Solved Examples

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Example 1: RSH (Thiols or Mercaptans) (pKa = 11) are more acidic than alcohols (pKa = 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 $9\sim330$ kJ) is much less than (O-H) bond of a alcohols $(\sim420$ kJ). Thiols undergo oxidative coupling reaction with mild OA alcohol do not undergo such reaction.

 $2RS-H + H_2O_2 \rightarrow RS-SR$ (Disulfide) + $2H_2O$

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 -

I. $H_2C = N = N$	II. $H_2C - N = N$
Θ⊕	e
III. H₂C−N≡N	IV. H₂C−N=N

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.

 $pK_{a1} = 1.27 \qquad 2.86 \ 4.21 \ 4.34 \ 4.41 \ 4.82$ $pK_{a2} = 4.27 \qquad 5.70 \ 5.64 \ 5.27 \ 5.28$

The above order of dibasic acid is due to an increasing number of alkyl group (e-donating group) or increasing number of σ -bonds between (–COOH) and (–COO⁻).

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 ₃ COOH
3. C ₂ H ₅ COOH	4. C ₆ H ₅ COOH
5. (CH ₃) ₂ CHCOOH	6. CH ₂ CICOOH

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

i.
$$1 > 4 > 2 > 3$$

 $CH_3 \rightarrow CH_2 \rightarrow CH_2 \rightarrow CH_2 - OH (+1 \text{ effect of } Bu > Me)$
 $(Me \rightarrow CH_2 \rightarrow CH \rightarrow CH_3, (+I)$
 OH

(+1 effect of Et and Me > Me) Me + OH +1 effect of three Me groups) Me

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

(In (6) -I effect of CI > (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. C ₆ H ₅ COOH
3. C ₆ H ₅ OH	4. HCl
iii. 1. RCOOH	2. ROH
3. RH	4. NH ₃
5. HOH	6. CH=CH

Sol: (i) 3 > 1 > 2

(3) Intramolecular H-bonding from two sides > (I) 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) H_2O > (2) Alcohol > (6) HC=CH (sp character) > (4) NH₂ > (3) Alkane (sp³ character)

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

i. 1. RCN	2. RNH ₂	3. R–N=CH–R
ii. 1. C ₂ H ₅ NH ₂	2. (iso-C ₃ H ₇) ₃ N	
3. CH ₃ CONH ₂	4. $CH_3 \overset{\oplus}{NHNa}^{\oplus}$	
iii. 1. NH₂ 4. ⁻OR	2. HC≡C⁻ 5. R⁻	3. ⁻OH 6. RCOO⁻

Sol: i. 2 > 3 > 1

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

Basicity: $sp^3 > sp^2 > sp$ character

ii. 4 > 1 > 2 > 3

(4) Anion of 1° amine
$$CH_3 - NH_2$$

LP e⁻s density increases > (1) 1° amine > (2) 3° amine > (3) amide due to the resonance, non-availability of LP electrons, hence weakest)

$$\begin{array}{c} C \\ C \\ R \\ - C \\ - NH_2 \\ \hline \end{array} \begin{array}{c} O \\ I \\ R \\ - C \\ - NH_2 \\ \hline \end{array} \begin{array}{c} O \\ I \\ R \\ - C \\ - NH_2 \\ \hline \end{array}$$

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

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

Acidity: RCOOH > H_2O > ROH (6) (3) (4) > CH=CH > NH_3 > RH (2) (1) (5) Basicity: RCOO^{Θ} < -OH < RO⁻ < CH=C^{Θ} < NH_2 < 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 dimmer due to H-bonding.

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

Example 9: Sulphonic acids are stronger acids than carboxylic acids

Sol:



Benzone sulphoric acid Benzone sulphonate ion



Oxygen being more EN than S, the sulphonyl group (– SO_2 –) having two oxygen atoms greatly facilitates the release of H atom of (– SO_2OH) group as hydronium ion as shown above.

i. Due to the release of a portion, the replacement of (–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 (H_2CO_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.

$$\begin{pmatrix} O & O^{\Theta} \\ \parallel & \parallel \\ HO - C - O^{\Theta} \leftrightarrow HO - C = O \\ I \end{pmatrix} + H_{3}O^{\Theta}$$

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.

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

Acid anion is stabilized by resonance as explained earlier.

$$\begin{array}{c} O \\ \parallel \\ R-C-O-OH + H_2O \rightarrow R-C-O^{\Theta} + H_3O^{\Theta} \\ Peroxy acids \end{array}$$

$$\begin{array}{c} & & \\ \parallel & \\ R-C-OH + H_2O \rightarrow R-C-O^{\Theta} + H_3O^{\Theta} \end{array}$$

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

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



exo-bicyclo [2,2,1]-2-heptanoic acid (I)



Here, exo (–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-otoluidine and N-dimethyl aniline.(b)Bemzoquinoclidine and N,N-dimethyl aniline(c) p=Cyanophenol and 5-methyl p-cyanophenol (d) 2,43,6-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 $(-CH_3)$ group at the o-position and $(-CH_3)$ 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^{-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⁻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-trinitro-aniline (I) by 40,000 times, whereas nearly triples the basicity of aniline.



(E) Basic character:

$$(CH_3)_3N > \bigcirc_N > CH_3 - C = N$$

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

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 α -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 α -H atoms (hyperconjugation).



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



(IV) is least stable; it has only two α -H atoms.



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

Example 5: Compare the basicity of substituted aromatic amines:



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

(p - > m - > Anilline > 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_2) group ; this results in the protonation of (NH_2) group becoming more difficult (salvation 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.



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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 Drawbond-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 ₆ H ₁₄	(ii) C ₆ H ₁₀
(iii) C ₈ H ₁₀	(iv) C ₈ H ₁₈
(v) C ₃ H ₈ O	(vi) C ₃ H ₈ O ₂
(vii) C ₄ H ₁₀ O	(viii) C ₆ H ₁₁ NO ₂

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

(i) Thioalochol	(ii) Isothiocyanate
(iii) Thiocyanate and	(iv) Sulhponic acid
(v) Suplhones	(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.

 $CH_2=CH-C_2H_5$, $CH_3CH=CHCH_3$, $CH_2=CHCH=CH_2$, $CH_3-CH=CH-CH=CH_2$ and $CH_2=C-C=CH_2$ I CH_3 CH_3

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 platinic 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) : CH_{3}^{-} (B) CH_{3}^{+} (C) BF_{4}^{-} (D) 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 sp³–sp² hybrid orbitals?

(A)
$$CH_3-C\equiv C CH_3$$
 (B) $CH_3-CH=CH-CH_3$
(C) $CH_2=CH-CH=CH_2$ (D) $HC\equiv C_2H_4$

Q.4 The bond between carbon atoms (1) and carbon atom (2) in compound, $1 \atop C=N$

(A) sp ³ and sp ²	(B) sp ² –sp ³	2
(C) sp and sp ²	(D) sp and sp	

Q.5 In the compound $CH_2 = CH - CH_2 - CH_2 - CH_2 - C \equiv CH$, the $C_2 - C_3$ bond is of the type is -

(A) sp – sp ²	(B) sp ³ – sp ³
(C) sp – sp ²	(D) sp ² – sp ³

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

(A)
$$CH_{3}^{-}$$
 (B) CH_{3}^{+} (C) BF_{4}^{-} (D) CH_{3}^{-}

Q.7 The stability order of alkenes is given as CH_3 - $CH=CH_2 > CH_2=CH_{2'}$ the reactivity order towards electrophilic addition reaction is given by

(A) $CH_2 = CH_2 > CH_3 - CH = CH_2$ (B) $CH_3 - CH = CH_2 > CH_2 = CH_2$ (C) $CH_3 - CH = CH_2$ equal to $CH_2 = CH_2$

(D) None of these

Q.8 Carbanion is

(A) An electrophile (B) A nucleophile

(C) A zwitter ion (D) A free radial

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) > > > V	(B) > > V >
(C) > > > V	(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 nonaromatic

(C) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons

(D) II is an acceptable canonical structure

Q.11 HC=CH $\xrightarrow{\text{HgSO}_4}_{\text{H_2SO}_4}$	(A) $\xrightarrow{\text{dil. OH}^-}$ (B). Give the
IUPAC name of B.	
(A) 2-butenal	(B) 3-hydroxybutanal
(C) 3-formyl 2-propanol	(D) 4-oxo-2-propanol





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

(A) $\overset{\delta}{C}H_2 = CH - \overset{\delta_+}{C}H = O$	(B) $CH_2 = CH - CH = CH_2$	Ċ Ċ
(C) $\overset{\delta_{-}}{C}$ H ₂ = $\overset{\delta_{+}}{C}$ H – CH = O	(D) $\overset{\delta_+}{C}H_2 - CH = CH - CH$	5

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 PO_4^{3-} using

(A) NaOH	(B) Na ₂ O
(C) Na ₂ O ₂	(D) NaO ₂

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



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

Q.20 The incorrect statement about S_N^1 reaction is (When only α -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-hloro

- (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.24 Magnesia mixture used during estimation of phosphorous is -

(A) $MgCl_2 + NH_4Cl$

(B) $HgCl_2 + NH_4Cl + little of NH_3$

(C) $HgCl_2 + NH_4Cl$

(D) $MgCl_2 + NH_4Cl + little of NH_3$

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 ${\rm CuSO}_{\rm 3}$

(C) K_2SO_4 is responsible for converting NH₃ to (NH₄)₂SO₄

(D) K_2SO_4 raises the boiling point of H_2SO_4

Q.26 The compound having maximum enol content -

(A) CH ₃ CH ₂ CHO	(B) CH ₃ COCH ₃
(C) CH ₃ CHO	(D) CH ₃ COCH ₂ COCH 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 carbine

(B) Singlet carbene = Triplet carbine

- (C) Singlet carbene < Triplet carbine
- (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

c) HCHO > AICHO > KCOK > AICOAI >

(D) None of these

Q.31 The number of meso forms for glucose are

(A) 1	(B) 2
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(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) Na₂S and NaCN are decomposed by HNO₃

(C) Ag_2S is soluble in HNO_3

(D) AgCN is soluble in HNO₃

Previous Years' Questions



The product A will be -



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

(1) CH ₃ -C ^{NH} _{NH₂}	(2) CH ₃ CH ₂ NH ₂
(3) (CH ₃) ₂ NH	(4) CH ₃ CONH ₂
(A) 2 > 1 > 3 > 4	(B) 1 > 3 > 2 > 4
(C) 3 > 1 > 2 > 4	(D) 1 > 2 > 3 > 4

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



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

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

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



(2003)

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

 $\begin{array}{cccc} H_{2}C = \stackrel{+}{N} = \stackrel{-}{N} & H_{2}C - N = \stackrel{-}{N} \\ (I) & (II) \\ H_{2}C - \stackrel{+}{N} = N & H_{2}C - N = \stackrel{+}{N} \\ (III) & (IV) \end{array}$

Q.7 In the following carbocation, H/CH_3 that is most likely to migrate to the positively charged carbon is (2009)



(A) CH ₃ at C-4	(B) H at C-4
(C) CH ₃ at C-2	(D) H at C-2

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

(A) σ-s (B) σ-p (C) p-p (D) π-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⁻ is correctly represented by – (2004)



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

(A)
$$p - O_2 N - C_6 H_4 - \overset{+}{C} H_2$$
 (B) $p - C H_3 O - C_6 H_4 - \overset{+}{C} H_2$
(C) $p - C I - C_6 H_4 - \overset{+}{C} H_2$ (D) $C_6 H_5 - \overset{+}{C} H_2$

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

(A) F^- (B) OH^- (C) CH_3^- (D) NH_2^-

- 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)



 $CH_2 = CH - \overset{\odot}{C}H_2$; $CH_3 - CH_2 - \overset{\odot}{C}H_2$;

$(A) \ \mathrm{III} > \mathrm{II} > \mathrm{I}$	(B) $II > III > I$
(C) $I > II > III$	(D) $III > I > II$



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(2013)

Exercise 1

is:

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

Q.22 The order of stability of the following carbocation:

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 $CX_2(X = F, CI, Br, I)$ 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) NaNH₂ is added to acetylene
- (b) gaseous NH₃ is add 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 1-hexanol why?

Q.15 1, 5-Pentanediol is soluble and 1-pentanol is slightly soluble in H₂O. Justify the statement.

Q.16 1° and 2° amides tend to exist as dimmer 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 $C_{3}H_{7}NO$ 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





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



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



Q.4 Which of the following is an electrophile?

(A) $AICI_4^{-}$ (B) BCI_3 (C) NH_3 (D) CH_3OH













- (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. \overbrace{O} B. $\overbrace{\bigcirc}$ (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

- (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/CH₃ that is most likely to migrate to the positively charged carbon is

$$\begin{array}{ccccccc} H & H \\ H_{3}C & C & C & C & C \\ H_{3}C & C & C & C & C \\ H_{3} & I & I \\ OH & H & CH_{3} \end{array}$$
(A) CH₃ at C-4
(B) CH₃COCH₃
(C) CH₃CHO
(D) H at C₂

Q.17 The compound having maximum enol content -

(A) CH ₃ CH ₂ CHO	(B) CH ₃ COCH ₃
(C) CH ₃ CHO	(D) CH ₃ COCH ₂ COCH

Q.18 Which of the following statement is correct?

(A) Trimethylmenthyl 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 σ 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
	(0) 000

(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: Trophylium cation is more stable than $(CH_3)_3C^+$.

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 $C \equiv C$ bond.

Q.30 Assertion: PH_3 is stronger nucleophile than NH_3 .

Reason: PH₃ is stronger base than NH₃.

Q.31 Assertion: The carbocation $CF_3 - CH_2$ is less stable than CF_3 .

Reason: In case of $CF_3 - CH_2$, CF_3 is strong electron withdrawing, therefore increases +ve, charge whereas

⊕

in CF_3 , 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 _N 2
(D)	Carbonyl compounds	(s)	C=C + HX

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

Colur	nn I	Colu	ımn II
(A)	C	(p)	Halogenation
(B)	$\bigcirc \bigcirc \bigcirc$	(q)	Electrophilic addition reactions
(C)	Me H Me Ph OH Ph	(r)	Nucleophilic addition reactions
(D)	OTs	(s)	Elimination reaction E_1 or E_2)
		(t)	Formation of carbocation intermediate

Q.34 Match the following:

Colur	Column I		mn ll
(A)	$(CH_3)_2C=CH_2 + HBr$	(p)	1° carbocation
(B)		(q)	2º carbocation
	+ CHBr ₃ +		
	(CH ₃) ₃ COK		
(C)	CH ₂ OH + H ⁺	(r)	3° carbocation
(D)	ОН	(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 adicals	(s)	Disproportionation	

Q.36 Match the following:

Colu	mn l	Column II	
(A)	H_3C Br e_{OH}	(p)	E ₂ (Major)
(B)	$\begin{array}{c} O \\ Ph \\ Ph \\ \end{array} \xrightarrow{Br} \xrightarrow{PhSNa} \end{array}$	(q)	E ₁ (Major)
(C)	$\overset{\text{Me}_{3}\text{C}}{} \overset{\text{O}}{\overset{\text{HBr}}{}} Br \overset{\text{HBr}}{} $	(r)	S _N 1(Major)
(D)	$\bigcup_{A} \stackrel{OH}{\longrightarrow} \xrightarrow{H_3PO_4} \xrightarrow{A}$	(s)	S _N 2(Major)
		(t)	E ₁ CB(Major)

Previous Years' Questions

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

(A)
$$CH_2 - CH - CH = CH - O - CH_3$$

(B) $CH_2 - CH = CH - CH = O - CH_3$
(C) $CH_2 = CH_2 - CH = CH - O - CH_3$
(D) $CH_2 = CH - CH - CH = O - CH_3$

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



Q.3 When benzene sulphonic acid and p-nitrophenol are treated with NaHCO₃, the gases released respectively (2006) are

(A) SO ₂ , NO ₂	(B) SO _{2'} NO
(C) SO _{2'} CO ₂	(D) CO ₂ , CO ₂

Q.8

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



Q.5 Phenol is less acidic than -				
(A) Acetic acid	(B) p-methoxy phenol			
(C) p-nitrophenol	(D) Ethanol			

Q.6 The compound in which C uses its sp³-hybrid orbitals for bond formation is (2000)

(A) HCOOH	(B) (H ₂ N) ₂ CO
(C) (CH ₃) ₃ COH	(D) CH ₃ 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)



(C) $H_2C=C=O$ (D) $H_2C=C=CH_2$

(2010)

	Column I		Column II
(A)	$N_2CI + OH \xrightarrow{NaOH/H_2O} N = N - OH$	(p)	Racemic mixture
(B)	$\begin{array}{cccc} OH & OH & & O \\ I & I \\ H_{3}C - C & - C - CH_{3} & \xrightarrow{H_{2}SO_{4}} & & C \\ I & I \\ CH_{3} & CH_{3} & & H_{3}C & I \\ \end{array} \begin{array}{c} C \\ H_{3}C \\ H_{3}C \\ \end{array} \begin{array}{c} C \\ H_{3} \\ CH_{3} \end{array} \begin{array}{c} C \\ H_{3} \\ CH_{3} \end{array}$	(q)	Addition reaction



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)



Q.10 Give reasons for the following $CH_2 = CH^-$ is more basic than $HC = C^-$. (2000)

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

(A)	Benzoic acid	(p)	10.2 × 10 ⁻⁵
(B)	p-nitrobenzoic acid	(q)	3.3 × 10 ⁻⁵
(C)	p-chlorobenzoic acid	(r)	6.4 × 10 ⁻⁵
(D)	p-methylbenzoic acid	(s)	36.2 × 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 sp₃ (B) sp and sp₂ (C) only sp² (D) sp² and sp³

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.



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(2014)
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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)



JEE Advanced/Boards

Q.23

MASTERJEE Essential Questions

JEE Main/Boards

Exercise 1				Exercise 1			
Q.1 (iii)	Q.3	Q.12 (iii)		Q.2	Q.6(4)	Q.7(4)	
Q.17 (vi, ii)	Q.19 (iv)	Q.22 (ii)	Q.27	Q.14	Q.23	Q.29	
Exercise 2				Exercise 2			
Q.2	Q.14	Q.19	Q.27	Q.8	Q.19	Q.21	
Previous Years' Questions				Previous	s Years' Qu	estions	
01	05	0.10		0.2	0.4		

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	2				
Single Corre	ect 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 Co	rrect Choice Type				
Q.21 A, B, C					
Comprehen	sion Type				
Q.22 C	Q.23 A	Q.24 A	Q.25 C	Q.26 A	Q.27 C

	Assertion	Reasoning	Туре
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Q.28 A	Q.29 A	Q.30 C	Q.31 A

Matric Match Type

Q.32 A \rightarrow p, s; B \rightarrow q; C \rightarrow r; D \rightarrow q	
Q.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
$\textbf{Q.34} \text{ A} \rightarrow p, \text{ r}; \text{ B} \rightarrow \text{r}, \text{ s}; \text{ C} \rightarrow p, \text{ r}; \text{ D} \rightarrow \text{q}, \text{ r}$	
Q.35 A \rightarrow p, r; B \rightarrow S; C \rightarrow p, s; D \rightarrow q, r, s	
Q.36 A \rightarrow t; B \rightarrow p; C \rightarrow r; D \rightarrow t, b \rightarrow p; C \rightarrow r; D \rightarrow 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 \rightarrow r, s ; B \rightarrow t	t;C→p,q;D→r	Q.9 A \rightarrow r, s, t ; B –	\rightarrow p, s ; C \rightarrow r, s ; D –	→q, r
Q.11 A \rightarrow r; B \rightarrow s;	$c \to p; D \to q$	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] 2s²2p²

It has four electrons in its outermost shell



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

Sol 2: Carbon undergo hybridization due to following reasons

(i) Hybridised orbitals are equivalent in energy (degenerate) and have more effective overlapping

(ii) Hybridised orbitals are directional in nature

Sol 3: Methane:



Sol 4: Fumaric acid has higher metling 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., sp³ 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-butylcylopentane



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 bukly NO_2 -group

Sol 8: (i) C₆H₁₄





(iii) C₈H₁₀

Degree of unsaturation = $8 - \frac{10}{2} + 1 = 4$ I am drawing those isomers only which contains a benzene ring.

Condensed

Bond line



(vi) $C_3H_6O_2$ Degree of unsaturation = 1





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:-SOH
- (ii) Isothiocyanate: S=C=N-
- (iii) Thiocyanate:-S=C=N-
- (iv) Sulphonic acid: -SO₃H



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)



Sol 11: Hydrazine (H–N=N–H) does not give a +ve test for Lassaigne's test of Nitrogen because it cannot produce NaCN.

Sol 12: (i)
$$CH_2 = CH - C_2H_5 \xrightarrow{HBr} CH_3 - \overrightarrow{C} H - C_2H_5 + \overrightarrow{C} H_2 - CH_2CH_2C_2H_5$$

(ii) $CH_3CH = CHCH_3 \xrightarrow{HBr} CH_3CH = CHCH_3 + CH_3\overrightarrow{C} HCH_3CH_5$

(iv)
$$CH_3 - CH = CH - CH = CH_2 \xrightarrow{HBr} CH_3 CH_2 - CH_2 CH_2 - CH_2 CH_2 CH_3 CH_2 - CH_2 CH_2 CH_2 - CH_2 CH_2 - CH_2 CH_2 - CH_2 CH_2 - CH_2 - CH_2 CH_2 - CH_2$$

+ minor but stable than III minor

(v)
$$CH_2=C$$
— $C=CH_2 \xrightarrow{HBr} CH_3 \xrightarrow{\oplus} CH_3 = CH_2$
 $| | | CH_3 CH_3 \xrightarrow{HBr} CH_3 \xrightarrow{\oplus} CH_3 = CH_2$
 $| | | CH_3 CH_3 \xrightarrow{HBr} CH_3 = CH_2$
 $| | CH_3 -C = CH - CH_2^{\oplus} + minor$
 $| | | CH_3 CH_3$

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 CH₃OH

Ethyl alcohol C₂H₅OH

Propyl alcohol C₃H₇OH

Butyl alcohol C₄H₀OH

Sol 14: Refer theory

Sol 15: $R_1Ag_2 \rightarrow 2Ag + other$

Let molecular weight of salt be M.

Then 1 mole of R₂ Ag gives 2 moles of Ag

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

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 platinic 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 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 α -H

For H_3C - max inductive effect (3 α H)

 $H_2CH_3C-2 \alpha H$

(CH₃) CH–1 α H

(CH₃)₃C–0 α H

Thus order of hypercongugation effect

 $CH_{3} - > CH_{3}CH_{2} - > (CH_{3})_{2}C - > (CH_{3})_{3}C -$

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 ($\sim 10 - 15K$)

Exercise 2

Single Correct Choice Type

Sol 1: (B) In CH_3^+ , C has a sp² structure, making its shape trigonal planar

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

Sol 3: (B) $CH_3 - CH = CH - CH_3$ $\downarrow_3 \qquad \downarrow_2 \qquad \downarrow_3 \qquad \downarrow_3$ $sp^3 \qquad sp^2 \qquad sp^2 \qquad sp^3$

Sol 4: (C) C_1 is sp and C_2 is sp²

Sol 5: (D)
$$CH_2 = CH - CH_2 - CH_2 - C \equiv CH$$

 $\downarrow_2 \qquad \downarrow_3$
 $sp^2 \qquad sp^3$

Sol 6: (B) In CH_3^+ , C has a sp² structure, making its shape trigonal planar

Sol 7: (B)

$$CH_{3}-CH = CH_{2} + X^{+} \rightarrow CH_{3}-CH_{2}-CH_{2}X$$

$$CH_{2} = CH_{2} + X^{+} \rightarrow CH_{2}-CH_{2}X$$

The resulting carbocation is more stable for CH_3 - $CH=CH_2$ due to more number of hyperconjugation structures

Sol 8: (B) Carbanion is a nucleophile as its has a negative 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 period 2 element



Are geometric isomers

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



Sol 14: (B) (D) is most stable because of the enhanced stability of resulting carbocation due to conjugation. In (A) lone pair of N is not conjugated and also CH_2C-N single bond have more +I effect than C–N double bond making it basic than (B) CH_3-C has least +I effect

Sol 15: (B) RSO₃⁻ group is the best leaving group. In 1 and 2, 2 will be more stable due to more – I effect of NH_3^+ and 3 > 4 in stability

∴ 2 > 1 > 3 > 4

Sol 16: (D)



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

Sol 17: (C) Its ring ontains 2π electrons, so it follows huckel s rule

Sol 18: (C) $5Na_2O_2+2P \xrightarrow{fuse} 2Na_3PO_4 + 2Na_2O_4$

Sol 19: (C) Reactivity order for S_N^1 reaction depends upon the stability of resulting carbocation.

Ph.CH₂⁺ > Ph⁺, since Ph–CH₂⁺ is a benzyl cation (due to –I and –M effect of NO₂⁻)



(:: tertiary carbocation > secondary carbocation)

Sol 20: (A) S_N1 reaction yield a racemic mixture

Sol 21: (B) –Cl group have –I effect which stabilizes the anion and it decreases with distance.



Sol 23: (D) For a compound to be reactive towards S_N^2 reaction, the resulting carbocation should be least stable. Here, the resulting carbocation is least stable in (d) due to strong –M effect of –NO₂ group.

Sol 24: (D) Magnesia mixture is $MgCl_2 + NH_4Cl + little of NH_3$

Sol 25: (D) K_2SO_4 raises the boiling point of water.





This structure is stabilised most by resonance

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



Which causes maximum difference in dipole moment between its cis and trans form. For others, 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 most positive charge density on carbonyl carbon. Noting this, order will be:

ArCOAr > ArCHO > ArCOR > HCHO > ArCOAr>

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

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

Previous Years' Questions

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

$$-C \equiv CH < ROH < H_2O < PhOH < R - COOH$$

Therefore, during stepwise neutralisation of given acid, -COOH will be neutralised first. In the second step, the phenolic –OH, assisted by –I effect of $-NO_2$ at Meta position will be neutralised.



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



IV is amide, least basic

$$\begin{array}{c} O & O \\ \parallel & \vdots \\ CH_3 - C - NH_2 \leftrightarrow CH_3 - C = NH_2 \end{array}$$

lone pair is part of delocation

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

Sol 3: (B) Carboxylic acid is stronger acid than ammonium ion, hence -COOH(X) is most acidic. $^{+}_{X}$ $Z(NH_3)$ is more acidic than $Y(NH_3)$ due to -I effect of -COOH on Z. Hence, overall acid strength order is X > Z > Y **Sol 4: (C)** A methylene $(-CH_2 -)$ with carbonyl on both side is highly acidic.

$$CH_{3}-C-CH_{2}-C-CH_{2}-CH_{3}$$



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 stabilized carbocation

Sol 8: (B) The σ -electrons of C-H bond is delocalized with p-orbitals of π -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 sp² 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 13: (B)

Nitro-group is electron withdrawing therefore decreases stability. Ŷ NO₂ ĊH₂

Methoxy group is electron releasing.

Therefore increases stability by donating electron.

Chlorine is also electron withdrawing but its effect is less than $-NO_2$ group.

Hence, correct order of stability.



Sol 14: (C) CH_3^- has the highest nucleophilicty.

Sol 15: (B) In cis isomer the carbon-chlorine dipole reinforces and henece ther is large molecualr dipole.

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

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

$$CH_3 - CH_2 - CH_2 - CH_2CI$$

1-chloro butane and $CH_3 - CH_2 - CH - CH_3$
|
CI
2-chloro butane

2-methyl propane as following two isomeric monochloro derivatives.

$$\begin{array}{c} \mathsf{CH}_3 & \mathsf{CH}_3 \\ | & | \\ \mathsf{CH}_3 - \mathsf{CH} - \mathsf{CH}_2\mathsf{CI} & \text{and} & \mathsf{CH}_3 - \mathsf{C} - \mathsf{CH}_3 \\ 2\text{-methyl-1-chloropropane} & | \\ \mathsf{CI} \end{array}$$

2-methyl-2-chloropropane

Sol 18: CO_3^{2-} shows resonance and thus all the three bonds are of identical bond length.

$$\begin{array}{c} \mathsf{O} = \mathsf{C} - \mathsf{O}^- \leftrightarrow \mathsf{O}^- - \mathsf{C} = \mathsf{O} \leftrightarrow \mathsf{O}^- - \mathsf{C} - \mathsf{O} \\ \\ \mathsf{O}_- & \mathsf{O}_- & \mathsf{O} \end{array}$$

Sol 19: Boiling points of isomeric compounds depend on dipole-dipole interactions and cis-isomers have 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 number of resonating structure (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

() +0-CH₃

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 on three different ways, because his valence shell orbitals allows him to do so.

He can hybridize (mix) his valence orbitals to generate sets of equivalent sp, sp2 or sp3 orbitals.

Sol 2: Methane: In methane, carbon is sp³ hybridised making the shape tetrahedral.

Ethane: In ethane, both the carbon atoms are sp³ hybridised making its shape tetrahedral with respect to each carbon atom

Ethene: In ethene both are carbon atoms are sp² 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.





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 (CH₃) N and (PH) ₃N making them Lewis base.

But, in (PH) $_{3}N$ 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 $\mbox{ } C_n\mbox{ } H_{2n+2}$

Example: methane, ethane

(b) Unsaturated hydrocarbons: These with one double bond are called akenes 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 compoundand that defines the structure of a family of compounds and determines theproperties 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 -CH2- 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 -NH₂)



 $(H^+ \text{ is less acidic the } -SO_3H)$

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

sp³ hybridization : Tetrahedrally coordinated carbon.e.g-Methane

sp² hybridisation: In ethene molecule carbon sp² hybridises, because one π (pi) bond is required for the double bond between the carbons and only three σ 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 σ bond and two additional π 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 tauromerization is called tautomerism

Keto-enol tautomerism refers to a chemical equailibrium 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) NaNH₂ + C₂H₂
$$\longrightarrow$$

NH₂-CH=C-NH₂ + Na⁺ + NH₃
Strong acid: NH₃⁻

Weak acid: C₂H₂ Weak base: NH₂ Strong base: H–C≡C[−] (b) EtLi $\xrightarrow{NH_3}$ LiNH₂ + Et (C₂H₆) Strong base: $Et^{-}(C_{2}H_{c})$ Weak acid: NH₃ Strong acid: Li* Weak base: NH, $\xrightarrow{\mathsf{HC}\equiv\mathsf{CNa}} \mathsf{C}_2\mathsf{H}_5\mathsf{O}^-\mathsf{Na}^+ + \mathsf{HC}\equiv\mathsf{CH}$ (c) $C_2H_5OH -$ Strong acid: Na⁺ Weak acid: C₂H₂OH Strong base: HC≡C⁻ Weak base: HC≡CH (d) NaH + CH₃OH \longrightarrow CH₃O⁻Na + H₂ Strong acid: Na⁺ Weak acid: CH,OH Strong acid: H-Weak base: H₂

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.

E.g.
$$\delta - \delta + \delta + \delta - \delta + \delta - \delta + \delta - CH_3 - O - H CH_3 - CI:$$

(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,

$$H_2C = CH - C - CH_3 \leftrightarrow H_2C^+ - CH = C - CH_3$$

(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.

$$R_2 \dot{N} = C = C = C$$

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

Condition: Presence of –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 π -orbitals with the p- or π -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, -NO₂, in nitrobenzene shows -M effect due to the delocalization of conjugated π 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 σ -electrons towards the multiple bond occurs when there are hydrogens on the α -carbon (which is adjacent to the multiple bond).

This results in the polarization of the multiple bond. In the formalism that separates bonds into σ and π types, hyper conjugation is the interaction of σ -bonds (e.g. C–H, C–C, etc.) with a π network. This conjugation between electrons of single (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. C—C bond length in propene is 1.488 Å as compared to 1.334Å 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: C-O, C-Cl, C-Br, C-I, C-C, C-H. Carbon free radicals are mainly generated by:

i. Photolysis (action of light) like acetone alpha cleavage

ii. Other radical initiator like allylic bromination by 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 C-X bond (where X is more electronegative) and thus has a positive charge.

Planar in shape (sp² 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 C-X bond (where X is less electronegative) and thus has a negative charge.
- Pyramidal is shape (sp3 hybridized) with the excess electrons placed in one sp3 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 a addition reaction.

E.g. $CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2 - Br$

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

E.g. $CH_3OH + HBr \longrightarrow CH_3Br + H_2O$

3. Elimination Reactions: These reactions are the reverse of the addition reaction and involve the loss of atoms or 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.

 $CH_{3}CH_{2} \xrightarrow{alc.KOH} CH_{2} = CH_{2} + HCI$

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

E.g.
$$CH_3 - CH - CH = CH_2 \xrightarrow{\Delta} CH_3 - CH = C - CH_2$$

X
X

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: H⁺, CH₃⁺

(ii) Netral electrophiles: SO₃, RCOCl

Nucleophiles: Those species which carry a negative cleavage / 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: Br⁻, CH₃⁻

(ii) Neutral electrophiles: NH₃, 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 go electrons (–I).

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



has a dipole moment which make this compound nonpolar and therefore, its solubility will be more in a polar solvent compared to a non-polar one. Now polarity of methyl alcohol (CH₃OH) > n-propyl alcohol



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

o-dichrolobenzene

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

(b) A: B $\longrightarrow A^{\Theta} + B^{\oplus}$

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 twostep 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 - NH₃ + group transfers its H⁺ to OH⁻ to form soluble salt P — $NH_2C_6H_4SO_3$ – Na^+ . On the other hand, — SO_3^+ group is a very weak base and does not accept H⁺ from dil HCl to form $NH_3C_6H_4SO_3H$ and therefore, it does not dissolve in dil HCl.

Exercise 2

Single Correct Choice Type

Sol 1: (A) Ph S⁻ will attack C–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) BCl_3 is an electrophile as B has only 6 valence electrons and needs electrons to complete its octet.

Sol 5: (B)



Sol 9: (C)



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



Sol 7: (A) (A) is antiaromatic (4 π electrons)

(B) is aromatic (6 π electrons)

Sol 8: (B) –Cl group have –l effect which stabilizes the anion and it decreases with distance.

Sol 10: (C) CCl_3 -CH (OH) ₂ is most stable as it can form hydrogen bonding most effectively due to more -l effect of CCl_3 - group

Sol 11: (A) CH₃–C–CH₂–COOH has most reactivity as || O

the resulting carbanion:CH₃–C–CH⁻ \longleftrightarrow CH₃–C=CH $\begin{tabular}{c} & & \\ & &$

This is stabilized by resonance

Sol 12: (B)



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









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



This structure is stabilised most by resonance

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

(B) This trend is not always nessarily followed

(C) ${}^{+}CH_{3}$ 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 π bonds – the resonance energy of benzene.

 \therefore Heat of hydrogenation of 3π bonds

= (49.8 + 36) K cal./mol = 85.8 k cal/mol

Heat of hydrogenation of cyclohexene involves.

Hydrogenation of 1 π bonds, therefore,

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

= 28.6 k cal/mole

Sol 20: (A) + H effect 9 α – H in (CH₃) ₃–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.



Making it optically active

Sol 26: (A) d-glucose and ℓ -glucose are enantionmers



Assertion Reasoning Type



This cation is aromatic and hence very stable due to resonance $(CH_3)_3C^+$ is stabilized only by +I effect



 C_1 and C_2 are sp hybridized as C_1-C_2 is triple bond

Sol 30: (C) PH₃ is stronger nucleophile than NH₃ due to big size of P and increased polarisability

 PH_3 is weak base than NH_3 as lone pair density is more in 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







(Tetrahedral transition state)



(Pentavalent transition state)

(D) Carbonyl compounds undergo nucleophilic addition

(A) Cannot undergo electrophillic 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 π bonds which can be broken

(D) Cannot undergo electrophilic addition reaction and elimination reaction

Sol 34: A
$$\rightarrow$$
 p, r; b \rightarrow r, s; C \rightarrow p, r; D \rightarrow q, r









(C)







Sol 35: A \rightarrow p, r ; B \rightarrow s ; C \rightarrow p, s ; D \rightarrow q, r, s

(A) Carbocations can undergo reaction with ethylene and rearrangement

(B) Carbanions undergo disproport-ionation

(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 \rightarrow t; B \rightarrow p; C \rightarrow r; D \rightarrow q

(A) E₁ CB mechanism



(B)



Will undergo E2 because of sterical hindrance and nucleophile $\mathsf{PhS}^{\scriptscriptstyle -}$

(C) Will undergo $\mathrm{S}_{\scriptscriptstyle N} 1$ due to stability of carbocation and weaker nucleophile





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

Previous Years' Questions

Sol 1: (C) $CH_2 = CH_2 - \overset{\oplus}{CH} = \overset{\Theta}{CH} - O - CH_3$

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 resoance effect, increases acid strength. Therefore, phenol is less acidic than p-nitro phenol.

On the other hand, methoxy group from para postion, 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 \longrightarrow



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



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



Sol 9: A
$$\rightarrow$$
 r,s,t ; B \rightarrow p, s ; C \rightarrow r, s ; D \rightarrow q, r





Sol 10: H-C=C-H is more acid than $CH_2=CH_2$.

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 +1 effect. Therefore,

p-methylbenzoic acid 3.3 × 10^{-5}

benzoic acid 6.4 \times 10⁻⁵

p-chlorobenzoic acid 10.2 × 10^{-5}

p-nitrobenzoic acid 36.2 × 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 14: (B)
$$\underset{H \xrightarrow{c} c = c = c}{\overset{H}{\underset{sp^{2} \text{ sp sp}}}} H$$
 (allene)

Sol 15: (A)

$$\begin{array}{c} H\\ H\\ CH_2 \\ -CH_3 \\ CH_3 \end{array} \sigma - p(empty) \text{ delocalisation} \\ GH_3 \\ CH_3 - CH = CH_2 \quad (\sigma - \pi^* \text{ electron}) \text{ delocalisation} \end{array}$$

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

Sol 17:



Sol 18: (A)

