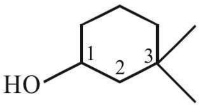
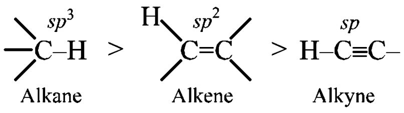
Chapter-12 : Organic Chemistry – Some Basic Principles and Techniques

1. (a) 

3, 3-Dimethyl -1- cyclohexanol

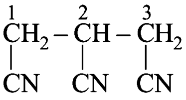
2. (a) Given structures are representing *cis-trans* isomerism (geometrical) hence differ only in configuration.

3. (a) Bond order follows the order



Thus ethane (C_2H_6), being alkane, has longest C–H bond.

4. (b) Chiral conformation will not have plane of symmetry. Since twist boat does not have plane of symmetry. So, it is chiral.

5. (c) 

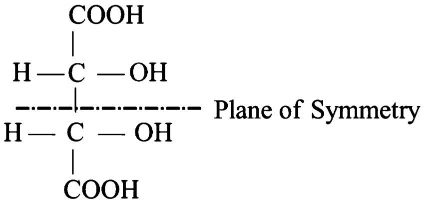
$$\underset{\underset{CN}{|}}{\overset{1}{C}H_2}-\underset{\underset{CN}{|}}{\overset{2}{C}H}-\underset{\underset{CN}{|}}{\overset{3}{C}H_2}$$

1, 2, 3-tricarbonitrile propane

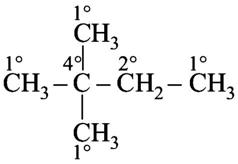
6. (d) Restricted rotation is essential condition for geometrical isomerism.

7. (c) The IUPAC name of the compound $CH_3CONHBr$ is N-bromoethanamide.

8. (a) Molecular symmetry



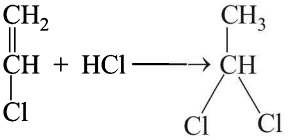
Meso-tartaric acid is optically inactive due to internal compensation *i.e.* the effect on half of the molecule is neutralized by other.

9. (d) 

$$\overset{1^\circ}{CH_3}-\underset{\underset{\underset{1^\circ}{CH_3}}{|}}{\overset{\overset{\overset{1^\circ}{CH_3}}{4^\circ|}}{C}}-\overset{2^\circ}{CH_2}-\overset{1^\circ}{CH_3}$$

Thus number of secondary hydrogens is two.

10. (c) The strength of nucleophile depends upon the nature of alkyl group R on which nucleophile has to attack and also on the nature of solvent. The order of strength of nucleophiles follows the order :
$CN^- > I^- > C_6H_5O^- > OH^- > Br^- > Cl^-$

11. (d) 

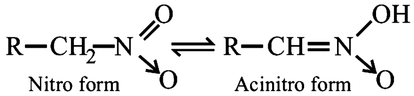
1,1-dichloroethane

It is an addition reaction, which is according to Markovnikov's rule.

12. (a)

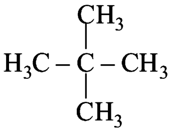
13. (a) A mixture of equal amounts of the two enantiomers is called a racemic mixture.

14. (d) Tautomerism is exhibited by the oscillation of hydrogen atom between two polyvalent atoms present in the molecule. As (d) has α-hydrogen atom therefore it shows tautomerism whereas other structures do not.



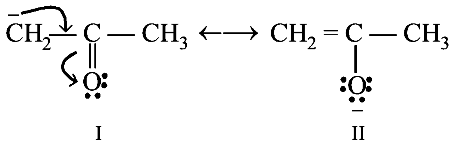
15. (c) The free rotation across C – C gives rise to many spatial arrangements. These arrangements are called conformers and property is called conformation.

16. (c) The structure of neopentane is



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

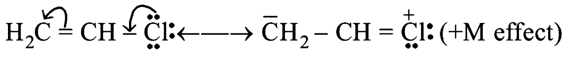
It has 1 quaternary and 4 primary carbons.

17. (a) 

both are resonating structures.

18. (c) Diastereomers, since they have different melting points, boiling points, solubilities etc.

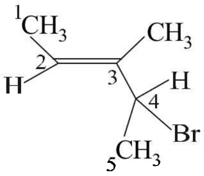
19. (a) The groups which donate electrons to the double bond or to a conjugated system are said to have +M effect or +R effect, e.g.



This criteria is fulfilled by option (a) only.

20. (a) Resolution.

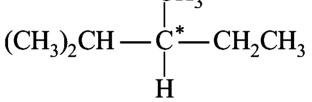
21. (b) The absolute configuration is (R, R)
(using priority rules to get the absolute configuration)
So the correct answer is (b)

22. (d) 

4-Bromo-3-methylpent-2-ene

23. (d)

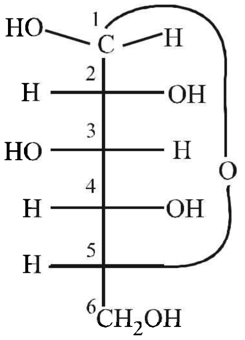
24. (a) A compound is said to exhibit optical isomerism if it atleast contains one chiral carbon atom, which is an atom bonded to 4 different atoms or groups.



$$(CH_3)_2CH-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C^*}}-CH_2CH_3$$

25. (d) Due to + I-effect of the CH_3 group, toluene has much higher electron density in the ring than benzene, nitrobenzene and benzoic acid as they show – I-effect and hence is most reactive towards nitration.

26. **(a)**

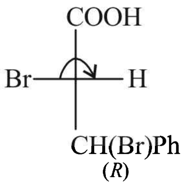


β – D –(+)– Glucose

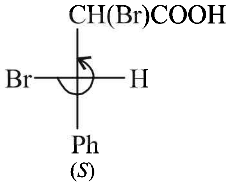
Carbon atoms from C_1 to C_5 are chiral.

27. **(d)** Due to + M effect of the – OH group in phenol, electron density in the ortho and para positions of the phenol nucleus increases hence phenol will undergo electrophilic substitution easily than benzene. The other three compounds have electron withdrawing groups, hence they will undergo electrophilic substitution with a difficulty than benzene.

28. **(d)** At C_2,

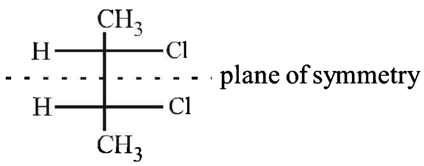


At C_3,



29. **(b)** – I group destablises carbocation and since inductive effect decreases with increasing length of carbon chain. Therefore (b) is the correct option.

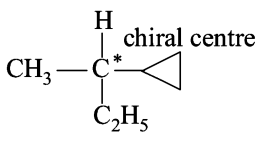
30. **(b)** The compound has two similar assymmetric C-atoms. It has plane of symmetry and exist in Meso form.



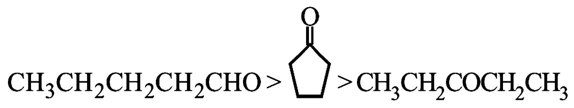
Meso - 2, 3 - dichlorobutane

31. **(a)** Triphenyl methyl cation has three benzene resonating ring so it is most stable compound.

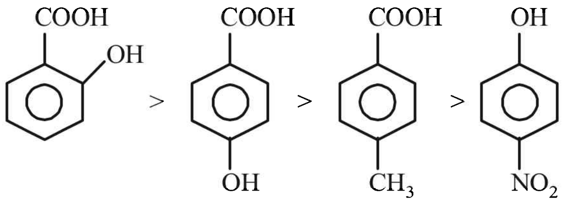
32. **(a)** Only 2- cylcopropyl butane has a chiral centre.



33. **(c)** More is the electron deficiency on the carbonyl carbon, greater will be the reactivity of the carbonyl compounds towards nucleophilic addition.



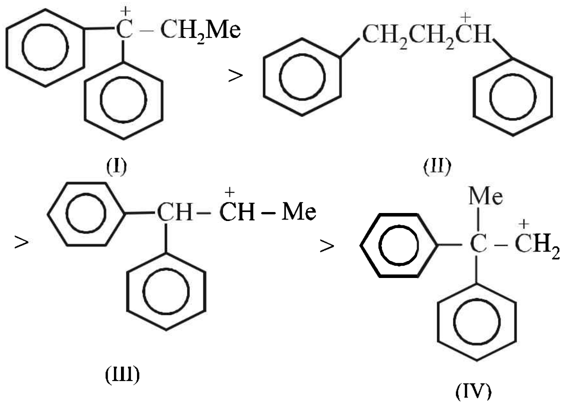
34. **(c)** *o*-Hydroxybenzoic acid is strongest acid and the decreasing order of acidity is



35. **(d)** Order of stability of carbocation is 3° > 2° > 1° and iodine is the best leaving group among halogens.

36. **(d)**

37. **(b)**

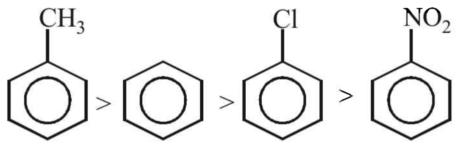


Stability of carbocation depends upon number of resonating structures and extent of +I, –I effect.

38. **(b)**

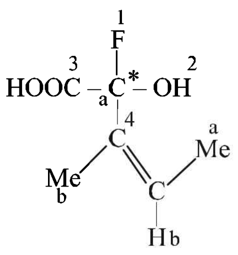
39. **(c)** $-CH_3$ is electron donating group, shows + I effect $-NO_2$ is electron withdrawing group as well as shows –M effect.

–Cl shows – I effect and is a weak deactivating group so the order of reactivity towards electrophilic substitution reaction is:



40. **(c)**

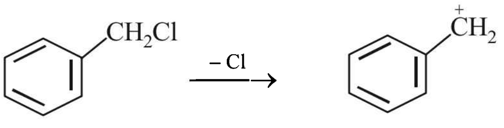
41. **(c)**



In the above compound, the configuration about the chiral carbon (C*) is R.

Since the groups with higher priority marked as (a) are on the same side of the double bond and those with lower priority are on the other side, thus the geometry about the C = C double bond is Z.

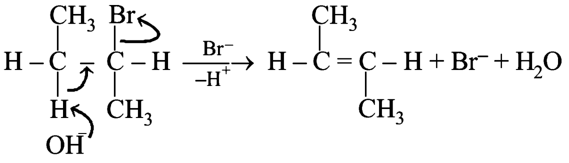
42. **(d)** S_N1 reactions involve the formation of carbocation, more is stability of carbocation, higher will be the probability of alkyl halide to undergo S_N1 mechanism. Thus decreasing order of S_N1 mechanisms follows order Benzyl > allyl > tertiary alkyl halide> secondary alkyl halide > primary alkyl halides



Benzyl cation

Obtained from S_N1 path. This molecule is resonance stabilised.

43. **(a)**

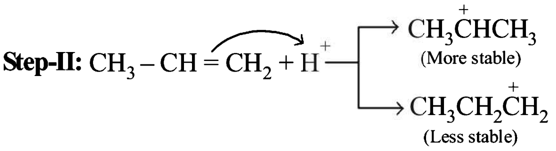


$$H-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{Br}{C}}-H \xrightarrow[-H^+]{Br^-} H-\underset{}{\overset{CH_3}{C}}=\underset{CH_3}{C}-H+Br^-+H_2O$$

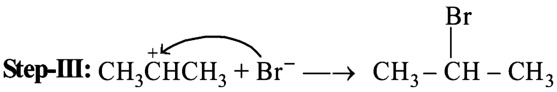
44. **(b)** Methyl carbanion is sp^3 hybridised, with three bond pairs and one lone pair same is the case with NH_3.

45. **(b)** Hyperconjugation is orbital interactions between π-systems and the adjacent σ bond of substituent groups. For hyperconjugation σ-carbon with respect to sp^2 hybrid carbon should have at least one hydrogen.

46. **(a)** **Step-I:** HBr $\longrightarrow$ H^+ + Br^- [Electrophile]

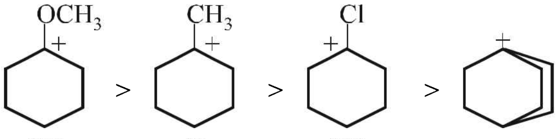


Step-II: $CH_3-CH=CH_2+\overset{+}{H}$ → $CH_3\overset{+}{C}HCH_3$ (More stable); → $CH_3CH_2\overset{+}{C}H_2$ (Less stable)



Step-III: $CH_3\overset{+}{C}HCH_3+Br^- \longrightarrow CH_3-\overset{Br}{CH}-CH_3$

47. **(a)**



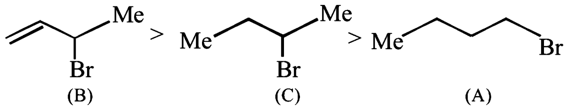
48. **(a)** The given compound contains only one double bond which can participate in geometrical isomerism. So, it shows two isomers.

49. **(c)** Order of basic nature of compounds depend on electron donating tendency.

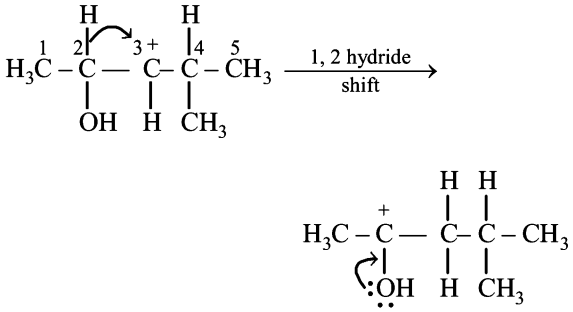
The compound (ii) is least basic among all given compounds due to sp^2 hybridisation of nitrogen atom.

Compound (iii) is most basic in given compounds due to resonance, one nitrogen carry negative charge and its conjugate acid have two equivalent resonating structure. Secondary amine (iv) is more basic than primary amine (i).

50. **(b)** Reactivity towards S_N1 depends on stability of carbocation



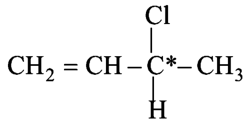
51. **(d)** Migrating tendency of hydride is greater than that of alkyl group. Further migration of hydride from C–2 gives more stable carbocation (stabilized by +R effect of OH group and +I and hyperconjugative effects of methyl group).



More stable carbocation

52. **(b)** Carboxylic acids are stronger acids than $-\overset{+}{N}H_3$ because the corresponding conjugate base ($-COO^-$) is more stable than $-NH_2$. Hence, Y is the strongest acid. Since – COOH has – I effect which decreases with distance, therefore, effect is more pronounced in Z than in X. As a result, Z is more acidic than X. Hence the correct option is Y > Z > X.

53. **(a)** Acyclic stereoisomers having molecular formula C_4H_7Cl



$$CH_2=CH-\underset{H}{\overset{Cl}{C^*}}-CH_3$$

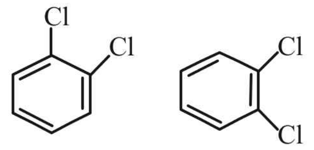
one asymmetric carbon

Therefore, number of optical isomers = $2^n = 2^1 = 2$. Two geometrical isomers of each compound are possible for the following structures.

$ClHC=CH-CH_2-CH_3$, $ClH_2C-CH=CH-CH_3$

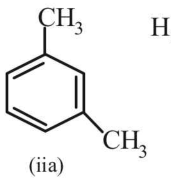
and $CH_3-\underset{Cl}{C}=CH-CH_3$

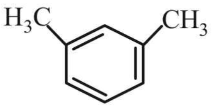
54. **(d)**



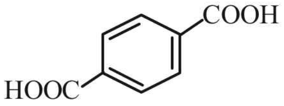
(ia) (ib)

Both 1, 2-dichloro benzene. Hence identical compounds


(iia)


(iib)

Both 1, 3-diemethyl benzene. Hence identical compounds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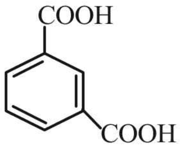
(iiib)

(iii a) and (iii b) are position isomers

55. (d) Chlorine atoms are strongly negative (show –I effect). They deactivate the ring towards electrophilic reaction.