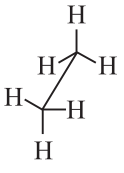
Hydrocarbons

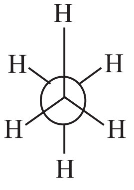
OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions (MCQs)

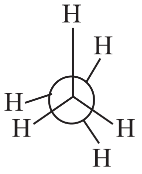
1. In the following structures, which two forms are staggered conformation of ethane?



(1)



(2)



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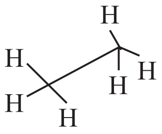


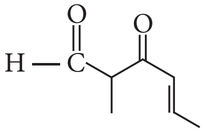
(4)

(a) 1 and 4 (b) 2 and 3
(c) 1 and 2 (d) 1 and 3

2. Which of the following molecules represents the order of hybridisation sp^2, sp^2, sp, sp from left to right atoms?

(a) $HC \equiv C - C \equiv CH$
(b) $CH_2 = CH - C \equiv CH$
(c) $CH_2 = CH - CH = CH_2$
(d) $CH_3 - CH = CH - CH_3$

3. The IUPAC name of the given compound is



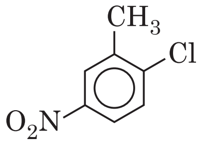
(a) 5-formylhex-2-en-3-one
(b) 5-methyl-4-oxohex-2-en-5-al
(c) 3-keto-2-methylhex-5-enal
(d) 3-keto-2-methylhex-4-enal

4. Arrange the following in decreasing order of their boiling points.

(I) *n*-Butane
(II) 2-Methylbutane
(III) *n*-Pentane
(IV) 2,2-Dimethylpropane

(a) I > II > III > IV (b) II > III > IV > I
(c) IV > III > II > I (d) III > II > IV > I

5. IUPAC name of



is

(a) 1-chloro-2-methyl-4-nitrobenzene
(b) 2-chloro-1-methyl-5-nitrobenzene
(c) 1-nitro-1-methyl-4-nitrobenzene
(d) 2-methyl-1-chloro-4-nitrobenzene.

6. The alkene that exhibits geometrical isomerism is

(a) propene (b) 2-methylpropene
(c) 2-butene (d) 2-methyl-2-butene.

7. During ozonolysis of $CH_2 = CH_2$ if hydrolysis is made in absence of Zn dust the products formed are

(a) HCHO (b) HCOOH
(c) CH_2OHCH_2OH (d) CH_3OH

8. Among the three conformations of ethane, the order of stability follows the sequence :

(a) eclipsed > gauche > staggered
(b) eclipsed > staggered > gauche
(c) staggered > gauche > eclipsed
(d) gauche > staggered > eclipsed

9. In the following sequence of reactions, the compound B is

$$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B$$

(a) CH_3CHO (b) CH_3CH_2CHO
(c) CH_3COCH_3 (d) $CH_3CH_2COCH_3$

10. Which of the following is Baeyer's reagent?

(a) alkaline $KMnO_4$ (b) acidic $K_2Cr_2O_7$
(c) alkaline $Na_2Cr_2O_7$ (d) MnO_2

11. The function of anhydrous $AlCl_3$ in Friedel–Crafts reaction is

(a) to absorb water
(b) to absorb HCl
(c) to produce attacking electrophile
(d) to produce nucleophile.

12. *Meta*-directing and deactivating group in aromatic electrophilic substitution is

(a) $-CH_3$ (b) $-OH$
(c) $-NO_2$ (d) $-Cl$

13. The numbers of σ and π-bonds present in 1, 3-butadiene are respectively
(a) 9 and 2 (b) 8 and 2
(c) 9 and 3 (d) 9 and 1

14. Which of the following reaction is not correct?
(a) Propene + HCl $\longrightarrow$ 2-chloropropane
(b) Propene + HBr $\xrightarrow{\text{peroxide}}$ 1-bromopropane
(c) Propene + HCl $\xrightarrow{\text{peroxide}}$ 2-chloropropane
(d) Propene + HBr $\longrightarrow$ 1-bromopropane

15. Which of the following species is most stable?
(a) $p\text{-}O_2N - C_6H_4 - \overset{+}{C}H_2$
(b) $C_6H_5 - \overset{+}{C}H_2$
(c) $p\text{-}Cl - C_6H_4 - \overset{+}{C}H_2$
(d) $p\text{-}CH_3O - C_6H_4 - \overset{+}{C}H_2$

16. Arrange the following hydrogen halides in order of their decreasing reactivity with propene.
(a) HCl > HBr > HI (b) HBr > HI > HCl
(c) HI > HBr > HCl (d) HCl > HI > HBr

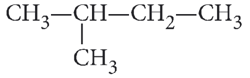
17. The IUPAC name of the compound having the formula $CH \equiv C - CH = CH_2$ is
(a) 1-butyn-2-ene (b) but-1-yn-3-ene
(c) 1-buten-3-yne (d) 3-buten-1-yne

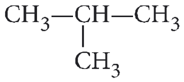
18. Which of the following reactions of methane is incomplete combustion?
(a) $2CH_4 + O_2 \xrightarrow{Cu/523K/100\ atm} 2CH_3OH$
(b) $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$
(c) $CH_4 + O_2 \longrightarrow C_{(s)} + 2H_2O_{(l)}$
(d) $CH_4 + 2O_2 \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$

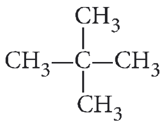
19. Benzene is obtained when
(a) acetylene is passed through red hot iron tube
(b) benzenesulphonic acid is treated with superheated steam
(c) both (a) and (b)
(d) none of these.

20. The molecule having net dipole moment is
(a) 2,2-dimethylpropane
(b) *trans*-pent-2-ene
(c) *trans*-but-2-ene
(d) 2, 2, 3, 3-tetramethylbutane.

21. In which of the following compounds only primary carbon atoms are present?

(a) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

(b) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(c) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

(d) CH_3-CH_3

22. The dihedral angle HCH in staggered conformation of C_2H_6 is
(a) 120° (b) 60° (c) 0° (d) 90°

23. The reaction, $RC \equiv CR \xrightarrow[\text{Lindlar's catalyst}]{H_2}$ gives the main product as
(a) *cis*-alkene (b) *trans*-alkene
(c) alkane (d) none of these.

24. Anti-Markownikoff addition of HBr is not observed in
(a) propene (b) 1-butene
(c) 2-butene (d) 2-pentene

25. Mark the correct decreasing order of stability.
(a) Aromatic > non-aromatic > anti-aromatic
(b) Aromatic > anti-aromatic > non-aromatic
(c) Non-aromatic > anti-aromatic > aromatic
(d) Anti-aromatic > non-aromatic > aromatic

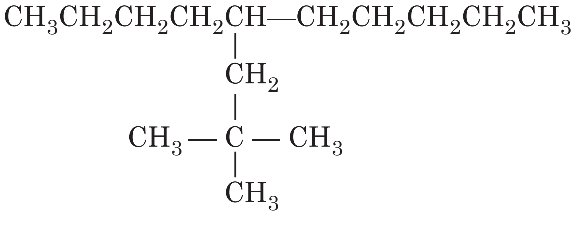
26. Which among the following is very strong *o*-, *p*-directing group ?
(a) $-Cl$ (b) $-OR$ (c) $-NH_2$ (d) $-NHR$

27. Electrolysis of an aqueous solution of sodium ethanoate gives
(a) methane (b) ethane
(c) butane (d) methyl ethanoate.

28. Which of the following compounds reacts with sodium to liberate hydrogen gas?
(a) Ethane (b) Propene
(c) Acetylene (d) Benzene

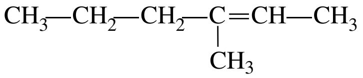
29. The correct order of reactivity towards electrophilic substitution is
(a) phenol > benzene > chlorobenzene > benzoic acid
(b) benzoic acid > chlorobenzene > benzene > phenol
(c) phenol > chlorobenzene > benzene > benzoic acid
(d) benzoic acid > phenol > benzene > chlorobenzene

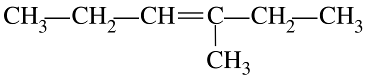
30. Which is the correct IUPAC name of the following compound?

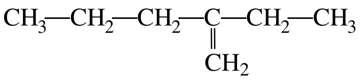

$$\begin{array}{c} CH_3CH_2CH_2CH_2CH-CH_2CH_2CH_2CH_2CH_3 \\ | \\ CH_2 \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array}$$

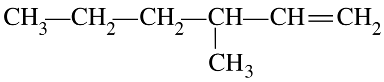
(a) 5-(2′, 2′-Dimethylpropyl)decane
(b) 4-Butyl-2,2-dimethylnonane
(c) 2,2-Dimethyl- 4-pentyloctane
(d) 2,2-Dimethyl- 4-butylnonane

31. An alkene on ozonolysis gave 2-pentanone and acetaldehyde. The alkene was

(a) 
$CH_3-CH_2-CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_3$

(b) 
$CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CH_2-CH_3$

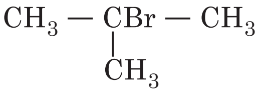
(c) 
$CH_3-CH_2-CH_2-\underset{CH_2}{\underset{\|}{C}}-CH_2-CH_3$

(d) 
$CH_3-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH=CH_2$

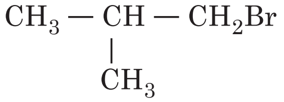
32. Which of the following compounds will not undergo Friedal-Crafts reaction easily?

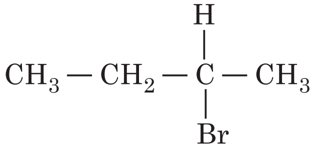
(a) Nitrobenzene (b) Toluene
(c) Cumene (d) Xylene

33. The reaction of HBr with $CH_3C(CH_3)=CH_2$ in the presence of peroxide will give

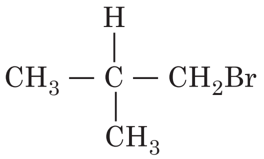
(a) 
$CH_3-\underset{CH_3}{\underset{|}{CBr}}-CH_3$

(b) $CH_3CH_2CH_2CH_2-Br$

(c) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2Br$

(d) 
$CH_3-CH_2-\overset{H}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3$

34. Arrange the following alkyl halides in decreasing order of the rate of β-elimination reaction with alcoholic KOH.

(I) 
$CH_3-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2Br$

(II) CH_3-CH_2-Br

(III) $CH_3-CH_2-CH_2-Br$

(a) I > II > III (b) III > II > I
(c) II > III > I (d) I > III > II

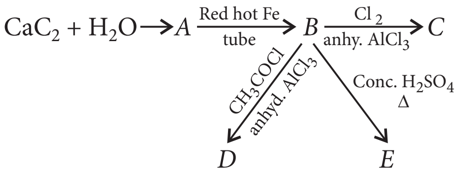
35. Benzene easily shows

(a) ring fission reactions since it is unstable
(b) addition reactions since it is unsaturated
(c) electrophilic substitution reactions due to stable ring and high π electron density
(d) nucleophilic substitution reactions due to stable ring and minimum electron density.

Case Based MCQs

Case I : Read the following and answer the questions from 36 to 40 given below.

Compound (*A*) is an important industrial feed stocks, but it's largest use as the fuel for the oxyacetylene torch. It is a colourless, foul smelling gas that burns in air with a yellow, sooty flame.



36. Identify the product *A*.

(a) ethane (b) ethyne
(c) ethene (d) methane

37. The compound (*B*) formed is

(a) cyclohexane (b) benzene
(c) hexane (d) cyclopentane.

38. The reaction $B \xrightarrow[\text{Anhy.AlCl}_3]{Cl_2} C$ follows

(a) nucleophilic substitution mechanism
(b) electrophilic addition mechanism
(c) electrophilic subsituition mechanism
(d) elimination reaction mechanism.

39. The product *E* is

(a) nitrobenzene
(b) benzene sulphonic acid
(c) both (a) and b (d) none of these.

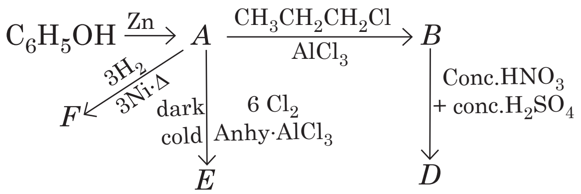
40. Identify the product '*D*'.

(a) Chlorobenzene (b) Bromobenzene
(c) Toluene (d) Acetophenonone

Case II : Read the following and answer the questions from 41 to 45 given below.

Compound '*A*' is the simplest and ideal aromatic compound. It is also one of the most basic petrochemicals which is mainly used to prepare a number of important chemicals such as toluene, phenol, aniline, biphenyl etc, which are used in manufacture of dyes, detergents, drugs, explosives, pesticides etc. But it is carcinogenic.

In the given sequence of reaction, compound *A* undergoes a number of changes



41. The name of compound *A* is

(a) cyclohexane

(b) benzene

(b) cyclohexene

(d) none of these.

42. The reaction $A \xrightarrow[AlCl_3]{CH_3CH_2CH_2Cl} B$ is an example of

(a) elimination reaction

(b) addition reaction

(c) electrophilic substitution reaction

(d) nucleophilic substitutional reaction.

43. The name of product *F* is

(a) benzene	(b) cyclohexene
(c) cyclohexane	(d) cyclohex-1 4-diene

44. The major product when '*A*' reacts with propyl chloride in the presence of $AlCl_3$ is

(a) propyl benzene

(b) isopropyl benzene

(c) chloro benzene

(d) ethyl benzene.

45. The major product '*D*' in the given series of reaction is

(a) 4-nitro isopropyl benzene

(b) 2-nitro isopropyl benzene

(c) 3-nitro propyl benzene

(d) none of these.

Assertion & Reasoning Based MCQs

For question numbers 46-55, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

46. Assertion : Boiling point of alkanes increases with increase in molecular weight.

Reason : van der Waal's forces increase with increase in molecular weight.

47. Assertion : Acetylene is acidic in nature.

Reason : Acetylene is sp hybridised.

48. Assertion : *Trans*-pent-2-ene is polar but *trans*-but-2-ene is non-polar.

Reason : The polarity of cis-isomer is more than trans which are either non-polar or less polar.

49. Assertion : Benzene on heating with conc. H_2SO_4 gives benzenesulphonic acid which when heated with superheated steam under pressure gives benzene.

Reason : Sulphonation is a reversible process.

50. Assertion : Sodium acetate on Kolbe's electrolysis gives methane.

Reason : Methyl free radical is formed at anode.

51. Assertion : $HC \equiv C^-$ is more stable than $H_2C = CH^-$.

Reason : $HC \equiv C^-$ has more *s*-character than $H_2C = CH^-$.

52. Assertion : All the hydrogen atoms in $CH_2 = C = CH_2$ are attached to sp^2 hybridised carbon atom.

Reason : All the carbon atoms in its are sp^2 hybridized.

53. Assertion : Methane cannot be obtained by Wurtz reaction.

Reason : Wurtz reaction leads to the formation of symmetrical alkane having an even number of carbon atoms.

54. Assertion : Saturated hydrocarbons are chemically less reactive.

Reason : All isomeric paraffins have same parent name.

55. Assertion : Nitrobenzene does not undergo Friedel Crafts reaction.

Reason : Nitrobenzene is a *m*-director.

SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

1. When alkyne is treated with bromine water then what will be the colour of product?

2. What product would you get from acid catalysed hydration of 1-methylcyclohexene? Explain.

3. Explain why the branching of an alkane chain lowers its boiling point.

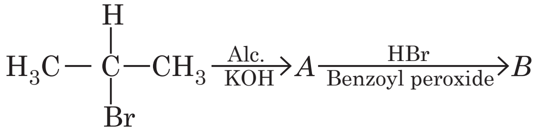
4. Give a brief account for the following statement :
CH_4 cannot be synthesized by Wurtz reaction.

5. Acetylene is acidic but it does not react with NaOH or KOH. Give reason.

6. Complete the following reaction :

$$CH_3-CH=CH_2 + HBr \xrightarrow{\text{Organic peroxide}}$$

7. Write structures of A and B in the following reaction :



$$H_3C-\overset{\overset{\large H}{|}}{\underset{\underset{\large Br}{|}}{C}}-CH_3 \xrightarrow[\text{KOH}]{\text{Alc.}} A \xrightarrow[\text{Benzoyl peroxide}]{\text{HBr}} B$$

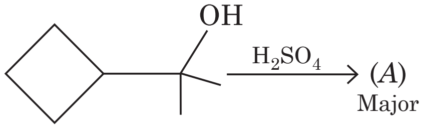
8. Name the chain isomer of C_5H_{12} which has a tertiary hydrogen atom.

9. Explain why dry ether is used as a solvent in Wurtz reaction.

10. Draw the Newmann projection formula for staggered and eclipsed conformation of ethane.

Short Answer Type Questions (SA-I)

11.



Identify A

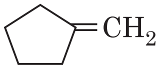
12. How will you convert methyl bromide to ethane?

13. Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms?

14. Ethyne reacts with dil. H_2SO_4 in presence of mercury salt to give acetaldehyde but with dil. HCl under similar conditions, it gives vinyl chloride. Explain why.

15. Which alkyne would you start with and what reagents would you use to prepare :
(i) *cis*-but-2-ene (ii) *trans*-pent-2-ene

16. What do the following compounds produce when passed through Cr_2O_3 supported over aluminia at 600°C?
(i) *n*-Hexane
(ii) *n*-Heptane

17. What will  produce on ozonolysis?

18. $Ph-CH_2-C\equiv CH \underset{Y}{\overset{X}{\rightleftharpoons}} Ph-C\equiv C-CH_3$

Identify X and Y .

19. Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour. Also, give reason for this behaviour.

20. Explain Friedel–Crafts alkylation reaction with chemical equation.

Short Answer Type Questions (SA-II)

21. An alkyne (X) has molecular formula C_5H_8. It reacts neither with sodamide nor with ammoniacal cuprous chloride. Identify X.

22. Complete the following reactions :

(i) $HC\equiv CH \xrightarrow{NaNH_2, CH_3Br} A$

(ii) $HC\equiv CH \xrightarrow{H_2O, HgSO_4/H_2SO_4} B$

(iii) $CH_3C\equiv CH + H_2 \xrightarrow{Pt/\ Pd/Ni} C \xrightarrow{H_2} D$

23. An alkene 'A' contains three C — C, eight C — H σ bonds and one C — C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'.

24. (a) Explain the order of stability of carbocations giving reason.
(b) Addition of HBr to propene in the presence of benzoyl peroxide yields 1-bromopropane. Explain with suitable mechanism.

25. (a) Write chemical reactions to illustrate the Kolbe's reaction
(b) Name the compound that will be required to obtain butane using Kolbe's electrolysis process.

26. Why *cis*-but-2-ene has higher boiling point than *trans*-but-2-ene?

27. Despite their –*I* effect, halogens are *o*- and *p*-directing in haloarenes. Explain.

28. An organic compound *A* with molecular formula C_3H_8O reacts with conc. H_2SO_4 to give *B*, which on reaction with HCl gives *C*. Compound *C* reacts with metallic sodium to give *D*. Identify compounds *A*, *B*, *C* and *D*.

29. Explain *ortho*- and *para*-directing influence of monosubstituted benzene giving suitable example.

30. Draw the Newman projections of the eclipsed and staggered conformers of ethane. Which of the two is stable and why?

31. Explain anti-Markovnikov addition or peroxide effect or Kharash effect with example.

32. What does ozonolysis of benzene yield?

33. Give two reactions to show acidic character of alkynes.

34. Identify a reagent which can easily distinguish between 1-butyne and 2-butyne.

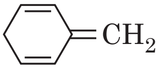
35. A hydrocarbon (*Z*) has molecular formula C_8H_{10}. It does not decolourise bromine water and is oxidised to benzoic acid on heating with $K_2Cr_2O_7$. It can also have three other isomers *A*, *B* and *C*. Write the structures of *Z, A, B* and *C*.

Long Answer Type Questions (LA)

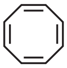
36. An alkyl halide $C_5H_{11}Br$ (*A*) reacts with ethanolic KOH to give an alkene '*B*', which reacts with Br_2 to give a compound '*C*', which on dehydrobromination gives an alkyne '*D*'. On treatment with sodium metal in liquid ammonia one mole of '*D*' gives one mole of the sodium salt of '*D*' and half a mole of hydrogen gas. Complete hydrogenation of '*D*' yields a straight chain alkane. Identify *A*,*B*,*C* and *D*. Give the reactions involved.

37. A hydrocarbon '*Y*' decolourises bromine water. On ozonolysis it gives 3-methylbutanal and formaldehyde. Give the name of the compound. Identify *Y*.

38. Explain why the following systems are not aromatic.

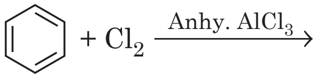
(a) 

(b) 

(c) 

39. Draw the resonating structure of C_6H_5OH (phenol) and C_6H_5CHO (benzaldehyde).

40. Give mechanism for the following reaction.

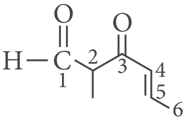


ANSWERS

OBJECTIVE TYPE QUESTIONS

1. (c) : In staggered conformation, the rotation about the C – C bond is such that the hydrogen atoms attached tetrahedrally to the two carbon atoms are completely staggered *i.e.* they are at maximum distance apart in space.

2. (b) : $\overset{sp^2}{CH_2}=\overset{sp^2}{CH}-\overset{sp}{C}\equiv\overset{sp}{CH}$

3. (d) : 

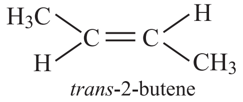
3-Keto-2-methylhex-4-enal

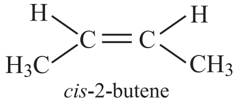
4. (d) : Boiling point increases with increase in molecular mass. Straight chain hydrocarbons have higher boiling points than branched chain hydrocarbons of comparable molecular mass.

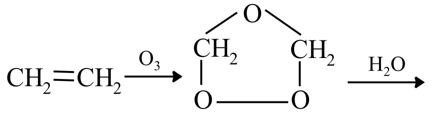
5. (a)

6. (c) : When two groups attached to a double bonded carbon atom are same, the compound does not exhibit geometrical isomerism.

Compounds in which the two groups attached to a double bonded carbon are different, exhibit geometrical isomerism, thus, only 2-butene exhibits *cis-trans* isomerism.


trans-2-butene


cis-2-butene

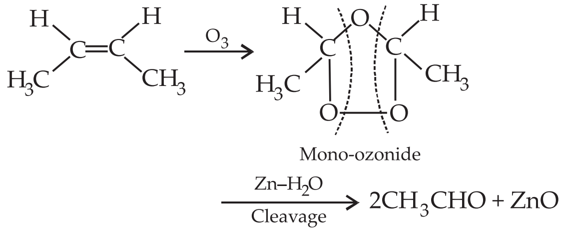
7. (b) : 

HCOOH + HCOOH

Reductive hydrolysis of ozonide with Zn dust gives carbonyl compound whereas oxidative hydrolysis yields carboxylic acid.

8. (c) : The eclipsed conformation is least stable because the hydrogens and bonding pairs of electrons on adjacent carbon atoms are as close to one another as possible. This causes maximum repulsion and least stability. Staggered conformation is most stable because of minimum repulsion. Gauche conformation lie between these two in stability. Thus, order of stability is : staggered > gauche > eclipsed.

9. (a) : The complete reaction sequence is as follows:

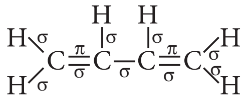


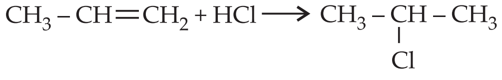
10. (a) : Baeyer's reagent is alkaline solution of cold potassium permanganate ($KMnO_4$).

11. (c) : $AlCl_3$ produces attacking electrophile.

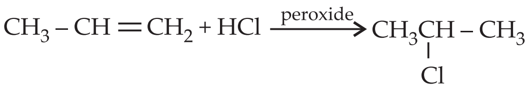
$$Cl_2 + AlCl_3 \longrightarrow \underset{\text{Electrophile}}{Cl^+} + AlCl_4^-$$

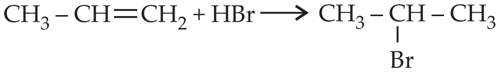
12. (c) : – CH_3 : Activating and *o*, *p*-directing
– OH : Activating and *o*, *p*-directing
– NO_2 : Deactivating and *m*-directing
– Cl : Deactivating and *o*, *p*-directing

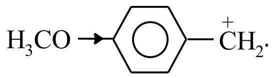
13. (a) : 

14. (d) : 
$CH_3-CH{=}CH_2 + HCl \longrightarrow CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}H-CH_3$

$CH_3-CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br$


$CH_3-CH{=}CH_2 + HCl \xrightarrow{\text{peroxide}} CH_3\underset{\displaystyle Cl}{\underset{|}{C}}H-CH_3$


$CH_3-CH{=}CH_2 + HBr \longrightarrow CH_3-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3$

15. (d) :  Electron donating group stabilizes the cation.

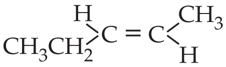
16. (c) : The decreasing order of reactivity of halo acids with propene is HI > HBr > HCl. As the size of halogen increases, the strength of H – *X* bond decreases and hence, reactivity increases.

17. (c) : $\overset{4}{CH} \equiv \overset{3}{C}-\overset{2}{CH}=\overset{1}{CH_2}$
1-Buten-3-yne

18. (c) : $CH_4 + O_2 \rightarrow C + 2H_2O$

Complete combustion will give CO_2 and H_2O.

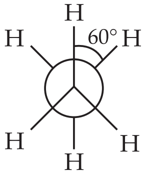
19. (c)

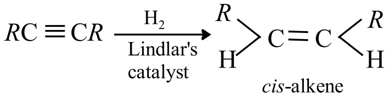
20. (b) : 

trans-pent-2-ene is unsymmetrical, therefore, show net dipole moment.

While 2,2-dimethylpropane, *trans*-but-2-ene and 2,2,3,3-tetramethylbutane are symmetrical, therefore do not show net dipole moment.

21. (d) : $\overset{1°}{CH_3}-\overset{1°}{CH_3}$

22. (b) : 

23. (a) : 

24. (c) : Anti-Markownikoff addition of HBr is observed only with unsymmetrical alkenes *i.e.*, propene, 1-butene, 2-pentene. As, 2-butene is symmetrical so in its case anti-Markownikoff addition will not be observed.

25. (a) : Aromatic are most stable followed by non-aromatic and anti-aromatics are least stable.

26. (d) : The directive influence order is

$O^- > NR_2 > NHR > NH_2 > OH > OCH_3 \approx NHCOCH_3 > CH_3 > X$

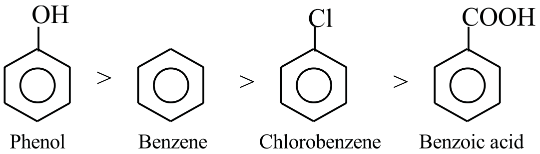
27. (b) : $\underset{\text{Sodium ethanoate}}{2CH_3COONa} + 2H_2O \xrightarrow[\text{(Kolbe's method)}]{\text{Electrolysis}}$

$\underset{\text{Ethane}}{CH_3{-}CH_3} + 2CO_2 + 2NaOH + H_2$

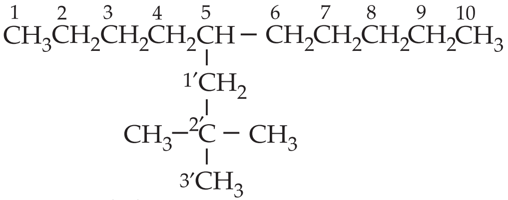
28. (c) : Only acetylene has acidic hydrogens and hence reacts with Na to evolve H_2 gas.

$2HC \equiv CH + 2Na \longrightarrow 2Na^+\bar{C} \equiv \bar{C}\overset{+}{Na} + H_2$

29. (a) : In general electron-releasing groups activate and electron withdrawing groups deactivate the benzene ring towards electrophilic substitutions. Thus order of reactivity is:



30. (a) :



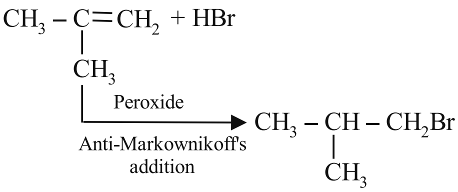
$$\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH}(\overset{1'}{CH_2}-\overset{2'}{C}(CH_3)_2-\overset{3'}{CH_3})-\overset{6}{CH_2}\overset{7}{CH_2}\overset{8}{CH_2}\overset{9}{CH_2}\overset{10}{CH_3}$$

5-(2′, 2′-Dimethylpropyl)decane
or 5-*neo*-Pentyldecane

31. (a)

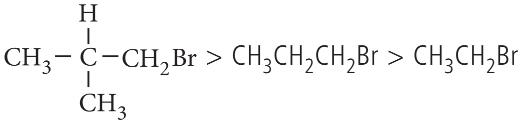
32. (a) : Nitrobenzene is strongly deactivated, hence will not undergo Friedel-Crafts reaction.

33. (c) :



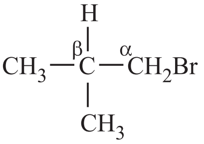
$$CH_3-C(CH_3)=CH_2 + HBr \xrightarrow[\text{Anti-Markownikoff's addition}]{\text{Peroxide}} CH_3-CH(CH_3)-CH_2Br$$

34. (d) :



$$CH_3-CH(CH_3)-CH_2Br > CH_3CH_2CH_2Br > CH_3CH_2Br$$

is the order of rate of β-elimination with alcoholic KOH.



$$\overset{\beta}{CH_3}-\overset{\alpha}{CH_2}-Br$$

(I) (II)

(has 2 β-substituents) (has no β-substituent)

$$CH_3-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-Br$$

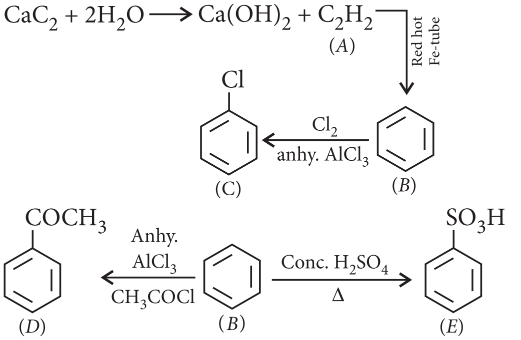
(III)

(has 1 β-substituent)

More the number of β-substituents (alkyl groups), more stable alkene it will form on β-elimination and more will be the reactivity. Thus, the decreasing order of the rate of β-elimination reaction with alcoholic KOH is : I > III > II.

35. (c) : The most common reactions shown by benzene are electrophilic substitution reactions.

36. (b) :

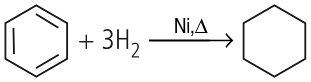


37. (c) **38. (c)**

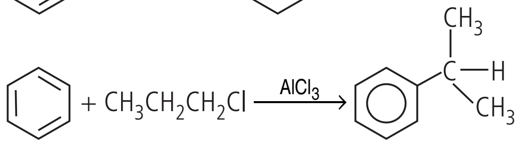
39. (b) **40. (d)**

41. (b) **42. (c)**

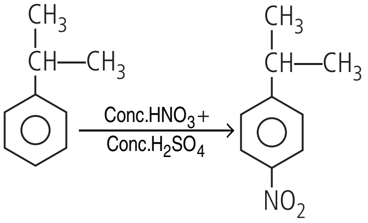
43. (c) :



44. (b) :



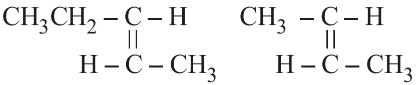
45. (a) :



46. (a) : Greater is the molecular mass, greater is the magnitude of van der Waal's forces of attraction and hence higher the boiling point.

47. (b) : The acidic nature in acetylene is described on the basis of higher electronegativity of sp hybridized carbon atom which pulls the C – H bond pair more effectively to lose H^+.

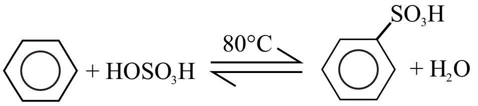
48. (b) : The vector sum of all polar bonds in *trans*-pent-2-ene is not zero but the vector sum is zero in *trans*-but-2-ene.



$$CH_3CH_2-C(H)=C(H)-CH_3 \qquad CH_3-C(H)=C(H)-CH_3$$

trans-2-pentene ($\mu \neq 0$) *trans*-2-butene ($\mu = 0$)

49. (a) : Sulphonation of benzene is an electrophilic substitution reaction in which SO_3 acts as the electrophile.



50. (d) : Sodium acetate on Kolbe's electrolysis gives ethane. It is formed at anode.

51. (a) : $HC\equiv C^-$ has 50% *s*-character and $H_2C=CH^-$ has 33% *s*-character. Stability of carbanions increases with an increase in the *s*-character at the carbanion. So, $HC\equiv C^-$ is more stable than $H_2C=CH^-$.

52. (c) : The two H-atom on first carbon and the two H-atoms on the third carbon atom are attached to sp^2 hybridised carbon atoms. The central carbon atom is *sp*-hybridized.

53. (a) : Wurtz reaction involves the formation of alkanes by heating alkyl halide with sodium in ether.

In this reaction two alkyl radicals join together to form an alkane. The net result in this reaction is the formation of symmetrical alkane (*R–R*) having an even number of carbon atoms.

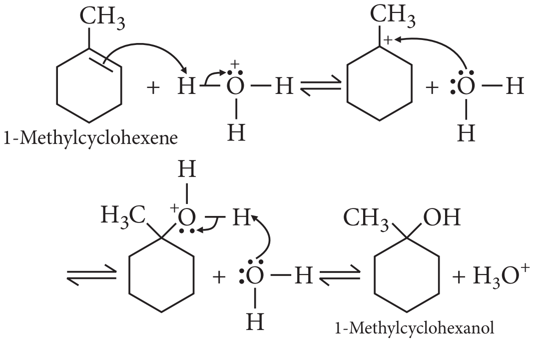
54. (c) : Less reactivity of saturated hydrocarbons is due to the presence of single bonds between carbon atoms. Paraffins (alkanes) may have straight chain or branched chain isomers which have different parent names.

55. (b) : The Friedel Crafts reaction does not take place with nitrobenzene because the ring has been too greatly deactivated. Moreover, any coordination of $AlCl_3$ with unshared electrons of oxygen of NO_2 group would further deactivate the ring making $-NO_2$ electrophilic.

SUBJECTIVE TYPE QUESTIONS

1. The product will be colourless.

2. 1-Methylcyclohexanol will be formed because a 3° carbocation will be formed as an intermediate.



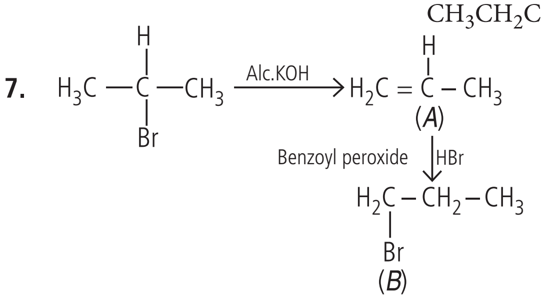
3. Boiling point decreases with increase in branching due to decrease in surface area of the molecule.

4. Wurtz reaction occurs between two alkyl halides to yield alkane. Methane has only one carbon atom, hence cannot be prepared by using Wurtz reaction.

5. Due to *sp*-hybridisation of C-atom in acetylene, proton is strongly attracted by nucleus and cannot be abstracted easily therefore, it does not react with NaOH or KOH.

6. $CH_3CH{=}CH_2 + HBr \xrightarrow{\text{Organic peroxide}} CH_3CH_2CH_2Br$

7.

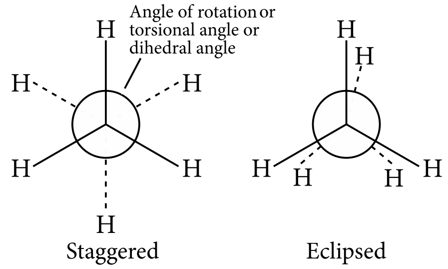


$H_3C-\underset{\large Br}{\overset{\large H}{C}}-CH_3 \xrightarrow{\text{Alc.KOH}} \underset{(A)}{H_2C=\overset{\large H}{C}-CH_3} \xrightarrow[\text{Benzoyl peroxide}]{HBr} \underset{(B)}{H_2\underset{\large Br}{C}-CH_2-CH_3}$

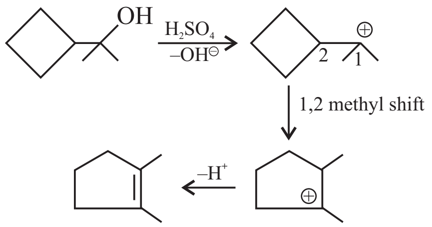
8. 2-Methylbutane, $(CH_3)_2CH - CH_2 - CH_3$.

9. In Wurtz reaction, pure sodium is used which is highly violent towards water therefore, dry ether is used.

10.



11.



12. Two moles of methyl bromide react with sodium metal in presence of dry ether as solvent to give ethane. This reaction is known as Wurtz reaction.

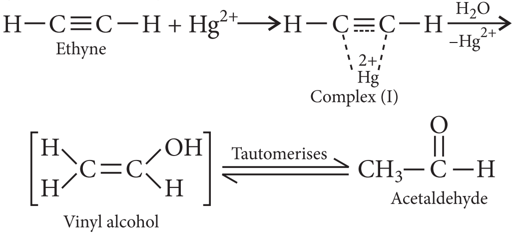
$$\underset{\text{Methyl bromide}}{CH_3-\boxed{Br + 2Na + Br}-CH_3} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

13. It is because mixture of alkanes will be formed *e.g.*,

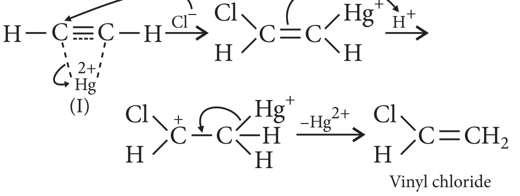
$$\underset{\text{Chloromethane}}{3CH_3Cl} + 6Na + \underset{\text{Chloroethane}}{3C_2H_5Cl} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Ethane}}{CH_3-CH_3}$$

$$+ \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + \underset{\text{Propane}}{CH_3-CH_2-CH_3} + 6NaCl$$

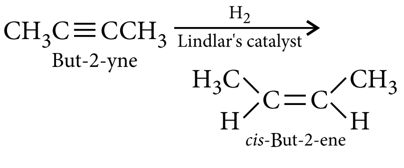
14. Mercuric ion forms a complex (I) with acetylene. Since, H_2O is more nucleophilic than SO_4^{2-} ion, it attacks the complex (I) to form first vinyl alcohol which further tautomerises to give acetaldehyde.



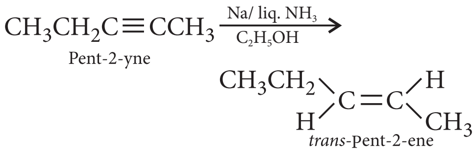
In case of dil. HCl, Cl^- ion is more nucleophilic than H_2O, it reacts with complex (I) to form vinyl chloride.

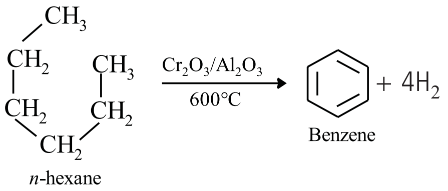


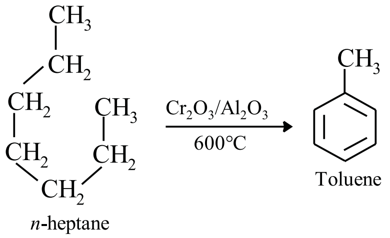
15. (i)

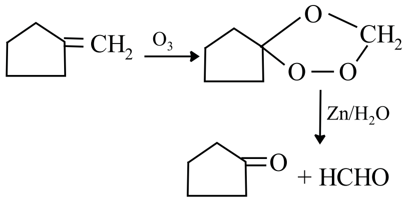


$\underset{\text{But-2-yne}}{CH_3C{\equiv}CCH_3} \xrightarrow[\text{Lindlar's catalyst}]{H_2}$ *cis*-But-2-ene

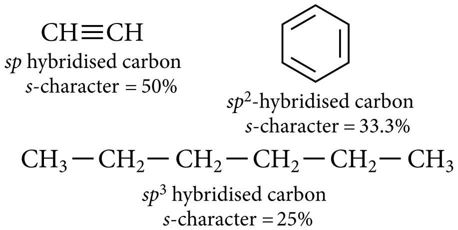
(ii) 

16. (i) 

(ii) 

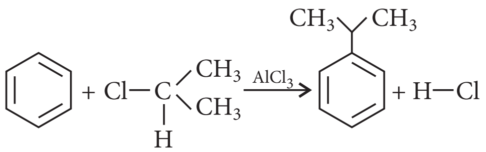
17. 

18. On heating with *alc*. KOH in inert solvent, the triple bond of 1-alkyne is shifted towards the centre to form an isomeric 2-alkyne. On heating with sodamide ($NaNH_2$ in liq. NH_3) the triple bond shifts towards end.

19. 

Since *s*-orbitals are closer to the nucleus, hence due to more *s*-character in ethyne (*sp* hybridised), the hybridised orbital is nearest to this carbon atom in comparison to sp^3 or sp^2 hybridised carbon. This leads to the movement of C — H bond pair more towards *sp* hybridised carbon, leading to the development of partial positive charge on the hydrogen attached to *sp* hybridised carbon. Thus, such a hydrogen behaves as acidic hydrogen. Hence, order of acidic nature is, ethyne > benzene > *n*-hexane.

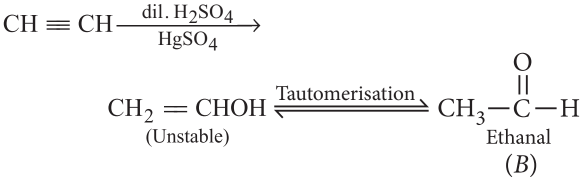
20. Friedel–Crafts alkylation is a Lewis acid-catalyzed electrophilic aromatic substitution reaction that allows the synthesis of alkylated products via the reaction of arenes with alkyl halides. With anhydrous aluminium chloride as a catalyst, the stable alkyl carbocation is generated which attacks the benzene ring. An example of this type of reaction is shown below :



21. Alkyne *X* is C_5H_8. Since it does not react with sodamide or ammoniacal cuprous chloride, the triple bond cannot be terminal.

∴ *X* is $CH_3CH_2C \equiv CCH_3$ (Pent-2-yne)

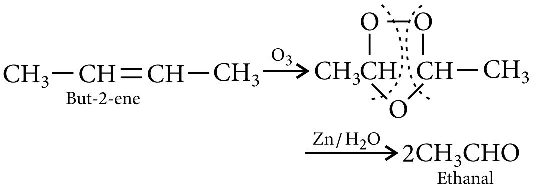
22. (i) $$HC\equiv CH \xrightarrow{NaNH_2} HC\equiv CNa \xrightarrow{CH_3Br} \underset{\substack{\text{Propyne}\\(A)}}{HC\equiv CCH_3}$$

(ii) 

$$CH\equiv CH \xrightarrow[HgSO_4]{\text{dil. } H_2SO_4} \underset{\text{(Unstable)}}{CH_2=CHOH} \xrightleftharpoons{\text{Tautomerisation}} \underset{\substack{\text{Ethanal}\\(B)}}{CH_3-\overset{\overset{O}{\|}}{C}-H}$$

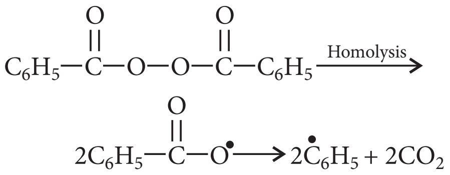
(iii) $$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\substack{\text{Propene}\\(C)}}{CH_3-CH=CH_2} \xrightarrow{H_2} \underset{\substack{\text{Propane}\\(D)}}{CH_3-CH_2-CH_3}$$

23. Alkene *A* contains 3C — C, 8C — H and one C=C bonds. An aldehyde containing one —CHO group and having molar mass of 44 amu has to be CH_3CHO and since two moles of CH_3CHO are obtained by ozonolysis of alkene *A*, the alkene has to be joined by two CH_3CH— groups by a double bond. It has to be $CH_3 — CH = CH — CH_3$, *i.e.*, but-2-ene. But-2-ene contains 3C—C σ bonds, 8C — H σ bonds and one C=C bond.



24. (a) Stability of carbocations decreases as 3° > 2° > 1°. Alkyl groups have $+I$ effect. when an alkyl group is attached to positively charged carbon atom of a carbocation, it tends to release electrons towards that carbon and reduces the positive charge on the carbon. Thus, positive charge gets dispersed. This dispersal of the positive charge stabilises the carbocation.

(b) Mechanism : Peroxide effect proceeds via free radical mechanism as given below :

(i) 

$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5 \xrightarrow{\text{Homolysis}} 2C_6H_5-\overset{\overset{O}{\|}}{C}-\dot{O} \longrightarrow 2\dot{C}_6H_5 + 2CO_2$$

(ii) $$\dot{C}_6H_5 + H-Br \xrightarrow{\text{Homolysis}} C_6H_6 + Br^{\bullet}$$

(iii) $CH_3-CH{=}CH_2 + Br^{\bullet} \xrightarrow{\text{Homolysis}}$

$$CH_3-\dot{C}H-CH_2-Br$$

(more stable free radical)

(iv) $CH_3-\dot{C}H-CH_2Br + H-Br \xrightarrow{\text{Homolysis}}$

$$CH_3-CH_2CH_2Br + Br^{\bullet}$$

25. (a) Kolbe's reaction : In this reaction, an aqueous solution of sodium or potassium salt of carboxylic acid on electrolysis gives alkane having even number of carbon atoms at anode.

$$2CH_3COO^-Na^+ + 2H_2O \xrightarrow{\text{electrolysis}} \underset{\text{Ethane}}{CH_3-CH_3} + 2CO_2 + H_2 + 2NaOH$$

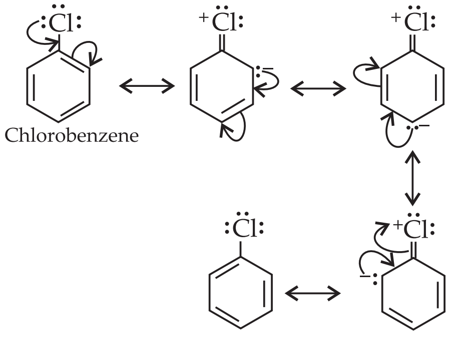
(b) Sodium propanoate,

$$2CH_3CH_2COONa + 2H_2O \xrightarrow{\text{electrolysis}} CH_3CH_2-CH_2CH_3 + 2CO_2 + H_2 + 2NaOH$$

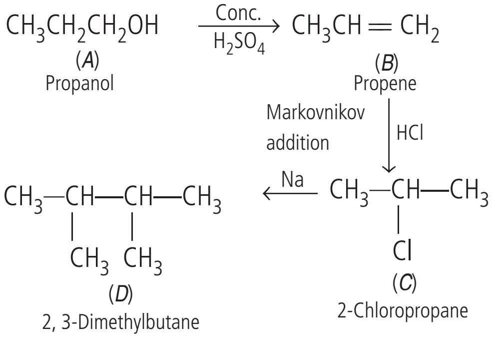
26. Due to higher dipole moment, the boiling point of *cis*-isomer is higher than the corresponding trans-isomer.

27. In case of aryl halides, halogens are little deactivating because of their strong –*I*-effect. Therefore, overall electron density on the benzene ring decreases. In other words, halogens are deactivating due to –*I*-effect. However, because of the +*R*-effect, *i.e.*, participation of lone pairs of electrons on the halogen atom with the π-electrons of the benzene ring, the electron density increases more at *o*- and *p*-positions than at *m*-positions.

As a result, halogens are *o*, *p*-directing. The combined result of +*R*-effect and –*I*-effect of halogens is that, halogens are deactivating but *o*, *p*-directing.



28. Compound *A* is an alcohol which on reaction with H_2SO_4 gives alkene *B*.

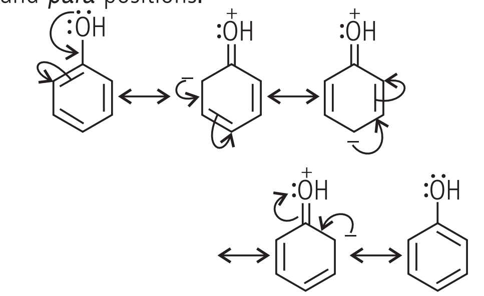


$$\underset{\substack{(A)\\ \text{Propanol}}}{CH_3CH_2CH_2OH} \xrightarrow[H_2SO_4]{\text{Conc.}} \underset{\substack{(B)\\ \text{Propene}}}{CH_3CH=CH_2}$$

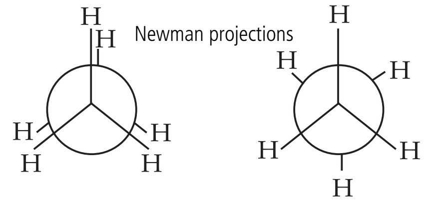
Markovnikov addition, HCl

$$\underset{\substack{(D)\\ \text{2, 3-Dimethylbutane}}}{CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3} \xleftarrow{Na} \underset{\substack{(C)\\ \text{2-Chloropropane}}}{CH_3-\underset{Cl}{CH}-CH_3}$$

29. —OH group attached to benzene ring release electrons and activate the benzene ring, direct the incoming groups to *ortho* and *para* positions.



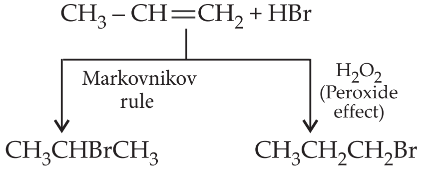
30.



Eclipsed Staggered

In staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon-hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. Thus, the molecule has more energy and therefore, has lesser stability.

31. Peroxide effect : Addition of HBr in presence of peroxide gives products opposite to Markovnikov rule.

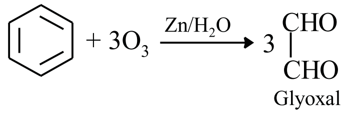


$CH_3-CH{=}CH_2 + HBr$

Markovnikov rule → $CH_3CHBrCH_3$

H_2O_2 (Peroxide effect) → $CH_3CH_2CH_2Br$

32.



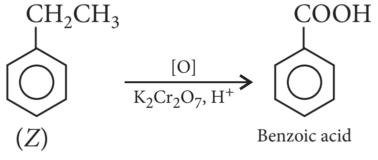
$$+ 3O_3 \xrightarrow{Zn/H_2O} 3\ \underset{\text{Glyoxal}}{\begin{matrix}CHO\\ |\\ CHO\end{matrix}}$$

33. $CH\equiv CH + Na \longrightarrow HC\equiv C^-Na^+ + \frac{1}{2}H_2$

$CH\equiv CH + NaNH_2 \longrightarrow CH\equiv C^-Na^+ + NH_3$

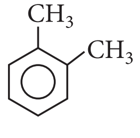
34. There will be no reaction between 2-butyne and Cu_2Cl_2 because it has no acidic hydrogen. In 1-butyne the terminal hydrogen is acidic ($CH_3CH_2-C\equiv CH$) so it will give a red ppt. with ammoniacal Cu_2Cl_2.

35. Since, it does not decolourise bromine water, it is arene. Thus,



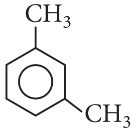
(*Z*)

The other three isomers are :



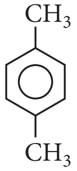
(A)

1, 2-Dimethylbenzene
(o-Xylene)



(B)

1, 3-Dimethylbenzene
(m-Xylene)



(C)

1, 4-Dimethylbenzene
(p-Xylene)

36. $\underset{(A)}{C_5H_{11}Br} \xrightarrow[-\,HBr]{\text{KOH (alcohol)}} \underset{(B)}{C_5H_{10}} \xrightarrow[CS_2]{Br_2 \text{ in}} \underset{(C)}{C_5H_{10}Br_2}$

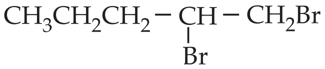
$\xrightarrow[-2HBr]{\text{alc. KOH}} \underset{(D)}{C_5H_8} \xrightarrow{\text{Na-liq } NH_3} \underset{\text{Sod. alkylide}}{C_5H_7Na} + \frac{1}{2}H_2$

$C_5H_8 \xrightarrow[Pt/Pd/Ni]{2H_2} C_5H_{12}$

Since, (*D*) an alkyne reacts with sodium in liq. NH_3, to give alkylide, it shows that (*D*) is a terminal alkyne. It yields straight chain alkane on hydrogenation it shows it is a straight chain terminal alkyne. Hence,

(*A*) $CH_3CH_2CH_2CH_2CH_2Br$

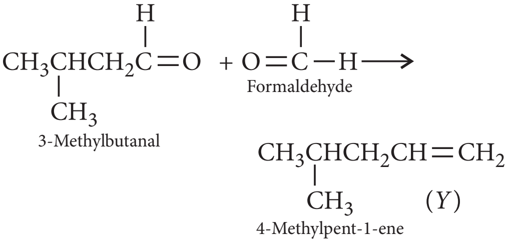
(*B*) $CH_3CH_2CH_2CH = CH_2$

(*C*) 

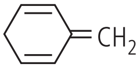
$CH_3CH_2CH_2-\underset{Br}{CH}-CH_2Br$

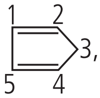
(*D*) $CH_3CH_2CH_2C \equiv CH$
n-Pentyne

37. Hydrocarbon '*Y*' is alkene because it decolourises bromine water. From the products of ozonolysis, the structure of alkene can be predicted.

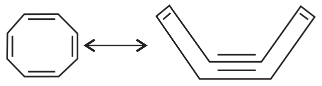


$$\underset{\text{3-Methylbutanal}}{CH_3\underset{CH_3}{CH}CH_2\overset{H}{C}=O} + \underset{\text{Formaldehyde}}{O=\overset{H}{C}-H} \longrightarrow \underset{\text{4-Methylpent-1-ene}}{CH_3\underset{CH_3}{CH}CH_2CH=CH_2}\ (Y)$$

38. (a)  it has 6π-electrons but not in the ring and one carbon atom has *sp*^{3}-hybridisation, hence it is non-aromatic.

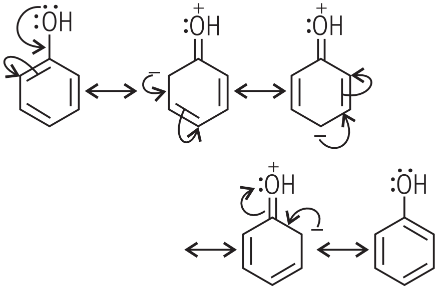
(b) In  3, due to the presence of *sp*^{3}-hybridised carbon (carbon 3) and only four π electrons, it does not contain planar delocalised cloud of (4*n* + 2)π electrons. Hence, it is non-aromatic compound.

(c) Cyclooctatetraene (COT) is not aromatic because of its non-planar tub-shaped structure. Athough according to electron-count it seems to be an anti-aromatic compound but, infact it is non-aromatic compound.

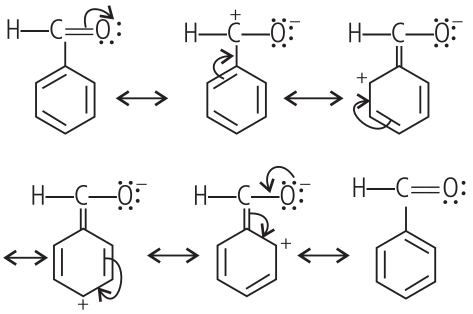


39. Resonating structures of phenol :

—OH group attached to benzene ring release electrons and activate the benzene ring, direct the incoming groups to *ortho-* and *para*-positions.

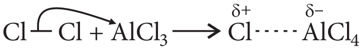


Resonating structures of benzaldehyde :



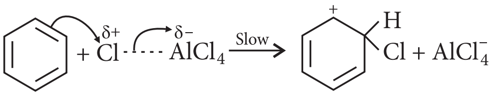
40. The halogenation of benzene proceeds by the following mechanism :

Step 1. Generation of an electrophile.

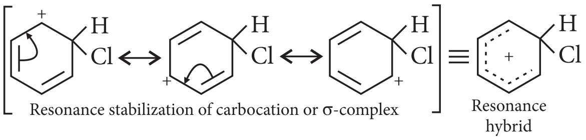


$\underset{\text{Chlorine}}{Cl-Cl} + AlCl_3 \longrightarrow \underset{\text{Electrophile}}{\overset{\delta+}{Cl}\cdots\overset{\delta-}{AlCl_4}}$

Step 2. Formation of σ-complex or carbocation intermediate.



σ-Complex

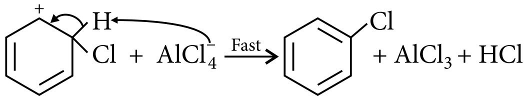


Resonance stabilization of carbocation or σ-complex

Resonance hybrid

This step is slow and hence is the rate-determining step of the reaction.

Step 3. Loss of a proton from the carbocation intermediate.



Chlorobenzene

This step is fast and hence does not affect the rate of the reaction.