Subjective questions of Organic Chemistry - Some Basic Principles & Technique

Fill in the Blanks

Q.1. Among the given cations, ... is most stable. (1981)

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

Ans. tert-butyl carbonium ion

Solution. tert-butyl carbonium ion is more stable due to liyperconjugation and +1 effect of methyl groups.

Q.2. The compound having both sp and sp^2 hybridized carbon atoms is ..... (1981)

(propene, propane, propadiene)

Ans. propadiene

Q.3. ..... ring is most strained. (1981)

(Cyclopropane, Cyclobutane, Cyclopentane)

Ans. cyclopropane

Solution. cyclopropane, because it has maximum deviation, from the normal bond angle of 109°28' present in alkanes. In it bond angle is 60°.

$$d = \frac{1}{2}(109°28' - 60°).$$

Q.4. The terminal carbon atom in butane is ..... hybridised. (1985)

Ans. sp^3

Solution. sp^3

Q.5. A ..... diol has two hydroxyl groups on ..... carbon atoms. (1986)
Ans. vicinal, adjacent

Solution. vicinal, adjacent (or stable, different).

Q.6. Isomers which are ..... mirror images are known as ..... (1988)

(superimposable, non-superimposable, enantiomers, diastereomers, epimers)

Ans. non-superimposable, enantiomers

Solution. non-superimposable, enantiomers;

Q.7. The valence atomic orbitals on carbon in silver acetylide is ..... hybridized. (1990)

Ans. sp

Solution. sp;

Q.8. The kind of delocalization involving sigma bond orbitals is called ..... (1994)

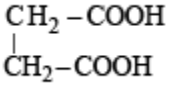
Ans. hyperconjugation

Solution. Hyperconjugation;

Q.9. The IUPAC name of succinic acid is ..... . (1994)

Ans. butane–1, 4-dioic acid

Solution. Butane-1, 4-dioic acid; Succinic acid has the formula.



True/False

Q.1. Iodide is a better nucleophile than bromide. (1985 - ½ Mark)

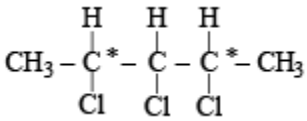
Ans. F

Solution. Iodide is bigger in size than bromide, hence its electrons are more dispersed than that of bromide, with the result it is weaker nucleophile than bromide.

Q.2. An electron donating substituent in benzene orients the incoming electrophilic group to the meta position. (1987)

Ans. F

Solution. An electron-donating group increases the electron density in o- and p-positions due to +M, +E and/or +I effects and hence orients the new electrophile to o- and p- positions.



Q.4. During S_N1 reaction, the leaving group leaves the molecule before the incoming group is attached to the molecule.

Ans. T

Solution. In S_N1 (un imolecular n ucleophilic substitution reaction), the leaving group leaves, thus producing a carbocation followed by the addition of the incoming group.

Subjective questions of Organic Chemistry - Some Basic Principles & Technique

Q.1. Arrange the following in :

(i) Increasing reactivity towards HCN

CH_3CHO, CH_3COCH_3, HCHO, C_2H_5COCH,

(ii) n-butane, n-butanol, n-butyl chlor ide, isobutane in increasing order of boiling point.

(iii) benzene, toluene, methoxybenzene, chlorobenzene in increasing order of reactivity towards sulphonation with fuming sulphuric acid.

(iv) Increasing order of acid strength

$ClCH_2COOH$ (I), CH_3CH_2COOH (II), $ClCH_2CH_2COOH$ (III), $(CH_3)_2CHCOOH$ (IV), CH_3COOH (V)

(v) Increasing reactivity in nucleophilic substitution reactions

CH_3F, CH_3I, CH_3Br, CH_3Cl

Ans. (i) $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

(ii) isobutane < n-butane < n-butyl chloride < n-butanol

(iii) chlorobenzene < benzene < toluene < methoxybenzene

(iv) IV < II < III < V < I

(v) $CH_3F < CH_3Cl < CH_3Br < CH_3I$

Solution.

(i) TIPS/Formulae : It is a case of nucleophilic addition reaction. More the electron deficiency of the carbonyl carbon, greater will be its reactivity towards nucleophilic addition.

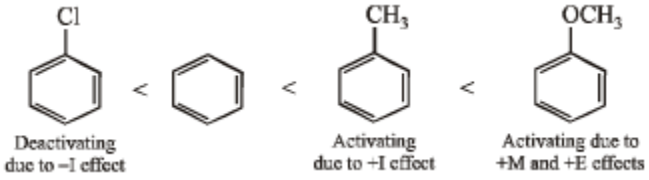
$C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

(*ii*) Isobutane < *n*-Butane < *n*-Butyl chloride < *n* - Butanol

van der Wall's 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 vander Waals attractive forces.

(iii) NOTE : $-OCH_3$ and $-CH_3$ groups are activating group while –Cl is a deactivating group for electrophilic substitution.



(iv) 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

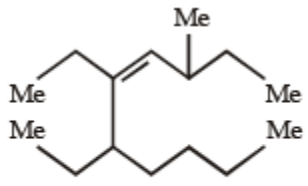
IV < II < V < III < I

(v) NOTE : 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.

Q.2. (i) Write the IUPAC name of :

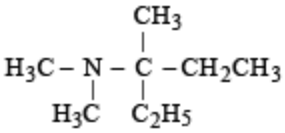
$CH_3CH_2CH = CHCOOH$

(ii) Give the IUPAC name of the following compound :



(Me = Methyl)

(iii) Write the IUPAC name for the following :

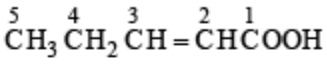


Ans. (i) Pent-2-en-1-oic acid or 2-Pentenoic acid

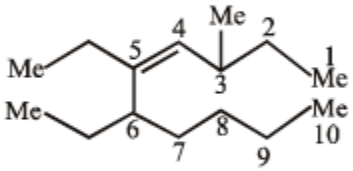
(ii) 5, 6-diethyl-3-methyl-4-decene

(iii) 3–(N, N dimethylamino)-3–methylpentane

Solution.

(i) 

Pent-2-en-1-oic acid *Or* 2-Pentenoic acid

(*ii*) 

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

(iii) IUPAC name is

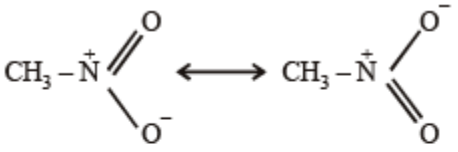
3–(N, N-dimethylamino)–3–methylpentane.

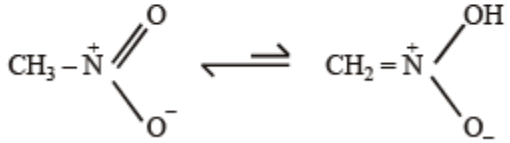
Q.3. For nitromethane molecule, write structure(s).

(i) showing significant resonance stabilisation.

(ii) indicating tautomerism.

Solution.

(*i*) 

(*ii*) 

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

Q.4. Give reasons for the following :

(i) 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.

(ii) Phenyl group is known to exert negative inductive effect. But each phenyl ring in biphenyl (C6H5 – C6H5) is more reactive than benzene towards electrophilic substitution .

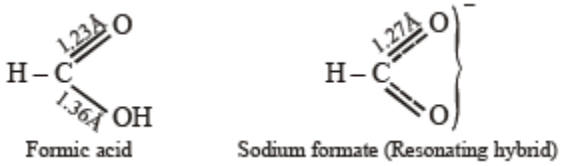
(iii) Aryl halides are less reactive than alkyl halides towards nucleophilic reagents

(iv) $CH_2=CH^-$ is more basic than $HC \equiv C^-$.

(v) Normally, ben zene gives electroph ilic substitution reaction rather than electrophilic addition reaction although it has double bonds.

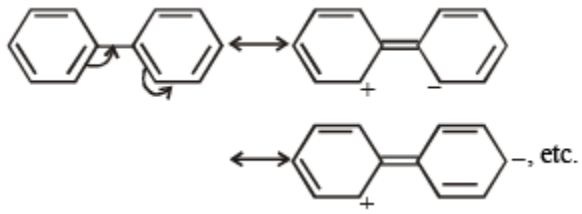
Solution.

(i) 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.

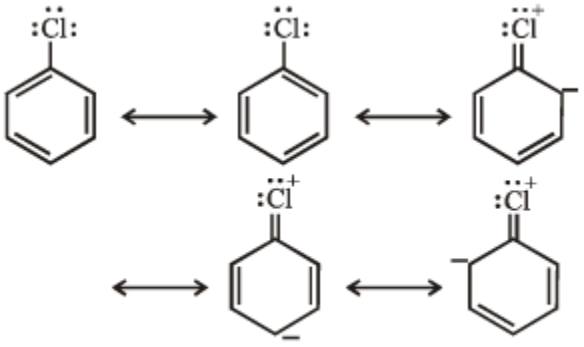


Formic acid Sodium formate (Resonating hybrid)

(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) The low reactivity of halogen atom in aryl and vinyl halides towards nucleophiles is due to resonance.



Resonating structures of chlorobenzene

NOTE : Due to resonance, carbon-chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be easily replaced by nucleophiles.

(iv) $CH \equiv C^-$, C^- is sp hybridised and more electronegative then the which is sp2 hybridised.

Thus the former can better accomodate electron pair hence less basic.

(v) Benzene gives electrophilic substitution reaction rather than electrophilic addition reactions because it will have a stable benzene ring in the product, whereas electrophilic addition on benzene destroys the benzenoid ring.

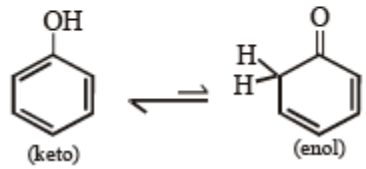
Q.5. Write the structural formula of 4-chloro-2-pentene.

Ans. $CH_3-\underset{Cl}{CH}-\underset{Cl}{CH}=CH-CH_3$

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

Q.6. Write tautomeric forms for phenol.

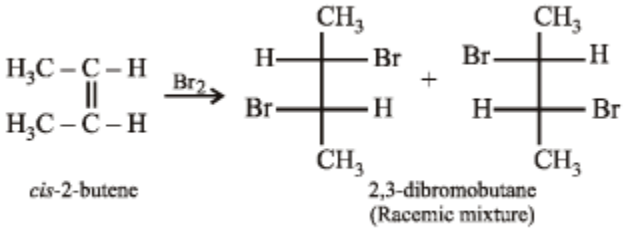
Solution.



(keto) (enol)

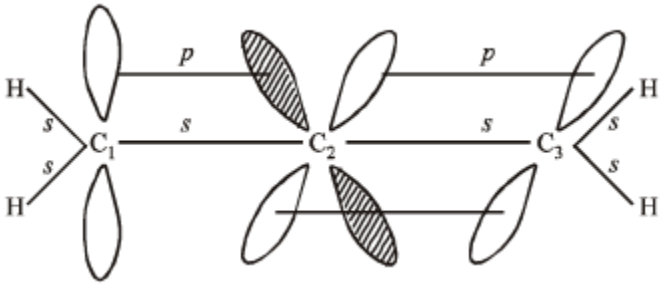
Q.7. Write down the structures of the stereoisomers formed when cis-2-butene is reacted with bromine.

Solution. cis-Alkenes add bromine to form racemic mixture.

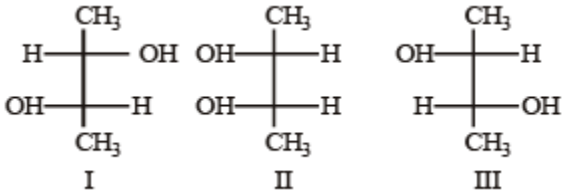


Q.8. Discuss the hybridisation of carbon atoms in allene (C_3H_4) and show the π-orbital overlaps.

Solution.



Q.9. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III



Ans. enantionmers – I & III; diastereomers – I & II and II & III.

Solution. In order to convert a molecule with two stereogenic centres to its enantiomer, the confuguration at both centres must be reversed. Reversing the configuration at only one stereogenic centre converts it to a distereomeric structure.

Thus structures I and III are enantiomers; while structures I and II as well as II and III are diastereomers.

Q.10. Which one is more soluble in diethyl ether - anhydrous $AlCl_3$ or hydrous $AlCl_3$? Explain in terms of bonding.

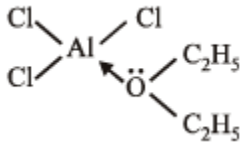
Ans. Anyhydrous $AlCl_3$

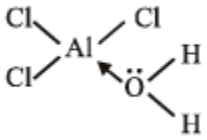
Solution.

TIPS/Formulae :

Diethyl ether acts as a lewis base and anhydrous $AlCl_3$ as a lewis acid.

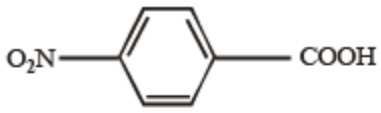
Anyhydrous $AlCl_3$ is more soluble in diethyl ether because the oxygen atom of ether donates its pair of electrons to the vacant orbital of electron deficient aluminium of $AlCl_3$ through the formation of coordinate bond. In case of hydrated $AlCl_3$ aluminium is not electron deficient as oxygen atom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



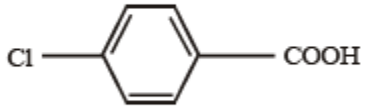


Q.11. Match the K_a values

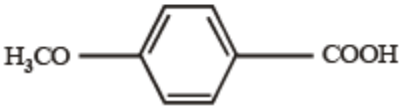
	K_a
(a) Benzoic acid	**6.4×10^{-5}**

(b) 

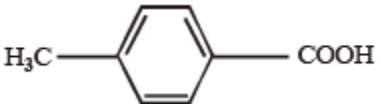
30.6×10^{-5}

(c) 

10.2×10^{-5}

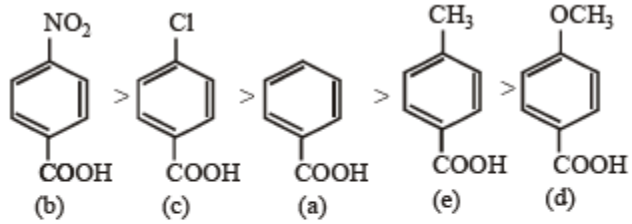
(d) 

3.3×10^{-5}

(e) 

4.2×10^{-5}

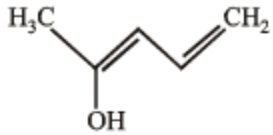
Solution. NOTE : Higher the Ka value, more stronger is the acid. Correct order of acidic strength of the given acids is



Hence the K_a values of the five acids will be in the order.

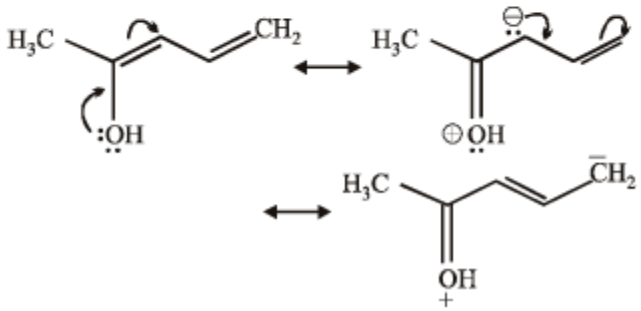
	(b)	(c)	(a)	(e)	(d)
K_a value	30.6×10^{-5}	10.2×10^{-5}	6.4×10^{-5}	4.2×10^{-5}	3.3×10^{-5}

Q.12.

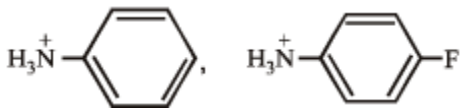


Write resonance structure of the given compound.

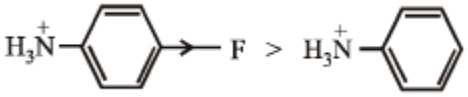
Solution.



Q.13. Which of the following is more acidic and why ?



Solution. Presence of an electron-attracting group increases acidity of the compound. Thus



Q.14. (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 : μ_{obs} = 1.0 D and $x_{(Anti)}$ = 0.82

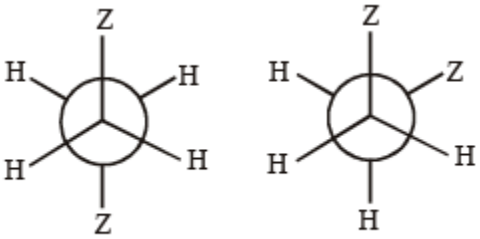
Draw all the stable conformers of Z – CH_2 – CH_2 – Z and calculate the value of $\mu_{(Gauche)}$.

(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.

Ans. (i) $\mu_{(gauche)}$ = 5.55 D

Solution.

(*i*)



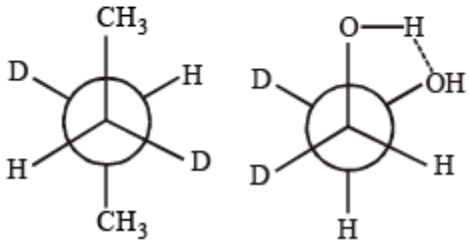
Anti conformer Gauche conformer

Given, mole fraction of anti conformer = 0.82

∴ mole fraction of gauche conformer = 0.18

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

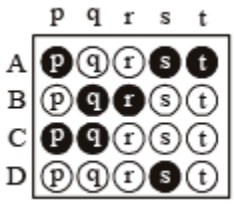
(*ii*)



Match the following of Organic Chemistry - Some Basic Principles & Technique

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.



Q.1. Given below are certain matching type questions, where two columns (each having 4 items) are given. Immediately after the columns the matching grid is given, where each item of Column I has to be matched with the items of Column II, by encircling the correct match(es). Note that an item of Column I can match with more than one item of Column II. All the items of Column II must be matched. Match the following :

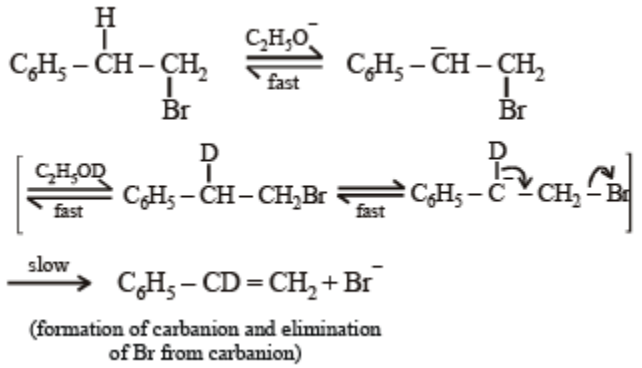
Column I	**Column II**
(A) $C_6H_5CH_2CD_2Br$ on reaction with $C_2H_5O^-$ gives $C_6H_5–CH=CD_2$	**(p) E_1 reaction**
(B) PhCHBrCH3 and PhCHBrCD3, both react with the same rate	**(q) E_2 reaction**
(C) $C_6H_5CH_2CH_2Br$ on treatment with $C_2H_5O^-$ and C_2H_5OD gives $C_6H_5CD=CH_2$	**(r) E_1cB reaction**
(D) C6H5CH2CH2Br reacts faster than $C_6H_5CD_2CH_2Br$ on reaction with $C_2H_5O^-$ in ethanol	**(s) First order reaction**

Ans. (A) - (q), (B) - (p, s), (C) - (r, s), (D) - (q)

Solution. E1 mechanisms are encountered only with tertiary or secondary substrates and in presence of either a weak base or a base in low concentration. So primary substrates will follow E_2 mechanism, i.e. (A) → E2 and (D) → E2.
Further E1 mechanism (similar to S_N1) proceeds by first order kinetics and is determined by the slower (first) step of the formation of carbocation. Hence (B)→E1 and first order reaction.

NOTE THIS STEP : Reaction of $C_6H_5CH_2CH_2Br$ on treatment with $C_2H_5O^-$ in presence of C_2H_5OD gives $C_6H_5CD = CH_2$.

This reaction follows E1CB (Elimination unimolecular conjugate base) mechanism. This 2 step mechanism follows the following path :



Although this mechanism involves 2 steps the overall rate of the reaction is limited to the slower second step and hence the rate of reaction depends only on the concentration of the carbanion, i.e. first order reaction. Hence, (C) → (r), (s).

Q.2. Match the compounds/ions in Column I with their properties/reactions in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

Column I	**Column II**
(A) C_6H_5CHO	**(p) gives precipitate with 2, 4-dinitrophenylhydrazine**
(B) $CH_3C \equiv CH$	**(q) gives precipitate with $AgNO_3$**
(C) CN^-	**(r) is a nucleophile**
(D) I^-	**(s) is involved in cyanohydrin formation**

Ans. (A) - (p, s); (B) - (q); (C) - (q, r, s); (D) - (q, r)

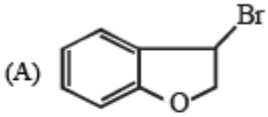
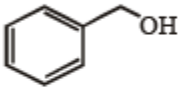
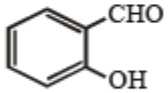
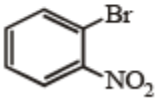
Solution. (A) C_6H_5CHO forms ppt. of 2, 4-dibromophenylhydrazone (p), forms silver mirror with ammonical silver nitrate – Tollen's reagent (q), forms cyanohydrin with CN– (s).

(B) $CH_3C \equiv CH$ gives ppt. with $AgNO_3$ (q)

(C) CN^- reacts with $AgNO_3$ to form ppt. of AgCN (q), it is a nucleophile (r) and forms cyanohydrin (s)

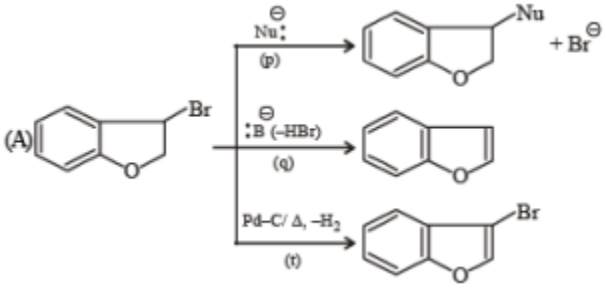
(D) I– gives ppt. of AgI with $AgNO_3$ (q), and it is a nucleophile (r)

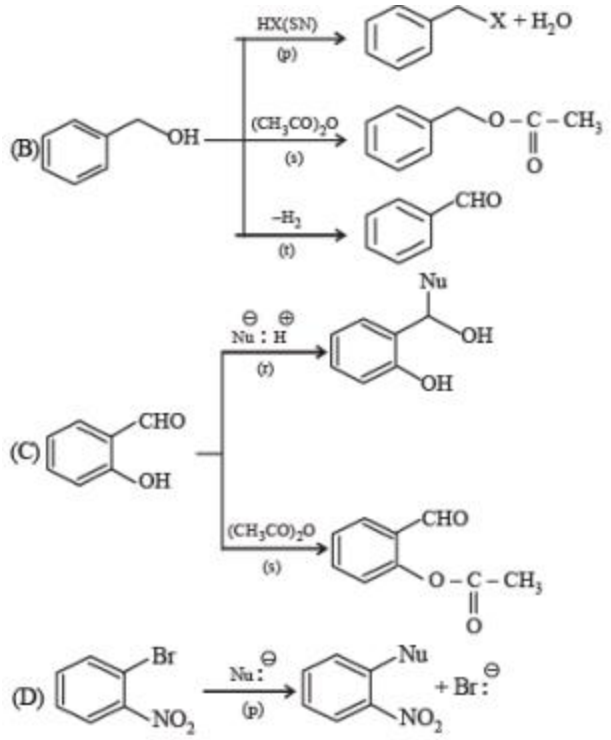
Q.3. Match each of the compounds given in Column-I with the reaction(s), that they can undergo, given in Column-II.

Column-I	Column-II
(A) 	(p) Nucleophilic substitution
(B) 	(q) Elimination
(C) 	(r) Nucleophilic addition
(D) 	(s) Esterification with acetic anhydride
	(t) Deh ydrogenation

Ans. (A) - (p,q,t); (B) - (p,s,t); (C) - (r,s); (D) - (p)

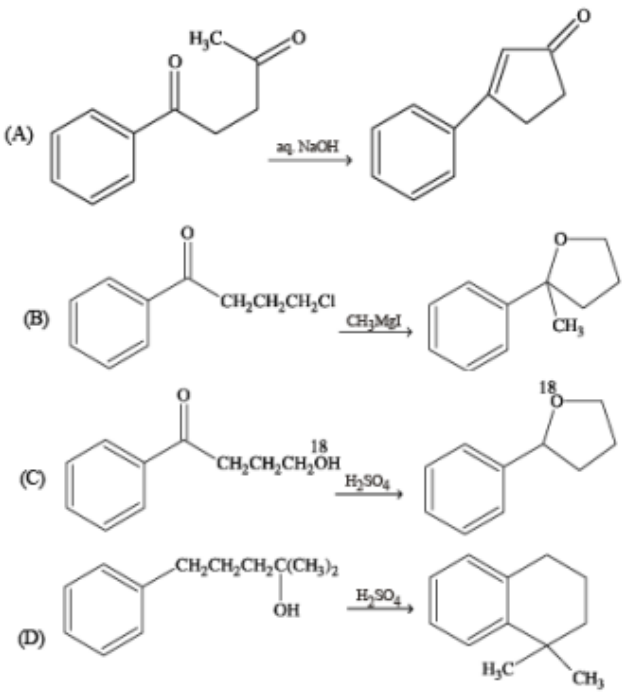
Solution.





Q.4. Match the reactions in Column I with appropriate types of steps/reactive intermediate involved in these reactions as given in Column II.

Column I **Column II**



(p) Nucleophilic substitution

(q) Electrophilic substitution

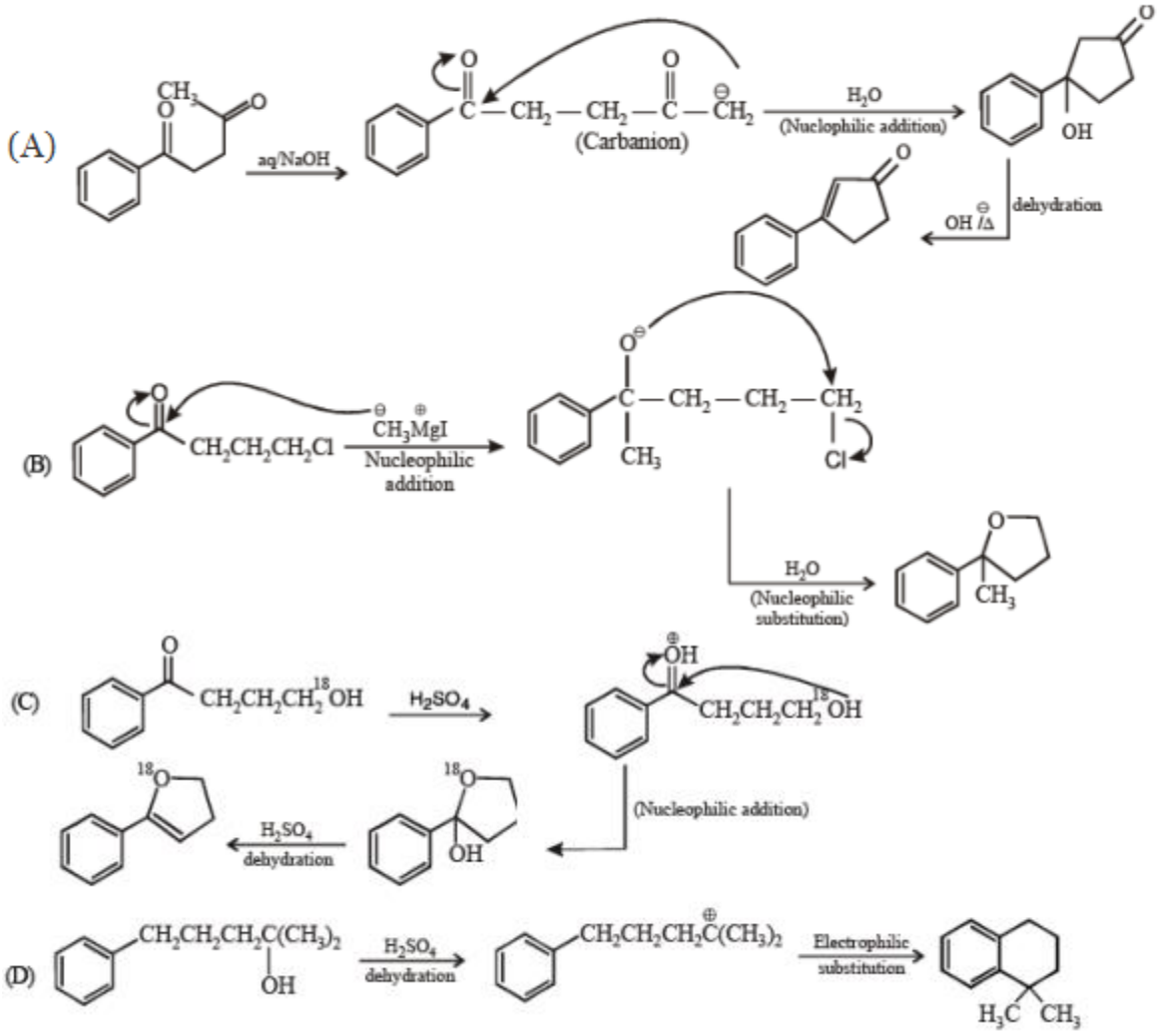
(r) Dehydration

(s) Nucleophilic addition

(t) Carbanion

Ans. (A) - (r,s,t); (B) - (p,s); (C) - (r,s); (D) - (q,r)

Solution.

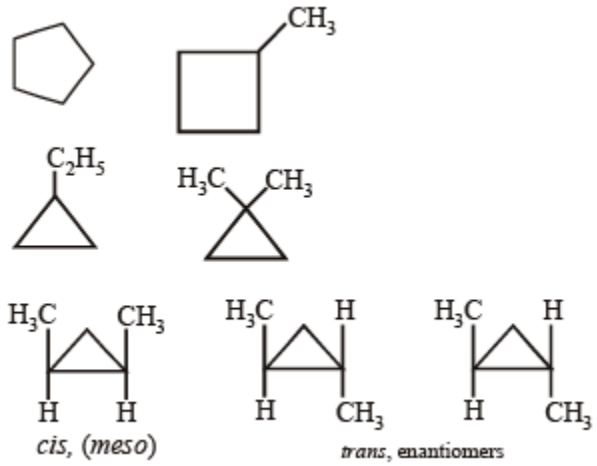


Integer Type ques of Organic Chemistry - Some Basic Principles & Technique

Q.1. The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula C_5H_{10} is

Ans. 7

Solution. The seven possible cyclic structural and stereoisomers are

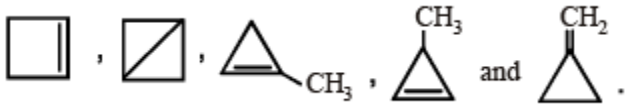


Q. 2. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is 5.

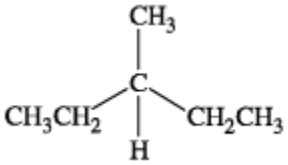
Ans. 5

Solution. The number of cyclic isomers for a hydr ocarbon with molecular formula C_4H_6 is 5.

The structures are

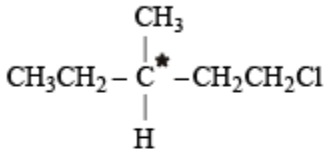


Q. 3. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound is

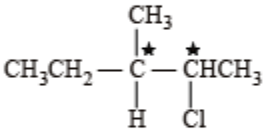


Ans. 8

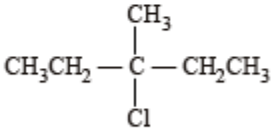
Solution.



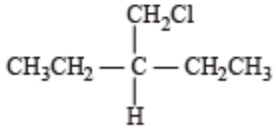
Enantiomeric pair = 2



Two enantiomeric pairs = 4



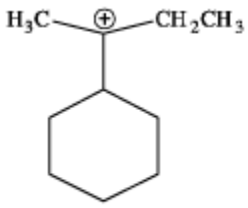
= 1



= 1

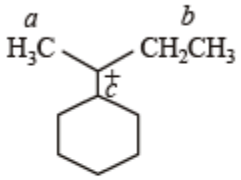
Total = 2 + 4 + 1 + 1 = 8

Q. 4. The total number of contributing structures showing hyperconjugation (involving C-H bonds) for the following carbocation is



Ans. 6

Solution.

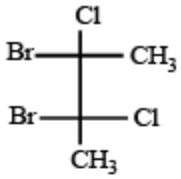


a = 3 Hyperconjugative H's

b = 2 Hyperconjugative H's

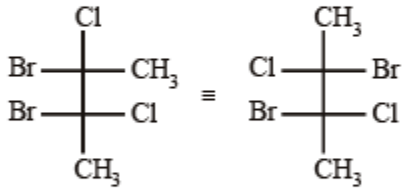
c = 1 Hyperconjugative H

Q. 5. The total number(s) of <u>stable</u> conformers with non-zero dipole moment for the following compound is (are)

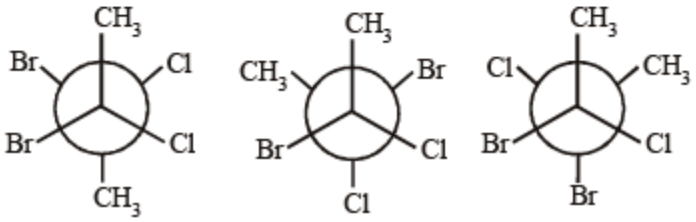


Ans. 3

Solution.



Following three conformers (with $\mu \neq 0$) are possible



Q. 6. The total number of stereoisomers that can exist for M is

Ans. 2

Solution. The molecule cannot show geometrical isomerism, so only its mirror image will be the other stereoisomer.