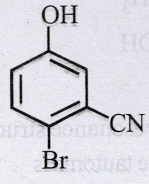
Chapter
Organic Chemistry - Some Basic Principles and Techniques

Topic-1: Classificiation and Nomenclature of Organic Compounds

1 MCQs with One Correct Answer

1. The IUPAC name of the following compound is **[2009]**



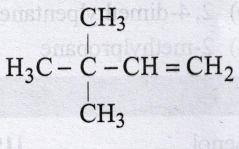
(a) 4-Bromo-3-cyanophenol
(b) 2-Bromo-5-hydroxybenzonitrile
(c) 2- Cyano-4-hydroxybromobenzene
(d) 6-Bromo-3-hydroxybenzonitrile

2. The IUPAC name of C_6H_5COCl is **[2006 - 3M, –1]**
(a) Benzene chloro ketone
(b) Benzoyl chloride
(c) Chloro phenyl ketone
(d) Benzene carbonyl chloride

3. The compound which has one isopropyl group is : **[1989]**
(a) 2, 2, 3, 3-tetramethylpentane
(b) 2, 2-dimethylpentane
(c) 2, 2, 3-trimethylpentane
(d) 2-methylpentane

4. The IUPAC name of the compound $CH_2=CH-CH(CH_3)_2$ is **[1987]**
(a) 1, 1-dimethyl –2-propene
(b) 3-methyl–1-butene
(c) 2-vinylpropane
(d) 1-isopropylethylene

5. The IUPAC name of the compound having the formula is: **[1984]**



(a) 3, 3, 3-Trimethyl-1-propene
(b) 1, 1, 1-Trimethyl-2-propene
(c) 3, 3-Dimethyl-1-butene
(d) 2, 2-Dimethyl-3-butene

4 Fill in the Blanks

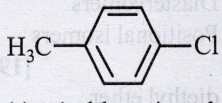
6. The IUPAC name of succinic acid is ..... . **[1990]**

7. The kind of delocalization involving sigma bond orbitals is called ..... . **[1994]**

8. A ..... diol has two hydroxyl groups on ..... carbon atoms. **[1986]**

6 MCQs with One or More than One Correct Answer

9. The IUPAC name(s) of the following compound is (are)

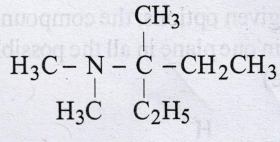


[Adv. 2017]

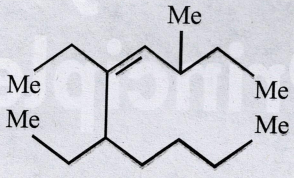
(a) 1-chloro-4-methylbenzene
(b) 4-chlorotoluene
(c) 4-methylchlorobenzene
(d) 1-methyl-4-chlorobenzene

10 Subjective Problems

10. (*i*) Write the IUPAC name for the following : **[1991]**



(*ii*) Give the IUPAC name of the following compound : [1990]



(Me = Methyl)

(*iii*) Write the IUPAC name of : $CH_3CH_2CH=CHCOOH$ [1986]

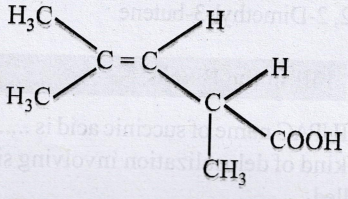
11. Write the structural formula of 4-chloro-2-pentene. [1988]

Topic-2: Isomerism in Organic Compounds

1 MCQs with One Correct Answer

1. The number of isomers of C_6H_{14} is [1987, 2007]
(a) 4 (b) 5 (c) 6 (d) 7

2. The number of isomers for the compound with molecular formula $C_2BrClFI$ is [2001S]
(a) 3 (b) 4 (c) 5 (d) 6

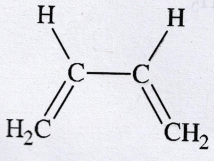
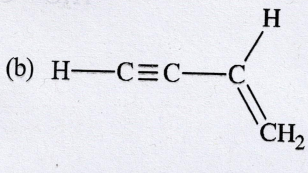
3. The structure  shows :
(a) geometrical isomerism [1995S]
(b) optical isomerism
(c) geometrical & optical isomerism
(d) tautomerism.

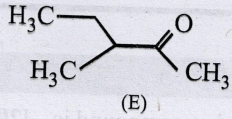
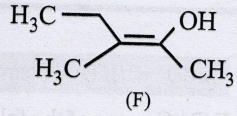
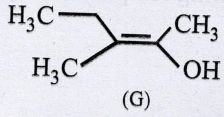
4. Isomers which can be interconverted through rotation around a single bond are [1992]
(a) Conformers (b) Diastereomers
(c) Enantiomers (d) Positional isomers

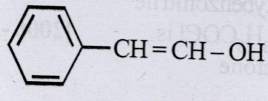
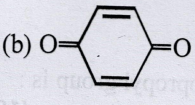
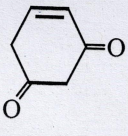
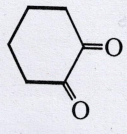
5. An isomer of ethanol is : [1986]
(a) methanol (b) diethyl ether
(c) acetone (d) dimethyl ether

6. The compound which is not isomeric with diethyl ether is [1981]
(a) *n*-propyl methyl ether (b) butan-1-ol
(c) 2-methylpropan-2-ol (d) butanone

6 MCQs with One or More than One Correct Answer

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

8. The correct statements(s) concerning the structures E,F and G is (are) – [2008]

(E)

(F)

(G)
(a) E, F and G are resonance structures
(b) E, F and E, G are tautomers
(c) F and G are geometrical isomers
(d) F and G are diastereomers

9. Tautomerism is exhibited by [1998]
(a) 
(b) 
(c) 
(d) 

10. Only two isomeric monochloro derivatives are possible for: [1986]
(a) *n*-butane (b) 2, 4-dimethylpentane
(c) benzene (d) 2-methylpropane

10 Subjective Problems

11. Write tautomeric forms for phenol. [1992]

Topic-3: Concepts of Reaction Mechanism in Organic Compounds and Purification

1 MCQs with One Correct Answer

1. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is **[1988]**
(a) C—C (b) C—O (c) C—H (d) O—H

2. The Cl—C—Cl angle in 1,1,2,2-tetrachloroethene and tetrachloromethane respectively will be about **[1988]**
(a) 120° and 109.5° (b) 90° and 109.5°
(c) 109.5° and 90° (d) 109.5° and 120°

3. The bond between carbon atom (1) and carbon atom (2) in compound $N \equiv \underset{1}{C} - \underset{2}{CH} = CH_2$ involves the hybrids as **[1987]**
(a) sp^2 and sp^2 (b) sp^3 and sp
(c) sp and sp^2 (d) sp and sp

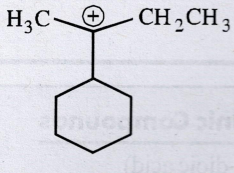
4. Out of the following compounds, which will have a zero dipole moment? **[1987]**
(a) 1, 1-dichloroethylene
(b) *cis*-1, 2-dichloroethylene
(c) *trans*-1, 2-dichloroethylene
(d) None of these compounds

5. The compound 1, 2-butadiene has **[1983]**
(a) only *sp* hybridized carbon atoms
(b) only sp^2 hybridized carbon atoms
(c) both *sp* and sp^2 hybridized carbon atoms
(d) *sp*, sp^2 and sp^3 hybridized carbon atoms

6. Molecule in which the distance between the two adjacent carbon atoms is largest is **[1981]**
(a) Ethane (b) Ethene (c) Ethyne (d) Benzene

2 Integer Value Answer

7. The total number of contributing structures showing hyperconjugation (involving C–H bonds) for the following carbocation is **[2011]**



4 Fill in the Blanks

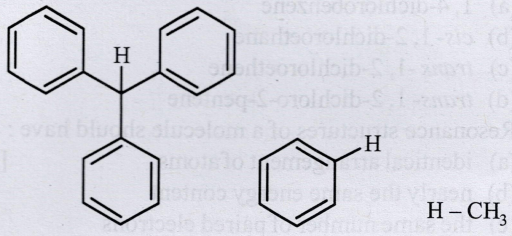
8. The valence atomic orbitals on carbon in silver acetylide is ..... hybridized. **[1990]**

9. The compound having both *sp* and sp^2 hybridized carbon atoms is ..... . **[1981]**
(propene, propane, propadiene)

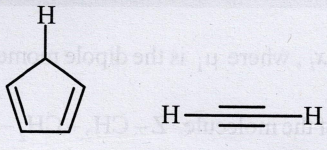
10. Among the given cations, ... is most stable. **[1981]**
(*sec*-butyl carbonium ion; *tert*-butyl carbonium ion; *n*-butyl carbonium ion)

6 MCQs with One or More than One Correct Answer

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



I **II** **III**

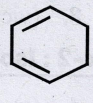
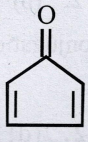
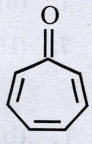


IV **V**

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

12. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to **[Adv. 2013]**
(a) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations
(b) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations
(c) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations
(d) p (filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations

13. Which of the following molecules, in pure form, is (are) **unstable** at room temperature? **[2012]**

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

14. Among the following compounds, the strongest acid is **[1998]**
(a) $HC \equiv CH$ (b) C_6H_6
(c) C_2H_6 (d) CH_3OH

15. What is the decreasing order of strength of the bases $OH^-, NH_2^-, HC \equiv C^-$ and $CH_3CH_2^-$? [1993]

(a) $CH_3 - CH_2^- > NH_2^- > H - C \equiv C^- > OH^-$

(b) $H - C \equiv C^- > CH_3 - CH_2^- > NH_2^- > OH^-$

(c) $OH^- > NH_2^- > H - C \equiv C^- > CH_3 - CH_2^-$

(d) $NH_2^- > H - C \equiv C^- > OH^- > CH_3 - CH_2^-$

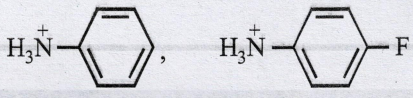
16. Dipole moment is shown by: [1986]
(a) 1, 4-dichlorobenzene
(b) *cis*- 1, 2-dichloroethane
(c) *trans* -1, 2-dichloroethene
(d) *trans*- 1, 2-dichloro-2-pentene

17. Resonance structures of a molecule should have :
(a) identical arrangement of atoms [1984]
(b) nearly the same energy content
(c) the same number of paired electrons
(d) identical bonding

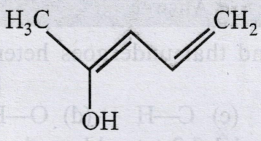
10 Subjective Problems

18. (*i*) $\mu_{obs} = \sum_i \mu_i x_i$, where μ_i is the dipole moment of a stable conformer of the molecule, $Z - CH_2 - CH_2 - Z$ and x_i is the mole fraction of the stable conformer.
Given : $\mu_{obs} = 1.0$ D and $x_{(Anti)} = 0.82$
Draw all the stable conformers of $Z - CH_2 - CH_2 - Z$ and calculate the value of $\mu_{(Gauche)}$.
(*ii*) Draw the stable conformer of $Y - CHD - CHD - Y$ (meso form), when $Y = CH_3$ (rotation about $C_2 - C_3$) and $Y = OH$ (rotation about $C_1 - C_2$) in Newman projection. [2005]

19. Which of the following is more acidic and why? [2004]



20. [2003]



Write resonance structure of the given compound.

21. Which one is more soluble in diethyl ether - anhydrous $AlCl_3$ or hydrous $AlCl_3$? Explain in terms of bonding. [2003]

22. Give reasons for the following :

(*i*) $CH_2{=}CH^-$ is more basic than $HC \equiv C^-$. [1994]

(*ii*) Phenyl group is known to exert negative inductive effect. But each phenyl ring in biphenyl ($C_6H_5 - C_6H_5$) is more reactive than benzene towards electrophilic substitution. [1992]

(*iii*) Carbon oxygen bond lengths in formic acid are 1.23Å and 1.36Å and both the carbon oxygen bonds in sodium formate have the same value i.e. 1.27Å. [1988]

23. *n*-butane, *n*-butanol, *n*-butyl chloride, isobutane in increasing order of boiling point. [1988]

24. For nitromethane molecule, write structure(s).
(*i*) showing significant resonance stabilisation. [1986]
(*ii*) indicating tautomerism. [1986]

Answer Key

Topic-1 : Classification and Nomenclature of Organic Compounds

1. (b) **2.** (b) **3.** (d) **4.** (b) **5.** (c) **6.** (Butane-1, 4-dioic acid)
7. (Hyperconjugation) **8.** (vicinal, adjacent or stable, different) **9.** (a, b)

Topic-2 : Isomerism in Organic Compounds

1. (b) **2.** (d) **3.** (b) **4.** (a) **5.** (d) **6.** (d) **7.** (b, c) **8.** (b, c, d)
9. (a, c, d) **10.** (a, d)

Topic-3 : Concepts of Reaction Mechanism in Organic Compounds and Purification

1. (d) **2.** (a) **3.** (c) **4.** (c) **5.** (d) **6.** (a) **7.** (6) **8.** (*sp* ; $Ag - C \equiv C - Ag$)
9. (propadiene) **10.** (*tert*-Butyl carbonium ion) **11.** (a, b, c) **12.** (a) **13.** (b, c)
14. (d) **15.** (a) **16.** (b, d) **17.** (a, b, c)

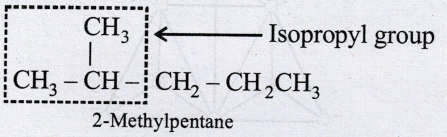
Hints & Solutions

Topic-1: Classification and Nomenclature of Organic Compounds

1. **(b)** – CN has highest priority. The nearest locant is at 2nd position.

2. **(b)** Carboxylic acids are named as *oyl chlorides*.

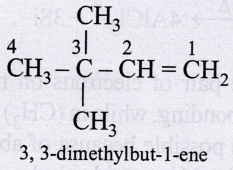
3. **(d)**



2-Methylpentane

4. **(b)** $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}(CH_3)-\overset{4}{CH_3}$ (3-Methyl-1-butene)

5. **(c)**



3, 3-dimethylbut-1-ene

6. **Butane-1, 4-dioic acid.**

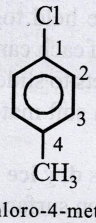
7. **Hyperconjugation.**

8. **vicinal, adjacent or stable, different.**

9. **(a, b)**

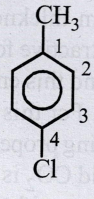
IUPAC name

(a)



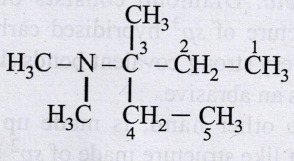
1-Chloro-4-methylbenzene

(b)



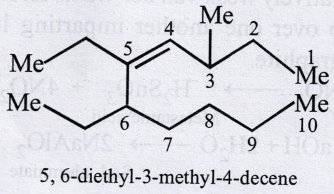
4-Chlorotoluene

10. (*i*) IUPAC name is



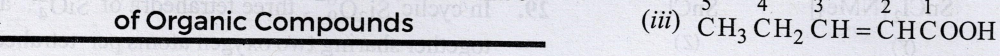
3–(*N*, *N*-dimethylamino)–3–methylpentane.

(*ii*)



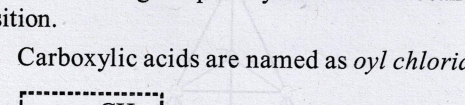
5, 6-diethyl-3-methyl-4-decene

(*iii*)



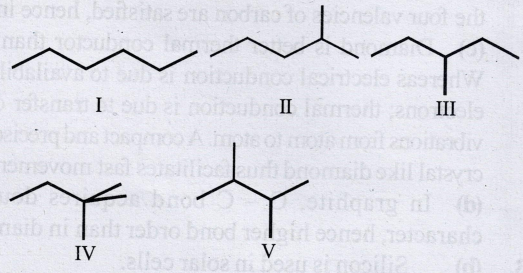
Pent-2-en-1-oic acid

11.

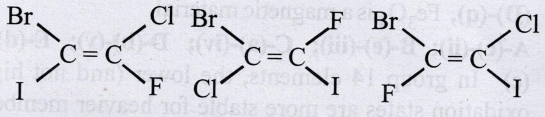


Topic-2: Isomerism in Organic Compounds

1. **(b)**



2. **(d)** Number of isomers (six) can be derived by keeping the position of any one halogen (say Br) fixed and changing the position of the other halogen one by one.



(Z and E) (Z and E) (Z and E)

3. **(b)** A compound which consists of at least one asymmetric carbon atom is capable of showing the phenomenon of optical isomerism.

The structure cannot show geometrical isomerism as one of the carbons along the double bond has identical group (methyl). Tautomerism is not possible because of the absence of –CO group.

4. **(a)** Stereoisomers which are mirror image of each other are *enantiomers* and the one which are not mirror images are *diasteromers*. **Conformation** of the molecule is the spatial arrangement of the atoms of a given molecular structure that are obtained merely by rotation about a sigma bond in the molecule.

5. **(d)** $\underset{\text{dimethyl ether}}{CH_3-O-CH_3}$ is an isomer of $\underset{\text{ethanol}}{CH_3CH_2OH}$

6. **(d)** The first three are isomers of diethyl ether, $C_2H_5OC_2H_5$ ($C_4H_{10}O$).

n-$C_3H_7OCH_3$ $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

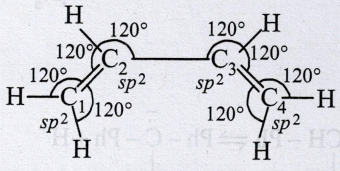
n-Propylmethylether , 2-Methylpropan-2-ol

n-C_4H_9OH , $CH_3\overset{\overset{O}{||}}{C}CH_2CH_3$

Butan-1-ol Butanone (C_4H_8O)

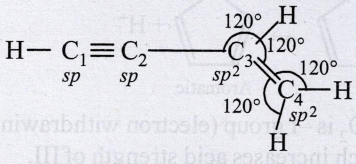
7. (b, c)

(a)



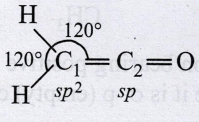
All carbons are sp^2 hybridised. Thus, they will form trigonal planar structure. But the conformer about C2–C3 bond can be in another plane. Hence, the molecule is non-planar in some of its conformations.

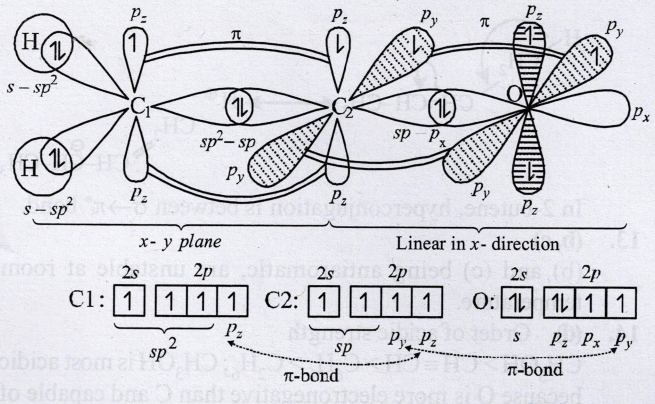
(b)



All carbons are either in sp or sp^2 hybridisation. Due to the presence of C2–C3 single bond, we can rotate the molecule about this bond. If we rotate the groups attached to C3 carbon, the molecule still remains planar as the C1–C2 part of the molecule is linear. The alkyne group has infinite rotational symmetry along its axis. After rotation the molecular plane will be different but the molecule will always remain in a plane.

(c)





C1 – carbon is sp^2 hybridised. Thus, it forms 3σ-bonds in x-y plane. It also forms a π-bond which must be perpendicular to this plane. Therefore, it will use the remaining p_z-orbital to form π-bond with C2-carbon.

C2 – carbon is sp-bybridised. Thus,it forms two linear sp-orbitals to form two σ-bonds, *i.e.* one with carbon and the other with oxygen. The remaining p_y orbital will form a π-bond with oxygen.

Oxygen atom will use its p_x orbital to form σ-bond with carbon, *i.e.* ($sp-p_x$) σ-bond. Its p_y-orbital is used in making π-bond and the p_z-orbital is already full. Hence, the C2 – O part of the molecule is linear in x-direction.

Hence, we can say that the whole moleucle is planar.

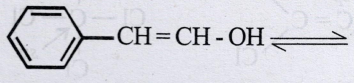
(d) The given compound is allene, which is non-planar as explained in page no.

8. (b, c, d) E and F ; and also E and G differ in position of atom (H), so these are tautomers (not resonating structures). Geometrical isomers are also diastereomers.

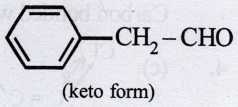
9. (a, c, d)

For a carbonyl compound to show tautomerism, it must have at least one H at the α – carbon atom.

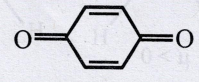
(a)



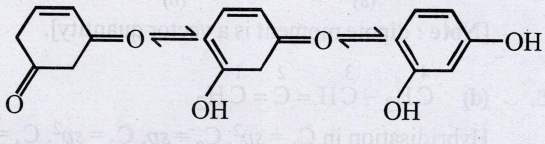
(enol form)



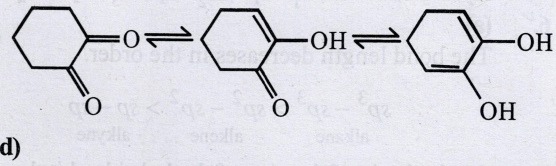
(keto form)

(b)  Tautomerism is not possible

(c)



(d)



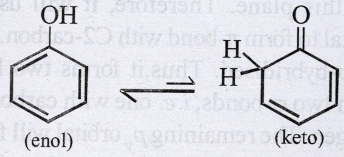
10. (a, d)

Option (a) In n-butane, Cl can add at either the first or second carbon giving two isomers.

Option (b) : $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$ will give three isomers with Cl group at either of the CH_3 groups, second C-atom and third C-atom.

Option (c) Benzene forms only one single derivative.

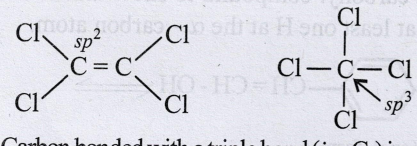
Option (d) : $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$ will again give two isomers with Cl at either one of the CH_3 groups or at the central C-atom.

11. 

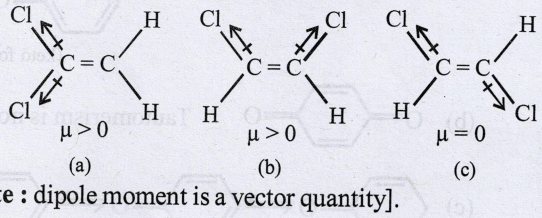
Topic-3: Concepts of Reaction Mechanism in Organic Compounds and Purification

1. **(d)** Heterolytic fission occurs when the two atoms differ considerably in their electronegativities.
O – H bond undergoes cleavage most readily because O and H differ markedly in their electronegativity and further oxygen being highly electronegative can accommodate the negative charge more effectively developed after the cleavage.

2. **(a)**
The bond angle in sp^3, sp^2 and sp hybridisad carbon atoms is respectively 109° 28', 120° and 180°.



3. **(c)** Carbon bonded with a triple bond (*i.e.* C_1) is *sp* hybridised. Carbon bonded with a double bond (C_2) is sp^2 hybridised.

4. **(c)** 

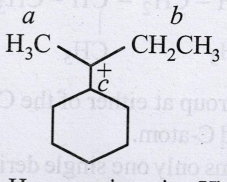
[**Note :** dipole moment is a vector quantity].

5. **(d)** $\overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}=\overset{1}{C}H_2$
Hybridisation in $C_1 = sp^2$, $C_2 = sp$, $C_3 = sp^2$, $C_4 = sp^3$.

6. **(a)**
The bond length decreases in the order.

$$\underset{\text{alkane}}{sp^3 - sp^3} > \underset{\text{alkene}}{sp^2 - sp^2} > \underset{\text{alkyne}}{sp - sp}$$

On the basis of the size of the hybrid orbitals, *sp* orbital should form the shortest and sp^3 orbital the longest bond with other atom.

7. **(6)** 

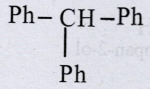
$a = 3$ Hyperconjugative H's
$b = 2$ Hyperconjugative H's
$c = 1$ Hyperconjugative H

8. ***sp*; Ag – C ≡ C – Ag**

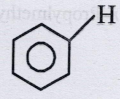
9. **propadiene;** $\overset{sp^2}{H_2C} = \overset{sp}{C} = \overset{sp^2}{CH_2}$

10. ***tert*-Butyl carbonium ion** is most stable due to hyperconjugation and +I effect of the three methyl groups.

11. **(a, b, c)**

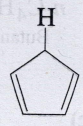
(I) 

$pk_a = 33.3$

(II) 

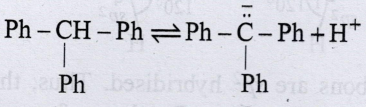
$pk_a = 43$

(III) $H - CH_3$
$pk_a = 50$

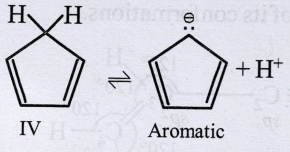
(IV) 

$pk_a = 16$

(V) $CH \equiv CH$
$pk_a = 25$

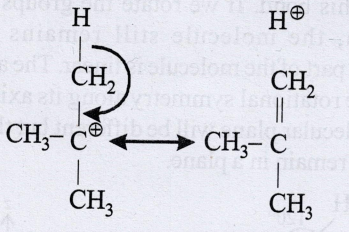
(a) 

I (Resonance stabilised anion of I)

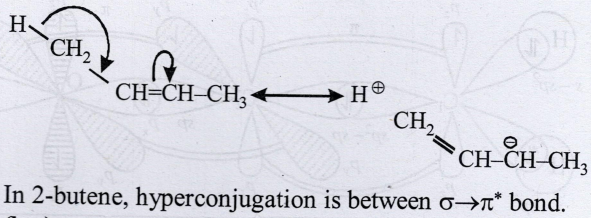
(b) 

(c) $-NO_2$ is –I group (electron withdrawing group), which increases acid strength of III.

(d) Acid strength order : IV > V > I > II > III

12. **(a)** 

In *tert*- butyl cation, carbon bearing positive charge has one vacant *p*-orbital hence it is σ–p (empty) conjugation or hyperconjugation.



In 2-butene, hyperconjugation is between $\sigma \rightarrow \pi^*$ bond.

13. **(b, c)**
(b) and (c) being antiaromatic, are unstable at room temperature.

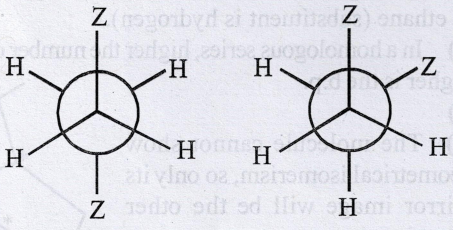
14. **(d)** Order of acidic strength
$CH_3OH > CH \equiv CH > C_6H_6 > C_2H_6$; CH_3OH is most acidic because O is more electronegative than C and capable of accommodating negative charge in CH_3O^-.
Although alcohols are neutral towards the litmus paper.

15. **(a)**
Conjugate base of strong acid is weak while conjugate base of a weak acid is strong.
Acidic strength of acids, of the given conjugate bases
$HOH > CH \equiv CH > NH_3 > CH_3 - CH_3$
Hence, the order of strength of bases,
$CH_3CH_2^- > NH_2^- > CH \equiv C^- > OH^-$

16. **(b,d)** 1, 4-Dichlorobenzene (*p*-dichlorobenzene) and *trans*-1, 2-dichloroethene have zero dipole moment because of their symmetrical structures.

17. **(a, b, c)**
Resonating structures differ in bonding pattern.

18. (i)

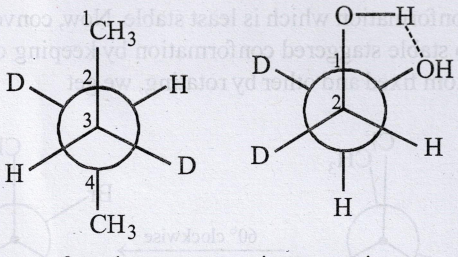


Anti conformer Gauche conformer

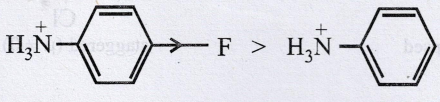
Given, mole fraction of anti conformer = 0.82
$\therefore$ mole fraction of gauche conformer = 0.18

$$\mu_{ob.} = \mu_{anti} \times \chi_{anti} + \mu_{gauche} \times \chi_{gauche}$$
$$1 = \mu_{(anti)} \times 0.82 + \mu_{(gauche)} \times 0.18$$
$$1 = 0 \times 0.82 + \mu_{(gauche)} \times 0.18$$
$[\because \mu_{(anti)} = 0]$
$$\therefore \ 1 = \mu_{(gauche)} \times 0.18$$
$$\mu_{(gauche)} = \frac{1}{0.18} = \mathbf{5.55\ D}$$

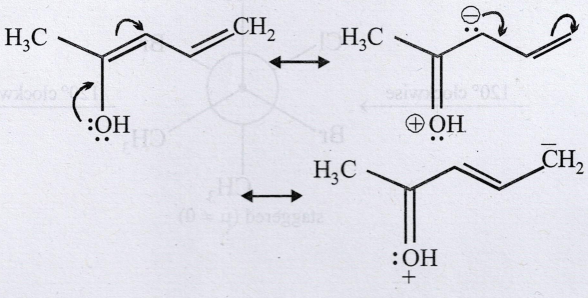
(ii)



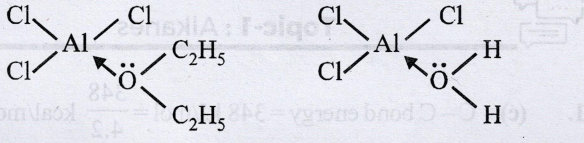
19. Presence of an electron-attracting group increases acidity of the compound. Thus, acidity order:



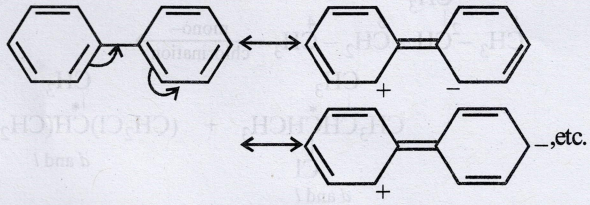
20.



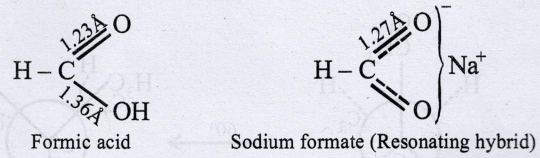
21. Diethyl ether acts as a Lewis base and anhydrous $AlCl_3$ as a Lewis acid.
Anyhydrous $AlCl_3$ is more soluble in diethyl ether because the oxygen atom of ether donates its pair of electrons to the vacant orbital of electron deficient aluminium of $AlCl_3$ through the formation of coordinate bond. In case of hydrated $AlCl_3$, aluminium is not electron deficient as oxygen atom of water molecule has already donated its pair of electrons to meet the electron deficiency of aluminium.



22. (i) $CH \equiv C^-$, C^- is *sp* hybridised and more electronegative than the $\bar{C}H$ of $CH_2 = \bar{C}H$ which is sp^2 hybridised. Thus, the former can better accommodate electron pair and hence, less basic.
(ii) In biphenyl, one of the phenyl groups acts as electron donor and the other electron acceptor due to mesomeric effect. This makes it more reactive than benzene.



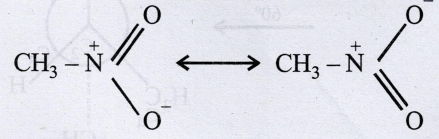
(iii) In formic acid, resonance is not possible, with the result, there are two types of C – O bonds. In sodium formate, resonance is possible, so both of the C – O bonds have same bond length.



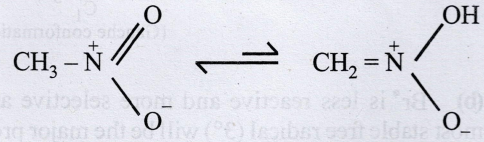
Formic acid Sodium formate (Resonating hybrid)

23. Isobutane < *n*-Butane < *n*-Butyl chloride < *n* - Butanol
Less van der Waals forces More dipole-dipole attraction H-bonding
Straight chain alkane isomer has higher boiling point than the isomeric branched chain isomer because the former isomer has larger surface area which leads to large van der Waals attractive forces.

24. (i)



(ii)



(*nitro* form) (*aci*-form)