SOME BASIC PRINCIPLES OF ORGANIC CHEMISTRY
[JEE ADVANCED PREVIOUS YEAR SOLVED PAPERS]

JEE Advanced

Single Correct Anser Type

1. The bond order of individual carbon–carbon bonds in benzene is

a. one **b.** two
c. between one and two **d.** one and two, alternately

(IIT-JEE 1981)

2. The compound in which the distance between the two adjacent carbon atoms is largest is

a. ethane **b.** ethene
c. ethyne **d.** benzene **(IIT-JEE 1981)**

3. Among the following, the compound that can be most readily sulphonated is

a. benzene **b.** nitrobenzene
c. toluene **d.** chlorobenzene

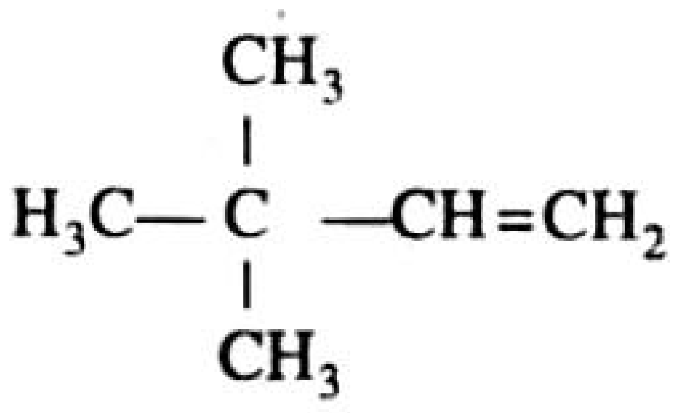
(IIT-JEE 1982)

4. The compound 1,2-butadiene has

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

(IIT-JEE 1983)

5. The IUPAC name of the compound having the formula



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2$$

is:

a. 3, 3, 3-Trimethyl-1-propene
b. 1, 1, 1-Trimethyl-2-propene
c. 3, 3-Dimenthyl-1-butene
d. 2, 2-Dimethyl-3-butene **(IIT-JEE 1984)**

6. The compound that is most reactive towards electrophilic nitration is

a. toluene **b.** benzene
c. benzoic acid **d.** nitrobenzene

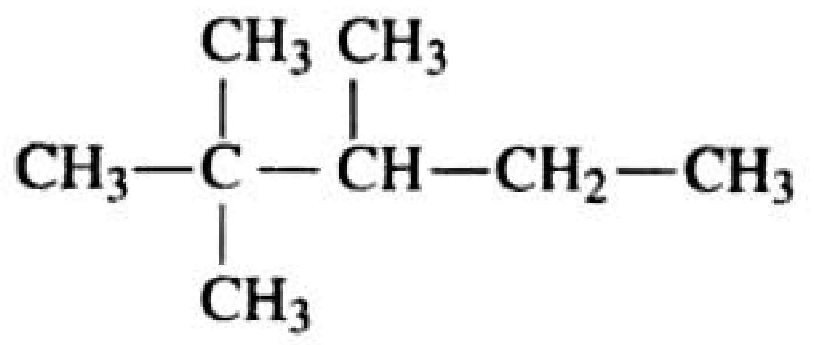
(IIT-JEE 1985)

7. Among the following compounds, the strongest acid is

a. $HC \equiv CH$ **b.** C_6H_6
c. C_2H_6 **d.** CH_3OH **(IIT-JEE 1986)**

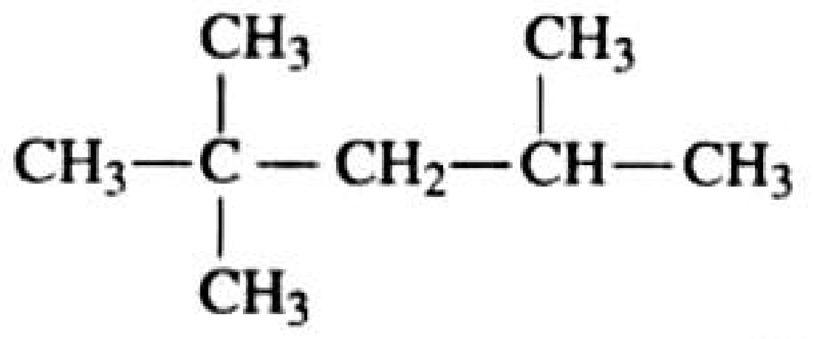
8. Which compound is 2,2,3-trimethyl hexane?

a.



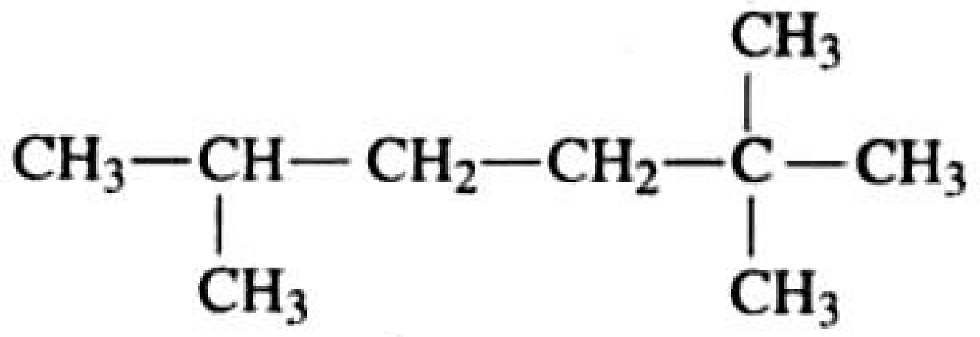
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{CH_3}{CH}-CH_2-CH_3$$

b.

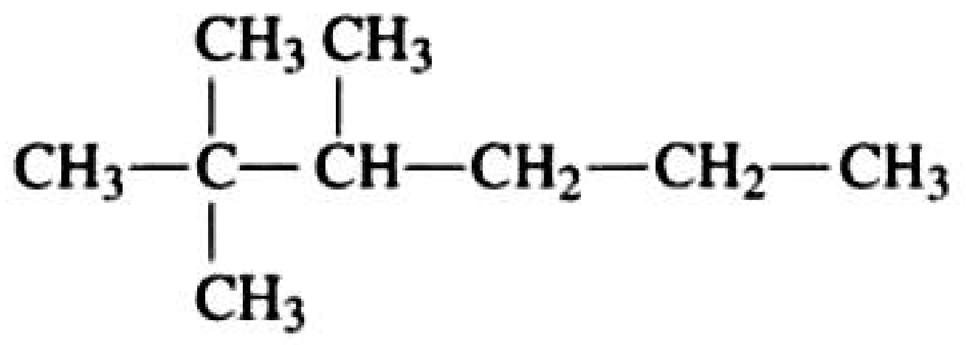


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3$$

c.



$$CH_3-\underset{CH_3}{CH}-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

d. 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{C}H-CH_2-CH_2-CH_3$ **(IIT-JEE 1986)**

9. If two compounds have the same empirical formula but different molecular formula, they must have
- **a.** different percentage composition
- **b.** different molecular weights
- **c.** same velocity
- **d.** same vapour density **(IIT-JEE 1987)**

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

11. 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
- **a.** sp^2 and sp^2
- **b.** sp^3 and sp
- **c.** sp and sp^2
- **d.** sp and sp

(IIT-JEE 1987)

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

13. The Cl – C – Cl angle in 1,1,2,2-tetrachloroethene and tetrachloromethane respectively will be about
- **a.** 120° and 109.5°
- **b.** 90° and 109.5°
- **c.** 109.5° and 90°
- **d.** 109.5° and 120°

(IIT-JEE 1988)

14. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is
- **a.** C – C
- **b.** C – O
- **c.** C – H
- **d.** O – H

(IIT-JEE 1988)

15. Polarisation of electrons in acrolein may be written as
- **a.** $\overset{-\delta}{C}H_2 = CH - \overset{+\delta}{C} = O$
- **b.** $\overset{-\delta}{CH_2} = CH - CH = \overset{+\delta}{O}$
- **c.** $\overset{-\delta}{CH_2} = \overset{+\delta}{CH} - CH = O$
- **d.** $\overset{+\delta}{CH_2} = CH - CH = \overset{-\delta}{O}$

(IIT-JEE 1988)

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

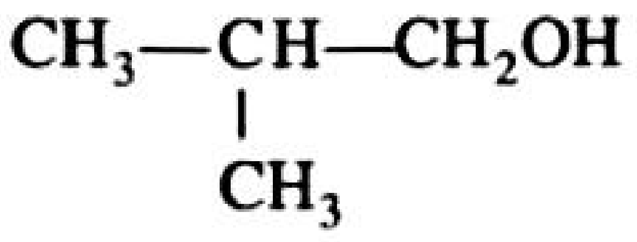
17. The C—H bond distance is the longest is
- **a.** C_2H_2
- **b.** C_2H_4
- **c.** C_2H_6
- **d.** $C_2H_2Br_2$

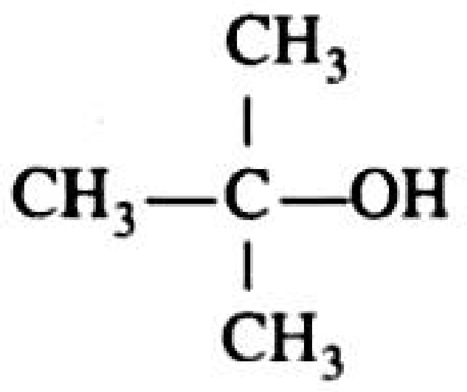
(IIT-JEE 1989)

18. The number of sigma and pi-bonds in 1-butene-3-yne are
- **a.** 5 sigma and 5 pi
- **b.** 7 sigma and 3 pi
- **c.** 8 sigma and 2 pi
- **d.** 5 sigma and 4 pi

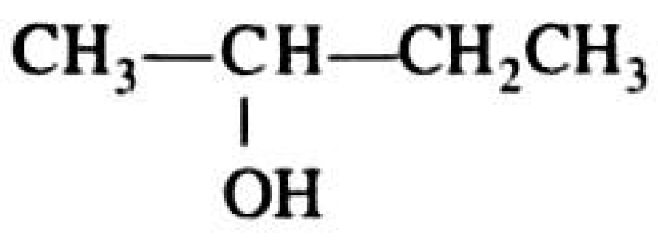
(IIT-JEE 1989)

19. The compound which gives the most stable carbonium ion on dehydration is

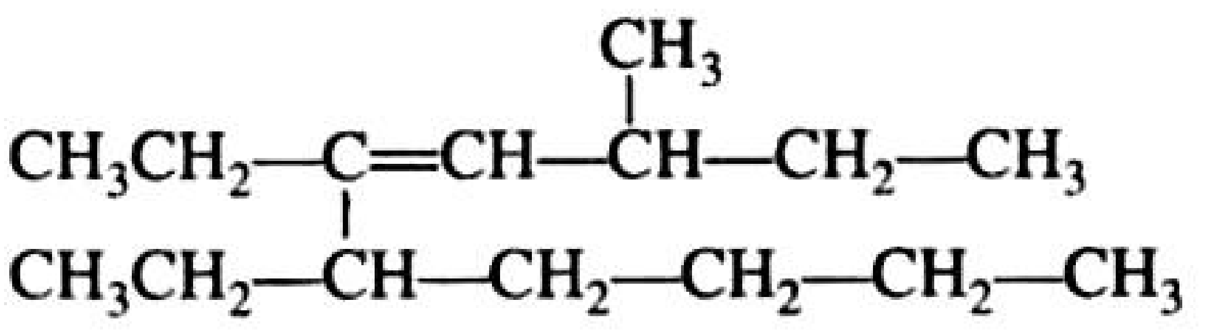
a. 
$CH_3-\underset{CH_3}{CH}-CH_2OH$

b. 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$

c. $CH_3 - CH_2 - CH_2 - CH_2OH$

d. 
$CH_3-\underset{OH}{CH}-CH_2CH_3$ **(IIT-JEE 1989)**

20. The correct IUPAC name of the compound is


$CH_3CH_2-\underset{CH_3CH_2-CH-CH_2-CH_2-CH_2-CH_3}{C}=CH-\overset{CH_3}{C}H-CH_2-CH_3$

- **a.** 5,6-Diethyl-3-methyl dec-4-ene
- **b.** 5,6-Diethyl-8-methyl dec-6-ene
- **c.** 6-Butyl-5-ethyl-3-methyl oct-4-ene
- **d.** 2,4,5-Triethyl-3-nonene **(IIT-JEE 1990)**

21. The hybridization of carbon atoms in C—C single bond of $HC \equiv C - CH = CH_2$ is
- **a.** $sp^3 - sp^3$
- **b.** $sp^2 - sp^3$
- **c.** $sp - sp^2$
- **d.** $sp^3 - sp$

(IIT-JEE 1991)

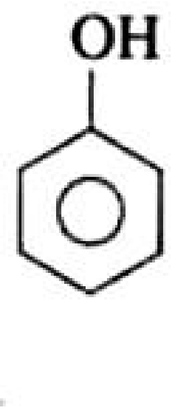
22. Allyl isocyanide has
- **a.** 9σ and 4π bonds
- **b.** 8σ and 5π bonds
- **c.** 9σ, 3π and 2 non-bonded electrons
- **d.** 8σ, 3π and 4 non-bonded electrons **(IIT-JEE 1995)**

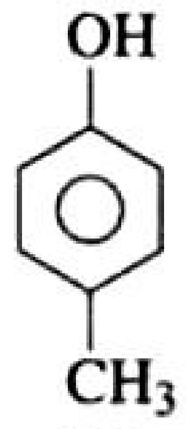
23. Arrange in order of decreasing trend towards S_E reactions: chlorobenzene, benzene, anilinium chloride, toluene
I II III IV
- **a.** II > I > III > IV
- **b.** III > I > II > IV
- **c.** IV > II > I > III
- **d.** I > II > III > IV

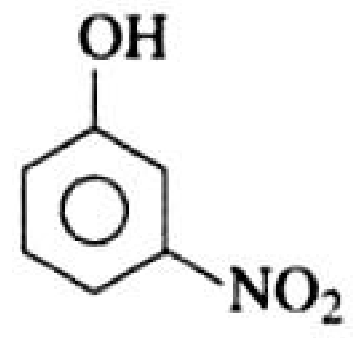
(IIT-JEE 1995)

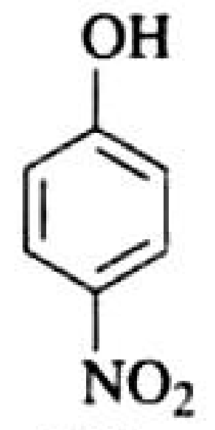
24. Most stable carbonium ion is
- **a.** $p - NO_2 - C_6H_4 - CH_2^+$
- **b.** $C_6H_5CH_2^+$
- **c.** $p - Cl - C_6H_4 - CH_2^+$
- **d.** $p - CH_3O - C_6H_4 - CH_2^+$ **(IIT-JEE 1996)**

25. In the following compounds,


(I)


(II)


(III)


(IV)

The order of acidity is

a. III > IV > I > II **b.** I > IV > III > II

c. II > I > III > IV **d.** IV > III > I > II

(IIT-JEE 1996)

26. Arrange the following compounds in order of increasing dipole moment.

Toluene (I) *m*-dichlorobenzene (II)

o-dichlorobenzene (III) *p*-dichlorobenzene (IV)

a. I < IV < II < III **b.** IV < I < II < III

c. IV < I < III < II **d.** IV < II < I < III

(IIT-JEE 1996)

27. In the following groups:

–OAc	–OMe	$-OSO_2Me$	$-OSO_2CF_3$
I	II	III	IV

the order of leaving group ability is

a. I > II > III > IV **b.** IV > III > I > II

c. III > II > I > IV **d.** II > III > IV > I

(IIT-JEE 1997)

28. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is

a. MeCOCl **b.** MeCHO

c. MeCOOMe **d.** MeCOOCOMe

(IIT-JEE 1997)

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

a. $sp - sp^2$ **b.** $sp^3 - sp^3$ **c.** $sp - sp^3$ **d.** $sp^2 - sp^3$

(IIT-JEE 1999)

30. Which of the following has the highest nucleophilicity?

a. F^- **b.** OH^- **c.** CH_3^- **d.** NH_2^-

(IIT-JEE 2000)

31. The order of reactivities of the following alkyl halides for an S_N2 reaction is

a. RF > RCl > RBr > RI **b.** RF > RBr > RCl > RI

c. RCl > RBr > RF > RI **d.** RI > RBr > RCl > RF

(IIT-JEE 2000)

32. Which of the following has the most acidic hydrogen?

a. 3-Hexanone **b.** 2, 4-Hexanedione

c. 2, 5-Hexanedione **d.** 2, 3-Hexanedione

(IIT-JEE 2000)

33. An S_N2 reaction at an asymmetric carbon of a compound always gives

a. an enantiomer of the substrate

b. a product with opposite optical rotation

c. a mixture of diastereomers

d. a single stereoisomer **(IIT-JEE 2001)**

34. Which of the following acids has the smallest dissociation constant?

a. $CH_3CHFCOOH$ **b.** FCH_2CH_2COOH

c. $BrCH_2CH_2COOH$ **d.** $CH_3CHBrCOOH$

(IIT-JEE 2002)

35. Identify the correct order of boiling points of the following compounds:

$CH_3CH_2CH_2CH_2OH$, 1

$CH_3CH_2CH_2CHO$, 2

$CH_3CH_2CH_2COOH$ 3

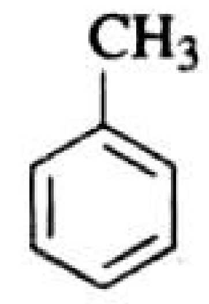
a. 1 > 2 > 3 **b.** 3 > 1 > 2

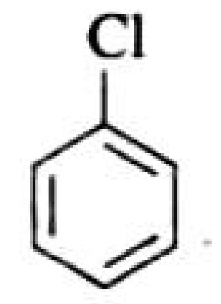
c. 1 > 3 > 2 **d.** 3 > 2 > 1

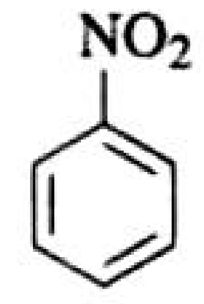
(IIT-JEE 2002)

36. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds


1


2


3

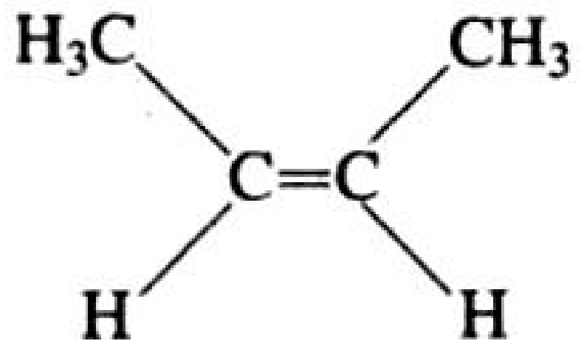

4

a. 1 > 2 > 3 > 4 **b.** 4 > 3 > 2 > 1

c. 2 > 1 > 3 > 4 **d.** 2 > 3 > 1 > 4

(IIT-JEE 2002)

37. Which of the following hydrocarbons has the lowest dipole moment?

a. 

b. $CH_3C \equiv CCH_3$

c. $CH_3CH_2C \equiv CH$ **d.** $CH_2 = CH - C \equiv CH$

(IIT-JEE 2002)

38. Which of the following represents the given mode of hybridization $sp^2 - sp^2 - sp - sp$ from left to right?

a. $H_2C = CH - C \equiv N$ **b.** $HC \equiv C - C \equiv CH$

c. $H_2C = C = C = CH_2$ **d.** 

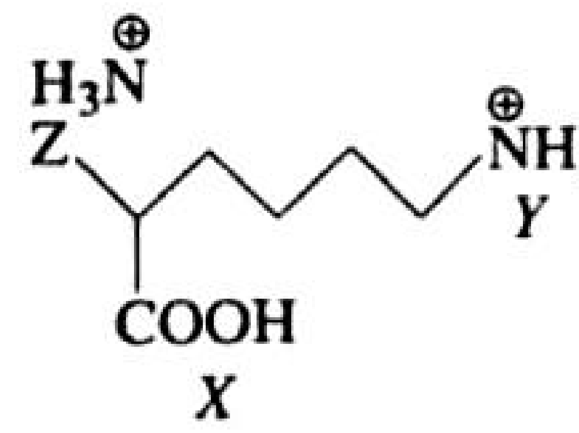
(IIT-JEE 2003)

39. Among the following, the molecule with the highest dipole moment is

a. CH_3Cl **b.** CH_2Cl_2 **c.** $CHCl_3$ **d.** CCl_4

(IIT-JEE 2003)

40. Arrange in the order of increasing acidic strengths.



a. X > Z > Y **b.** Z < X > Y

c. X > Y > Z **d.** Z > X > Y

(IIT-JEE 2004)

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

a. $\overset{\ominus}{C}H_2 - CH = CH - CH = \overset{\oplus}{O} - CH_3$

b. $CH_2 = CH - \overset{\ominus}{C}H - CH = \overset{\oplus}{O} - CH_3$

c. $\overset{\ominus}{C}H_2 - \overset{\oplus}{CH} - CH = CH - O - CH_3$

d. $CH_2 = CH - \overset{\ominus}{C}H - \overset{\oplus}{C}H - O - CH_3$ **(IIT-JEE 2005)**

42. The IUPAC name of C_6H_5COCl is

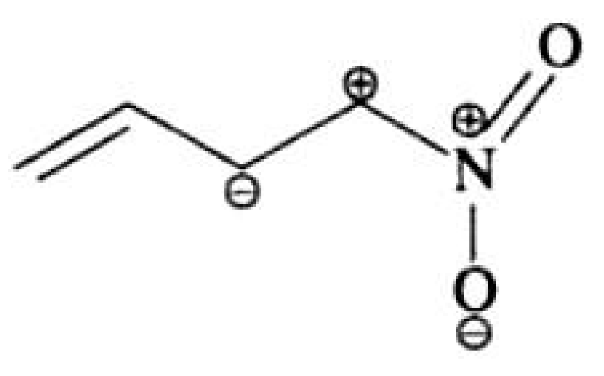
a. benzene chloro ketone **b.** benzoyl chloride

c. chloro phenyl ketone **d.** benzene carbonyl chloride

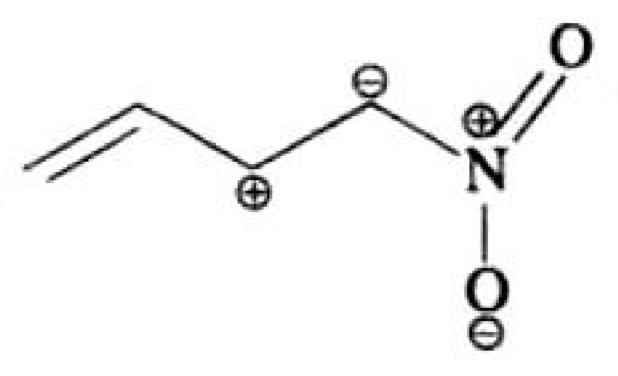
(IIT-JEE 2006)

43. Among the following, the least stable resonance structure is

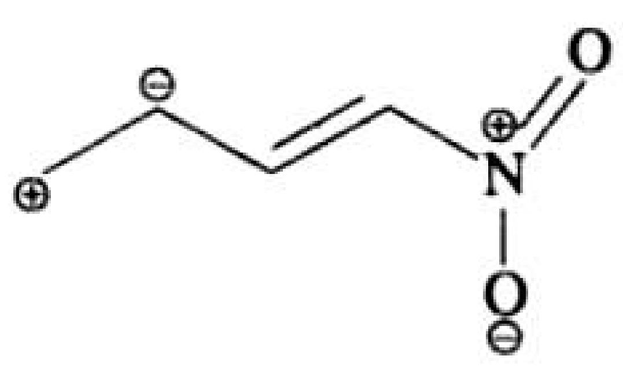
a.



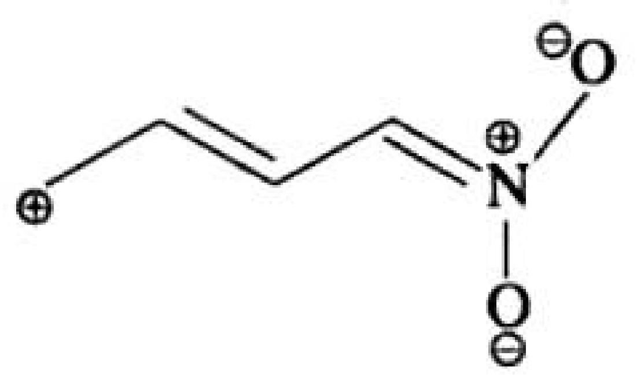
b.



c.



d.



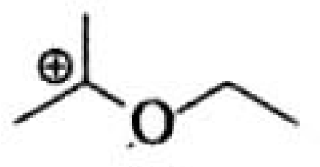
(IIT-JEE 2007)

44. Hyperconjugation involves overlap of the following orbitals:

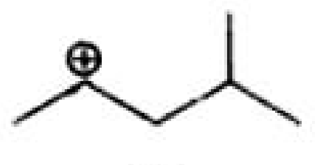
a. $\sigma - \sigma$ **b.** $\sigma - \pi$ **c.** $p - p$ **d.** $\pi - \pi$

(IIT-JEE 2008)

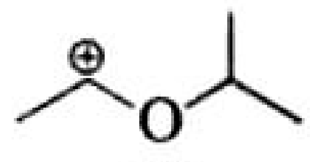
45. The correct stability order for the following species is



(I)



(II)



(III)

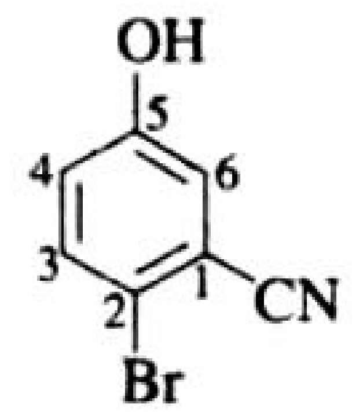
(IV)

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

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

(IIT-JEE 2008)

46. The IUPAC name of the following compound is



a. 4-Bromo-3-cyanophenol

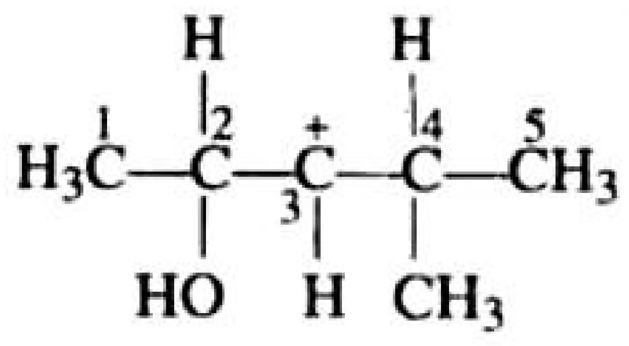
b. 2-Bromo-5-hydroxybenzonitrile

c. 2-Cyano-4-hydroxybromobenzene

d. 6-Bromo-3-hydroxybenzonitrile

(IIT-JEE 2009)

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



a. CH_3 at C – 4 **b.** H at C – 4

c. CH_3 at C – 2 **d.** H at C – 2

(IIT-JEE 2009)

48. The correct order of stabilities of the following resonance structure is

$H_2C = \overset{\oplus}{N} = \overset{\ominus}{N}$ (I) $H_2\overset{\oplus}{C} - N = \overset{\ominus}{N}$ (II)

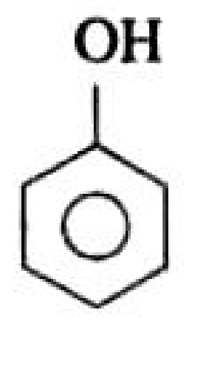
$H_2\overset{\ominus}{C} - \overset{\oplus}{N} \equiv N$ (III) $H_2\overset{\ominus}{C} - N = \overset{\oplus}{N}$ (IV)

a. I > II > IV > III **b.** I > III > II > IV

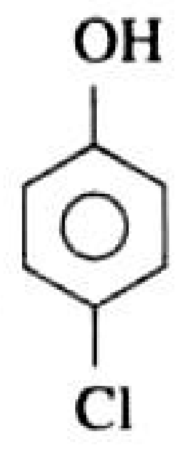
c. II > I > III > IV **d.** III > I > IV > II

(IIT-JEE 2009)

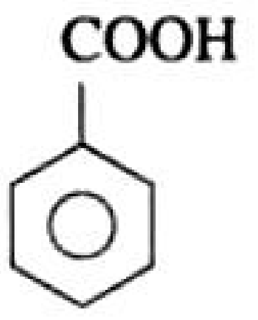
49. The correct order of acidities of the following is



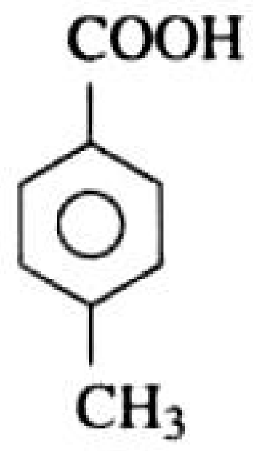
I



II



III



IV

a. III > IV > II > I **b.** IV > III > I > II

c. III > II > I > IV **d.** II > III > IV > I

(IIT-JEE 2009)

50. Among the following compounds, the most acidic is

a. *p*-nitrophenol **b.** *p*-hydroxybenzoic acid

c. *o*-hydroxybenzoic acid **d.** *p*-toluic acid

(IIT-JEE 2011)

51. In allene (C_3H_4), the type(s) of hybridization of the carbon atoms is (are)

a. sp and sp^3 **b.** sp and sp^2

c. only sp^2 **d.** sp^2 and sp^3

(IIT-JEE 2012)

52. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to

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

(JEE Advanced 2013)

Multiple Correct Answers Type

1. Resonance structures 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 **(IIT-JEE 1984)**

2. Phenol is less acidic than

a. acetic acid **b.** *p*-methoxyphenol

c. *p*-nitrophenol **d.** ethanol

(IIT-JEE 1986)

3. Dipole moment is shown by

a. 1, 4-dichlorobenzene

b. cis 1,2-dichloroethane

c. trans-1,2-dichloroethene

d. trans-1,2-dichloro-2-pentene **(IIT-JEE 1986)**

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

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. $NH_2^- > H - C \equiv C^- > OH^- > CH_3 - CH_2^-$

(IIT-JEE 1993)

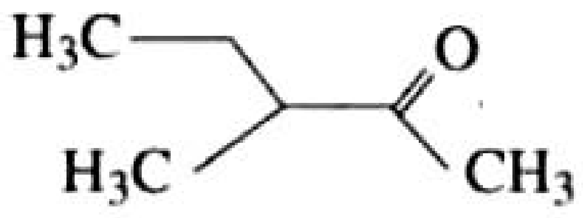
5. An aromatic molecule will

a. have $4n$ π electrons **b.** have $(4n + 2)$ π electrons

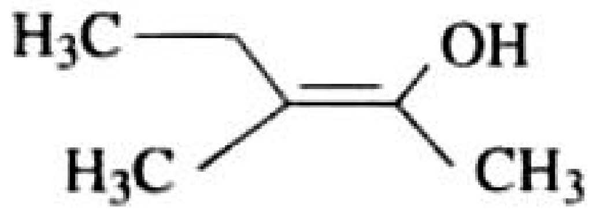
c. be planar **d.** be cyclic

(IIT-JEE 1999)

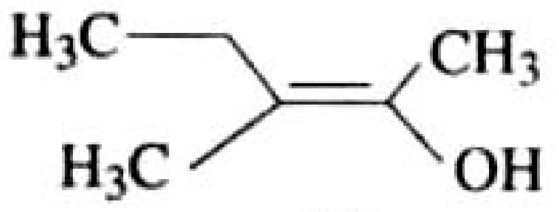
6. The correct statements(s) concerning the structures E, F and G is (are)–



(E)



(F)



(G)

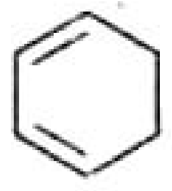
a. E, F and G are resonance structures

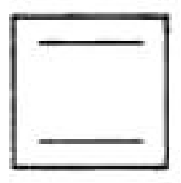
b. E, F and E, G are tautomers

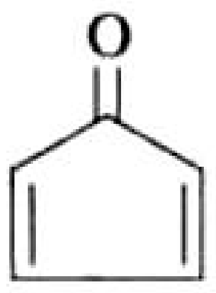
c. F and G are geometrical isomers

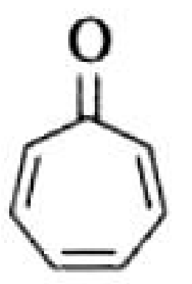
d. F and G are diastereomers **(IIT-JEE 2008)**

7. Which of the following molecules, in pure form, is (are) unstable at room temperature?

a. 

b. 

c. 

d. 

(IIT-JEE 2012)

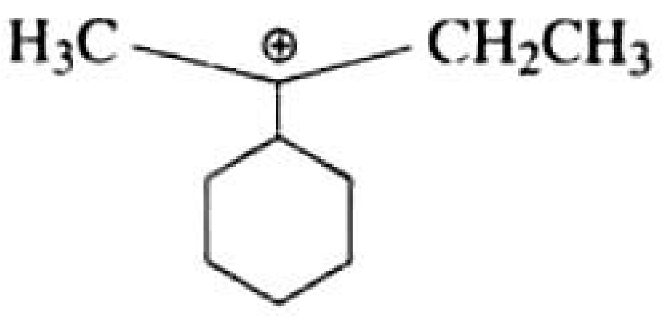
8. The compounds in which C uses its sp^3-hybrid orbitals for bond formation are:

a. HCOOH **b.** $(H_2N)_2CO$

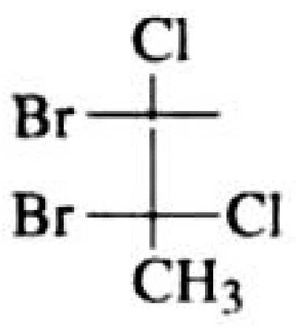
c. $(CH_3)_3COH$ **d.** CH_3CHO

Integer Answer Type

1. The total number of contributing structures showing hyperconjugation (involving C – H bonds) for the following carbocation is **(IIT-JEE 2011)**



2. The total number(s) of stable conformers with non-zero dipole moment for the following compound is (are) **(JEE Advanced 2014)**



Assertion-Reasoning Type

Read the following Statement 1 and Statement 2 and answer as per the options given below:

a. If both Statement 1 and Statement 2 are correct, and Statement 2 is the correct explanation of the Statement 2.

b. If both Statement 1 and Statement 2 are correct, but Statement 2 is not the correct explanation of the Statement 1.

c. If Statement 1 is correct but Statement 2 is incorrect.

d. If Statement 1 is incorrect but Statement 2 is correct.

1. Statement 1: Aryl halides undergo nucleophilic substitution with ease.

Statement 2: The carbon–halogen bond in aryl halides has partial double bond character. **(IIT-JEE 1991)**

2. Statement 1: Phenol is more reactive than benzene towards electrophilic substitution reactions.

Statement 2: In the case of phenol, the intermediate carbocation is more resonance stabilized.

(IIT-JEE 2000)

3. Statement 1: Molecules that are not superimposable on their mirror images are chiral.

Statement 2: All chiral molecules have chiral centres.

(IIT-JEE 2007)

Fill in the Blanks Type

1. Among the given cations, ______ is most stable.

(IIT-JEE 1981)

(sec butyl carbonium ion; tert-butyl carbonium ion; *n*-butyl carbonium ion)

2. The compound having both sp and sp^2 hybridized carbon atoms is ______. **(IIT-JEE 1981)**

(propene, propane, propadiene)

3. ______ ring is most strained. **(IIT-JEE 1981)**

(Cyclopropane, Cyclobutane, Cyclopentane)

4. The terminal carbon atom in butane is ______ hybridized.

(IIT-JEE 1985)

5. A ______ diol has two hydroxyl groups on ______ carbon atoms. **(IIT-JEE 1986)**

6. The valence atomic orbitals on carbon in silver acetylide is ______ hybridized. **(IIT-JEE 1990)**

7. The shape $(CH_3)^{\oplus}$ is ______. **(IIT-JEE 1990)**

8. The bond dissociation energy needed to form the benzyl radical from toluene is ______ than the formation of the methyl radical from methane. **(IIT-JEE 1994)**

9. The kind of delocalization involving sigma bond orbitals is called ______. **(IIT-JEE 1994)**

10. The IUPAC name of succinic acid is ______.

(IIT-JEE 1994)

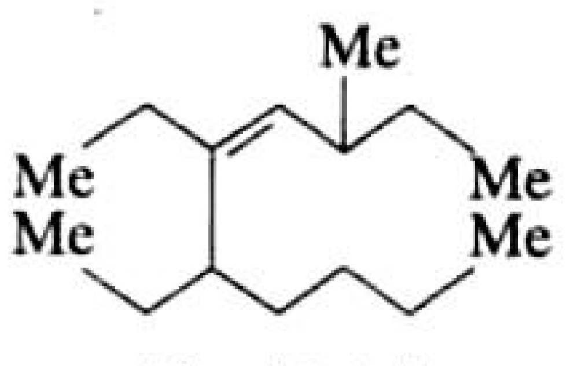
11. Among PCl_3, CH_3^+, NH_2^- and NF_3, ______ is least reactive towards water. **(IIT-JEE 1997)**

True / False Type

1. Iodide is a better nucleophile than bromide. **(IIT-JEE 1985)**
2. An electron donating substituent in benzene orients the incoming electrophilic group to the meta position. **(IIT-JEE 1987)**
3. During S_N1 reaction, the leaving group leaves the molecule before the incoming group is attached to the molecule. **(IIT-JEE 1990)**

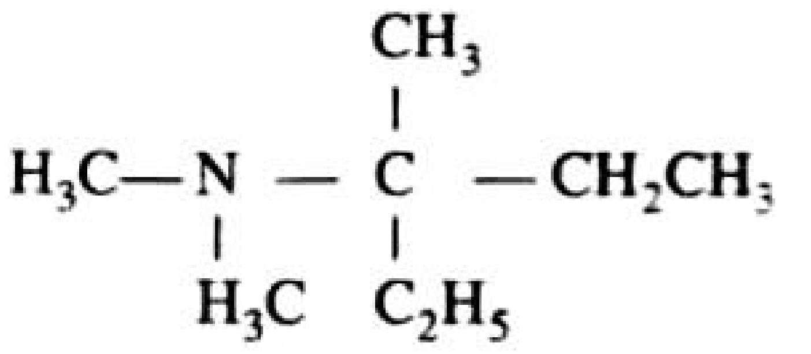
Subjective Type

1. Arrange the following in the increasing reactivity towards HCN:
CH_3CHO, CH_3COCH_3, HCHO, $C_2H_5COCH_3$ **(IIT-JEE 1985)**
2. Arrange the following in the increasing order of their basicities.
I. *p*-Toluidine **II.** *N, N*-Dimethyl-*p*-toluidine
III. *p*-Nitroaniline **IV.** Aniline
(IIT-JEE 1986)
3. Write the IUPAC name of:
$CH_3CH_2CH = CHCOOH$ **(IIT-JEE 1986)**
4. For nitromethane molecule, write structure(s):
   i. Showing significant resonance stabilization.
   ii. Indicating tautomerism. **(IIT-JEE 1986)**
5. Give the IUPAC name of the following compound: $CH_2 = CH - CH(CH_3)_2$. **(IIT-JEE 1987)**
6. Arrange the following in
   i. *n*-butane, *n*-butanol, *n*-butyl chloride, isobutane in increasing order of boiling point.
   ii. benzene, toluene, methoxybenzene, chlorobenzene in increasing order of reactivity towards sulphonation with fuming sulphuric acid. **(IIT-JEE 1988)**
7. Give reason:
"Carbon oxygen bond lengths in formic acid are 1.23 Å and both the carbon oxygen bonds in sodium formate have the same value i.e. 1.27 Å." **(IIT-JEE 1988)**
8. Write the structural formula of 4-chloro-2-pentene. **(IIT-JEE 1988)**
9. Give the IUPAC name of the following compound: **(IIT-JEE 1990)**



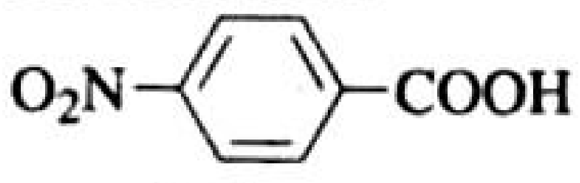
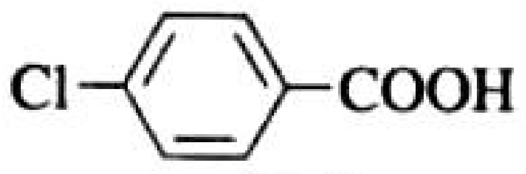
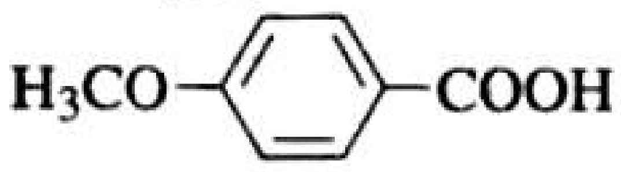
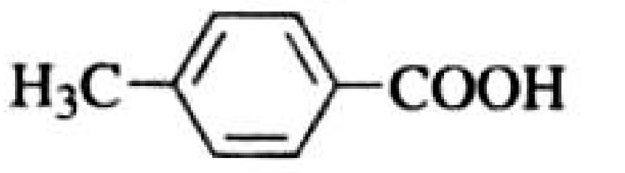
(Me = Methyl)

10. Arrange the following in increasing order of acid strength:
$ClCH_2COOH$ (I), CH_3CH_2COOH (II), $ClCH_2CH_2COOH$ (III), $(CH_3)_2CHCOOH$ (IV), CH_3COOH (V) **(IIT-JEE 1991)**
11. Write the IUPAC name for the following:

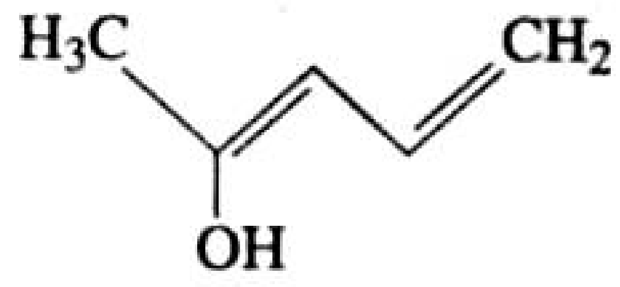


$H_3C-N(CH_3)-C(CH_3)(C_2H_5)-CH_2CH_3$

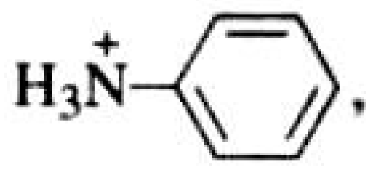
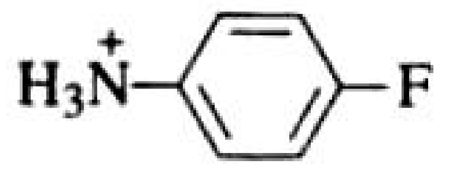
(IIT-JEE 1991)
12. Arrange the following in increasing reactivity in nucleophilic substitution reactions
CH_3F, CH_3I, CH_3Br, CH_3Cl **(IIT-JEE 1992)**
13. Phenyl group is known to exert negative inductive effect. But each phenyl ring in biphenyl ($C_6H_5 - C_6H_5$) is more reactive than benzene towards electrophilic substitution. Explain. **(IIT-JEE 1992)**
14. Give reasons for the following:
   i. Aryl halides are less reactive than alkyl halides towards nucleophilic reagents
   ii. $CH_2 = CH^-$ is more basic than $HC \equiv C^-$.
   iii. Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds. **(IIT-JEE 1994)**
15. Discuss the hybridization of carbon atoms in allene (C_3H_4) and show the π-orbital overlaps. **(IIT-JEE 1999)**
16. Match the K_a values

		K_a values
a.	Benzoic acid	6.4×10^{-5}
b.		30.6×10^{-5}
c.		10.2×10^{-5}
d.		3.3×10^{-5}
e.		4.2×10^{-5}

(IIT-JEE 2003)
17. Write resonance structures of the given compound.



(IIT-JEE 2004)
18. Which of the following is more acidic and why?

,  **(IIT-JEE 2004)**

19. **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 Newmann projection. **(IIT-JEE 2005)**

Answer Key

JEE Advanced

Single Correct Answer Type

1. c. **2.** a. **3.** c. **4.** d. **5.** c.
6. a. **7.** d. **8.** d. **9.** b. **10.** c.
11. c. **12.** b. **13.** a. **14.** d. **15.** d.
16. d. **17.** c. **18.** b. **19.** b. **20.** a.
21. c. **22.** c. **23.** c. **24.** d. **25.** d.
26. b. **27.** b. **28.** a. **29.** d. **30.** c.
31. d. **32.** b. **33.** d. **34.** c. **35.** b.
36. c. **37.** b. **38.** a. **39.** a. **40.** a.
41. c. **42.** b. **43.** a. **44.** b. **45.** d.
46. b. **47.** d. **48.** b. **49.** a. **50.** c.
51. b. **52.** a.

Multiple Correct Answers Type

1. a., b., c. **2.** a., c. **3.** b., d. **4.** a.
5. b., c., d. **6.** b., c., d. **7.** b., c. **8.** c., d.

Integer Answer Type

1. (7) 2. (3)

Assertion–Reasoning Type

1. d. **2.** a. **3.** c.

Fill in the Blanks Type

1. tert-butyl carbonium ion **2.** propadiene
3. cyclopropane **4.** sp^3
5. vicinal, adjacent **6.** sp
7. planer **8.** less
9. hyperconjugation **10.** butane-1, 4-dioic acid
11. $NH_2^{\ominus}$

True/False Type

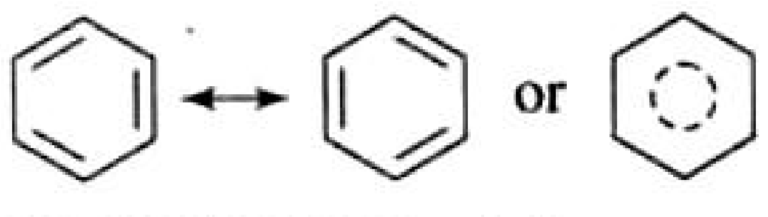
1. False **2.** False **3.** True

Hints and Solutions

JEE Advanced

Single Correct Anser Type

1. c. The phenomenon of resonance gives identical bonding, so identical bond lengths.

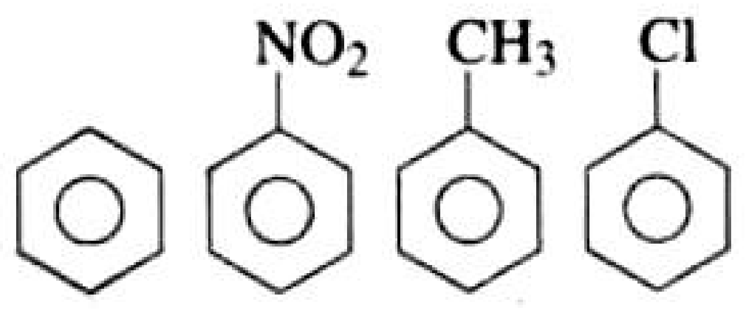


C – C bond order in benzene = 1.5

2. a. Bond length order: $\underset{154}{C–C} > \underset{134}{C=C} > \underset{120\text{ pm}}{C \equiv C}$

In benzene, due to resonance, the bond length lies in between single and double bonds and is 139 pm.

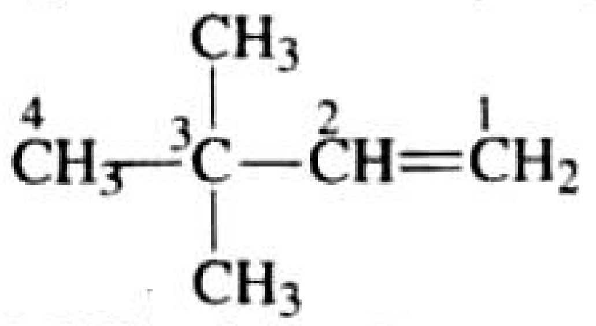
3. c. Sulphonation is electrophilic substitution reaction. Any factor that increases e^- density on benzene increases its rate.
$-NO_2$, $-Cl$ and $-OH$ are electron-attracting or withdrawing group due to –M, –E and/or –I effects whereas $-CH_3$ shows +I effect (electron releasing).
Because of the +I effect of the CH_3 group, toluene has the highest electron density in the *o*- and *p*-positions and hence can be most readily sulphonated.



order is c > a > d > b

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

5. c.



$$\overset{4}{C}H_3-\overset{3}{\underset{CH_3}{\overset{CH_3}{C}}}-\overset{2}{C}H=\overset{1}{C}H_2$$

3, 3-Dimethylbut-1-*ene*

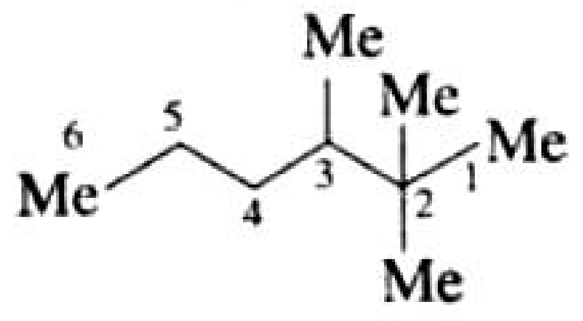
6. a. +I effect of $(-CH_3)$ group increases the electron density on the benzene ring, hence it is most reactive towards electrophilic nitration.

7. d. Order of acidic strength is

$$CH_3OH > HC \equiv CH > C_6H_6 > C_2H_6$$

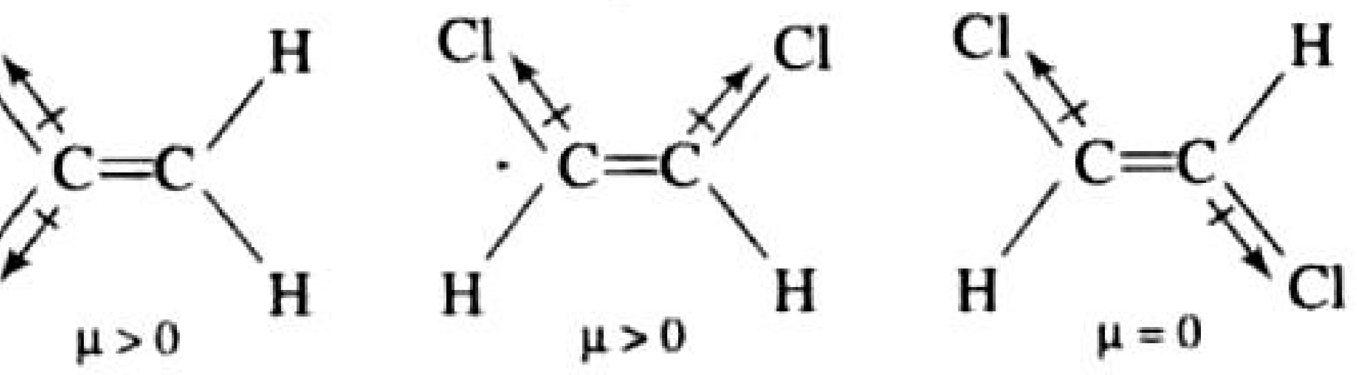
CH_3OH is most acidic because O is more electronegative than C and capable of accommodating negative charge in CH_3O^-.

8. d. Structure of 2,2,3-trimethyl hexane.



9. b. Different molecular weights.

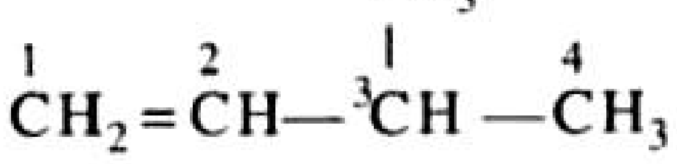
10. c. Dipole moment is a vector quantity



μ > 0 (a) μ > 0 (b) μ = 0 (c)

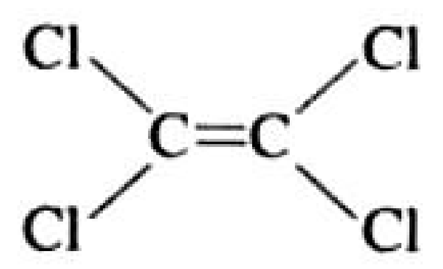
11. c. Carbon bonded with a triple bond (i.e. C_1) is sp hybridized.
Carbon bonded with a double bond (C_2) is sp^2 hybridised.
If C makes 4σ-bonds then C is sp^3 hybridized.
If C makes 3σ + 1π bonds then C is sp^2 hybridized.
If C makes 2σ + 2π bonds then C is sp hybridized.

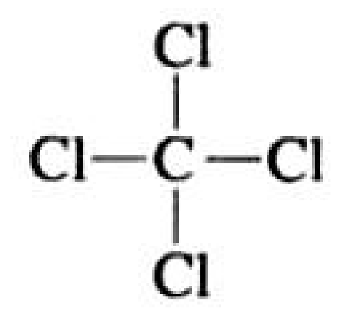
12. b.



$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{\underset{}{\overset{CH_3}{C}}}H-\overset{4}{C}H_3 \text{ (3-Methyl-1-butene)}$$

13. a. The bond angle in sp^3, sp^2 and sp hybridization is respectively 109.28°, 120° and 180°.
Tetrachloroethene being an alkene has sp^2 hybridised C-atoms and hence the Cl – C – Cl angle is 120°, whereas in tetrachloromethane, carbon is sp^3 hybridised, so the angle is 109°.28′.



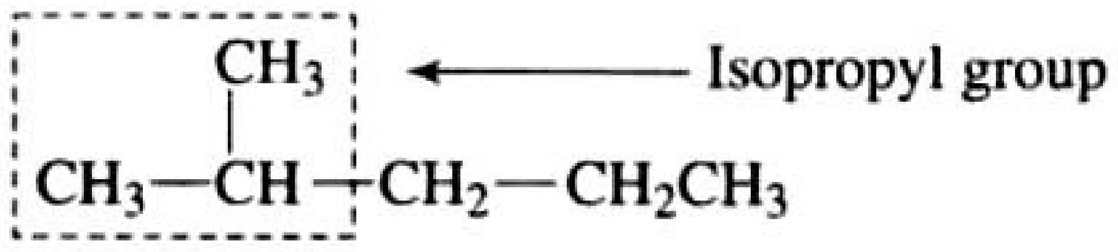


14. d. Heterolytic fission occurs when the two atoms differ considerably in their electronegativities.

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.

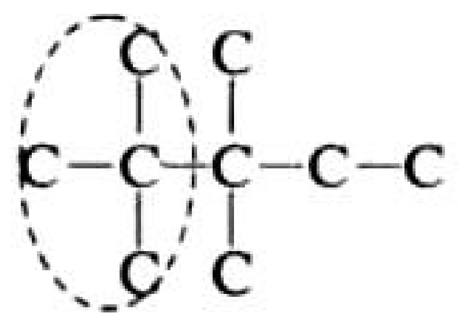
15. d. O atom is more electronegative than C atom, so it acquires (–δ) charge and C atom acquires (+δ) charge which is transferred to the last atom.

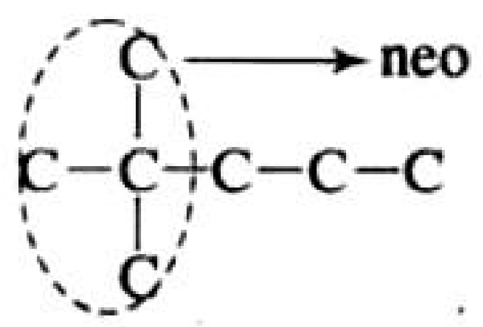
16. d.



$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_2CH_3$ ← Isopropyl group

2-Methylpentane

a. 

b. 

17. c. C_2H_6 is a saturated hydrocarbon and its carbon is sp^3 hybridised. Hence it is least electronegative among alkanes, alkenes and alkynes, with the result C – H bond length will be maximum.

18. b. $CH_2=CH-C\equiv CH$;

No. of σ bonds = 2 + 1 + 1 + 1 + 1 + 1 = 7;

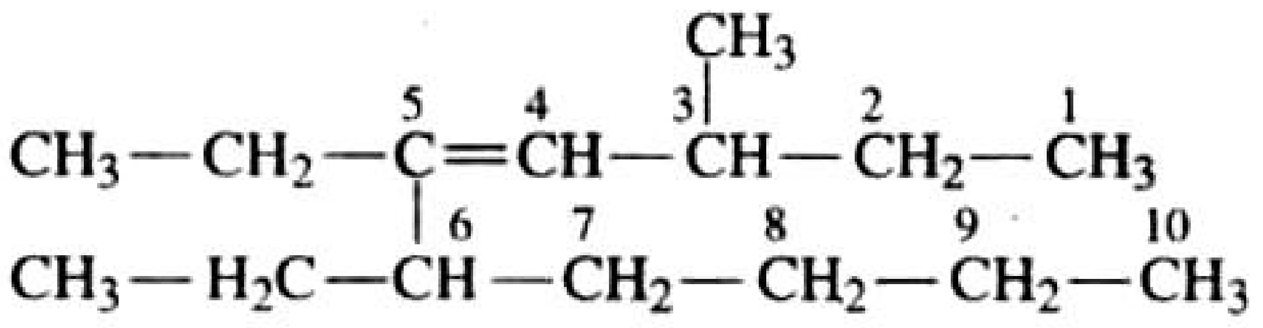
No. of π bonds = 1 + 2 = 3

19. b. The order of stability of carbonium ion is

tertiary > secondary > primary > methyl

Tertiary carbonium ions (in b) are more stable because of electron releasing (+ I effect) nature of CH_3 group due to which the +ve charge gets dispersed to maximum extent.

20. a.



$CH_3-CH_2-\overset{5}{C}=\overset{4}{C}H-\overset{3}{C}H(CH_3)-\overset{2}{C}H_2-\overset{1}{C}H_3$, with C-5 bearing $\overset{6}{C}H(CH_2CH_3)-\overset{7}{C}H_2-\overset{8}{C}H_2-\overset{9}{C}H_2-\overset{10}{C}H_3$

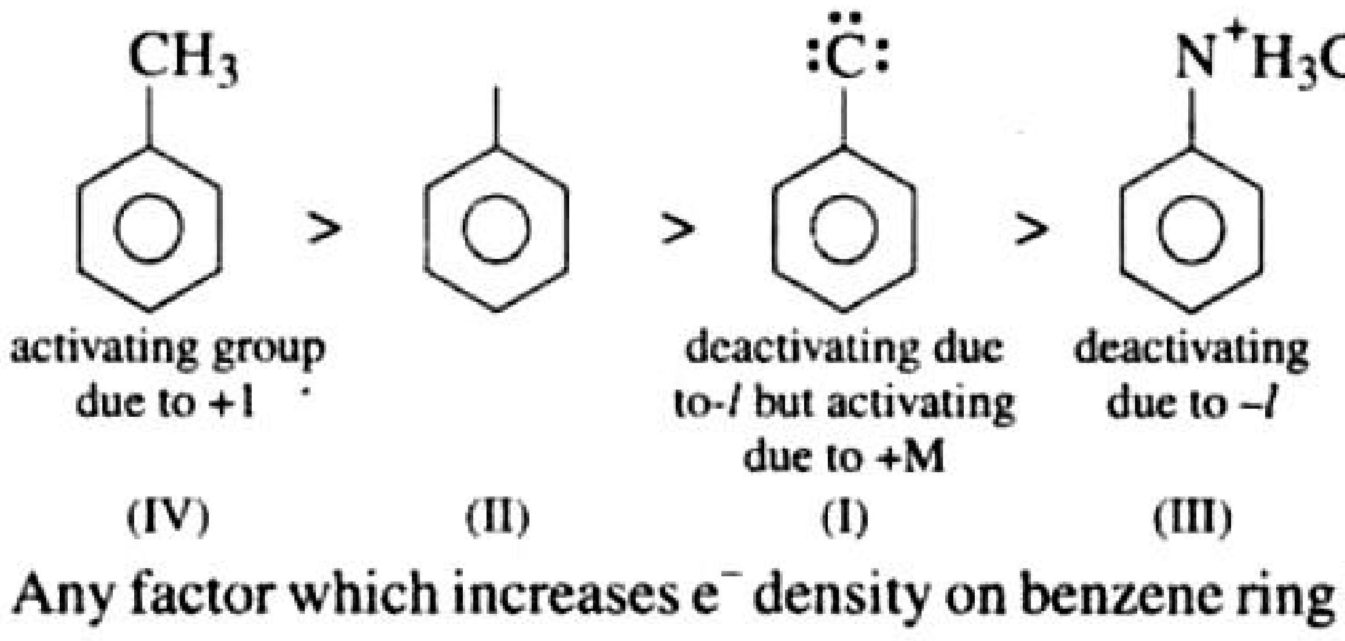
(5,6-Diethyl-3-methyl dec-4-ene)

21. c. $HC\equiv\overset{sp}{C}-\overset{sp^2}{C}H=CH_2$

22. c. $CH_2=CH-CH_2-N\overset{\rightarrow}{=}C:$

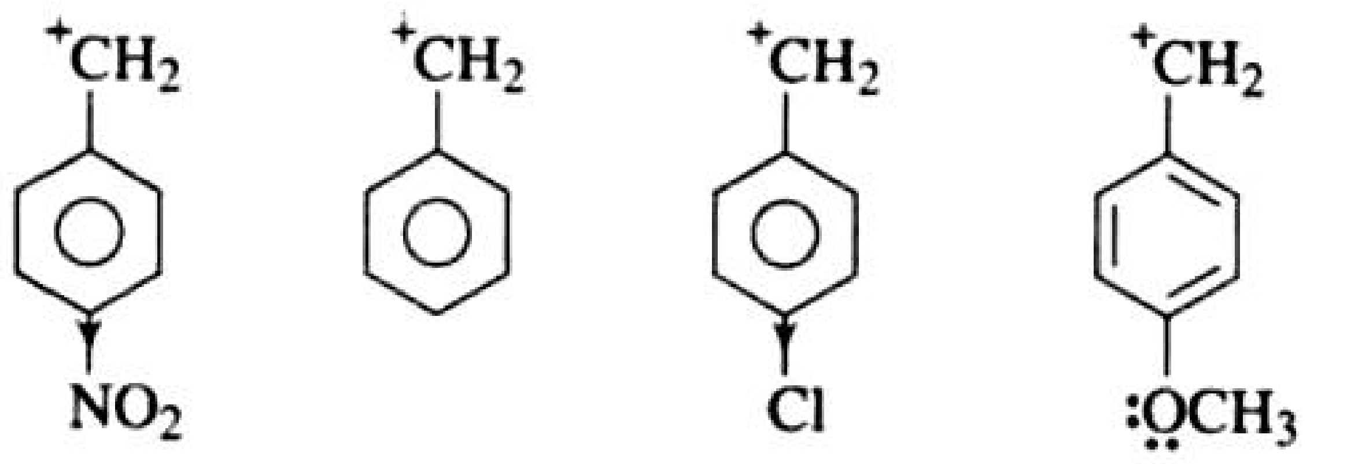
Allyl isocyanide structure shows 5C – H (σ), 2C – C (σ), 1C – N(σ), 1N – C (σ), 1C – C (π) 2N – C (π) bonds, i.e. 9σ and 3π bonds in all. There are 2 non-bonded electrons on the C-atom (coordinate bond between N and C, the electron pair of N is shifted towards C).

23. c.



Any factor which increases e⁻ density on benzene ring increases rate towards electrophilic substitution.

24. d. The stability of carbonium ion is influenced by both resonance and inductive effect.



NO₂ intensifies +ve charge on benzyl cation due to –I and –M effects

Benzyl stable due to resonance

Cl intensifies +ve charge on C due to –I effect

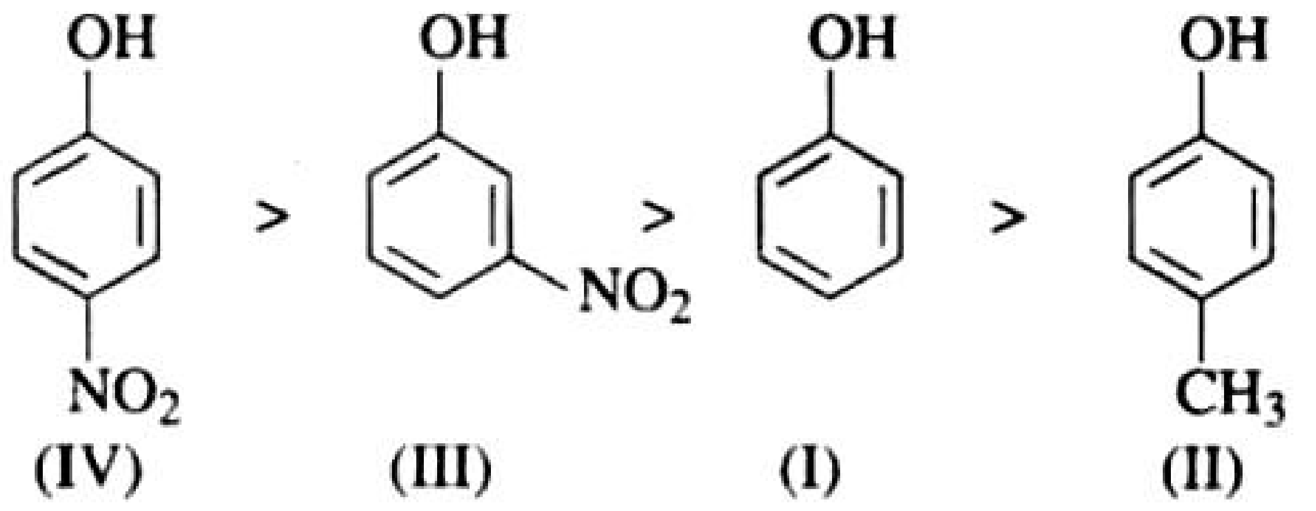
Positive charge of benzyl cation is more dispersed due to +M effect of the –OCH₃ group

25. d. Any factor which stabilizes phenoxide ion makes the corresponding phenol more acidic.

$-NO_2$ is an electron-attracting group whereas $-CH_3$ is an electron-releasing group.

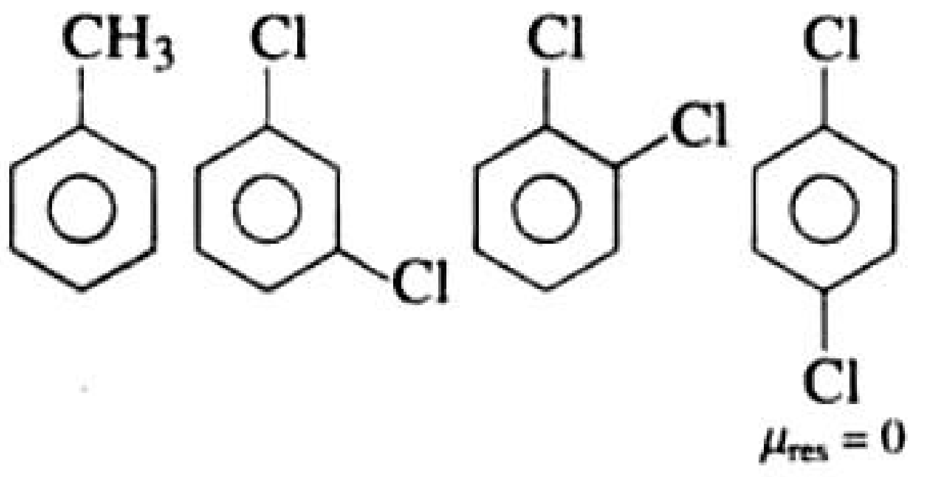
An electron-attracting substituent tends to disperse the negative charge of the phenoxide ion and thus, makes it more stable. which, in turn, increases the acid strength of phenol. The substituent in para position is more effective than in the meta-position, as the former involves a resonating structure bearing negative charge on the carbon attached to the electron- withdrawing substituent.

An electron-releasing substituent tends to intensify the negative charge of the phenoxide ion and thus makes it more unstable. which, in turn, decreases the acid strength of phenol. Hence, the order of acid strength is



26. b. Dipole moment of *p*-dichlorobenzene is zero because of symmetrical structure. *o*-and *m*-dichlorobenzene have higher dipole moments than toluene due to high electronegativity of chlorine than $-CH_3$ group. Further, the *o*-dichlorobenzene has higher dipole moment due to lower bond angle of the *m*-isomer. Hence, the order of increasing dipole moment is: *p*-dichlorobenzene (IV) < toluene (I) < *m*-dichlorobenzene (II) < *o*-dichlorobenzene (III)

27. b. Weaker the base better is the leaving ability.



$(\mu_{res}=\sqrt{\mu_1^2+\mu_2^2+2\mu_1\mu_2\cos\theta})$

A weak base has a strong conjugate acid. The corresponding conjugate acids of the four species in decreasing acidity and so is the order of leaving group ability.

$HOSO_2CF_3$ > $HOSO_2Me$ > HOAc > HOMe

i.e. IV > III > I > II

28. a. Greater the ease of leaving group, easier will be the nucleophilic substitution.

Weaker the base, the better is its leaving characteristic which lies in the following order.

$$\underset{\text{very weak base}}{Cl^-} > OCOCH_3 > {}^-OCH_3 > \underset{\text{strongest base}}{H^-}$$

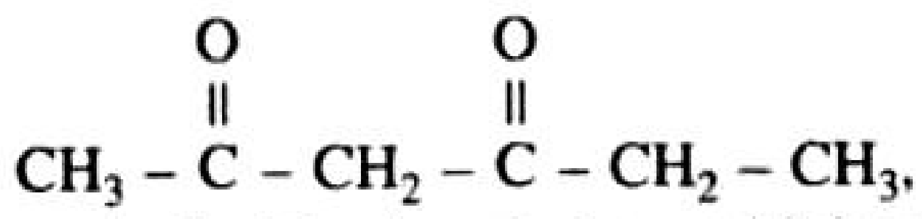
Hence CH_3COCl will be most reactive for nucleophilic substitution at acyl carbon.

29. d. $\underset{sp^2}{\overset{1}{C}H_2} = \underset{sp^2}{\overset{2}{C}H} - \underset{sp^3}{\overset{3}{C}H_2} - \overset{4}{C}H_2 - \overset{5}{C} \equiv \overset{6}{C}H$

30. c. $-CH_3$ is the best nucleophile because carbon is least electronegative among the given options. The order is

$$H_3\bar{C} > \bar{N}H_2 > \bar{O}H > F^-$$

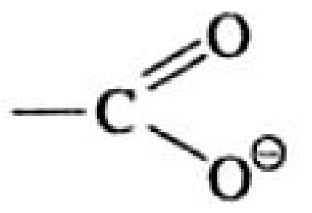
31. d. As I^- is the best, while F^- is the poorest leaving groups among halide ions. Therefore, rate of reaction will be $R-I > R-Br > R-Cl > R-F$.



32. b. $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$, $(-CH_2-)$ group is flanked on both sides by electron-withdrawing groups and hence its hydrogens are most acidic. Once a carbanion is formed, it is stabilised due to resonance.

33. d. S_N2 reactions proceed with inversion of configuration. Since the attacking nucleophile is not necessarily the same as that of leaving group, the product cannot be enantiomer of the substrate and thus necessarily will not have opposite optical rotation. Moreover since only one product is obtained, we cannot obtain diastereomers.

34. c.



Carboxylate ion

Charge dispersal stabilizes and charge intensification destabilizes.

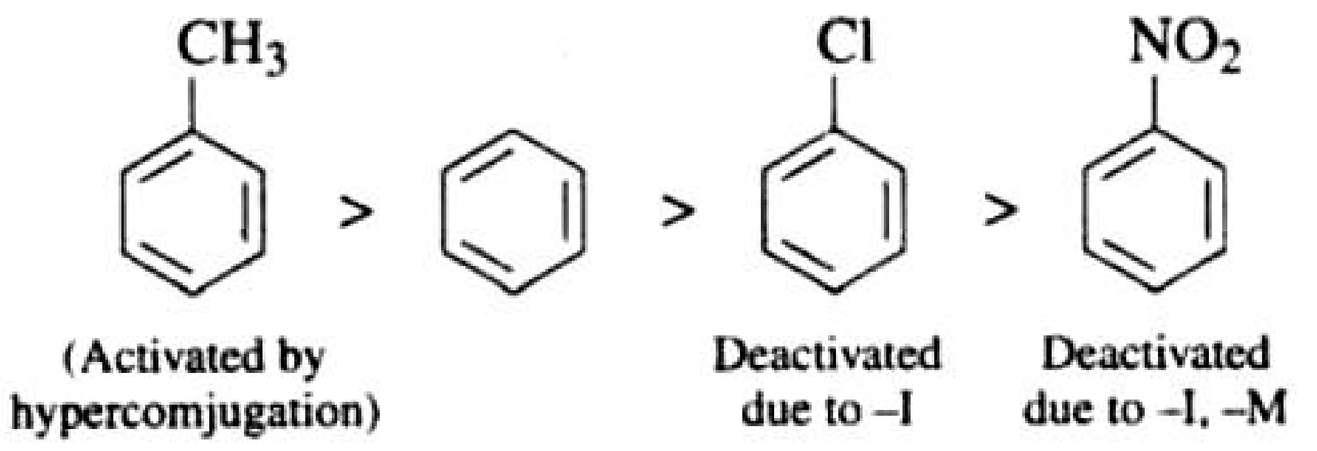
i. The inductive effect decreases with increase in distance of halogen atom from the carboxylate ion and hence the strength of acid proportionally decreases due to decrease in stability of carboxylate ion.

ii. The acidity increases with the increase in electronegativity of the halogen present due to –I effect of stronger electronagative group.

Smallest dissociation constant means weakest acid, which is $BrCH_2\ CH_2COOH$ because here Br (less electronegative than F) is two carbon atoms away from –COOH.

35. b. In carboxylic acids, molecules are more strongly associated followed by alcohols due to H-bonding and in aldehydes the dipole interactions.

36. c.



37. b. $CH_3C \equiv CCH_3$ is linear and symmetrical; thus, it has lowest dipole moment.

38. a. $\underset{}{\overset{sp^2}{H_2C}} = \overset{sp^2}{C}H - \overset{sp}{C} \equiv \overset{sp}{N}$.

39. a. Methane molecule being symmetrical, has zero dipole moment. Replacement of one of the H-atoms by Cl atom increases the dipole moment. The increase in dipole moment is more because the bond dipole moment of C – H bond and that of C – Cl bond reinforce one another.

Replacement of another H atom by Cl increases the bond angle due to lone pair – lone pair repulsion between two Cl – atoms thereby reducing the dipole moment of the molecule.

Increase in angle is again caused by the introduction of the third Cl – atom.

When the fourth Cl – atom is introduced, the molecule (CCl_4) again becomes symmetrical and dipole moment reduces to zero.

So, CH_3Cl will have the maximum dipole moment.

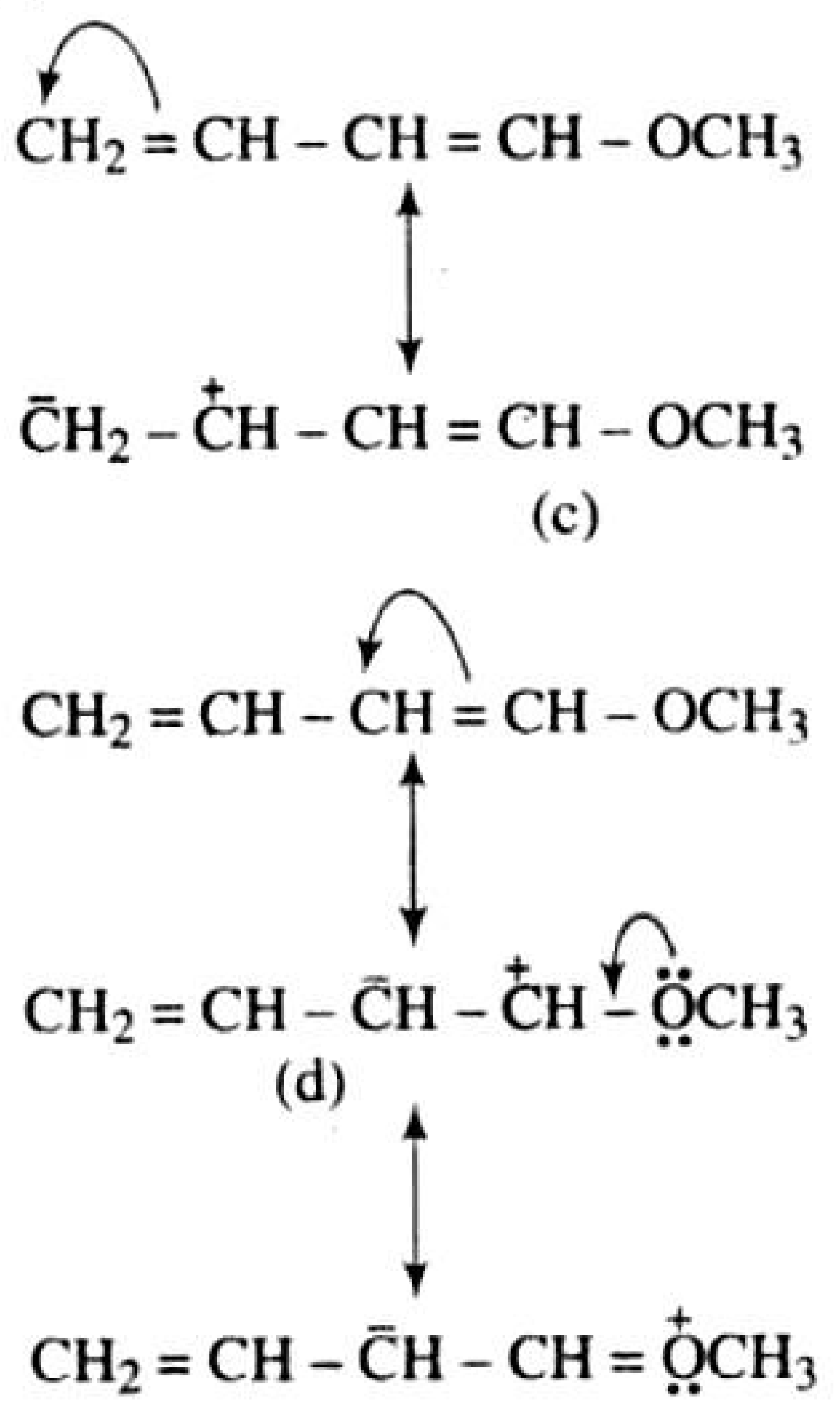
40. a. Carboxylic acids are stronger acid than $\overset{\oplus}{N}H_3$ in amino acid and $-\overset{\oplus}{N}H_3$ (Y). (Z) is more acidic than (Y) due to –I effect of (–COOH) group which is nearer to (Z) than (Y). Hence, the acidic order: X > Z > Y.

41. c. Structures (a) and (b) are quite stable because every atom has complete octet

Structures (c) and (d) are less stable than (a) and (b), because in these every atom does not have complete octet.

Structure (d) is stabilised by resonance, which is not possible in (c).

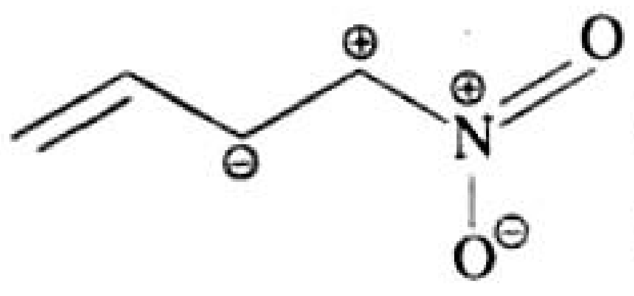
Therefore (c) is least stable.



42. b. General IUPAC name is alkanoyl halide.

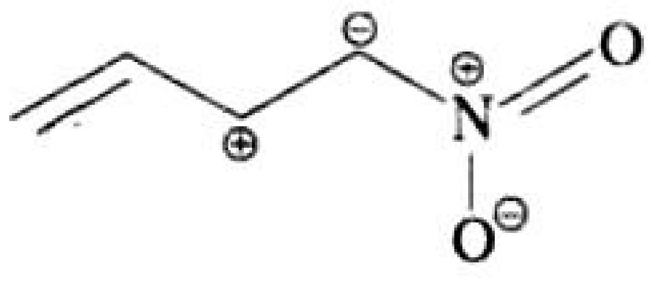
43. a.

a.

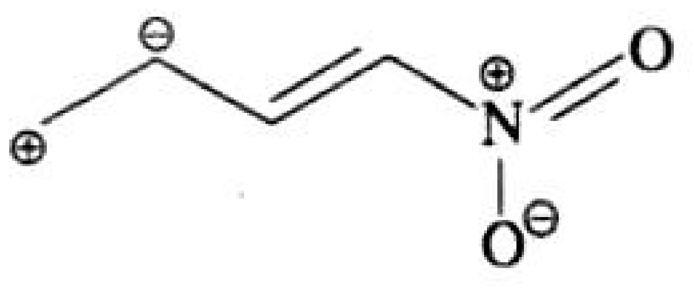


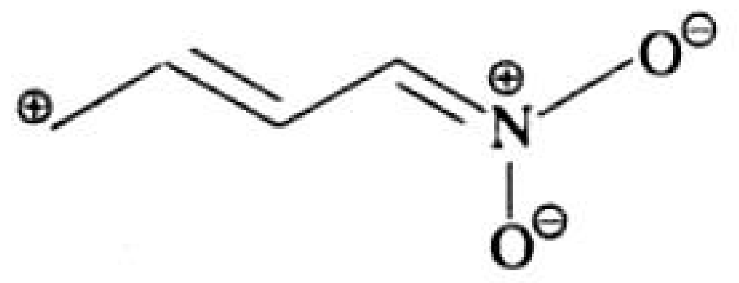
Same charges are present at nearest position (less stable)

b.



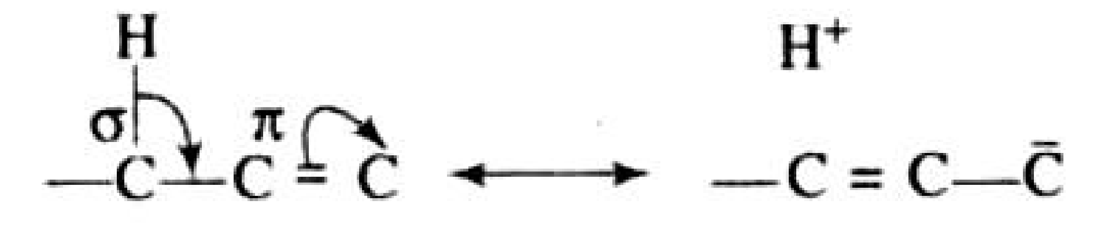
c.



d. 

Hence (a) is correct.

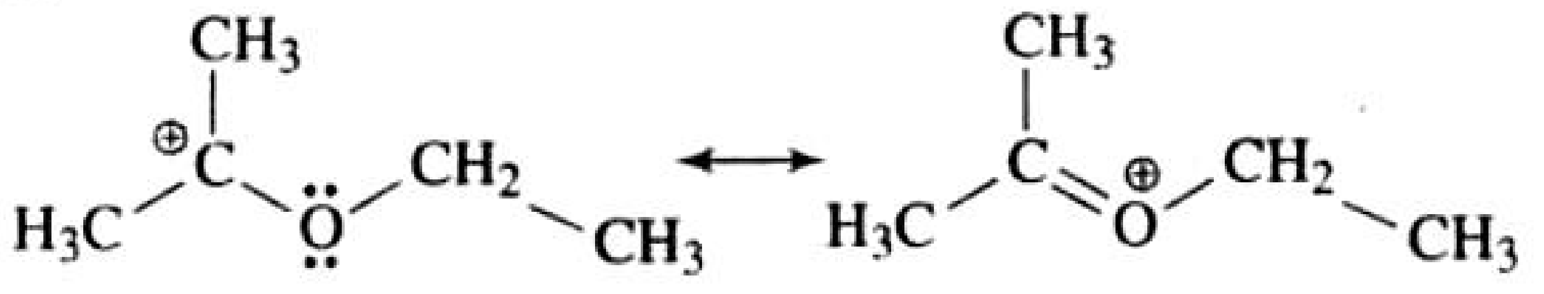
44. b. Alkyl groups with at least one hydrogen atom on the α-carbon atom, attached to an unsaturated carbon atom, are able to release electrons in the following way.



Note that the delocalization involves σ and π bond orbitals (or *p* orbitals in case of free radicals); thus it is also known as σ–π *conjugation*. This type of electron release due to the presence of the system H – C – C = C is known as *hyperconjugation*. This is also known as no bond resonance.

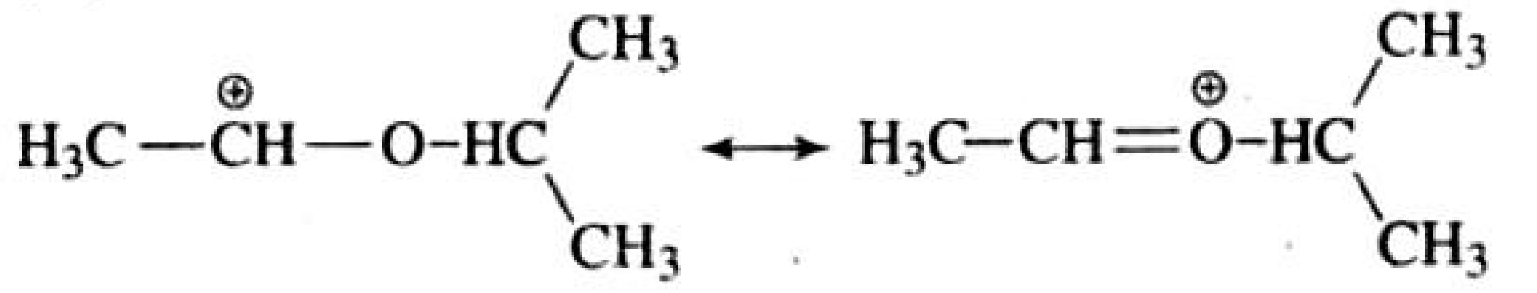
45. d.

(I)



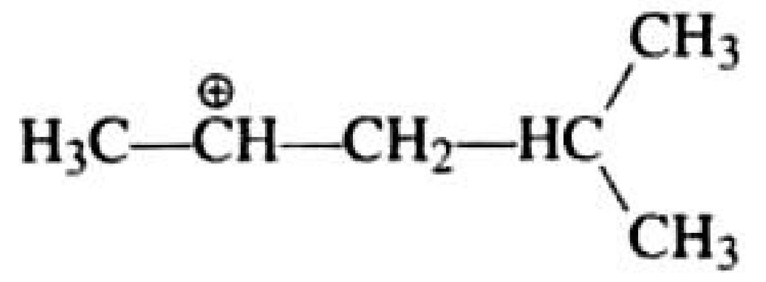
Stabilizes by resonance and have six α-hydrogen atoms (hyperconjugation)

(III)



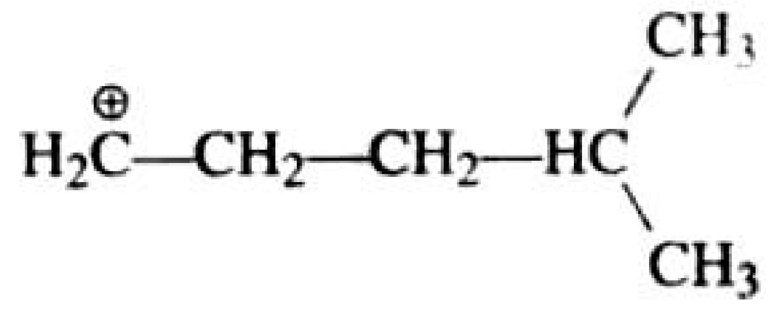
Stabilizes by resonance and have only three α-hydrogen atoms.

(II)



have five α-hydrogen atoms.

(IV)



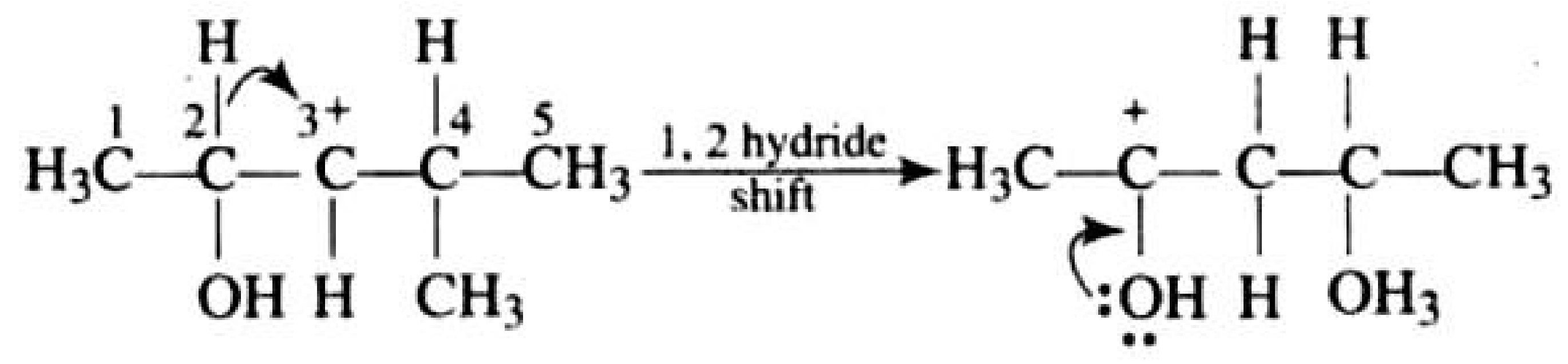
have only two α- hydrogen atoms.

∴ I > III > II > IV

46. b. –CN has highest priority.

47. d. Migrating tendency of hydride is greater than that of alkyl group.

Migration of hydride from C-2 gives more stable carbocation (stabilized by +R effect of OH group and +I and hyperconjugative effects of methyl group).



48. b. i. The lesser the charge separation, the more stable the resonating structure. (I) and (III) have less charge separation. But in (III), charge is on 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).

ii. 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.

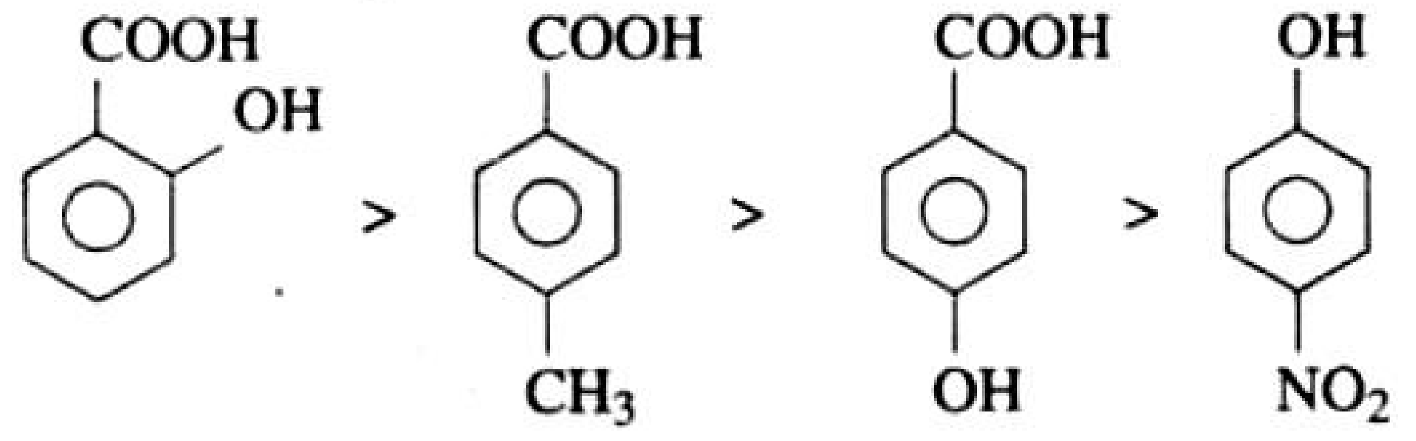
49. a. III > IV > II > I > (III acids) > IV (acid with (Me) group at *p*-position (+I and H.C. effect of Me)) > II (phenol with Cl at *p*-position (–I effect of Cl)) > I (standard).

–COOH is more acidic than –OH.

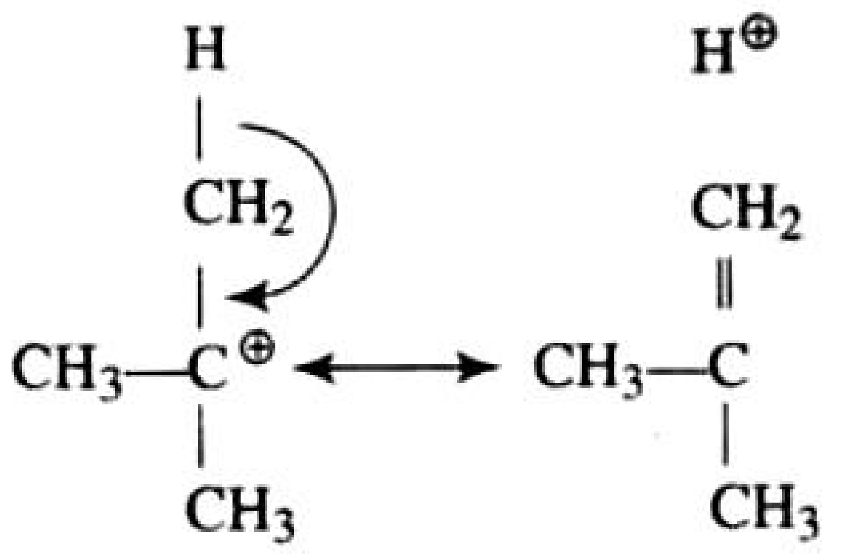
$-CH_3$ decreases stability of benzoate ion as well as phenoxide ion.

50. c. Any factor which stabilizes benzoate ion makes corresponding benzoic acid more stable.

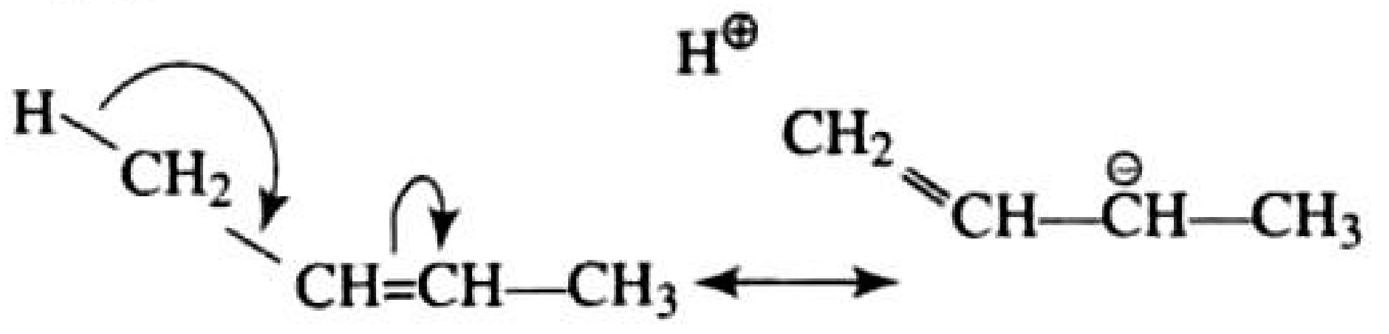
o-Hydroxybenzoic acid is strongest acid and the decreasing order of acidity is



51. b. $\overset{sp^2}{H_2C}=\overset{sp}{C}=\overset{sp^2}{CH_2}$

52. 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, hyperconjugate is between σ → π* bond.

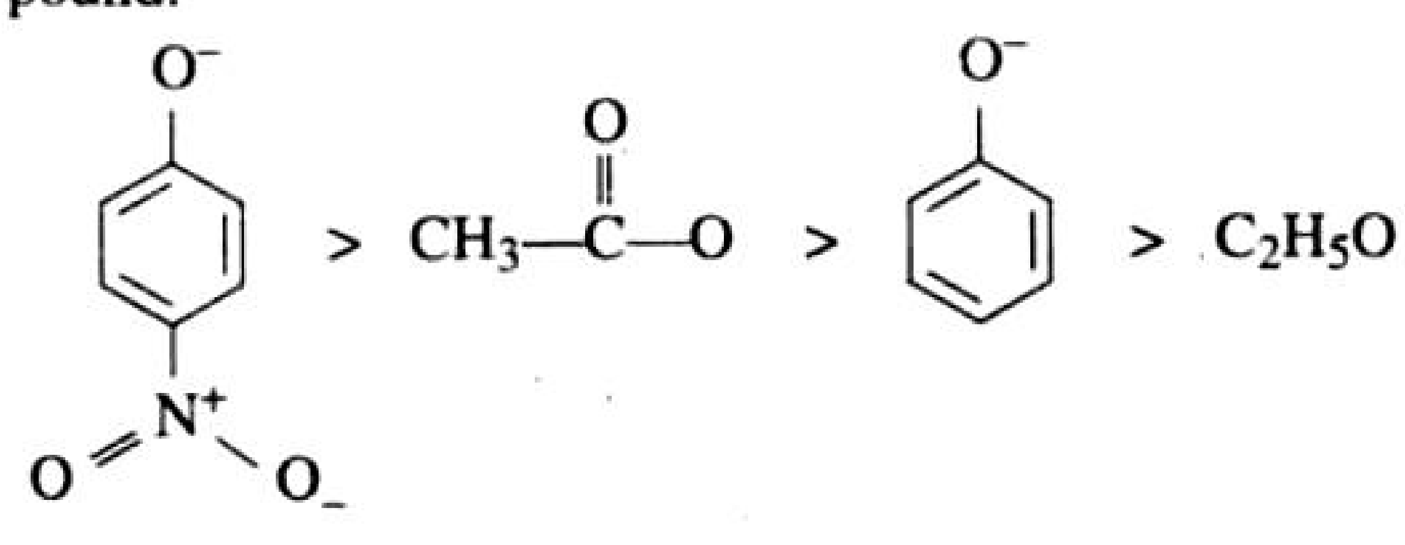
Multiple Correct Answers Type

1. **a., b., c.**

Because resonating structures differ in bonding pattern.

2. **a., c.**

As we know that higher the stability of the corresponding anion, more will be the acidic character of the parent compound.



So, acetate ions will have higher stability than phenoxide ion due to equivalent resonating structures in the former.

3. b., d.

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

4. a.

As we know that conjugate base of strong acid is weak while conjugate base of a weak acid is stronger.

Acidic strength of acids,

$$HOH > CH \equiv CH > NH_3 > CH_3 \cdot CH_3$$

So, the order of strength of bases,

$$CH_3CH_2^- > NH_2^- > CH \equiv C^- > OH^-$$

5. b., c., d.

An aromatic species will have:

⇒ $(4n + 2)$ π electrons (by Huckel's Rule)

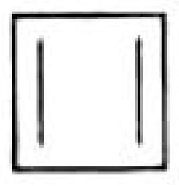
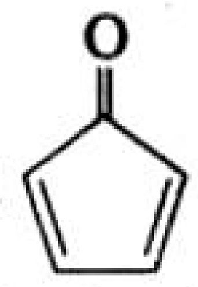
⇒ Planar structure (due to resonance)

⇒ Cyclic structure (due to presence of sp^2-hybrid carbon atoms).

6. b., c., d.

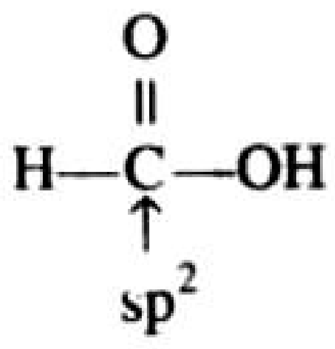
As (E and F) and (E and G) differ in position of atom (H), so these are tautomers (not resonating structures. Geometrical isomers are also diastereomers).

7. b., c.

Compound  and  being antiaromatic are unstable at room temperature. As they follow $(4n)\pi$ rule.

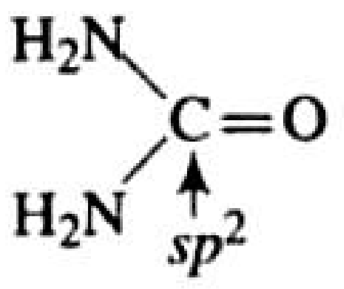
8. c., d.

a.

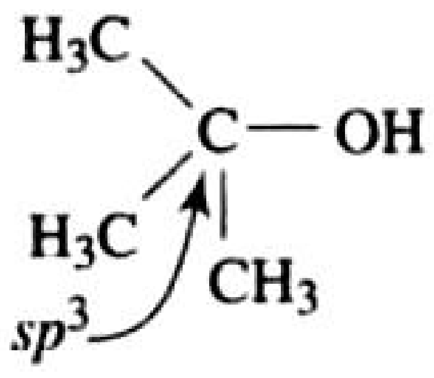


$$H-\overset{\overset{O}{\|}}{C}-OH$$

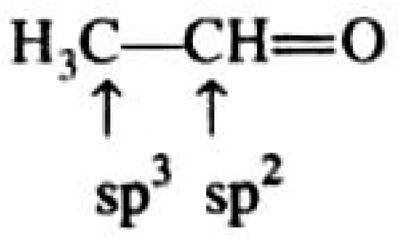
b.



c.



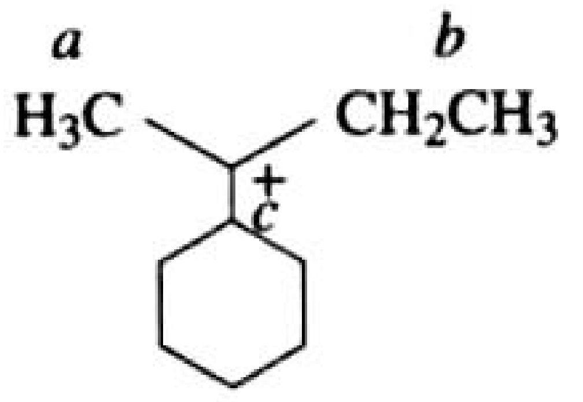
d.



$$\underset{sp^3}{\underset{\uparrow}{H_3C}}-\underset{sp^2}{\underset{\uparrow}{CH}}=O$$

Integer Answer Type

1. (7)



No. of hyperconjugating structures = No. of $\propto_H + 1$

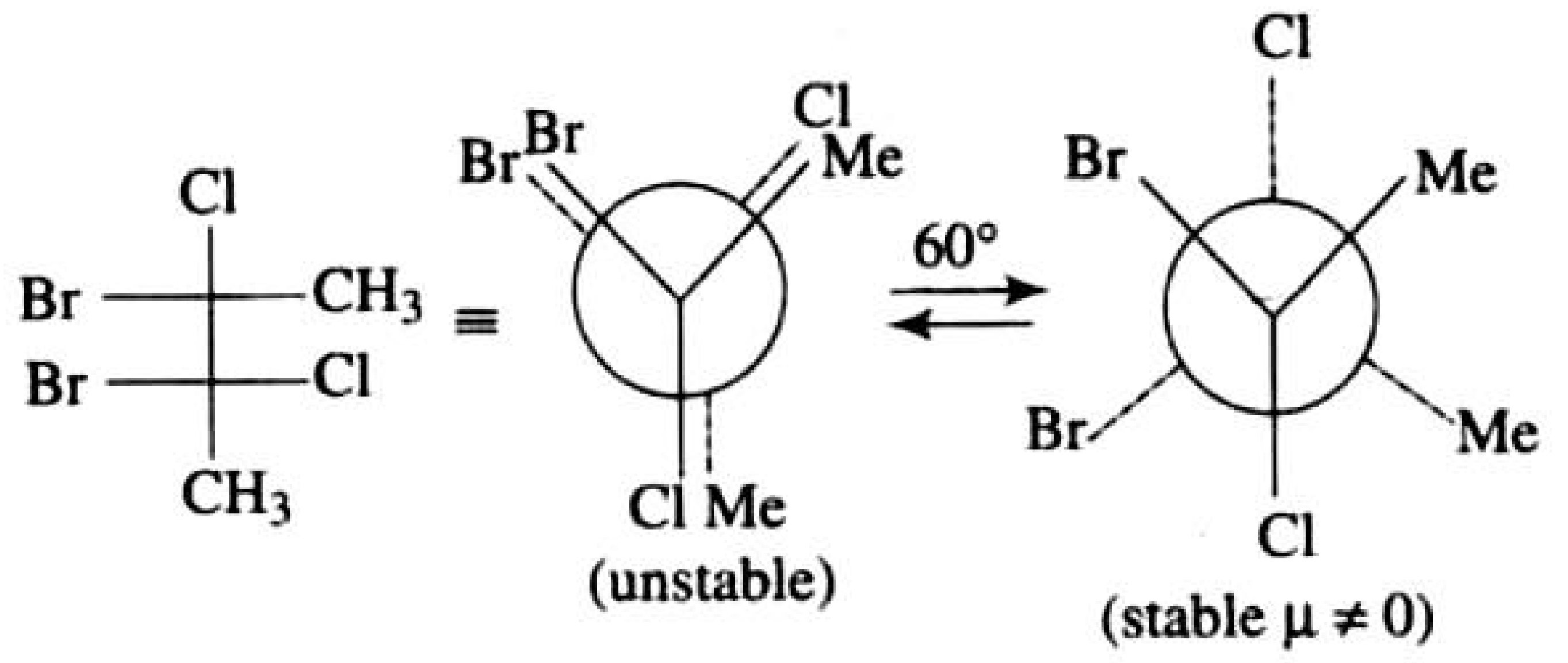
⇒ Structures = 6 + 1 = 7

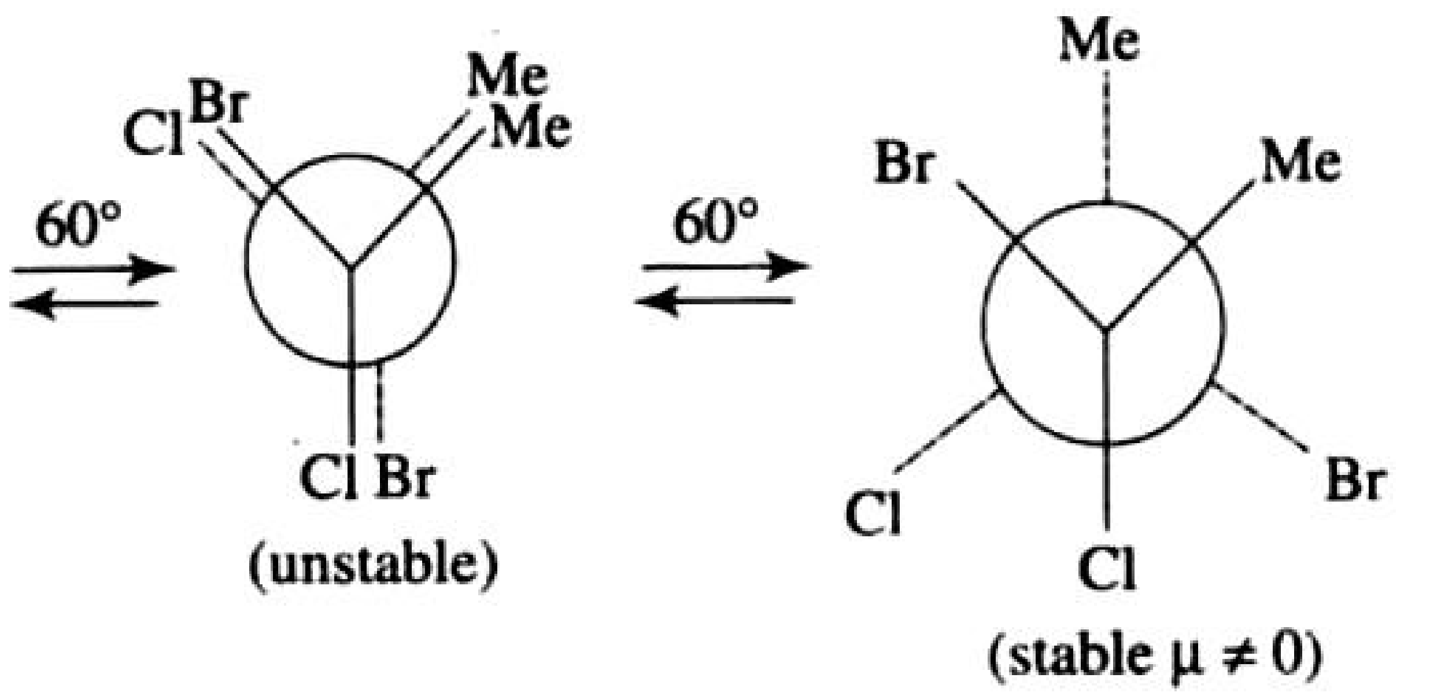
$a = 3$ Hyperconjugative H's

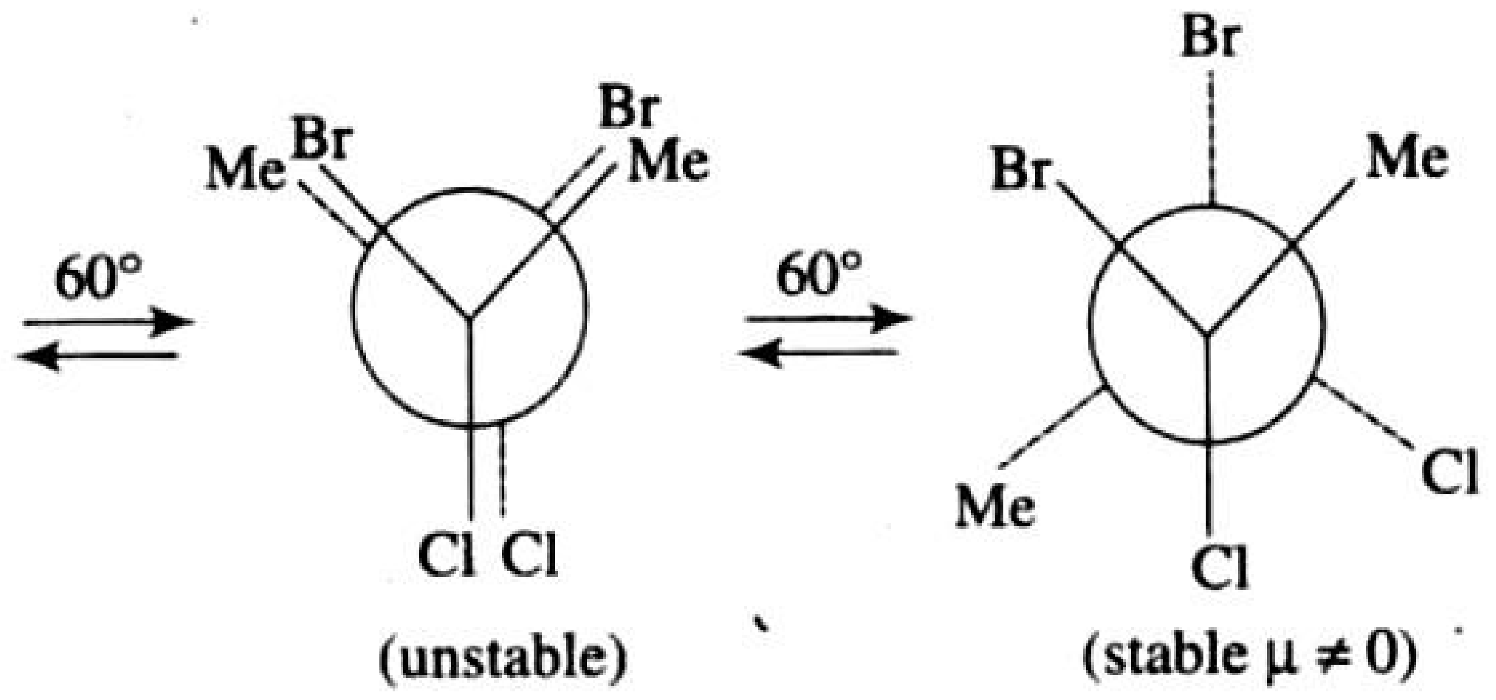
$b = 2$ Hyperconjugative H's

$c = 1$ Hyperconjugative H

2. (3)







Assertion-Reasoning Type

1. d. Statement 1 is incorrect because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon–chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles.

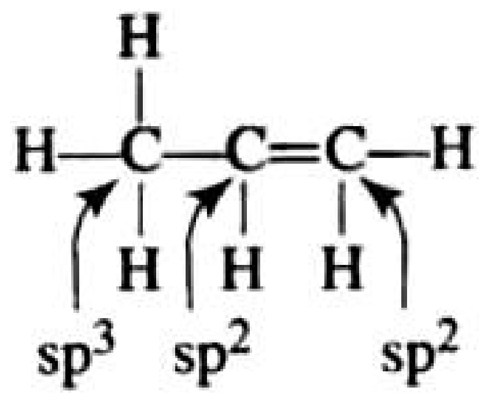
2. a. Due to +M effect of $-\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}H$, its intermediate carbocation is more stable than the one in benzene.

3. c. Statement 1 is correct. Statement 2 is incorrect because compound can be chiral even in the absence of chiral atoms.

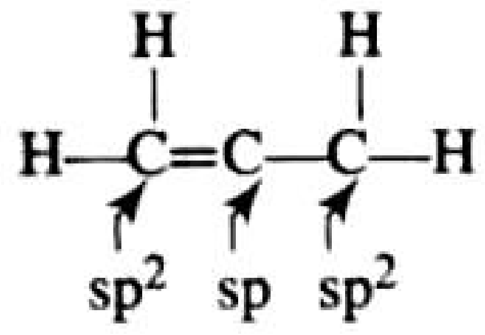
Fill in the Blanks Type

1. Tert-butyl carbonium ion is more stable due to hyperconjugation and +I effect of methyl groups.
2. Propadiene, in it carbon–carbon is sp hybridized.

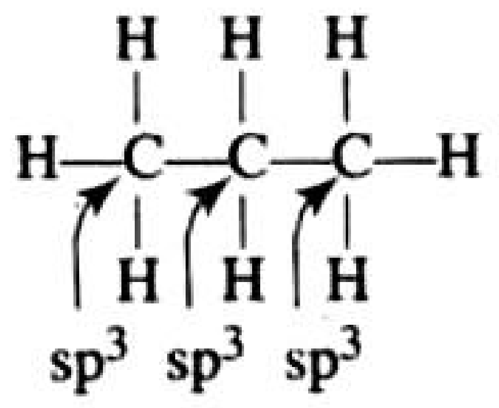
Propene :



Propadiene :



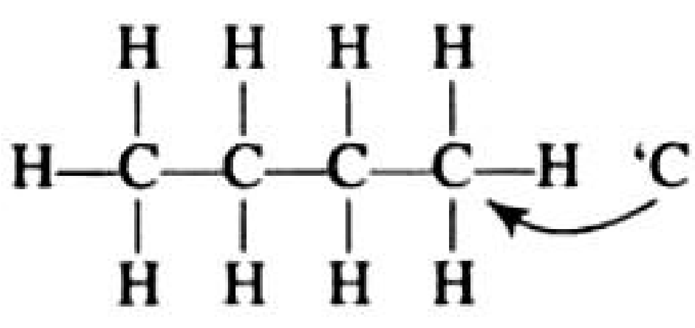
Propane :



3. Cyclopropane, because it has maximum deviation, from the normal bond angle of 109°28′ present in alkanes. In it bond angle is 60°.

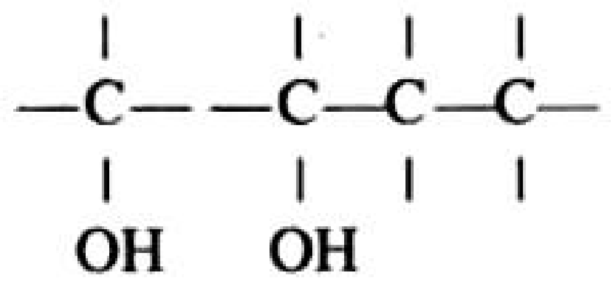
$$d = \frac{1}{2}(109°28' - 60°).$$

4. sp^3

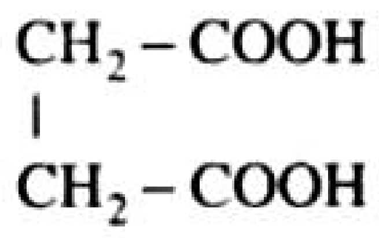


'C' making 4σ bonds is sp^3 hybridized.

5. Vicinal, adjacent



6. sp; $Ag-C\equiv C-Ag$, here 'C' makes 2σ and 2π bonds.
7. The shape $(CH_3)^{\oplus}$ is planer.
8. Less
9. Hyperconjugation
10. Butane-1, 4-dioic acid; Succinic acid has the formula.



$$\begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array}$$

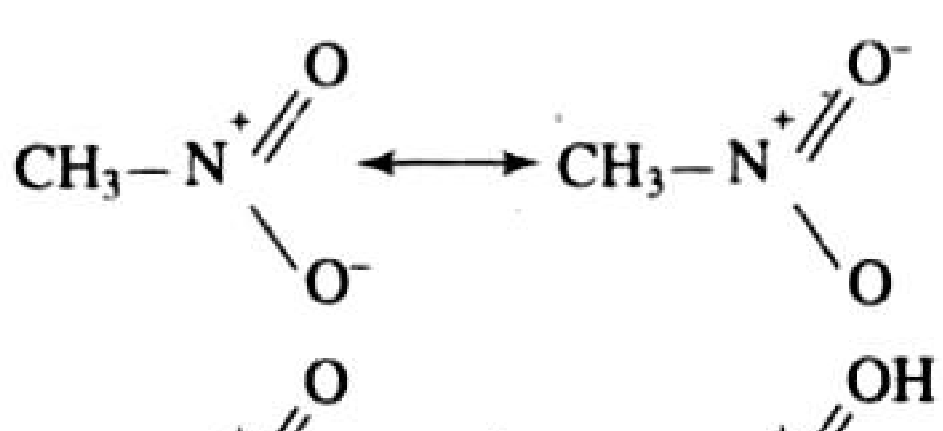
11. $NH_2^{\ominus}$ is a nucleophile, hence it is least reactive towards water. H_2O is e^- rich due to two lone pair of electrons on it.

True / False Type

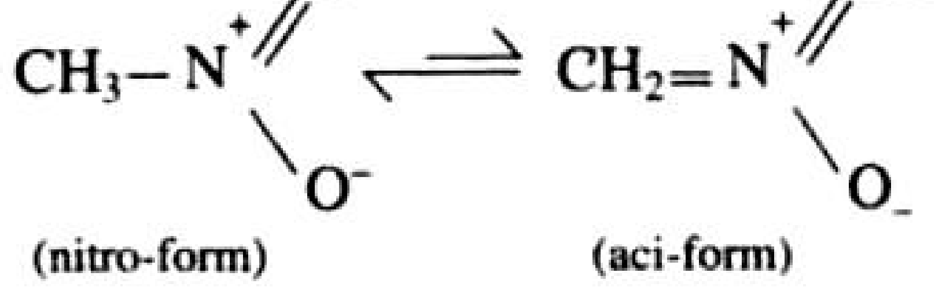
1. **False:**
   Iodide is bigger in size than bromide, hence its electrons are more dispersed than of bromide, with the result it is weaker nucleophile than bromide.
2. **False:**
   An electron-donating group increases the electron density in *o*- and *p*-position due to +M, +E and/or +I effects and hence orients the new electrophile to *o*-and *p*-positions.
3. **True:**
   In S_N1 (unimolecular nucleophilic substitution reaction), the leaving group leaves, thus producing a carbocation followed by the addition of the incoming group.

Subjective Type

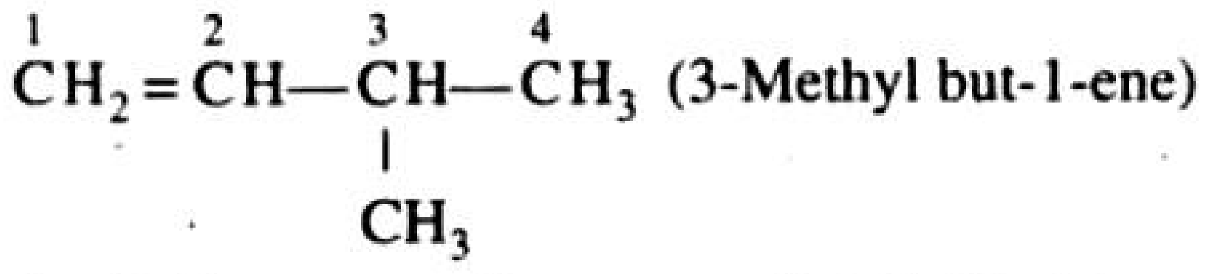
1. More the electron deficiency of the carbonyl carbon and less is steric hindrance around carboxyl carbon, greater will be its reactivity towards nucleophilic addition (case of nucleophilic addition reaction)
   $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$
2. III < IV < I < II or II > I > IV > III
   (II) (+I effect of two Me groups of N atom and Me group at *p* position (+I and H.C. effects) highest basic).
   (I) +I and H.C. effects of (Me) group at *p* position.
   (IV) (Standard) (Aniline)
   (III) –I and –R effect of $(-NO_2)$ group at *p* position.
3. $\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}OOH$
   Pent-2-en-1-oic acid or 2-Pentenoic acid
4. i.



ii.



5.



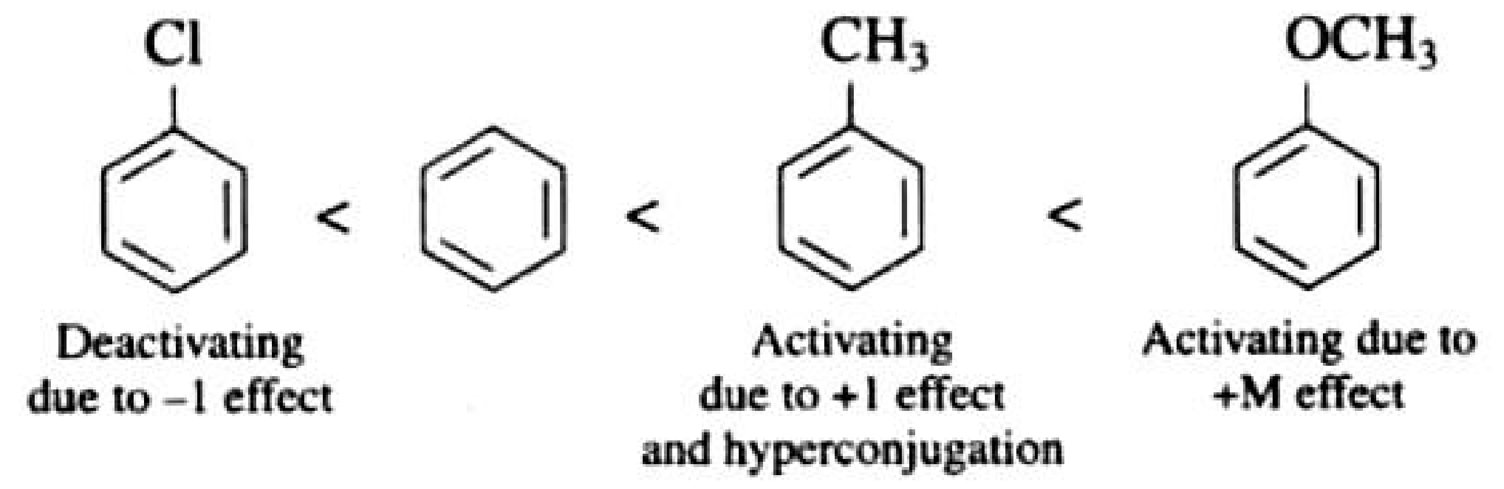
$$\overset{1}{C}H_2=\overset{2}{C}H-\underset{\displaystyle CH_3}{\overset{3}{C}H}-\overset{4}{C}H_3$$ (3-Methyl but-1-ene)

6. i. Isobutane < n-Butane < n-Butyl chloride < n-Butanol

van der Walls forces	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.

   ii. OCH_3 and $-CH_3$ groups are activating group while –Cl is a deactivating group for electrophilic substitution. Any factor which increases electron density on benzene ring makes it more susceptible towards electrophilic substitution.

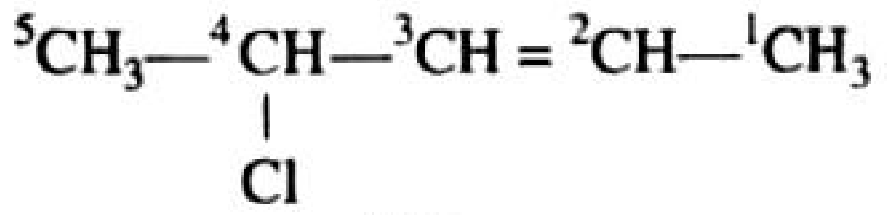


7. In formic acid, resonance is not possible, with the result there are two types of C – O bonds. In sodium formate, resonance is possible, so both of the C – O bonds have same bond length.

Formic acid

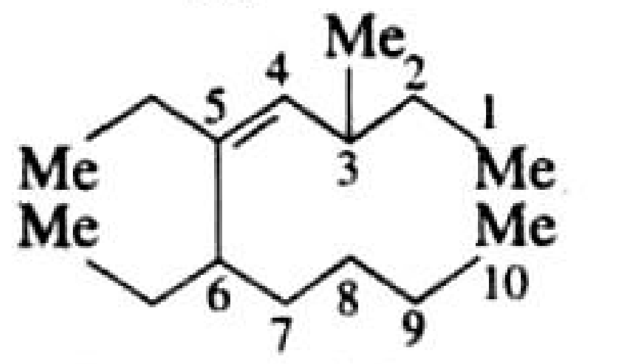
Sodium formate (Resonating hybrid)

8.



$$^5CH_3-{}^4\underset{\displaystyle Cl}{CH}-{}^3CH={}^2CH-{}^1CH_3$$

9.



5, 6-diethyl-3-methyldec-4-ene

10. Presence of electron withdrawing group increases the acidic character of the –COOH due to –I effect, while presence of electron-donating group (alkyl groups) decreases the acidic character due to +I effect. Thus
    IV < II < V < III < I
    Any factor which stabilizes carboxylate ion makes corresponding acid more strong
    $RCOOH \rightleftharpoons RCOO^- + H^+$
    –I group stabilizes carboxylate ion
    +I group destabilizes carboxylate ion
11. IUPAC name is
    3-(N, N-dimethylamino)-3-methylpentann
12. A weaker base is a better leaving group.
    Rate of reaction will be R – I > R – Br > R – Cl > R – F. because I^- is the best, while F^- is the poorest leaving groups among halide ions.
13. 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.