CHAPTER

Hydrocarbons

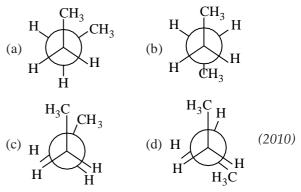
13.2 Alkanes

- **1.** Which of the following alkane cannot be made in good yield by Wurtz reaction?
 - (a) *n*-Hexane
 - (b) 2, 3-Dimethylbutane
 - (c) *n*-Heptane
- (d) *n*-Butane (*NEET* 2020)
- 2. The alkane that gives only one monochloro product on chlorination with Cl₂ in presence of diffused sunlight is
 - (a) 2,2-dimethylbutane (b) neopentane
 - (c) *n*-pentane (d) isopentane.

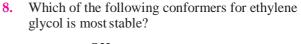
(OdishaNEET2019)

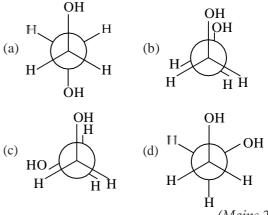
- **3.** Hydrocarbon (*A*) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms. (*A*) is
 - (a) CH = CH (b) $CH_2 = CH_2$
 - (c) $CH_3 CH_3$ (d) CH_4 (*NEET2018*)
- 4. With respect to the conformers of ethane, which of the following statements is true?
 - (a) Bond angle changes but bond length remains same.
 - (b) Both bond angle and bond length change.
 - (c) Both bond angle and bond length remain same.
 - (d) Bond angle remains same but bond length changes. (NEET 2017)
- 5. The correct statement regarding the comparison of staggered and eclipsed conformations of ethane, is
 - (a) the eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
 - (b) the staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain
 - (c) the staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain

- (d) the eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain. (NEET-I 2016)
- 6. In the following the most stable conformation of *n*-butane is



- 7. Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by
 - (a) oxidation
 - (b) cracking
 - (c) distillation under reduced pressure
 - (d) hydrolysis. (2010)





(Mains 2010)

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9. Dihedral angle in staggered form of ethane is $(a) 0^{\circ}$

(a)
$$0^{\circ}$$
 (b) 120°
(c) 60° (d) 180° (2000)

10. Which of the following reaction is expected to readily give a hydrocarbon product in good yields?

(a) CH CH
$$_{3}$$
 $\xrightarrow{Cl_{2}}$ (b) (CH) CHCl $\xrightarrow{C_{2}H_{3}OH}$ (c) RCOOK $\xrightarrow{Electrolysis}_{Oxidation}$ (d) RCOOAg $\stackrel{L_{2}}{\xrightarrow{L_{2}}}$ (1997)

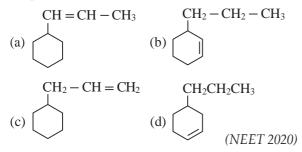
- **11.** In the commercial gasolines, the type of hydrocarbons which are more desirable is
 - (a) linear unsaturated hydrocarbon
 - (b) toluene
 - (c) branched hydrocarbon

- **12.** The most stable conformation of *n*-butaneis
 - (a) gauche (b) staggered
 - (c) skew boat (d) eclipsed. (1997)
- **13.** Which of the following is used as an antiknocking material?
 - (a) Glyoxal (b) Freon
 - (c) T.E.L. (d) Ethyl alcohol (1996)
- 14. Reactivity of hydrogen atoms attached to different carbon atoms in alkanes has the order
 - (a) tertiary > primary > secondary
 - (b) primary > secondary > tertiary
 - (c) both (a) and (b)

(d) tertiary > secondary > primary. (1993)

13.3 Alkenes

15. An alkene on ozonolysis gives methanal as one of the product. Its structure is



16. An alkene *A* on reaction with O_3 and ZnH_2O gives propanone and ethanal in equimolar ratio. Addition of HCl to alkene *A* gives *B* as the major product. The structure of product *B* is

(b)
$$C_1 - CH_2 - CH_2 - CH_2 - CH_3$$

(c) $H_3C - CH_2 - CH_2 - CH_3$
(d) $H_3C - CH_2 - CH_3 - CH_3$
(d) $H_3C - CH_2 - CH_3 - CH_3$
(NEET 2019)

17. The most suitable reagent for the following conversion, is

H₃C
$$-C \equiv C - CH_3 \longrightarrow H_3C - CH_3 \xrightarrow{H_3C} H_3C - CH_3$$

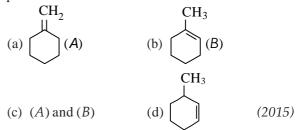
(a) Hg²⁺/H⁺, H₂O (b) Na/liquid NH₃
(c) H₂, Pd/C, quinoline (d) Zn/HCl (*NEET 2019*)

18. Which of the following compounds shall not produce propene by reaction with HBr followed by elimination or direct only elimination reaction?

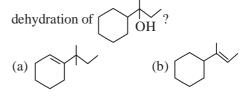
(a)
$$H_2C - CH_2$$

(b) $H_3C - C^2 - CH_2OH$
(c) $H_2C = C = O$
(d) $H_3C - C^2 - CH_2Br$ (NEET-II 2016)

- **19.** The compound that will react most readily with gaseous bromine has the formula
 - (a) C_3H_6 (b) C_2H_2
 - (c) C_4H_{10} (d) C_2H_4 (*NEET-II* 2016)
- **20.** In the reaction with HCl, an alkene reacts in accordance with the Markovnikov's rule to give a product 1-chloro-1-methyl-cyclohexane. The possible alkene is



21. Which of the following is not the product of



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(c)
$$(-)$$
 $(-)$

(b) (d) $\stackrel{R}{\underset{R}{\overset{}}}_{\underset{R}{}}}_{\underset{R}{}}_{\underset{R}{\overset{}}}_{\underset{R}{}}}_{\underset{R}{}}_{\underset{R}{}}}_{\underset{R}{}}}_{\underset{R}{}}_{\underset{R}{}}}_{\underset{R}{}}_{\underset{R}{}}}_{\underset{R}{}}}_{\underset{R}}{}}_{\underset{R}{}}}_{\underset{R}{}}}_{\underset{R$ (R = alkyl substituent)(2005)eaction of HBr with propene in the presence of roxide gives) isopropyl bromide (b) 3-bromopropane) allyl bromide (d) n-propyl bromide. (2004)CH₃ he compound, $CH_3-C = CH \cdot CH_3$ on reaction ith NaIO₄ in the presence of KMnO₄ gives) CH₃COCH₃) $CH_3COCH_3 + CH_3COOH$) $CH_3COCH_3 + CH_3CHO$) $CH_3CHO + CO_2$ (2003)eometrical isomers differ in) position of functional group) position of atoms) spatial arrangement of atoms) length of carbon chain. (2002)preparation of alkene from alcohol using Al₂O₃ hich is the effective factor?) Porosity of Al₂O₃) Temperature) Concentration) Surface area of Al_2O_3 (2001)'hich reagent converts propene to 1-propanol?) H_2O, H_2SO_4) B_2H_6 , H_2O_2 , OH^-) $Hg(OAc)_2$, $NaBH_4/H_2O$) Aq. KOH (2000)'hich is maximum stable?) 1-Butene) cis-2-Butene) trans-2-Butene (2000)) All have same stability. Butene shows geometrical isomerism due to) restricted rotation about double bond) free rotation about double bond) free rotation about single bond (2000)) chiral carbon. Bromopentane is heated with potassium ethoxide ethanol. The major product obtained is) *trans*-2-pentene (b) 1-pentene

(c) 2-ethoxy pentane (d) 2-*cis*-pentene.

(1998)

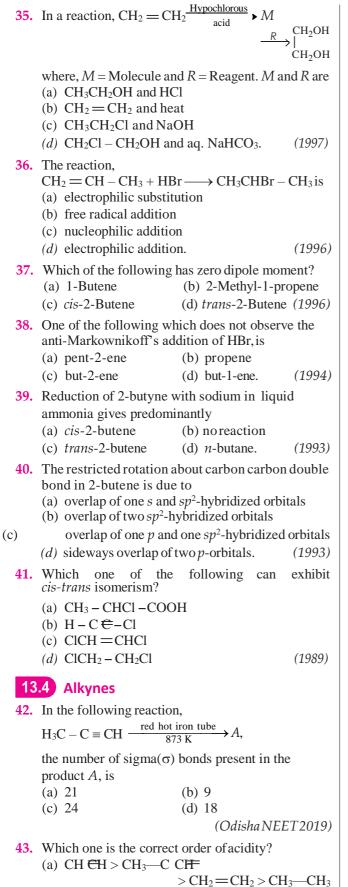
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(b)
$$CH \equiv CH > CH_2 = CH_2$$

 $> CH_3 \rightarrow CCH > CH_3 \rightarrow CH_3$
(c) $CH_3 \rightarrow CH_2 = CH_2$
 $> CH_3 \rightarrow CCH > CHCH$
(d) $CH_2 = CH_2 > CH_3 \rightarrow CH = CH_2$
 $> CH_3 \rightarrow CEH > CH = CH_2$

44. Predict the correct intermediate and product in the following reaction :

$$H_{3}C - C \equiv CH \xrightarrow{H_{2}O, H_{2}SO_{4}} \text{Intermediate} \xrightarrow{(A)} Product$$
(a) $A: H_{3}C - C = CH_{2}, B: H_{3}C - C = CH_{2}$
(b) $A: H_{3}C - C - CH_{3}, B: H_{3}C - C \equiv CH$
(c) $A: H_{3}C - C = CH_{2}, B: H_{3}C - C \equiv CH_{3}$
(d) $A: H_{3}C - C = CH_{2}, B: H_{3}C - C = CH_{3}$
(d) $A: H_{3}C - C = CH_{2}, B: H_{3}C - C = CH_{3}$
(d) $A: H_{3}C - C = CH_{2}, B: H_{3}C - C = CH_{3}$
(n) $OH = O$
(n) OH

45. The pair of electrons in the given carbanion, CH₃C ⊂ , is present in which of the following orbitals?
(a) sp²
(b) sp
(c) 2p
(d) sp³
(NEET-I 2016)

46. In the reaction

$$H C CH \xrightarrow{(i) NaNH / liq.NH}_{(ii) CH_3CH_2Br} X$$

(i) NaNH₂/liq. NH₃ K (ii) CH₃CH₂Br

X and Y are (a) X = 2-butyne, Y = 2-hexyne (b) X = 1-butyne, Y = 2-hexyne (c) X = 1-butyne, Y = 3-hexyne (d) X = 2-butyne, Y = 3-hexyne. (NEET-I 2016) 47. Which of the following organic compounds has same hybridization as its combustion product $(CO_2)?$ (a) Ethane (b) Ethyne (c) Ethene (d) Ethanol (2014)**48.** In the following reaction : HC \in H H2 SO_4 $\cdot p$ $_{Hg^{2+}}$

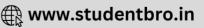
Product 'P' will not give

- (a) Tollens' reagent test
- (b) Brady's reagent test
- (c) Victor Meyer test
- (d) Iodoform test.

(Karnataka NEET 2013)

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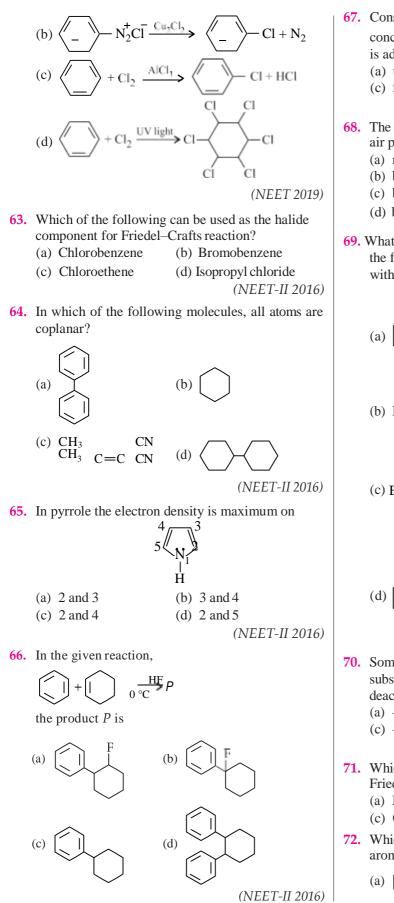


- **49.** Which of the following reagents will be able to distinguish between 1-butyne and 2-butyne? (a) NaNH₂ (b) HCl (c) O₂ (d) Br_2 (Mains 2012) 50. Considering the state of hybridization of carbon atoms, find out the molecule among the following which is linear? (a) $CH_3 - CH = CH - CH_3$ (b) $CH_3 - C \in -CH_3$ (c) $CH_2 = CH - CH_2 - C = CH$ (d) $CH_3 - CH_2 - CH_2 - CH_3$ (2011)**51.** Base strength of H_3CCH_2 , $H_2C = CH$ and $H - C \equiv C$ (ii) (i) is in the order of (a) (i) > (iii) > (iii) (b) (i) > (ii) > (iii) (d) (iii) > (ii) > (i) (2008) (c) (ii) > (i) > (iii) 52. Predict the product *C* obtained in the following reaction of 1-butyne. $\frac{HI}{C} C H C H C C C$ В CH≯ HCl ≻ (a) $CH_3CH_2CH_2CH_1^{\dagger}$ (b) CH₃-CH₂ CH CH₂Cl (c) CH₃CH₂C CH₃ (2007)(d) $CH_3 CH CH_2 CH_2 I$ 53. Products of the following reaction: CH C CCH CH 2 ³ (ii) hydrolysis are (a) $CH_3COOH + CO_2$ (b) CH₃COOH + HOOCCH₂CH₃ (c) $CH_3CHO + CH_3CH_2CHO$ (*d*) $CH_3COOH + CH_3COCH_3$ (2005)54. When CH CH CHCl is treated with NaNH, the product formed is (a) $CH_3 - CH = CH_2$ (b) $CH_3 - C \equiv CH$ (c) CH CH CH \sim NH₂ (d) CH_3CH_2CH (2002)
- 55. When acetylene is passed through dil. H_2SO_4 in the presence of HgSO₄, the compound formed is (a) acetic acid (b) ketone (c) ether (d) acetaldehyde. (1999) 56. The cylindrical shape of an alkyne is due to (a) two sigma C - C and one $\pi C - C$ bonds (b) one sigma C - C and two $\pi C - C$ bonds (c) three sigma C - C bonds (d) three $\pi C - C$ bonds. (1997)**57.** $R - CH_2 - CCl_2 - R \xrightarrow{\text{Reagent}} R - C \xleftarrow{=} R$ The reagent is (a) Na (b) HCl in H₂O (c) KOH in C_2H_5OH (d) Zn in alcohol. (1993) 58. A compound is treated with NaNH₂ to give sodium salt. Identify the compound. (a) C_2H_2 (b) C₆H₆ (c) C_2H_6 (d) C_2H_4 (1993)**59.** The shortest C–C bond distance is found in (a) diamond (b) ethane (c) benzene (d) acetylene. (1991)60. Acetylenic hydrogens are acidic because (a) sigma electron density of C - H bond in acetylene is nearer to carbon, which has 50% s-character (b) acetylene has only open hydrogen in each carbon (c) acetylene contains least number of hydrogens among the possible hydrocarbons having two carbons (d) acetylene belongs to the class of alkynes with molecular formula, $C_n H_{2n-2}$. (1989)61. Which is the most suitable reagent among the following to distinguish compound (3) from rest of the compounds? (1) $CH_3 - C \equiv C - CH_3$ (2) $CH_3 - CH_2 - CH_2 - CH_3$ (3) $CH_3 - CH_2C \in H$ (4) $CH_3 - CH = CH_2$ (a) Bromine in carbon tetrachloride (b) Bromine in acetic acid (c) Alk. KMnO₄ (d) Ammoniacal silver nitrate (1989)13.5 Aromatic hydrocarbons 62. Among the following the reaction that proceeds through an electrophilic substitution is

(a)
$$\bigcirc$$
 CH₂OH + HCl \xrightarrow{heat} CH₂Cl + H₂O

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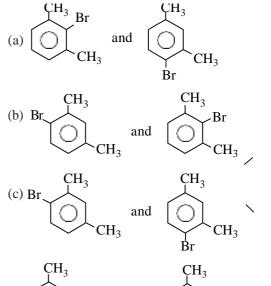
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- 67. Consider the nitration of benzene using mixed conc. H₂SO₄ and HNO₃. If a large amount of KHSO₄ is added to the mixture, the rate of nitration will be
 (a) unchanged
 (b) doubled
 (c) faster
 (d) slower.
 - (NEET-I 2016)
- $\label{eq:V2O5} \textbf{68.} \quad \text{The oxidation of benzene by } V_2O_5 \text{ in the presence of air produces}$
 - (a) maleic anhydride
 - (b) benzoic acid
 - (c) benzaldehyde
 - (d) benzoic anhydride.
- **69.** What products are formed when the following compound is treated with Br_2 in the presence of FeBr₃?



(2015)



(d)
$$\bigcirc$$
 CH_3 and Br CH_3 CH_3 (2014)

70. Some *meta*-directing substituents in aromatic substitution are given. Which one is most deactivating?

a)
$$-COOH$$
 (b) $-NO_2$
c) $-C \equiv N$ (d) $-SO_3H$

- **71.** Which of the following compounds will not undergo Friedel-Crafts reaction easily?
 - (a) Nitrobenzene (b) Toluene
 - (c) Cumene (d) Xylene (*NEET* 2013)
- **72.** Which of the following chemical system is non aromatic?

(a)



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(NEET 2013)

	(c) $\langle c \rangle$	(d)	
	3	• (Karnataka NEET 2013)	
73.	Among the following co most reactive towards el (a) benzoic acid (c) toluene	lectrophilic nitration is	8
74	The reaction of toluene y	with Cl_2 in presence of FeCl ₃	
74.	gives X and reaction in Thus, X and Y are (a) $X =$ benzal chloride, Y = o-chlorotoluene (b) $X = m$ -chlorotoluene Y = p-chlorotoluene (c) $X = o$ - and p -chlorot Y = trichloromethyl (d) $X =$ benzyl chloride	presence of light gives Y. e, toluene, benzene	8
	Y = m-chlorotoluene	e. (2010)	
75.	Benzene reacts with CH anhydrous AlCl ₃ to form (a) chlorobenzene	1	
	(c) xylene	(d) toluene. (2009)	
	the mixture, nitric acid a (a) acid (c) catalyst	HNO_3 and conc. H_2SO_4 . In	
	electrophilic attack?		
	(a) OH	(b) CH ₂ OH	8
	(c)	(d) (2008)	
78.	(i) benzene(iii) chlorobenzene	r the following would be (ii) toluene (iv) phenol	
	(a) (ii) > (iv) > (i) > (iii) (b) (iv) > (iii) > (ii) > (ii) (c) (iv) > (ii) > (i) > (ii) > (iii))	8
	(d) (i) > (ii) > (iii) > (iv)) (2007)	
79.	Using anhydrous AlCl ₃ a	as catalyst, which one of the	

79. Using anhydrous AlCl₃ as catalyst, which one of the following reactions produces ethylbenzene (PhEt)?
(a) H₃C - CH₂OH + C₆H₆

- (b) $CH_3 CH = CH_2 + C_6H_6$ (c) $H_2C CH_2 + C_6H_6$ (d) $H_3C - CH_3 + C_6H_6$ (2004)
- **80.** Which one of the following is a free-radical substitution reaction?

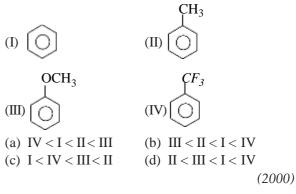
(a)
$$(1)^{CH_3} + Cl_2 \xrightarrow{\text{Boiling}} CH_2Cl$$

(b) $(1)^{-1} + CH_3Cl \xrightarrow{\text{anhy. AlCl}_3} CH_3$
(c) $(1)^{-CH_2Cl} + AgNO_2 \rightarrow (1)^{-CH_2NO_2}$

(d) $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$ (2003)

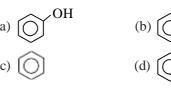
81. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I), benzene (II) and nitrobenzene (III) is

- (a) III > II > I (b) II > III > I
- (c) I < II > III (d) I > II > III (2003)
- **82.** Increasing order of electrophilic substitution for following compounds



83. In Friedel-Crafts reaction, toluene can be prepared by

- (a) $C_6H_6 + CH_3Cl$ (b) $C_6H_5Cl + CH_4$ (c) $C_6H_6 + CH_2Cl_2$ (d) $C_6H_6 + CH_3COCl$ (2000)
- **84.** In Friedel-Crafts alkylation, besides AlCl₃ the other reactants are
 - (a) $C_6H_6 + CH_3Cl$ (b) $C_6H_6 + CH_4$ (c) $C_6H_6 + NH_3$ (d) $C_6H_6 + CH_3COCl$ (1999)
- **85.** Which of the following compounds will be most easily attacked by an electrophile?



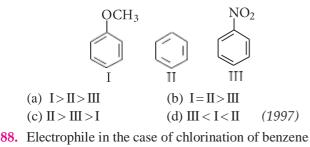
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- **86.** Which one of these is not compatible with arenes?
 - (a) Electrophilic additions (b) Delocalisation of π -electrons
 - (c) Greater stability
 - (d) Resonance
- **87.** Among the following compounds (I-III) the correct order of reaction with electrophile is



- in the presence of FeCl₃ is
- (a) Cl (b) FeCl₃ (c) Cl⁺ (d) Cl⁻ (1996)

- 89. The reactive species in the nitration of benzene is
 (a) NO₃
 (b) HNO₃
 (c) NO₁
 (d) NO₁
 (1994)
- **90.** Which is the correct symbol relating the two Kekule structures of benzene?

$$\begin{array}{ccc} (a) & & & (b) & \longrightarrow \\ (c) & & & (d) & \longleftrightarrow & (1993) \end{array}$$

- **91.** Select the true statement about benzene amongst the following
 - (a) because of unsaturation benzene easily undergoes addition
 - (b) there are two types of C C bonds in benzene molecule
 - (c) there is cyclic delocalisation of π -electrons in benzene
 - (d) monosubstitution of benzene gives three isomeric products. (1992)

ANSWER KEY																			
1.	(c)	2.	(b)	3.	(d)	4.	(c)	5.	(b)	6.	(b)	7.	(b)	8.	(d)	9.	(c)	10.	(c)
11.	(c)	12.	(b)	13.	(c)	14.	(d)	15.	(c)	16.	(d)	17.	(c)	18.	(c)	19.	(a)	20.	(c)
21.	(a)	22.	(a)	23.	(d)	24.	(d)	25.	(d)	26.	(a)	27.	(d)	28.	(b)	29.	(c)	30.	(b)
31.	(b)	32.	(c)	33.	(a)	34.	(a)	35.	(d)	36.	(d)	37.	(d)	38.	(c)	39.	(c)	40.	(d)
41.	(c)	42.	(a)	43.	(a)	44.	(c)	45.	(b)	46.	(c)	47.	(b)	48.	(c)	49.	(a)	50.	(b)
51.	(b)	52.	(c)	53.	(b)	54.	(b)	55.	(d)	56.	(b)	57.	(c)	58.	(a)	59.	(d)	60.	(a)
61.	(d)	62.	(c)	63.	(d)	64.	(a)	65.	(d)	66.	(c)	67.	(d)	68.	(a)	69.	(c)	70.	(b)
71.	(a)	72.	(d)	73.	(c)	74.	(c)	75.	(d)	76.	(b)	77.	(a)	78.	(c)	79.	(c)	80.	(a)
81.	(d)	82.	(a)	83.	(a)	84.	(a)	85.	(a)	86.	(a)	87.	(a)	88.	(c)	89.	(c)	90.	(d)
91.	(c)																		

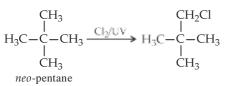
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Hints & Explanations

5.

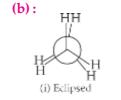
1. (c) : Wurtz reaction is used for the preparation of higher alkanes containing even number of C-atoms. Thus this reaction cannot be used for the preparation of *n*-heptane.

2. (b): In chlorination of alkanes, hydrogen is replaced by chlorine. In *neo*-pentane, only one type of hydrogen is present, hence replacement of any hydrogen atom will give the same product.



3. (d):
$$CH_4 \xrightarrow{Br_2/hv} CH_3$$
 Br $\xrightarrow{Wardzreaction} CH_3 \xrightarrow{(Less than 4 caron atoms)} CH_3 \xrightarrow{(Less than 4 c$

4. (c) : Conformers of ethane have different dihedral angles but same bond angle and bond lengths.



Angle of rotation or angle of torsion or dihedral angle

н

H

(ii) Staggered Newman's projections of ethane

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Magnitude of torsional strain depends upon the angle of rotation about C—C bond. Staggered form has the least torsional strain and the eclipsed form has the maximum torsional strain. So, the staggered conformation of ethane is more stable than the eclipsed conformation.

6. (b) : The anti-conformation is the most stable conformation of *n*-butane as in this, the bulky methyl groups are as far apart as possible thereby keeping steric repulsion at a minimum.

7. (b) : The process of cracking converts higher

alkanes into smaller alkanes and alkenes. This process can be used for production of natural gas.

8. (d): The conformation (d) is most stable because of intermolecular H-bonding.

9. (c) : The staggered form of ethane has the following structure and the dihedral angle is 60° , which means 'H' atoms are at an angle of 60° to each other.



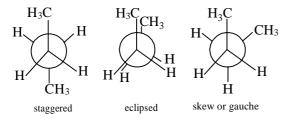
10. (c): When an aqueous solution of sodium or potassium salt of carboxylic acid is electrolysed, hydrocarbon is evolved at anode.

$$2RCOOK \xrightarrow{\text{Electrolysis}}_{\text{Oxidation}} 2RCOO^{-} + 2K^{+}_{\text{Cathode}}$$

At anode : $2RCOO^{-} - 2e^{-} \rightarrow R - R + 2CO_{2}_{\text{Alkane}}$

11. (c) : The branching of chain increases the octane number of a fuel. High octane number means better fuel.

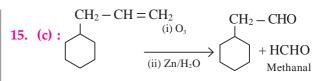
12. (b) : Newman projections for *n*-butane are



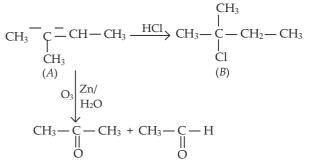
The staggered conformation has minimum repulsion between the hydrogen atoms attached tetrahedrally to the two carbon atoms. Thus, it is the most stable conformation.

13. (c) : Tetraethyl lead $(C_2H_5)_4Pb$, is used as an antiknocking agent in gasoline used for running automobiles.

14. (d) : The reactivity of H-atom depends upon the stability of free radicals, therefore reactivity of H-atom follows the order : $3^{\circ} > 2^{\circ} > 1^{\circ}$.



16. (d) :



Addition of HCl to an alkene (A) will take place according to Markownikoff's rule.

17. (c) : CH₃ C C~~CH~~₃
$$\xrightarrow{H_2, Pd/C}_{quinoline}$$
 $\xrightarrow{H_3C}_{C}$ \xrightarrow{C}_{C} CH₃
H \xrightarrow{C}_{H} C C $\xrightarrow{CH_3}_{H}$
18. (c) :
H $\xrightarrow{2}_{C}$ C H $\xrightarrow{2}_{H}$ C H $\xrightarrow{2}_{S}$ C H \xrightarrow{C}_{H} C \xrightarrow{C}_{H} C

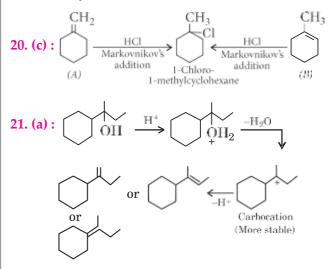
$$\begin{array}{c} \mathsf{Br} \qquad \qquad \mathsf{F}_{2} \\ \mathsf{H}_{2} \\ \mathsf{H}_{3}\mathsf{CCH} \neq \mathsf{H}_{2} \end{array}$$

 $CH_3CH_2CH_2OH \xrightarrow{HBr} \xrightarrow{Elimination} H_3C-CH = CH_2$

$$CH_2 \neq O \xrightarrow{HBr} H_2 C \neq O \xrightarrow{HBr} H_3 C \in Br$$

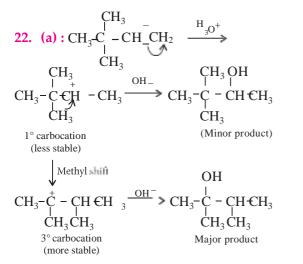
 $CH_3CH_2CH_2Br$ <u>Elimination</u> $CH_3CH = CH_2$

19. (a) : Rate of free radical substitution with $Br_{2(g)}$ depends upon the stability of free radical. Propenyl free radical is allylic free radical which is more stable.

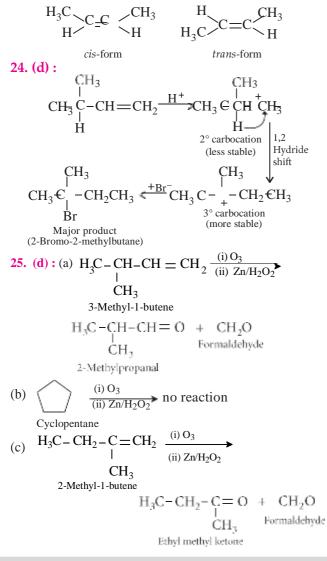


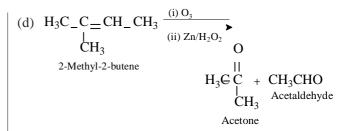
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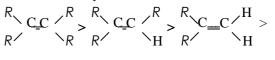
23. (d): *Cis-trans* isomerism is exhibited by compounds having C = C, C = N and N N-groups, due to restricted rotation around the double bond. Among the given options, only 2-butene exhibits geometrical isomerism.

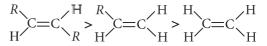




26. (a) : The relative rates of hydrogenation decrease with the increase of steric hindrance. Most stable the alkene, slowly it undergoes hydrogenation to give the product. Least substituted alkene is less stable and more reactive.

Order of stability is :





Hence, alkene which will react faster with H₂ is that which is most unstable.

27. (d) : The formation of *n*-propyl bromide in presence of peroxide can be explained as follow :

Step 1 : Peroxide undergoes fission to give free radicals. $R-O-O - R \longrightarrow 2R-O$

Step 2 : HBr combines with free radical to form bromine free radical.

$$R-O + HBr \longrightarrow R-OH + Br$$

Step 3 : Br attacks the double bond of the alkene to form a more stable free radical. $_{\mathbf{Pr}}$

$$CH CH_{3} = CH_{2} + Br < CH_{3}CH - CH_{2} (1^{\circ} \text{ free radical, less stable})$$

 $(2^{\circ} \text{ free radical, more stable})$

Step 4 : More stable free radical attacks on HBr.

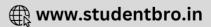
 $CH_{3}CHCH_{2}Br + HBr \longrightarrow CH_{3}CH_{2}CH_{2}Br + Br$ *n*-Propyl bromide

Step 5 : Br + Br
$$\longrightarrow$$
 Br₂

28. (b): CH₃-
$$\overset{CH_3}{\overset{\circ}{=}}$$
 CH-CH₃ $\xrightarrow{\text{NaIO}_4}$ CH₃- $\overset{I}{\underset{\leftarrow}{\leftarrow}}$ CH₃- $\overset{I}{\underset{\leftarrow}{\leftarrow}}$ =O
CH₃COOH

29. (c) : Geometrical isomers are those isomers which possess the same molecular and structural formula but differ in the arrangement of atoms or groups in space due to hindered rotation around the double bonded atoms.

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Hydrocarbons

30. (b) : Temperature is an effective factor because at different temperature it forms different products.

$$CH_3CH_2OH \xrightarrow{Al_2O_3, 620 \text{ K}}{-H_2O} \rightarrow CH_2 = CH_2$$

This is intramolecular dehydration. At lower temperature, intermolecular dehydration takes place between two molecules of alcohol and ether will be formed.

31. (b) : Propene adds to diborane (B_2H_6) giving an addition product. The addition compound on oxidation gives 1-propanol. Here addition of water takes place according to anti-Markownikoff's rule.

32. (c):
$$\begin{array}{c} H_3C \\ C \\ H \end{array} \xrightarrow{C \\ CH_3} H (trans-2-butene) \\ H \end{array}$$

This is most stable as the repulsion between two methyl groups is least.

33. (a) : Due to restricted rotation about double bond, 2-butene shows geometrical isomerism.

$$\underset{(trans)}{\overset{H_3C}{\longrightarrow}} C = C \underbrace{\overset{H}{\underset{CH_3}{\longrightarrow}} H}_{CH_3} C = C \underbrace{\overset{H}{\underset{(cis)}{\longrightarrow}} H}_{CH_3}$$

34. (a) : $CH_3 - CH - CH_2 - CH_2 - CH_3 + C_2H_5 - OK$ Br 2 Bromopentane

$$\rightarrow$$
 CH₃-CH=CH-CH₂-CH₃+KBr
trans-2-Pentene +C₂H₅-OH

35. (d):
$$CH_2 = CH_2 + HOCl \xrightarrow{CH_2OH}_{CH_2Cl} \xrightarrow{aq. NaHCO_3}_{CH_2OH} \xrightarrow{CH_2OH}_{CH_2OH}$$

Therefore, $M = CH_2Cl$ — CH_2OH and R = aq. NaHCO₃

36. (d) : In this reaction, HBr undergoes heterolytic fission as HBr \longrightarrow H⁺ + Br⁻

$$CH_{2} = CH - CH_{3} + HBr \longrightarrow CH_{3} - CH_{3} - CH_{3}$$
$$\xrightarrow{Br} CH - CHBr - CH_{3}$$
$$\xrightarrow{3} 3$$

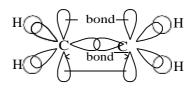
This is an example of electrophilic addition reaction. **37. (d)**

38. (c) : In case of but-2-ene ($CH_3 - CH CH - CH_3$) both double bonded carbons are identical. Therefore, it does not observe the anti-Markownikoff's addition of HBr.

39. (c) : Reduction of non-terminal alkynes with Na in liq. NH₃ at 195 - 200 K gives *trans*-2-butene.

$$CH_3 - C \equiv C - CH_3 \xrightarrow{\text{Na in liq. NH}_3} \xrightarrow{\text{CH}_3} \xrightarrow{\text{CH}_3} \xrightarrow{\text{CH}_3} \xrightarrow{\text{H}_3} \xrightarrow{\text{CH}_3} \xrightarrow$$

40. (d): C = C'



Restricted rotation is due to sideways overlap of two *p*-orbitals.

41. (c) :
$$CI - C - H$$
 $CI - C - H$
 $||$ $||$ $||$ $CI - C - H$ $||$ $H - C - CI$
(*cis*) (*trans*)

1, 2-Dichloroethene exhibits *cis-trans* (geometrical) isomerism.

42. (a): CH₃—C=CH—red hot iron tube

$$H_3C$$
 (A) CH₃
 H_3C (A) CH₃

There are 21 σ bonds.

43. (a) : Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour :

$$\begin{array}{c} sp _ sp & sp^2 & sp^2 \\ HC \ \hline CH > H_2C \ CH_2 \rightarrow \hline CH_3 & - CH_3 \end{array}$$

This is because *sp*-hybridised carbon is more electronegative than sp^2 -hybridised carbon which is further more electronegative than sp^3 -hybridised carbon. Hence, in ethyne proton can be released more easily than ethene and ethane.

Among alkynes the order of acidity is :

$$HC \underline{=} CH > CH_3 - C \underline{=} CH > CH_3 - C \underline{=} C - CH_3$$

This is due to +*I* effect of - CH₃ group.

44. (c) : In case of unsymmetrical alkynes addition of H_2O occurs in accordance with Markownikoff's rule.

$$CH_{3}-C \equiv CH + H - OH \xrightarrow{H_{2}SO_{2}, H_{3}SO_{4}}{333 \text{ K}}$$

$$\begin{bmatrix} OH \\ CH_{3}-C = CH_{2} \\ (A) \end{bmatrix} \xrightarrow{\text{Tautomerises}} CH_{3}-C - CH_{3}$$

$$\xrightarrow{\text{Propanone}} (B)$$

$$45. (b): CH_{3}-C = C^{-}$$

Thus, pair of electrons is present in *sp*-hybridised orbital.

46. (c):
$$HC \equiv CH \xrightarrow{NaNH_2/liq.NH_3} HC \equiv CNa \xrightarrow{CH_3CH_2Br} \\CH_3CH_2C \equiv CNa \xleftarrow{NaNH_2/liq.NH_3} CH_3CH_2C \equiv CH \\ \downarrow CH_3CH_2Dr \\CH_3CH_2C \equiv CCH_2CH_3 \\3 - Hexyne(Y)$$

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47. (b) : $C_2H_2 + O_2 \longrightarrow 2CO_2 + H_2O_2$ Both ethyne and CO₂ have *sp*-hybridisation.

sh

$$\begin{array}{c} sp & sp sp \\ \bigoplus C \oplus & HC \equiv CH \\ 48. (c): HC \equiv CH \xrightarrow{H_3 5O_4} \\ \left[\begin{array}{c} CH_2 \\ Hg^{2+} \end{array} \right] \xrightarrow{Tautomerises} \begin{array}{c} CH_3 \\ I \\ CHOH \\ Vinyl \ alcohol \end{array} \end{array}$$

Acetaldehyde does not give Victor Meyer test.

49. (a) : Terminal alkynes (1-butyne) react with NaNH₂ to form sodium acetylide and evolve hydrogen but 2butyne do not.

50. (b) : CH₃ – C C= CH₃

In case of sp^3 hybridised carbon, bond angle is 109° 28'; sp^2 hybridised carbon, bond angle is 120° and sphybridised carbon, bond angle is 180°.

So, only
$$CH_3 - C = C - CH_3$$
 is linear.
 $\downarrow \qquad \downarrow \qquad \downarrow \qquad \downarrow \qquad \downarrow$
51. (b) : $H - C = C - H > CH_2 = CH_2 > CH_3 CH_3$
 $sp \qquad sp \qquad sp^2 \qquad sp^2 \qquad sp^2 \qquad sp^3 \qquad sp^3$

(Acidic character)

Conjugate base of the given acid :

$$\overline{C} \equiv C - H < \overline{C}H = CH_2 < \overline{C}H_2CH_3$$

(Basic character)

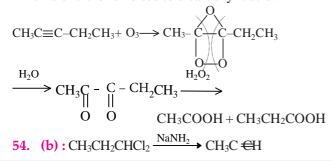
Conjugate base of stronger acid is weaker and vice-versa.

52. (c):
$$CH_3-CH_2-C \equiv CH + HCl \longrightarrow$$

 $CH_3-CH_2-C \equiv CH_2 \xrightarrow{HI} CH_3 CH_2 C CH_3^{I} -$
 $I \qquad I \qquad I$
 $Cl \qquad Cl \qquad Cl$
 $(B) \qquad (C)$

Markownikoff's According to rule. during hydrohalogenation to unsymmetrical alkene, the negative part of the addendum adds to less hydrogenated (*i.e.* more substituted) carbon atom.

53. (b) : On ozonolysis, higher alkynes form diketones which are further oxidised to dicarboxylic acid.



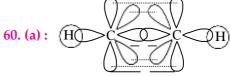
55. (d) : CH CH + H₂O ^{dil.}
$$\xrightarrow{H^2SO_4}$$
 CH
Acetylene $\xrightarrow{H_{gSO_4}}$ $\xrightarrow{H_{gSO_4}}$ $\xrightarrow{H_{gSO_4}}$ $\xrightarrow{H_{gSO_4}}$ $\xrightarrow{H_{gSO_4}}$ $\xrightarrow{H_{gSO_4}}$ $\xrightarrow{H_{gSO_4}}$

56. (b) : In alkyne, two carbon atoms constituting the triple bond are sp-hybridised.Carbon undergoes sphybridisation to form two sp-hybrid orbitals. The two 2p-orbitals remain unhybridised. Hybrid orbitals form one sigma bond while two π -bonds are formed by unhybridised orbitals.

57. (c) : A powerful base is needed to carry out second dehydrohalogenation reaction e.g., hot alcoholic KOH solution or alkoxide ion.

58. (a) : Alkynes react with strong bases like $NaNH_2$ to form sodium acetylide derivative known as acetylides.

H−C≡C−H + NaNH₂ → H−C≡
$$\overline{C}Na^{+}$$
 + 1/2H₂
59. (d) : Shortest C−C distance (1.20 Å) is in acetylene.



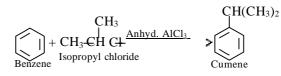
The formation of C – H bond in acetylene involves sphybridised carbon atom. Since s-electrons are closer to the nucleus than *p*-electrons, the electrons present in a bond having more s-character will be more closer to the nucleus. In alkynes s character is 50%, the electrons constituting this bond are more strongly bonded by the carbon nucleus. Thus, acetylenic C-atom becomes more electronegative in comparison to sp^2 , sp^3 and hence the hydrogen atom present on carbon atom ($\neq -H$) can be easily removed.

61. (d) : All the three reagents except ammoniacal AgNO₃ reacts with 1, 2 and 4 compounds. The compound 3 possessing the terminal alkyne only reacts with ammoniacal AgNO3 and thus can be distinguished from 1, 2 and 4 compounds.

62. (c) : The attacking species in the reaction given

in option (c) is an electrophile *i.e.*, Cl. Therefore, it is an electrophilic substitution reaction.

63. (d) : Friedel–Crafts reaction :



Chlorobenzene, bromobenzene and chloroethene are not suitable halide components as C-X bond acquires

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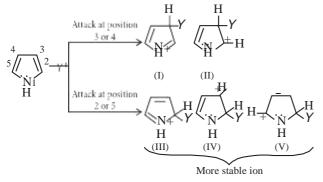


Hydrocarbons

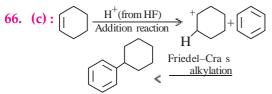
some double bond character due to resonance of lone pair of electrons with π -bond.

64. (a) : Biphenyl is coplanar as all C-atoms are sp^2 hybridised.

65. (d) : Pyrrole has maximum electron density on 2 and 5. It generally reacts with electrophiles at the C-2 or C-5 due to the highest degree of stability of the protonated intermediate.

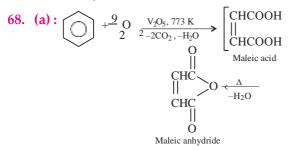


Attack at position 3 or 4 yields a carbocation that is a hybrid of structures (I) and (II). Attack at position 2 or 5 yields a carbocation that is a hybrid not only of structures (III) and (IV) (analogous to I and II) but also of structure (V). The extra stabilization conferred by (V) makes this ion the more stable one. Also, attack at position 2 or 5 is faster because the developing positive charge is accommodated by three atoms of the ring instead of only two.

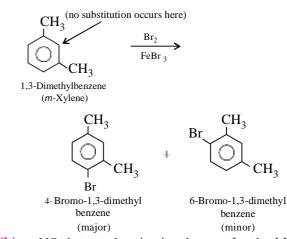


67. (d) : Mechanism of nitration is : HNO₃ + 2H₂SO₄ \rightarrow NO⁺₂+ 2HSO⁻₄+ H₃O⁺

If a large amount of KHSO₄ is added then conc. of HSO_4^- ions increases and the reaction will be shifted in backward direction hence, the rate of nitration will be slower.



69. (c) : — CH₃ group is o,p-directing. Because of crowding, no substitution occurs at the carbon atom between the two — CH₃ groups in *m*-xylene, even though two — CH₃ groups activate that position.

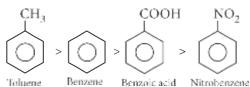


70. (b): $-NO_2$ is most deactivating due to -I and -M effect.

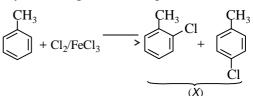
71. (a) : Nitrobenzene is strongly deactivated, hence will not undergo Friedel-Crafts reaction.

72. (d): The molecules which do not satisfy Huckel rule or $(4n + 2)\pi$ -electron rule are said to be non-aromatic. The compound (d) has total $4\pi e^-$. It does not follow $(4n + 2)\pi$ rule. So, it is non-aromatic compound.

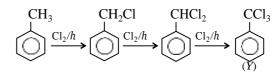
73. (c) : As the +I effect increases reactivity towards electrophilic reactions increases and as -I or -M effect increases, reactivity towards electrophilic reactions decreases. Thus, the order is



74. (c) : The reaction of Cl_2 , in presence of FeCl₃, with toluene yields a ring substitution product.



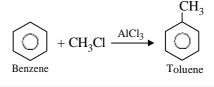
In presence of sunlight, free radical reaction takes place.



75. (d) : This is Friedel-Crafts alkylation.

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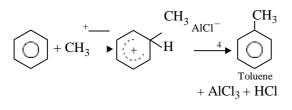
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Mechanism: $CH_3Cl + AlCl_3 \rightarrow AlCl_4^- + CH_3^+$ Lewis acid Electrophile



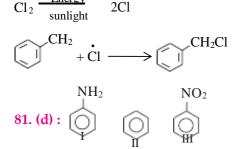
76. (b): $H^+ + H\ddot{O} - NO_2 \rightarrow [H_2O^+ - NO_2]$ (From H_2SO_4) (Base) $H_2O + NO_2^+$

77. (a): Groups like, — Cl and — NO₂ shows –*I*effect. –*I* groups attached to the benzene ring decrease the electron density and hence less prone to electrophilic attack. — OH not only shows –*I* effect but also +*M* effect which predominates the –*I* character and electron density is increased in the benzene ring which facilitates electrophilic attack.

78. (c) : Benzene having any activating group *i.e.*, — OH, — *R* undergoes electrophilic substitution easily as compared to benzene itself. Thus, toluene and phenol undergo electrophilic substitution easily. Chlorine due to –*I*-effect deactivates the ring. So, it is difficult to carry out the electrophilic substitution in chlorobenzene. Hence, the order is $C_6H_5OH > C_6H_5CH_3 > C_6H_6 > C_6H_5Cl$.

79. (c) :
$$C_6H_5H + H_2C == CH_2 \xrightarrow{AlCl_3, HCl} C_6H_5CH_2CH$$

80. (a) : $CH_3 \xrightarrow{heat} CH_2 \xrightarrow{CH_2} H_2$
Benzyl free radical

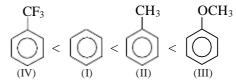


Energy

— NH₂ group is electron donating hence increases electron density on ring. Benzene is also electron rich due to delocalisation of electrons. — NO₂ group is electron withdrawing hence, decreases electron density on ring. Thus, correct order for electrophilic substitution is I > II > III.

82. (a) : Due to -I effect of F atom, —CF₃ on benzene ring, deactivates the ring and does not favour electrophilic

substitution. While — CH₃ and — OCH₃ are electrondonating group which favours electrophilic substitution in the benzene ring at '*ortho*' and '*para*' positions. The +*I* effect of — OCH₃ is more than — CH₃, therefore the correct order for electrophilic substitution is



83. (a) : In Friedel-Crafts reaction toluene is obtained by the action of CH_3Cl on benzene in presence of $AlCl_3$.

$$\bigcirc + CH_3Cl \xrightarrow{AlCl_3} \qquad \blacktriangleright \bigcirc \\Toluene \qquad + HCl$$

84. (a) : In Friedel-Crafts reaction, an alkyl group is introduced into the benzene ring in presence of a Lewis acid (AlCl₃) catalyst. The reaction is

$$\bigcup_{\text{Benzene}} + \text{CH}_3\text{Cl} \xrightarrow{\text{AlCl}_3} \bigoplus_{\text{Toluene}} + \text{HCl}$$

85. (a) : -OH, -Cl and $-CH_3$ groups in benzene

are *ortho*, *para* directing groups. But among these — OH group is strongly activating while — CH₃ is weakly activating and — Cl is deactivating. Thus, phenol will be most easily attacked by an electrophile.

86. (a) : Arenes undergo electrophilic substitution reactions and are resistant to addition reactions, due to

delocalisation of π -electrons. These are also stabilized by resonance.

87. (a) : In structure III, withdrawal of electrons by —NO₂ causes decrease in reaction rate while in structure I, there is electron releasing effect by —OCH₃ group which accelerates the reaction.

The order of reactivity towards electrophile is :

88. (c): $Cl_2 + FeCl_3 \longrightarrow FeCl_4^- + Cl^+$

89. (c) : Nitronium ion (NO⁺) is an electrophile that actually attacks the benzene ring.

90. (d) : Benzene shows Kekule structures which are resonating structures and these structures are separated by a double headed arrow (\leftrightarrow) .

91. (c) : Due to resonance all the C – C bonds in the benzene possess same nature and the resonating structures are obtained because of the delocalisation of π -electrons.



