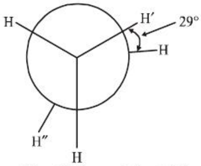
# 13

# Hydrocarbons

## TOPIC 1 Alkanes

**1.** In the following skew conformation of ethane, H′ – C – C – H3 dihedral angle is : **[April 12, 2019 (II)]**



(a) 58°  (b) 149°  (c) 151°  (d) 120°

**2.** 25 g of an unknown hydrocarbon upon burning produces 88 g of $CO_2$ and 9 g of $H_2O$. This unknown hydrocarbon contains: **[April 12, 2019 (II)]**

(a) 20 g of carbon and 5 g of hydrogen
(b) 22 g of carbon and 3 g of hydrogen
(c) 24 g of carbon and 1 g of hydrogen
(d) 18 g of carbon and 7 g of hydrogen

**3.** At 300 K and 1 atmospheric pressure, 10 mL of a hydrocarbon required 55 mL of $O_2$ for complete combustion, and 40 mL of $CO_2$ is formed. The formula of the hydrocarbon is : **[April 10, 2019 (I)]**

(a) $C_4H_{10}$ (b) $C_4H_6$ (c) $C_4H_7Cl$ (d) $C_4H_8$

**4.** Which of these factors does not govern the stability of a conformation in acyclic compounds ? **[April 10, 2019 (II)]**

(a) Steric interactions
(b) Torsional strain
(c) Electrostatic forces of interaction
(d) Angle strain

**5.** The major product obtained in the photo catalysed bromination of 2-methylbutane is: **[2005, Online May 19, 2012; Online April 12, 2014]**

(a) 1-bromo-2-methylbutane
(b) 1-bromo-3-methylbutane
(c) 2-bromo-3-methylbutane
(d) 2-bromo-2-methylbutane

**6.** Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide ? **[2012]**

(a) Tertiary butyl chloride (b) Neopentane
(c) Isohexane (d) Neohexane

**7.** Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is **[2005]**

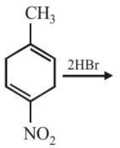
(a) 2-methylpentane (b) 2, 2-dimethylbutane
(c) 2, 3-dimethylbutane (d) n-hexane

**8.** On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be **[2003]**

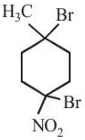
(a) pentane (b) isopentane
(c) neopentane (d) propane

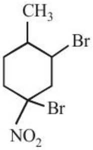
## TOPIC 2 Alkenes

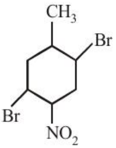
**9.** The major product of the following reaction is :

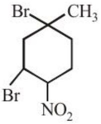


**[Sep. 06, 2020 (I)]**

(a)


(b)


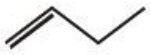
(c)


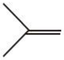
(d)


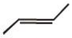
**10.** Which of the following compounds shows geometrical isomerism? **[Sep. 06, 2020 (I)]**

(a) 2-methylpent-2-ene (b) 4-methylpent-2-ene
(c) 4-methylpent-1-ene (d) 2-methylpent-1-ene

**11.** The increasing order of the boiling point of the major products A, B and C of the following reactions will be: **[Sep. 06, 2020 (II)]**

(a)  $+ HBr \xrightarrow{(C_6H_5\overset{O}{\overset{\|}{C}}O)_2}$ A

(b)  $+ HBr \longrightarrow$ B

(c)  $+ HBr \longrightarrow$ C

(a) B < C < A (b) C < A < B
(c) A < B < C (d) A < C < B

**12.** The major product formed in the following reaction is :

$CH_3CH = CHCH(CH_3)_2 \xrightarrow{HBr}$ **[Sep. 05, 2020 (II)]**

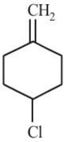
(a) $CH_3CH(Br)CH_2CH(CH_3)_2$

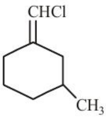
(b) $CH_3CH_2CH(Br)CH(CH_3)_2$

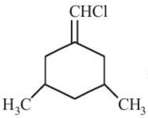
(c) $Br(CH_2)_3CH(CH_3)_2$

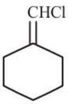
(d) $CH_3CH_2CH_2C(Br)(CH_3)_2$

**13.** Among the following compounds, geometrical isomerism is exhibited by : **[Sep. 05, 2020 (II)]**

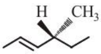
(a) 

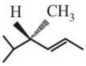
(b) 

(c) 

(d) 

**14.** Which of the following compounds produces an optically inactive compound on hydrogenation? **[Sep. 03, 2020 (I)]**

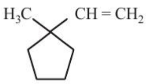
(a) 

(b) 

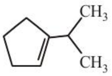
(c) 

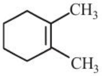
(d) 

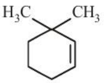
**15.** The major product in the following reaction is : **[Sep. 02, 2020 (I)]**

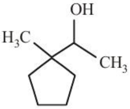


$\xrightarrow[\text{Heat}]{H_3O^+}$

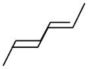
(a) 

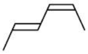
(b) 

(c) 

(d) 

**16.** The correct order of heat of combustion for following alkadienes is: **[Jan. 09, 2020 (I)]**

(A) 

(B) 

(C) 

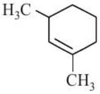
(a) (A) < (B) < (C) (b) (A) < (C) < (B)
(c) (C) < (B) < (A) (d) (B) < (C) < (A)

**17.** Which of the following has the shortest C–Cl bond? **[Jan. 09, 2020 (II)]**

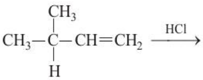
(a) $Cl–CH=CH_2$ (b) $Cl–CH=CH–NO_2$
(c) $Cl–CH=CH–CH_3$ (d) $Cl–CH=CH–OCH_3$

**18.** Which of the following reactions will not produce a racemic product? **[Jan. 09, 2020 (II)]**

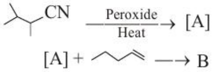
(a) 
$CH_3-\overset{O}{\overset{\|}{C}}CH_2CH_3 \xrightarrow{HCN}$

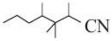
(b)  $\xrightarrow{HCl}$

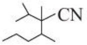
(c) $CH_3CH_2CH=CH_2 \xrightarrow{HBr}$

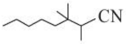
(d) 
$CH_3-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH=CH_2 \xrightarrow{HCl}$

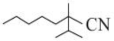
**19.** The major products A and B in the following reactions are: **[Jan. 08, 2020 (I)]**



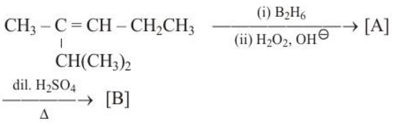
(a) A =  and B = 

(b) A =  and B = 

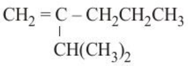
(c) A =  and B = 

(d) A =  and B = 

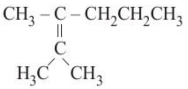
**20.** The major product [B] in the following sequence of reactions is: **[Jan. 08, 2020 (II)]**



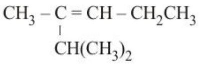
$$CH_3-\underset{\underset{CH(CH_3)_2}{|}}{C}=CH-CH_2CH_3 \xrightarrow[\text{(ii) } H_2O_2,\ OH^{\ominus}]{\text{(i) } B_2H_6} [A] \xrightarrow[\Delta]{\text{dil. } H_2SO_4} [B]$$

(a) 

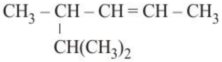
$$CH_2=\underset{\underset{CH(CH_3)_2}{|}}{C}-CH_2CH_2CH_3$$

(b) 

$$CH_3-\underset{\underset{H_3C\ \ CH_3}{\overset{\|}{C}}}{C}-CH_2CH_2CH_3$$

(c) 

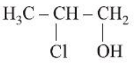
$$CH_3-\underset{\underset{CH(CH_3)_2}{|}}{C}=CH-CH_2CH_3$$

(d) 

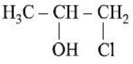
$$CH_3-\underset{\underset{CH(CH_3)_2}{|}}{CH}-CH=CH-CH_3$$

**21.** The major product of the following addition reaction is

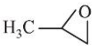
$H_3C-CH=CH_2 \xrightarrow{Cl_2/H_2O}$ **[April 12, 2019 (I)]**

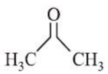
(a) 

$$H_3C-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$$

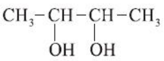
(b) 

$$H_3C-\underset{\underset{OH}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$$

(c) 

(d) 

**22.** But 2-ene on reaction with alkaline $KMnO_4$ at elevated temperature followed by acidification will give : **[April 12, 2019 (I)]**

(a) 

$$CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3$$

(b) one molecule of $CH_3CHO$ and one molecule of $CH_3COOH$

(c) 2 molecules of $CH_3COOH$

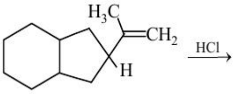
(d) 2 molecules of $CH_3CHO$

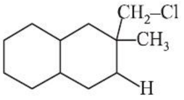
**23.** Which one of the following alkenes when treated with HCl yields majorly an anti Markovnikov product ? **[April 8, 2019 (II)]**

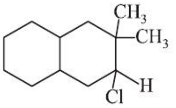
(a) $CH_3O-CH=CH_2$ (b) $Cl-CH=CH_2$

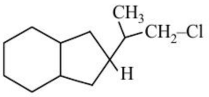
(c) $H_2N-CH=CH_2$ (d) $F_3C-CH=CH_2$

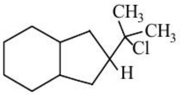
**24.** The major product of the following reaction is : **[Jan. 12, 2019 (II)]**



(a) 

(b) 

(c) 

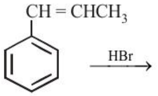
(d) 

**25.** The *trans*-alkenes are formed by the reduction of alkynes with: **[2018]**

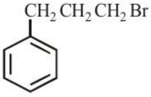
(a) $H_2$-Pd/C, $BaSO_4$ (b) $NaBH_4$

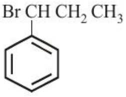
(c) Na/liq. $NH_3$ (d) Sn - HCl

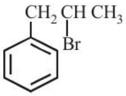
**26.** The major product of the following reaction is :

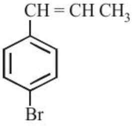


**[Online April 16, 2018]**

(a) 

(b) 

(c) 

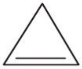
(d) 

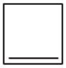
**27.** 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is : **[2017]**

(a) Six (b) Zero

(c) Two (d) Four

**28.** Which of the following compounds is most reactive to an aqueous solution of sodium carbonate ? **[Online April 9, 2017]**

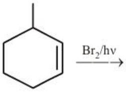
(a) 

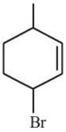
(b) 

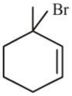
(c) 

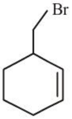
(d) 

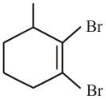
**29.** The major product of the following reaction is : **[Online April 9, 2017]**



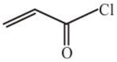
(a) 

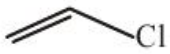
(b) 

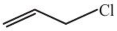
(c) 

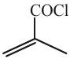
(d) 

**30.** Which of the following compounds will not undergo Friedel Craft's reaction with benzene ? **[Online April 8, 2017]**

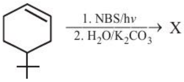
(a) 

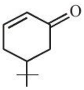
(b) 

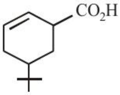
(c) 

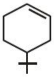
(d) 

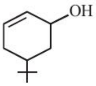
**31.** The product of the reaction given below is: **[2016]**



(a) 

(b) 

(c) 

(d) 

**32.** The reaction of propene with HOCl ($Cl_2 + H_2O$) proceeds through the intermediate: **[2016]**

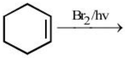
(a) $CH_3-CH(OH)-CH_2^+$

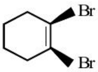
(b) $CH_3-CHCl-CH_2^+$

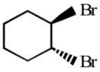
(c) $CH_3-CH^+-CH_2-OH$

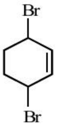
(d) $CH_3-CH^+-CH_2-Cl$

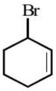
**33.** Bromination of cyclohexene under conditions given below yields : **[Online April 10, 2016]**



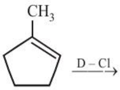
(a) 

(b) 

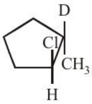
(c) 

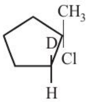
(d) 

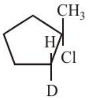
**34.** What is the major product expected from the following reaction ? **[Online April 11, 2015]**

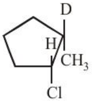


Where D is an isotope of hydrogen

(a) 

(b) 

(c) 

(d) 

**35.** In the hydroboration - oxidation reaction of propene with diborane, $H_2O_2$ and NaOH, the organic compound formed is: **[Online April 9, 2014]**

(a) $CH_3CH_2OH$ (b) $CH_3CHOHCH_3$

(c) $CH_3CH_2CH_2OH$ (d) $(CH_3)_3COH$

**36.** The gas liberated by the electrolysis of dipotassium succinate solution is: **[Online April 11, 2014]**
(a) Ethane (b) Ethyne
(c) Ethene (d) Propene

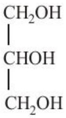
**37.** In the presence of peroxide, HCl and HI do not give anti-Markownikoff's addition of alkenes because: **[Online April 12, 2014]**
(a) One of the steps is endothermic in HCl and HI
(b) Both HCl and HI are strong acids
(c) HCl is oxidizing and the HI is reducing
(d) All the steps are exothermic is HCl and HI

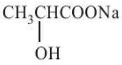
**38.** The addition of HI in the presence of peroxide catalyst does not follow anti-Markovnikov's rule because : **[Online April 9, 2013]**
(a) HI is a strong reducing agent.
(b) H-I bond is too strong to be broken homolytically.
(c) I atom combines with H atom to give back HI.
(d) Iodine atom is not reactive enough to add across a double bond.

**39.** Consider the following sequence of reactions

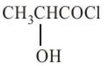
$$CH_3CH=CH_2 \xrightarrow[700K]{Cl_2} A \xrightarrow[420K,12atm]{Na_2CO_3} B \xrightarrow[(ii)\ NaOH]{(i)\ HOCl} C$$

Compound 'C' is **[Online May 26, 2012]**

(a) 
$CH_2OH-CHOH-CH_2OH$

(b) 
$CH_3CH(OH)COONa$

(c) $HOCH_2-CH=CH_2$

(d) 
$CH_3CH(OH)COCl$

**40.** Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds: **[2011RS]**
(a) 1 – Pentene
(b) 2 – Pentene
(c) 2 – Methyl – 2 – pentene
(d) 2 – Methyl – 1 – pentene

**41.** One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is **[2010]**
(a) propene (b) 1-butene
(c) 2-butene (d) ethene

**42.** In the following sequence of reactions, the alkene affords the compound 'B'

$$CH_3-CH=CH-CH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B.$$

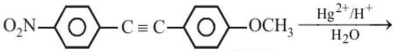
The compound B is **[2008]**
(a) $CH_3CH_2CHO$ (b) $CH_3COCH_3$
(c) $CH_3CH_2COCH_3$ (d) $CH_3CHO$

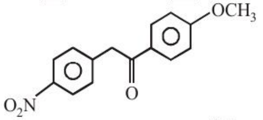
**43.** Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at 40 °C gives predominantly **[2005]**
(a) 1-bromo-2-butene under kinetically controlled conditions
(b) 3-bromobutene under thermodynamically controlled conditions
(c) 1-bromo-2-butene under thermodynamically controlled conditions
(d) 3-bromobutene under kinetically controlled conditions

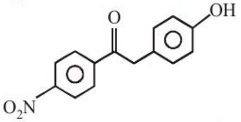
**44.** Butene-1 may be converted to butane by reaction with **[2003]**
(a) Sn – HCl (b) Zn – Hg
(c) $Pd/H_2$ (d) Zn – HCl

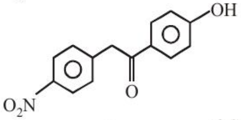
## TOPIC 3 Alkynes

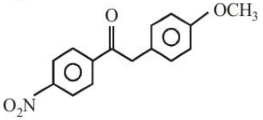
**45.** The major product obtained from the following reaction is: **[Sep. 06, 2020 (I)]**



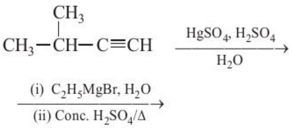
(a) 

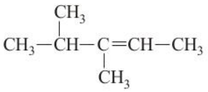
(b) 

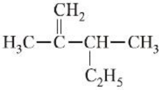
(c) 

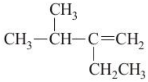
(d) 

**46.** The major product (Y) in the following reactions is: **[Jan. 09, 2020 (I)]**

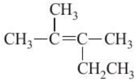

$$CH_3-CH(CH_3)-C\equiv CH \xrightarrow[H_2O]{HgSO_4,\ H_2SO_4} \xrightarrow[(ii)\ Conc.\ H_2SO_4/\Delta]{(i)\ C_2H_5MgBr,\ H_2O}$$

(a) 
$CH_3-CH(CH_3)-C(CH_3)=CH-CH_3$

(b) 
$H_3C-C(=CH_2)-CH(C_2H_5)-CH_3$

(c) 

$CH_3-CH(CH_3)-C(CH_2CH_3)=CH_2$

(d) 

$CH_3-C(CH_3)=C(CH_2CH_3)-CH_3$

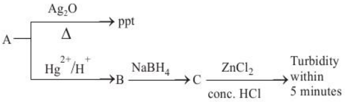
**47.** In the following sequence of reactions the maximum number of atoms present in molecule '*C*' in one plane is ______.

$$A \xrightarrow[\text{Cu tube}]{\text{Red hot}} B \xrightarrow[\text{Anhydrous } AlCl_3]{CH_3Cl(1\text{ eq.})}$$

(A is a lowest molecular weight alkyne)

**[NV. Jan. 08, 2020 (II)]**

**48.** Consider the following reaction :

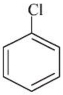


'A' is: **[April 12, 2019 (II)]**

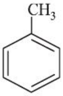
(a) $CH\equiv CH$ (b) $CH_3-C\equiv C-CH_3$

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

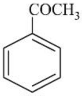
**49.** The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reactions is : **[April 10, 2019 (I)]**



(I)



(II)

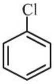


(III)

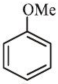
(a) II < I < III (b) III < II < I

(c) III < I < II (d) I < III < II

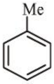
**50.** The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is: **[April 9, 2019 (I)]**



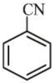
A



B



C



D

(a) D < A < C < B (b) B < C < A < D

(c) A < B < C < D (d) D < B < A < C

**51.** The major product of the following reaction is:

$$CH_3C\equiv CH \xrightarrow[\text{(ii) DI}]{\text{(i) DCI (1 equiv.)}}$$ **[April 9, 2019 (I)]**

(a) $CH_3CD(I)CHD(Cl)$ (b) $CH_3CD(Cl)CHD(I)$

(c) $CH_3CD_2CH(Cl)(I)$ (d) $CH_3C(I)(Cl)CHD_2$

**52.** The correct order for acid strength of compounds $CH\equiv CH$, $CH_3-C\equiv CH$ and $CH_2=CH_2$ is as follows: **[Jan. 12, 2019 (I)]**

(a) $CH\equiv CH > CH_2=CH_2 > CH_3-C\equiv CH$

(b) $CH_3-C\equiv CH > CH\equiv CH > CH_2=CH_2$

(c) $CH_3-C\equiv CH > CH_2=CH_2 > HC\equiv CH$

(d) $HC\equiv CH > CH_3-C\equiv CH > CH_2=CH_2$

**53.** When 2-butyne is treated with $H_2$/Lindlar's catalyst, compound X is produced as the major product and when treated with Na/liq. $NH_3$ it produces Y as the major product. Which of the following statements is correct? **[Online April 15, 2018 (II)]**

(a) Y will have higher dipole moment and higher boiling point than X

(b) Y will have higher dipole moment and lower boiling point than X

(c) X will have lower dipole moment and lower boiling point than Y

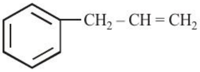
(d) X will have higher dipole moment and higher boiling point than Y

**54.** The reagent needed for the given conversion is

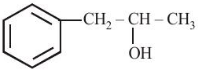
**[Online April 11, 2014]**

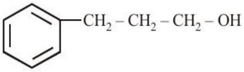
(a) Cat. hydrogenation (b) $H_2$/ Lindlar Cat.

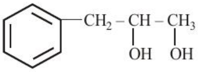
(c) Li/$NH_3$ (d) $LiAlH_4$

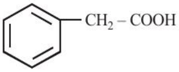
**55.** 

On mercuration-demercuration produces the major product: **[Online April 12, 2014]**

(a) 

(b) 

(c) 

(d) 

**56.** Which one of the following class of compounds is obtained by polymerization of acetylene? **[Online April 9, 2014]**

(a) Poly-yne (b) Poly-ene

(c) Poly-ester (d) Poly-amine

**57.** 2-Hexyne gives *trans*-2-hexene on treatment with: **[2012]**

(a) Pt/$H_2$ (b) Li / $NH_3$

(c) Pd/$BaSO_4$ (d) Li $AlH_4$

**58.** The hydration of propyne results in formation of **[Online May 26, 2012]**

(a) Acetone (b) Propanol-1

(c) Propene (d) Propanal

**59.** The hydrocarbon which can react with sodium in liquid ammonia is **[2008]**

(a) $CH_3CH_2CH_2C \equiv CCH_2CH_2CH_3$

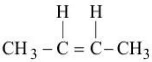
(b) $CH_3CH_2C \equiv CH$

(c) $CH_3CH = CHCH_3$

(d) $CH_3CH_2C \equiv CCH_2CH_3$

**60.** The treatment of $CH_3MgX$ with $CH_3C \equiv C-H$ produces **[2008]**

(a) $CH_3-CH=CH_2$ (b) $CH_3C \equiv C-CH_3$

(c) 
$CH_3-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-CH_3$ (d) $CH_4$

**61.** Which of the following reactions will yield 2, 2-dibromopropane? **[2007]**

(a) $CH_3-CH=CH_2+HBr \rightarrow$

(b) $CH_3-C\equiv CH+2HBr \rightarrow$

(c) $CH_3CH=CHBr+HBr \rightarrow$

(d) $CH \equiv CH+2HBr \rightarrow$

**62.** Which one of the following has minimum boiling point? **[2004]**

(a) 1 - Butene (b) 1 - Butyne

(c) *n*- Butane (d) Isobutane

**63.** Which of these will not react with acetylene? **[2002]**

(a) dil. NaOH (b) ammonical $AgNO_3$

(c) Na in liq. $NH_3$ (d) HCl.

**64.** What is the product when acetylene reacts with hypochlorous acid? **[2002]**

(a) $CH_3COCl$ (b) $ClCH_2CHO$

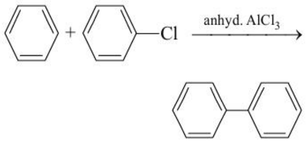
(c) $Cl_2CHCHO$ (d) $ClCH_2COOH$.

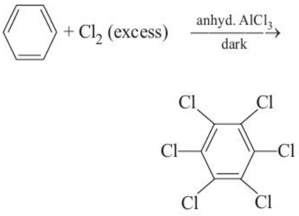
## TOPIC 4 Aromatic Hydrocarbons

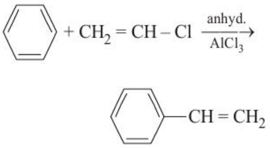
**65.** The number of $sp^2$ hybrid orbitals in a molecule of benzene is: **[Jan. 09, 2020 (II)]**

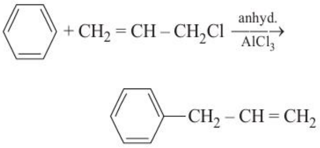
(a) 24 (b) 6 (c) 18 (d) 12

**66.** Consider the following reactions:

(A) 

(B) 

(C) 

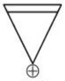
(D) 

Which of these reactions are possible ? **[Jan. 07, 2020 (II)]**

(a) (A) and (B) (b) (A) and (D)

(c) (B), (C) and (D) (d) (B) and (D)

**67.** Which compound (s) out of the following is/are not aromatic? **[Jan. 11, 2019 (I)]**


(A)


(B)


(C)

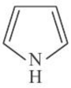

(D)

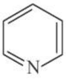
(a) (B), (C) and (D) (b) (C) and (D)

(c) (B) (d) (A) and (C)

**68.** Which of the following compounds is not aromatic? **[Jan. 9, 2019 (II)]**

(a) 

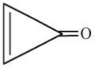
(b) 

(c) 

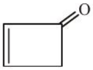
(d) 

**69.** Which of the following compounds will show highest dipole moment ? **[Online April 9, 2017]**

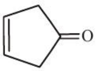
(I)



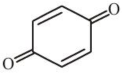
(II)



(III)



(IV)



(a) (I) (b) (II)

(c) (III) (d) (IV)

**70.** In the following sequence of reactions :

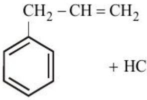
$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

the product C is : **[2015]**

(a) $C_6H_5CH_2OH$ (b) $C_6H_5CHO$

(c) $C_6H_5COOH$ (d) $C_6H_5CH_3$

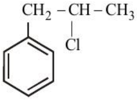
**71.**



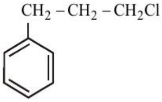
+ HCl ⟶ X,

X is : **[Online April 9, 2013]**

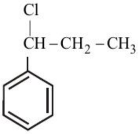
(a)



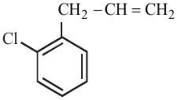
(b)



(c)



(d)



**72.** Which of the following would not give 2-phenylbutane as the major product in a Friedel-Crafts alkylation reaction ? **[Online April 22, 2013]**

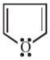
(a) 1-butene + HF

(b) 2-butanol + $H_2SO_4$

(c) Butanoyl chloride + $AlCl_3$ then Zn, HCl

(d) Butyl choloride + $AlCl_3$

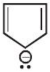
**73.** Which of the following compounds are antiaromatic



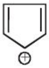
(I)

(II)

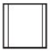
(III)



(IV)



(V)



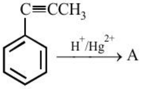
(VI)

**[Online May 26, 2012]**

(a) (I) and (V) (b) (II) and (V)

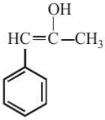
(c) (I) and (IV) (d) (III) and (VI)

**74.** In the given reaction, **[Online May 12, 2012]**

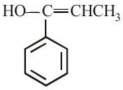


the product 'A' is

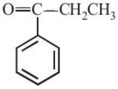
(a)



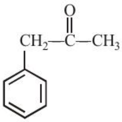
(b)



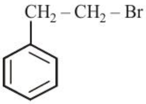
(c)

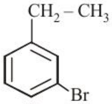


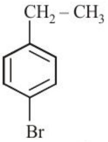
(d)

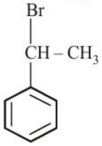


**75.** The product of the reaction between ethyl benzene and N-bromosuccinamide is **[Online May 19, 2012]**

(a) 

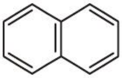
(b) 

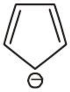
(c) 

(d) 

**76.** The non aromatic compound among the following is : **[2011RS]**

(a) 

(b) 

(c) 

(d) 

**77.** Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated wth cuprous bromide. The reaction mixture so formed contains **[2008]**

(a) mixture of *o*- and *p*-bromotoluenes
(b) mixture of *o*- and *p*-dibromobenzenes
(c) mixture of *o*- and *p*-bromoanilines
(d) mixture of *o*- and *m*-bromotoluenes

**78.** The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is **[2007]**

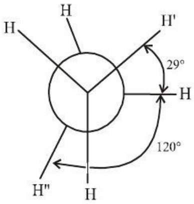
(a) benzyl alcohol
(b) benzophenone
(c) acetophenone
(d) benzoic acid.

**79.** The reaction of toluene with $Cl_2$ in presence of $FeCl_3$ gives predominantly **[2007]**

(a) *m*-chlorobenzene
(b) benzoyl chloride
(c) benzyl chloride
(d) *o*- and *p*-chlorotoluenes.

# Hints & Solutions

1. **(b)**



$\therefore$ Angle between H' and H" = 120° + 29° = 149°

2. **(c)** Let the hydrocarbon be $C_xH_y$.

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

25g (excess) 88g 9g

2 mol $\frac{1}{2}$ mol

x = 2 y = 1

$\because$ x = 2 and y = 1, the hydrocarbon will be $(C_2H)_n$

2 mol carbon contains 24 g and 1 mol hydrogen contains 1g.

3. **(b)** Let the hydrocarbon be $C_xH_y$

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

| | | | |
|---|---|---|---|
| Before combustion: | 10 mL | 55 mL | 0 |
| After combustion: | 0 | $55-10\left(x+\frac{y}{4}\right)$ | 10 x |

Volume of $CO_2$, 10x = 40; x = 4

$55-10\left(x+\frac{y}{4}\right)=0$; y = 6

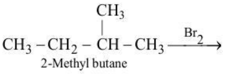
$\therefore$ Hydrocarbon is $C_4H_6$

4. **(d)** In a cyclic or open chain compounds, angle strain is absent.

5. **(d)** The order of substitution in different alkanes is

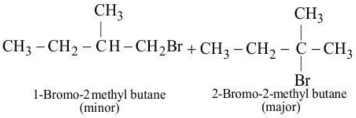
$$3° > 2° > 1°$$

Thus the bromination of 2-methyl butane mainly gives 2 Bromo - 2 - methyl butane



$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3 \xrightarrow{Br_2}$$

2-Methyl butane

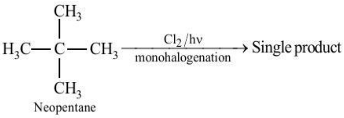


$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2Br + CH_3-CH_2-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

1-Bromo-2 methyl butane (minor)

2-Bromo-2-methyl butane (major)

6. **(b)**

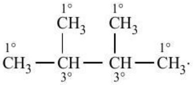


$$H_3C-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \xrightarrow[\text{monohalogenation}]{Cl_2/hv} \text{Single product}$$

Neopentane

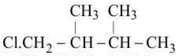
In neopentane, all hydrogen atoms are equivalent.

7. **(c)**



$$\overset{1°}{CH_3}-\underset{3°}{\overset{\overset{\displaystyle \overset{1°}{CH_3}}{|}}{CH}}-\underset{3°}{\overset{\overset{\displaystyle \overset{1°}{CH_3}}{|}}{CH}}-\overset{1°}{CH_3}.$$

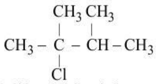
Since it contains only two types of H-atoms hence it will give only two monochlorinated compounds viz.



$$Cl.CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

1-Chloro-2, 3-dimethyl butane

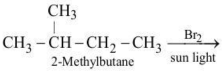
and



$$CH_3-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

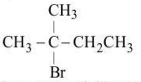
2-Chloro-2,3-dimethylbutane

8. **(c)**



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3 \xrightarrow[\text{sun light}]{Br_2}$$

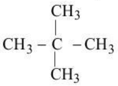
2-Methylbutane



$$CH_3-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2CH_3$$

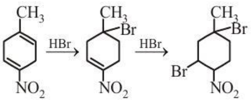
2-Bromo-2-methyl butane

Ease of replacement of H-atoms 3° > 2° > 1°.
In neopentane all H atoms are equivalent (1°).

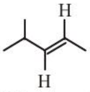


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

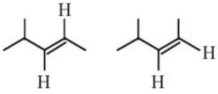
9. **(d)**



**10.** **(b)**

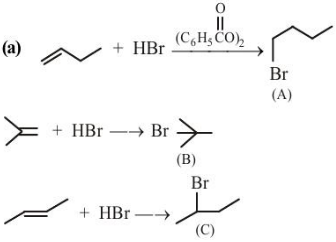


4-Methylpent-2-ene



Geometrical isomers

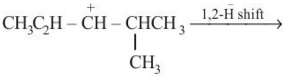
**11.** **(a)**



The boiling points of isomeric haloalkanes decrease with increase in branching.

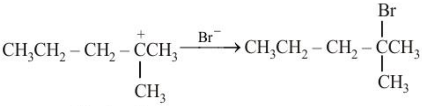
So order of B.P. is A > C > B.

**12.** **(d)** $CH_3CH = CHCH(CH_3)_2 \xrightarrow{H^+}$



$CH_3C_2H-\overset{+}{C}H-\underset{CH_3}{C}HCH_3 \xrightarrow{1,2\text{-}\bar{H}\text{ shift}}$

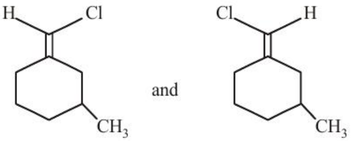
2° carbocation



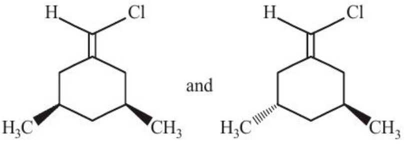
$CH_3CH_2-CH_2-\underset{CH_3}{\overset{+}{C}}CH_3 \xrightarrow{Br^-} CH_3CH_2-CH_2-\underset{CH_3}{\overset{Br}{C}}CH_3$

3° carbocation

**13.** **(b, c)**

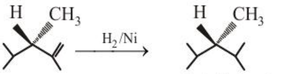


Geometrical isomers



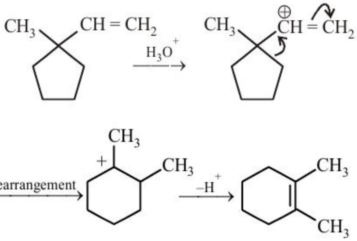
Geometrical isomers

**14.** **(d)**



Optically inactive
(No chiral centre)

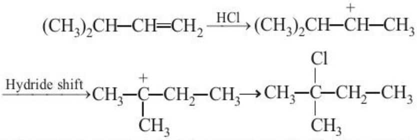
**15.** **(b)**



**16.** **(a)** In isomers of hydrocarbon heat of combustion is inversely proportional to the stability.
Stability order : $A > B > C$
Order of heat of combustion : $A < B < C$

**17.** **(b)** In Cl–CH=CH–$NO_2$ double bond character in carbon-chlorine bond is maximum due to resonance and so the bond length is shortest.

**18.** **(d)**

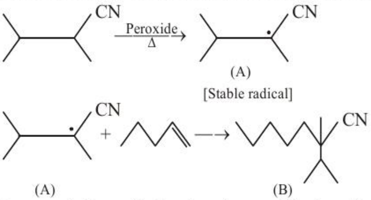


$(CH_3)_2CH-CH=CH_2 \xrightarrow{HCl} (CH_3)_2CH-\overset{+}{C}H-CH_3$

$\xrightarrow{\text{Hydride shift}} CH_3-\underset{CH_3}{\overset{+}{C}}-CH_2-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{Cl}{C}}-CH_2-CH_3$

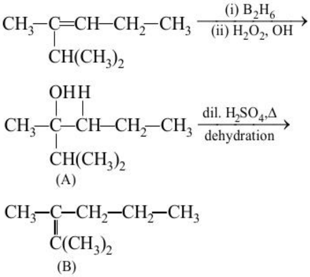
There is no chiral carbon in the product of this reaction.

**19.** **(d)**



(A) is more stable radical and undergoes Markovnikov addition to form (B).

**20.** **(b)**



$CH_3-\underset{CH(CH_3)_2}{C}=CH-CH_2-CH_3 \xrightarrow[(ii)\ H_2O_2,\ OH]{(i)\ B_2H_6}$

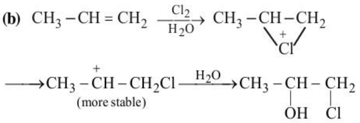
$CH_3-\underset{CH(CH_3)_2}{\overset{OH}{C}}-\overset{H}{C}H-CH_2-CH_3 \xrightarrow[\text{dehydration}]{\text{dil. }H_2SO_4,\Delta}$

(A)

$CH_3-\underset{\overset{\|}{C(CH_3)_2}}{C}-CH_2-CH_2-CH_3$

(B)

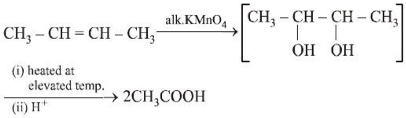
**21.** **(b)**



$CH_3-CH=CH_2 \xrightarrow[H_2O]{Cl_2} CH_3-CH-CH_2 \,(\overset{+}{Cl}) \longrightarrow CH_3-\overset{+}{C}H-CH_2Cl \xrightarrow{H_2O} CH_3-\underset{OH}{CH}-\underset{Cl}{CH_2}$

(more stable)

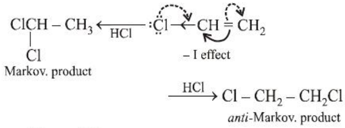
**22.** **(c)**



$CH_3-CH=CH-CH_3 \xrightarrow{alk.KMnO_4} \left[CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3\right] \xrightarrow[(ii)\ H^+]{(i)\ heated\ at\ elevated\ temp.} 2CH_3COOH$

**23.** **(d)**

(a)



$\underset{Cl}{ClCH}-CH_3 \xleftarrow{HCl} :\ddot{Cl}\leftarrow CH=CH_2$

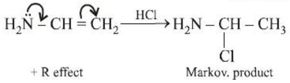
Markov. product

– I effect

$\xrightarrow{HCl} Cl-CH_2-CH_2Cl$

*anti*-Markov. product

(b)

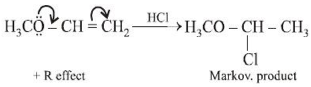


$H_2\ddot{N}-CH=CH_2 \xrightarrow{HCl} H_2N-\underset{Cl}{CH}-CH_3$

+ R effect

Markov. product

(c)

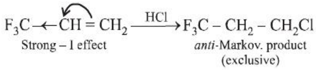


$H_3C\ddot{O}-CH=CH_2 \xrightarrow{HCl} H_3CO-\underset{Cl}{CH}-CH_3$

+ R effect

Markov. product

(d)

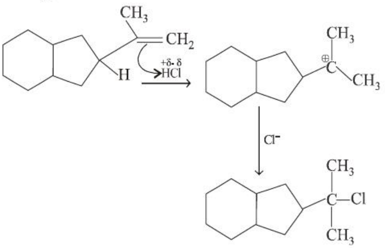


$F_3C\leftarrow CH=CH_2 \xrightarrow{HCl} F_3C-CH_2-CH_2Cl$

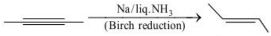
Strong – I effect

*anti*-Markov. product (exclusive)

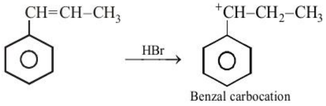
**24.** **(d)**

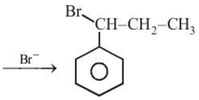


**25.** **(c)**

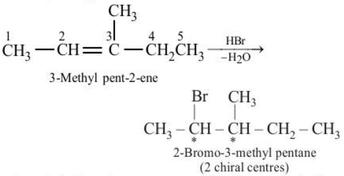


**26.** **(b)**





**27.** **(d)** Addition of HBr on 3-methylpent-2-ene in presence of peroxide, takes place in anti-Markownikov's rule.

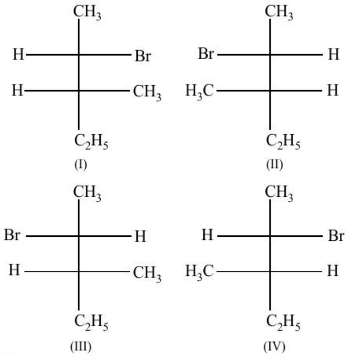


$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}(CH_3)-\overset{4}{C}H_2\overset{5}{C}H_3 \xrightarrow[-H_2O]{HBr} CH_3-\underset{*}{\overset{Br}{CH}}-\underset{*}{\overset{CH_3}{CH}}-CH_2-CH_3$

3-Methyl pent-2-ene

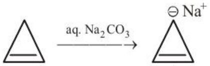
2-Bromo-3-methyl pentane (2 chiral centres)

Since two chiral centres are present in the product, four stereoisomers ($n^2$) are possible.



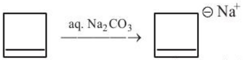
**28.** **(c)**

(a)



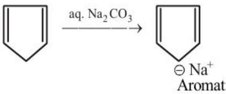
Antiaromatic ($4\pi e^-$) **Unstable.**

(b)



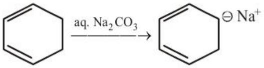
Antiaromatic ($4\pi e^-$) **Unstable.**

(c)



Aromatic ($6\pi e^-$) **Stable.**

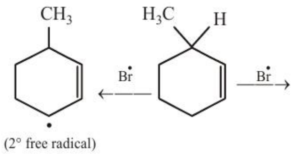
(d)

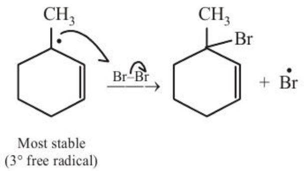


Homoaromatic ($6\pi e^-$)

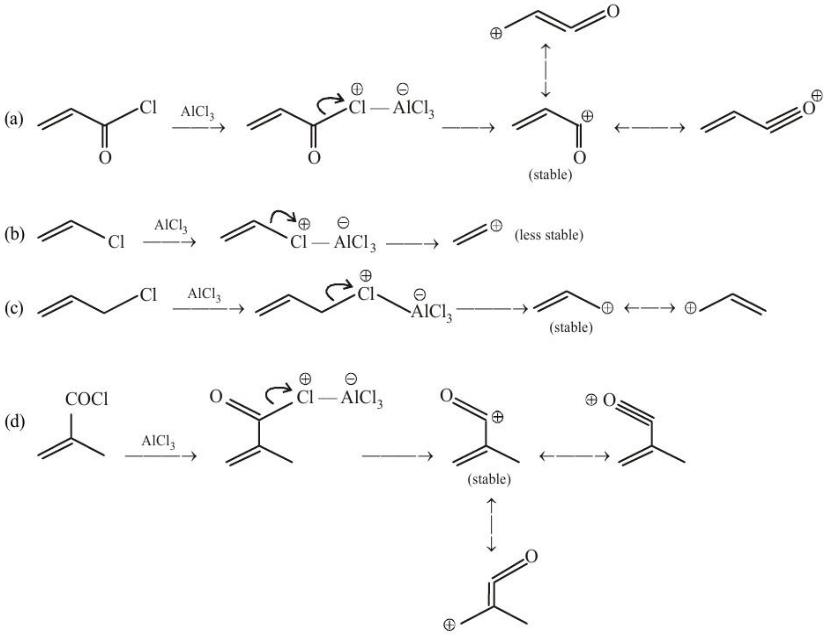
No delocalization of electron in whole ring **Unstable.**

**29.** **(b)** $Br_2 \xrightarrow{h\nu} 2\dot{B}r$



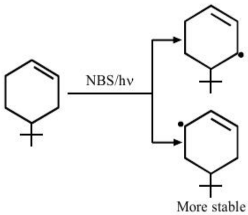


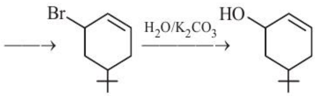
**30.** **(b)**



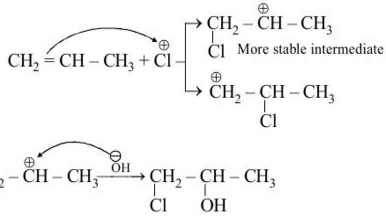
Hence formation of carbocation is not possible in the case of vinyl halide.

**31.** **(d)** N – bromosuccinimide results into bromination at allylic and benzylic positions

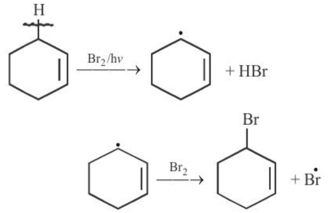




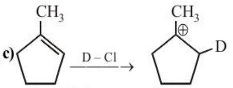
**32.** **(d)**



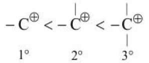
33. **(d)** In presence of sunlight alkenes undergo free radical substitution.



34. **(b, c)**

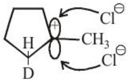


Formation of above species is more favourable. The stability order of carbocations is

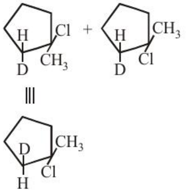


$$\underset{1^\circ}{-\overset{\oplus}{C}} < \underset{2^\circ}{-\overset{|}{C}{}^{\oplus}} < \underset{3^\circ}{-\underset{|}{\overset{|}{C}}{}^{\oplus}}$$

Now, carbocation formed is $sp^2$ hybridised that is triangular planar as shown below

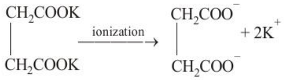


$Cl^\ominus$ ion can attack either from above or below the plane of the molecule, so there is probability of resultant product as shown below i.e., both product will form.



35. **(c)** $CH_3CH=CH_2 \xrightarrow[H_2O_2,NaOH]{B_2H_6} CH_3CH_2CH_2OH$

36. **(c)** Ethene is obtained by electrolysis of dipotassium succinate as follows

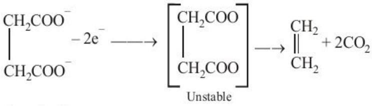


$$\begin{array}{l}CH_2COOK\\ |\\ CH_2COOK\end{array} \xrightarrow{\text{ionization}} \begin{array}{l}CH_2COO^-\\ |\\ CH_2COO^-\end{array} + 2K^+$$

Pot. Succinate

$$2H_2O \xrightleftharpoons{\text{ionization}} 2OH^- + 2H^+$$

At anode :



$$\begin{array}{l}CH_2COO^-\\ |\\ CH_2COO^-\end{array} - 2e^- \longrightarrow \underset{\text{Unstable}}{\left[\begin{array}{l}CH_2COO\\ |\\ CH_2COO\end{array}\right]} \longrightarrow \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + 2CO_2$$

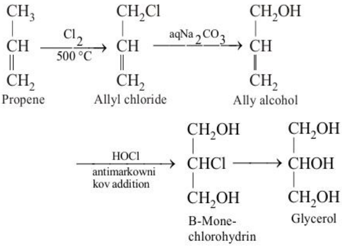
At cathode :

$$2H^+ + 2e^- \longrightarrow [2H] \longrightarrow H_2$$

37. **(a)** Anti-Markownikov addition is possible only in case of HBr and not in HCl and HI. In HBr both the chain initiation and propagation steps are exothermic, while in HCl, first step is exothermic, and second step is endothermic and in HI, no step is exothermic. Hence HCl and HI do not undergo anti-Markownikov's addition.

38. **(d)** HI does not exhibit peroxide effect. HI bond although dissociates easily into iodine radicals, they being bigger in size are not much reactive but recombine together to form iodine molecule.

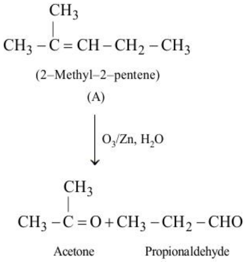
39. **(a)**



$$\underset{\text{Propene}}{\begin{array}{l}CH_3\\ |\\ CH\\ \|\\ CH_2\end{array}} \xrightarrow[500\,^\circ C]{Cl_2} \underset{\text{Allyl chloride}}{\begin{array}{l}CH_2Cl\\ |\\ CH\\ \|\\ CH_2\end{array}} \xrightarrow{aqNa_2CO_3} \underset{\text{Ally alcohol}}{\begin{array}{l}CH_2OH\\ |\\ CH\\ \|\\ CH_2\end{array}}$$

$$\xrightarrow[\text{antimarkowni kov addition}]{HOCl} \underset{\text{B-Mone-chlorohydrin}}{\begin{array}{l}CH_2OH\\ |\\ CHCl\\ |\\ CH_2OH\end{array}} \longrightarrow \underset{\text{Glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}}$$

40. **(c)** From the products formed it is clear that the compound has 5 carbon atoms with a double bond and methyl group on 2nd carbon atom.

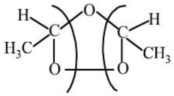


$$\underset{\underset{(A)}{(2\text{–Methyl–2–pentene})}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_3}$$

$$\Big\downarrow O_3/Zn,\ H_2O$$

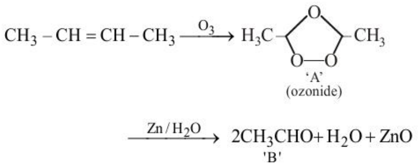
$$\underset{\text{Acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} + \underset{\text{Propionaldehyde}}{CH_3-CH_2-CHO}$$

41. **(c)** $\underset{\text{2-Butene}}{CH_3CH=CHCH_3} \xrightarrow{O_3}$

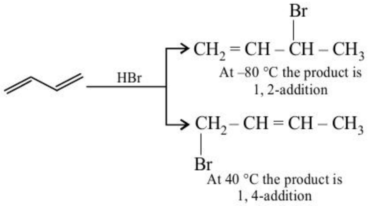


$$\xrightarrow{Zn/H_2O} 2CH_3CHO + H_2O_2$$

**42.** **(d)** Completing the sequence of given reactions,



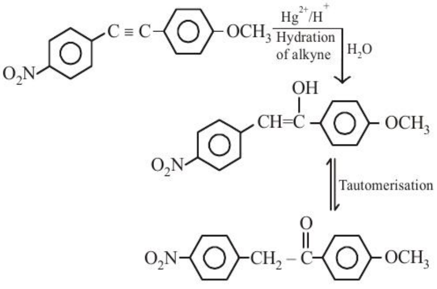
**43.** **(c)**



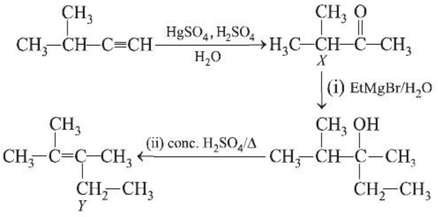
**44.** **(c)** Alkenes combine with hydrogen under pressure and in presence of a catalyst (Ni, Pt or Pd) and form alkanes.

Butene - 1 $\xrightarrow{H_2/Pd}$ Butane

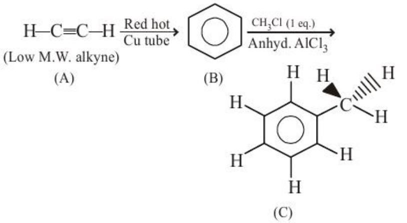
**45.** **(a)**



**46.** **(d)**



**47.** **(13)**

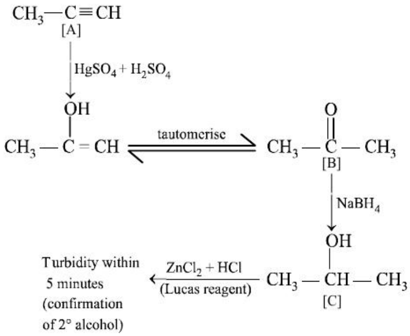


Number of atoms present in molecule (C) in one plane = 13

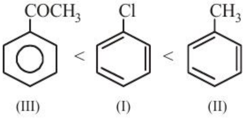
**48.** **(c)**

(i) Reaction of 'A' with $Ag_2O$ to give ppt indicates – C ≡ CH type of linkage.

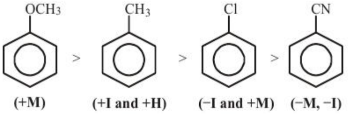
(ii) Going backward in the second set, compound 'C' when heated with $ZnCl_2$ and conc. HCl gives turbidity within 5 minutes, it indicates that 'C' is a 2° alcohol, (C) hence 'B' is a ketone and 'A' is prop-1-yne.



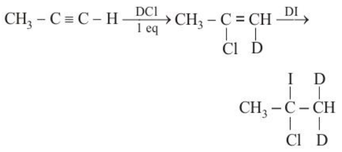
**49.** **(c)** $CH_3$ group when bonded to benzene increases the electron density of benzene ring due to +I and hyper conjugation effects. –Cl group decreases the electron density of benzene ring due to –I effect, and $-COCH_3$ group strongly decreases the electron density of benzene ring due to –I and –R effects. Therefore, correct increasing order of the given compounds towards electrophilic aromatic substitution is



**50.** **(a)**



51. **(d)**



$$CH_3-C\equiv C-H \xrightarrow[1\ eq]{DCl} CH_3-\underset{Cl}{C}=\underset{D}{CH} \xrightarrow{DI} CH_3-\overset{I}{\underset{Cl}{C}}-\overset{D}{\underset{D}{CH}}$$

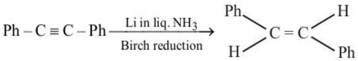
Both additions follow Markovnikov's rule.

52. **(d)** Alkynes having *sp*-hybridised carbon has max. *s*-character and hence max. electronegativity with the result it attracts the electron pair of the bond C – H to a greater extent and makes the removal of proton easier than the alkenes having $sp^2$ hybridised carbon. Now presence of electron donating group ($-CH_3$) in alkyne $CH_3-C\equiv CH$ decreases acidic strength of the compound. Hence the correct order of acidic strength is

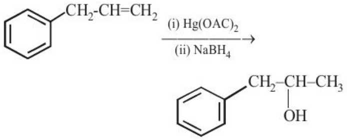
$$HC\equiv CH > H_3C \rightarrow C\equiv CH > CH_2=CH_2$$

53. **(d)** When 2-butyne is treated with $H_2$/Lindlar's catalyst, compound X (*cis*-2-butene) is produced as the major product; and when treated with Na/liq $NH_3$ it produces Y (*trans* -2- butene) as the major product. *Cis*-isomer(X) will have higher dipole moment and higher boiling point than *trans* (Y).

54. **(c)** With Lithium in liquid ammonia, trans-alkene is almost an exclusive product.

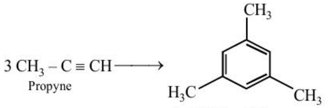


55. **(a)**



56. **(b)** Poly-ene. e.g

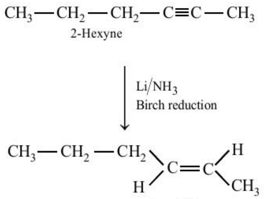
$$\underset{\text{acetylene}}{3\,CH\equiv CH} \longrightarrow \underset{\text{Benzene}}{C_6H_6}$$



1, 3, 5-Trimethylbenzene

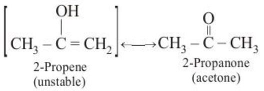
57. **(b)** Anti addition of hydrogen atoms to the triple bond occurs when alkynes are reduced with sodium (or lithium) metal in liq. ammonia, ethylamine, or alcohol at low temperatures. This reaction called, a dissolving metal reduction, produces an (E)- or *trans*-alkene.

Sodium in liq. $NH_3$ is used as a source of electrons in the reduction of an alkyne to a *trans* alkene.



*trans*-2-Hexene

58. **(a)** $\underset{\text{Propyne}}{CH_3-C\equiv CH} + H_2O \xrightarrow[HgSO_4]{H_2SO_4}$



$$\left[CH_3-\overset{OH}{C}=CH_2\right] \longleftrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

2-Propene (unstable) 2-Propanone (acetone)

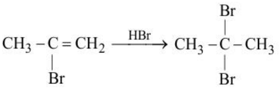
59. **(b)** Alkynes having terminal $-C\equiv H$ react with Na in liquid ammonia to yield $H_2$ gas

$$CH_3CH_2C\equiv CH \xrightarrow[\text{liquid }NH_3]{\text{Na in}} CH_3CH_2C\equiv C^-Na^+ + \frac{1}{2}H_2(g)$$

60. **(d)** $CH_3MgX + CH_3-C\equiv C-H \longrightarrow CH_3-C\equiv CMgX + CH_4(g)$

61. **(b)** The reaction follows Markownikoff rule which states that when unsymmetrical reagent adds across unsymmetrical double or triple bond, the negative part adds to carbon atom having lesser number of hydrogen atoms.

$$CH_3-C\equiv CH + HBr \longrightarrow$$



$$CH_3-\underset{Br}{C}=CH_2 \xrightarrow{HBr} CH_3-\overset{Br}{\underset{Br}{C}}-CH_3$$

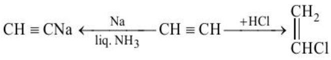
2,2-Dibromopropane

62. **(d)** **Note:** Among isomeric alkanes, the straight chain isomer has higher boiling point than the branched chain isomer. The greater the branching of the chain, the lower is the boiling point. Further due to the presence of π electrons, these moleculs are slightly polar and hence have higher boiling points than the corresponding alkanes.

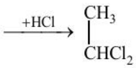
Thus B.pt. follows the order

alkynes > alkenes > alkanes (straight chain) > branched chain alkanes.

63. **(a)** Acetylene reacts with the other three reagents as:



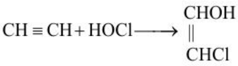
$$CH\equiv CNa \xleftarrow[\text{liq. }NH_3]{Na} CH\equiv CH \xrightarrow{+HCl} \underset{CHCl}{\overset{CH_2}{\|}}$$



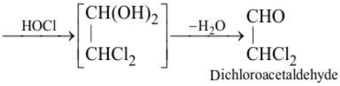
$\xrightarrow{+HCl} \begin{array}{c} CH_3 \\ | \\ CHCl_2 \end{array}$

$CH \equiv CH \xrightarrow{[AgNO_3 + NH_4OH]} \underset{\text{white ppt.}}{AgC \equiv CAg} + NH_4NO_3$

**64.** **(c)**



$CH \equiv CH + HOCl \longrightarrow \begin{array}{c} CHOH \\ \| \\ CHCl \end{array}$



$\xrightarrow{HOCl} \left[\begin{array}{c} CH(OH)_2 \\ | \\ CHCl_2 \end{array}\right] \xrightarrow{-H_2O} \begin{array}{c} CHO \\ | \\ CHCl_2 \end{array}$

Dichloroacetaldehyde

**65.** **(c)** In benzene each carbon atom is $sp^2$ hybridised. Therefore total 18 $sp^2$ hybrid orbitals are present in benzene.

**66.** **(d)** Vinyl halides and aryl halides are unreactive towards Friedel Craft's reaction.
Therefore reactions (A) and (C) are not possible.

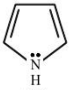
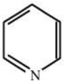
**67.** **(a)**  is aromatic; $(4 \times 0 + 2) = 2\,\pi e^-$ in conjugation

 and  are antiaromatic

$4\pi e^-$ $8\pi e^-$
$(4 \times 1)\,\pi e^-$ $(4 \times 2)\,\pi e^-$

 is non aromatic due to the presence of $sp^3$ carbon.

**68.** **(a)** Compounds (b), (c) and (d) are containing $6\pi e^-$ in complete conjugation and are aromatic.


(b)
;

(c)
;

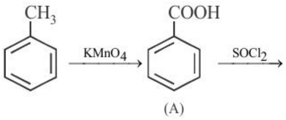
(d)

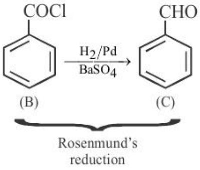
 Compound (a) is anti-aromatic as it has $4\pi e^-$ in complete conjugation and doesn't obey Hückel rule.

**69.** **(a)**

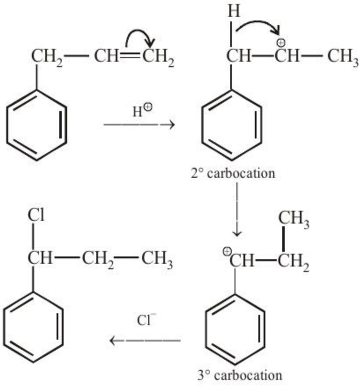
A dipolar resonance structure has aromatic character in the ring and would be expected to make a major contribution to the overall structure.

**70.** **(b)**





**71.** **(c)**



**72.** **(c)** The Friedal-crafts alkylation reaction will give propyl phenyl ketone which further on Clemmenson's reduction will give butyl benzene

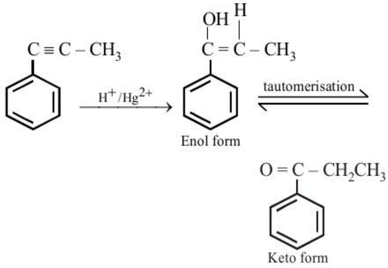
$C_6H_6 + CH_3CH_2CH_2COCl \xrightarrow{AlCl_3}$

$C_6H_5COCH_2CH_2CH_3 \xrightarrow{Zn\text{-}Hg/HCl}$

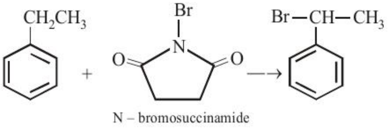
$C_6H_5CH_2CH_2CH_2CH_3$
Butyl benzene

**73.** **(d)** For a compound to be aromatic it must have $(4n + 2)\,\pi e^-$ where $n$ is an integer. (III) have 8 and (VI) have 4 $e^-$. Hence are antiaromatic

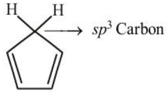
**74.** **(c)**



**75.** **(d)**

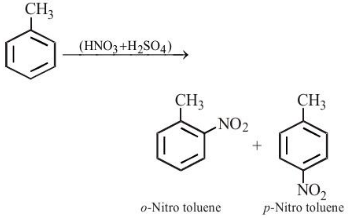


76. **(d)**

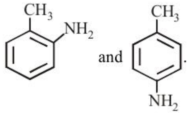


Cyclopentadiene does not obey Huckel's Rule, as it has $sp^3$ carbon in the ring.

77. **(a)** **Note:** Toluene ($C_6H_5CH_3$) contains $-CH_3$ group which is *o*-, *p*- directing group so on nitration of toluene the $-NO_2$ group will occupy *o*-, *p*- positions.

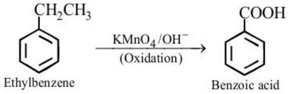


On reduction with Sn/HCl they will form corresponding anilines in which $-NO_2$ group changes to $-NH_2$. The mixture now contains



These anilines when diazotized and then treated with CuBr form *o*-, *p*- bromotoluenes (Sandmeyer reductions).

78. **(d)** When alkyl benzenes are oxidised with alkaline $KMnO_4$ (strong oxidising agent), the entire alkyl group is oxidised to $-COOH$ group regardless of length of side chain.



79. **(d)** $FeCl_3$ is Lewis acid. In presence of $FeCl_3$ and $Cl_2$ toluene undergoes electrophilic substitution in *o*- and *p*-positions.