Chapter 13. Hydrocarbons

- Which one is the correct order of acidity?
 - (a) CH≡CH>CH₃—C≡CH

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

(c) CH_3 — CH_3 > CH_2 = CH_2

(d) $CH_2 = CH_2 > CH_3 - CH = CH_2$

(NEET 2017)

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

$$H_3C - C \equiv CH \xrightarrow{H_2O, H_2SO_4} Intermediate$$

$$\xrightarrow{H_3SO_4} Intermediate$$

$$\longrightarrow \text{FIOCUC}_{(B)}$$

(a)
$$A: H_3C - C = CH_2$$
 $B: H_3C - C = CH_2$ OH SO_4

(b)
$$A: H_3C - C - CH_3$$
 $B: H_3C - C = CH$

(c)
$$A: H_3C - C = CH_2$$
 $B: H_3C - C - CH_3$ OH

(d)
$$A: H_3C - C = CH_2$$
 $B: H_3C - C - CH_3$
 SO_4 O

- 3. 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 (NEET 2017) changes.
- Which of the following can be used as the halide component for Friedel-Crafts reaction?
 - (a) Chlorobenzene
- (b) Bromobenzene
- (c) Chloroethene
- (d) Isopropyl chloride

(NEET-II 2016)

In which of the following molecules, all atoms are coplanar?

(c)
$$CH_3$$
 $C=C$ CN CH_3

6. In pyrrole the electron density is maximum on

$$5\sqrt[4]{\frac{1}{N_1}}$$

- (a) 2 and 3
- (b) 3 and 4
- (c) 2 and 4
- (d) 2 and 5

(NEET-II 2016)

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

(a)
$$H_2C \longrightarrow CH_2$$

 C
 H_2

(b)
$$H_3C - C^2 - CH_2OH$$

(c) $H_2C = C = O$

(c)
$$H_2C = C = C$$

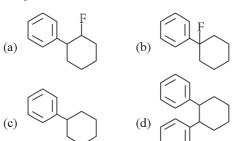
(d)
$$H_3C - C^2 - CH_2Br$$

(NEET-II 2016)



8. In the given reaction,

the product P is



(NEET-II 2016)

- **9.** The compound that will react most readily with gaseous bromine has the formula
 - (a) C_3H_6
- (b) C,H,
- (c) C_4H_{10}
- (d) C_2H_4

(NEET-II 2016)

- 10. 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)
- 11. 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)

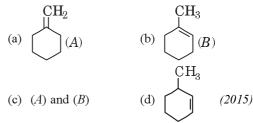
12. The pair of electrons in the given carbanion, CH₃C ≡ C⁻, is present in which of the following orbitals?

- (a) s_I
- (b) *sp*
- (c) 2p
- (d) sp³ (NEET-I 2016)

13. In the reaction

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)
- **14.** In the reaction with HCl, an alkene reacts in accordance with the Markovnikov's rule to give a product 1-chloro-1 methylcyclohexane. The possible alkene is



- **15.** 2,3-Dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid?
 - (a) (CH₂)₂CCH=CH₂
 - (b) (CH₂),C=CHCH,CH,
 - (c) (CH₂),CHCH₂CH=CH₃

(d)
$$(CH_3)_2CH-CH-CH=CH_2$$
 (2015) CH_3

16. A single compound of the structure,

$$\begin{array}{cccc} & CH_3 & CH_3 \\ & & & \\ OHC & C & C \\ & & C & C \\ & & & C & O \\ & & & & \\ H_2 & & & H_2 \end{array}$$

is obtainable from ozonolysis of which of the following cyclic compounds?

(a)
$$H_3C$$
 CH_3 (b) CH_3 CH_3 (c) H_3C CH_3 (d) H_3C CH_3 (2015, Cancelled)

17. Given :

$$\operatorname{III.} \begin{array}{c} \operatorname{H_2C} \\ \\ \operatorname{CII_2} \end{array}$$

The enthalpy of hydrogenation of these compounds will be in the order as

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

(2015, Cancelled)

18. What products are formed when the following compound is treated with Br2 in the presence of FeBr₃?

$$\begin{array}{c} CH_3 \\ CH$$

19. Identify
$$Z$$
 in the sequence of reactions :
$$CH_3CH_2CH = CH_2 \xrightarrow{HBr/H_2O_2} Y \xrightarrow{C_2H_5ONa} Z$$
(a) CH_3 - $(CH_2)_3$ - O - CH_2CH_3

- (b) $(CH_3)_2CH O CH_2CH_3$
- (c) $CH_3(\tilde{C}H_2)_4 O CH_3$ (d) $CH_3CH_2 CH(CH_3) O CH_2CH_3$ (2014)
- 20. Which of the following organic compounds has same hybridization as its combustion product (CO₂)?
 - (a) Ethane
- (b) Ethyne
- (c) Ethene
- (d) Ethanol (2014)
- 21. Which of the following compounds will not undergo Friedal-Craft's reaction easily?
 - (a) Nitrobenzene
- (b) Toluene
- (c) Cumene
- (d) Xylene

(NEET 2013)

22. Which of the following chemical system is non aromatic?

$$\text{(d)} \ \, \bigotimes$$

(Karnataka NEET 2013)

23. In the following reaction:

$$HC \equiv CH \frac{H_2SO_4}{Hg^{2+}} \rightarrow P'$$

Product 'P' will not give

- (a) Tollen's reagent test
- (b) Brady's reagent test
- (c) Victor Meyer test
- (d) Iodoform test (Karnataka NEET 2013)
- 24. In the following reaction

$$\begin{array}{c} \text{CH}_{3} \\ \text{H}_{3}\text{C} - \text{C} - \text{CH} = \text{CH}_{2} \xrightarrow{\text{H}_{2}\text{O}/\text{H}^{\oplus}} A + B \\ \text{Major Minor product product} \end{array}$$

The major product is

$$\begin{array}{c} \text{CH}_{3} \\ \text{(a)} \quad \text{H}_{3}\text{C} - \text{C} - \text{CH} - \text{CH}_{3} \\ \text{OH} \quad \text{CH}_{3} \\ \end{array}$$

$$\begin{array}{c} \text{CH}_3 \\ \text{(d)} \ \ \text{H}_3\text{C} - \text{C} - \text{CH}_2 - \text{CH}_2 \\ \text{CH}_3 \ \ \ \text{OH} \end{array}$$



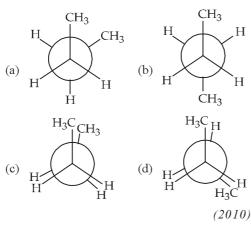
- 25. Which of the following acids does not exhibit optical isomerism?
 - (a) Maleic acid
- (b) α-amino acids
- (c) Lactic acid
- (d) Tartaric acid

(2012)

- 26. 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)

27. In the following the most stable conformation of n-butane is



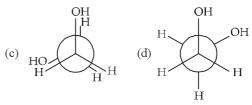
- 28. Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by
 - (a) oxidation
- (b) cracking
- (c) distillation under reduced pressure
- (d) hydrolysis.

- 29. The reaction of toluene with Cl₂ in presence of FeCl₃ gives X and reaction in presence of light gives Y. Thus, X and Y are
 - (a) X = Benzal chloride, Y = o-chlorotoluene
 - (b) X = m-chlorotoluene, Y = p-chlorotoluene
 - (c) X = o- and p-chlorotoluene,
 - Y = Trichloromethyl benzene
 - (d) X = Benzyl chloride, Y = m-chlorotoluene
- 30. In a set of reactions, ethylbenzene yielded a

(a)
$$\bigcirc$$
 CH_2 $-CH$ $-COOC_2H_5$ $\stackrel{\circ}{|}$ $\stackrel{\circ}{|}$ $\stackrel{\circ}{|}$ $\stackrel{\circ}{|}$ $\stackrel{\circ}{|}$ $\stackrel{\circ}{|}$ $\stackrel{\circ}{|}$

$$(d) \bigcup_{Br}^{COOC_2H_5}$$

31. Which of the following conformers for ethylene glycol is most stable?



(Mains 2010)

32. The state of hybridisation of C2, C3, C5 and C₆ of the hydrocarbon,

$$CH_3$$
 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_4 CH_5 CH_5

is in the following sequence

- (a) sp^3 , sp^2 , sp^2 and sp
- (b) sp, sp^2 , sp^2 and sp^3 (c) sp, sp^2 , sp^3 and sp^2 (d) sp, sp^3 , sp^2 and sp^3

- 33. Which of the following compounds will exhibit cis-trans (geometrical) isomerism?
 - (a) Butanol
- (b) 2-Butyne
- (c) 2-Butenol
- (d) 2-Butene

(2009)

(2009)

- 34. Benzene reacts with CH₃Cl in the presence of anhydrous AlCl₃ to form
 - (a) chlorobenzene
- (b) benzyl chloride
- (c) xylene
- (d) toluene.

(2009)



35.
$$H_3C - CH - CH = CH_2 + HBr \longrightarrow A$$

$$CH_3$$

A (predominantly) is

(b)
$$CH_3 - CH - CH - CH_3$$

 $CH_3 Br$

$$\begin{array}{ccc} \text{(c)} & \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 \text{Br} \\ & \text{CH}_3 \end{array}$$

(d)
$$CH_3 - \overset{Br}{\underset{C}{\vdash}} - CH_2CH_3$$
 (2008)

36. In the hydrocarbon,

$$CH_3 - CH = CH - CH_2 - C = CH$$

$$\begin{pmatrix} CH_3 - CH_2 - CH_2 - C - CH_2 -$$

The state of hybridization of carbons 1, 3 and 5 are in the following sequence (a) sp, sp^2 , sp^3 (b) sp^3 , sp^2 , sp(c) sp^2 , sp, sp^3 (d) sp, sp^3 , sp^2

(a)
$$sp$$
, sp^2 , sp^3

(b)
$$sp^{3}$$
, sp^{2} , sp

(c)
$$sp^2$$
, sp , sp

$$sp, sp^-, sp^-$$

37. Predict the product *C* obtained in the following reaction of 1-butyne.

$$CH_{3}CH_{2} - C \equiv CH + HC1 \longrightarrow B \xrightarrow{HI} C$$
(a)
$$CH_{3} - CH_{2} - CH_{2} - C - H$$

$$CI$$
(b)
$$CH_{3} - CH_{2} - CH - CH_{2}CI$$

(d)
$$CH_3 - CH - CH_2CH_2I$$
 (2007)

- **38.** Which of the compound with molecular formula C₅H₁₀ yields acetone on ozonolysis?
 - (a) 3-Methyl-1-butene (b) Cyclopentane
 - (c) 2-Methyl-1-butene (d) 2-Methyl-2-butene (2007)
- 39. Which one of the following alkenes will react faster with H₂ under catalytic hydrogenation conditions?

40. Products of the following reaction:

$$CH_3C \equiv CCH_2CH_3 \xrightarrow{(i) O_3}$$
 are

- (a) $CH_3COOH + CO_2$
- (b) CH₃COOH + HOOC.CH₂CH₃
- (c) CH₃CHO + CH₃CH₂CHO
- (d) CH₃COOH + CH₃COCH₃ (2005)
- 41. Using anhydrous AlCl₃ as catalyst, which one of the following reactions produces ethylbenzene (PhEt)?
 - (a) $H_3C CH_2OH + C_6H_6$
 - (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)
- 42. Reaction of HBr with propene in the presence of peroxide gives
 - (a) isopropyl bromide
 - (b) 3-bromopropane
 - (c) allyl bromide
 - (d) *n*-propyl bromide.

(2004)

43. The compound
$$CH_3 - C = CH - CH_3$$
 on reaction with NaIO₄ in the presence of KMnO₄ gives

- (a) CH₃COCH₃
- (b) CH₃COCH₃ + CH₃COOH
- (c) CH₃COCH₃+CH₃CHO
- (d) $CH_3CHO + CO_2$

(2003)

44. Which one of the following is a free-radical substitution reaction?

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

(b) $CH_3Cl \xrightarrow{anh. AlCl_3} CH_3$

(b)
$$CH_3Cl \xrightarrow{anh. AlCl_3} CH_3$$

$$(c) \hspace{0.2in} \overbrace{\hspace{0.2in}}^{\hspace{0.2in} \operatorname{CH}_2\operatorname{Cl}} \hspace{0.2in} + \operatorname{AgNO}_2 \hspace{0.2in} \longrightarrow \hspace{0.2in} \overbrace{\hspace{0.2in}}^{\hspace{0.2in} \operatorname{CH}_2\operatorname{NO}_2}$$

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

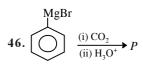
45. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I), benzene (II) and nitrobenzene (III) is



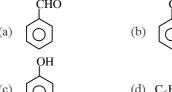


- (a) III > II > I
- (b) II > III > I
- (c) I < II > III
- (d) I > II > III

(2003)



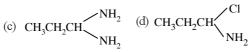
In the above reaction product P is



(2002)

47. When CH₃CH₂CHCl₂ is treated with NaNH₂, the product formed is

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



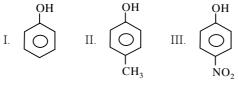
(2002)

- 48. In preparation of alkene from alcohol using Al₂O₃ which is the effective factor?
 - (a) Porosity of Al₂O₃
 - (b) Temperature
 - (c) Concentration
 - (d) Surface area of Al₂O₃.

(2001)

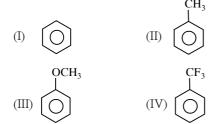
(2001)

49. The correct acidic order of the following is



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

50. Increasing order of electrophilic substitution for following compounds



- (a) IV < I < II < III
- (b) III < II < IV
- (c) I < IV < III < II
- (d) II < III < I < IV(2000)

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

- (a) $C_6H_6 + CH_3C1$
- (b) $C_6H_5Cl + CH_4$
- (c) $C_6H_6 + CH_2Cl_2$
- (d) $C_6H_6 + CH_3COC1$ (2000)

52. Which reagent converts propene to 1-propanol?

- (a) H_2O , H_2SO_4
- (b) B_2H_6 , H_2O_2 , OH^-
- (c) Hg(OAc)₂, NaBH₄/H₂O

(d) Aq. KOH

(2000)

53. Which is maximum stable?

- (a) 1-Butene
 - (b) cis-2-Butene
- (c) trans-2-Butene
- (d) All have same stability.

(2000)

- 54. 2-Butene shows geometrical isomerism due to
 - (a) restricted rotation about double bond
 - (b) free rotation about double bond
 - (c) free rotation about single bond
 - (d) chiral carbon.

(2000)

55. Dihedral angle in staggered form of ethane is

- (a) 0°
- (b) 120°
- (c) 60°
- (d) 180° (2000)

56. When acetylene is passed through dil. H₂SO₄ in the presence of HgSO₄, the compound formed is

- (a) acetic acid
- (b) ketone
- (c) ether
- (d) acetaldehyde

(1999)

57. In Friedel-Craft's alkylation, besides AlCl₃ the other reactants are

- (a) $C_6H_6 + CH_3C1$
- (c) $C_6H_6 + NH_3$
- $\begin{array}{ll} \text{(b)} & \mathrm{C_6H_6} + \mathrm{CH_4} \\ \text{(d)} & \mathrm{C_6H_6} + \mathrm{CH_3COCl} \end{array}$

(1999)

58. Which of the following compounds will be most easily attacked by an electrophile?









59. Which one of these is not compatible with arenes?

- (a) Electrophilic additions
- (b) Delocalisation of π -electrons
- (c) Greater stability
- (d) Resonance

(1998)



- 60. 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is
 - (a) trans-2-pentene
- (b) 1-pentene
- (c) 2-ethoxy pentane
- (d) 2-cis-pentene

(1998)

- 61. Which of the following reaction is expected to readily give a hydrocarbon product in good yields?
 - (a) $CH_3CH_3 \xrightarrow{Cl_2} h_1$
 - (b) $(CH_3)_2CHC1 \xrightarrow{C_2H_5OH}$
 - (c) RCOOK Electrolysis Oxidation
 - (d) $RCOOAg \xrightarrow{I_2}$

(1997)

62. In a reaction $CH_2 = CH_2 \xrightarrow{\text{Hypochlorous}} M \xrightarrow{R}$

where M = Molecule and R = Reagent. M and R are

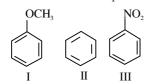
- (a) CH₃CH₂OH and HCl
- (b) $CH_2 = CH_2$ and heat
- (c) CH₃CH₂Cl and NaOH
- (d) CH₂Cl CH₂OH and aq. NaHCO₃.

(1997)

- **63.** 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 π C C bonds

(1997)

- 64. In the commercial gasolines, the type of hydrocarbons which are more desirable is
 - (a) linear unsaturated hydrocarbon
 - (b) toluene
 - (c) branched hydrocarbon
 - (d) straight-chain hydrocarbon. (1997)
- 65. Among the following compounds (I-III) the correct reaction with electrophile is



- (a) I > II > III
- (b) I = II > III
- (c) II > III > I
- (d) III < I < II

(1997)

- **66.** The most stable conformation of n-butane is
 - (a) gauche
- (b) staggered
- (c) skew boat
- (d) eclipsed

(1997)

- 67. Electrophile in the case of chlorination of benzene in the presence of FeCl₃ is
 - (a) Cl
- (b) FeCl₃
- (c) Cl⁺
- (d) Cl

(1996)

68. The reaction,

$$CH_2 = CH - CH_3 + HBr \rightarrow CH_3CHBr - CH_3$$
 is

- (a) electrophilic substitution
- (b) free radical addition
- (c) nucleophilic addition
- (d) electrophilic addition.

(1996)

- 69. Which of the following has zero dipole moment?
 - (a) 1-Butene
- (b) 2-Methyl-1-propene
- (c) cis-2-Butene
- (d) trans-2-Butene

(1996)

- **70.** The alkene $R CH = CH_2$ reacts readily with B₂H₆ and the product on oxidation with alkaline hydrogen peroxides produces
- (b) R—CH—CH₂ OH OH
- (c) $R CH_2 CHO$
- (d) $R CH_2 CH_2 OH$

(1995)

- 71. One of the following which does not observe the anti-Markownikoff's addition of HBr, is
 - (a) pent-2-ene
- (b) propene
- (c) but-2-ene
- (d) but-1-ene

(1994)

- 72. The reactive species in the nitration of benzene
 - (a) NO₃
- (b) HNO₃
- (c) NO_2^+
- (d) NO_2^-
 - (1994)
- 73. $R CH_2 CCl_2 R \xrightarrow{\text{Reagent}} R C \equiv C R$ The reagent is
 - (a) Na
- (b) HCl in H₂O
- (c) KOH in C₂H₅OH
- (d) Zn in alcohol.

(1993)

- 74. Reduction of 2-butyne with sodium in liquid ammonia gives predominantly
 - (a) cis-2-butene
- (b) no reaction
- (c) trans-2-butene
- (d) n-butane.

(1993)

- **75.** A compound is treated with NaNH₂ to give sodium salt. Identify the compound.
 - (a) C_2H_2
- (b) C₂H₂
- (c) C₂H₆
- (d) C_2H_4 (1993)
- **76.** 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)
- 77. Which is the correct symbol relating the two Kekule structures of benzene?
 - (a) **(c) (a)**
- (b) → (d) ← →

(1993)

- **78.** 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)
- 79. 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_nH_{2n-2} . (1989)
- **80.** 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) $CH_3 CH_2C \equiv CH$
 - (4) $CH_3 CH = CH_2$
 - (a) Bromine in carbon tetrachloride
 - (b) Bromine in acetic acid
 - (c) Alk. KMnO₄
 - (d) Ammoniacal silver nitrate. (1989)

Answer Key

1. (d) 5. (a) (c) (c) (a) (d) (c) (c) (a) 10. (d) 11. (d) 12. (b) 15. (c) 17. 20. 13. (c) 14. (c) (a) **16.** 18. (c) 19. (a) (b) 21. 22. (d) 23. 24. 25. 27. 28. 29. **30**. (a) (c) (a) (a) **26**. (a) (b) (b) (c) (d) 31. (d) **32.** (d) 33. (d) 34. (d) **35.** (d) **36**. (d) 37. (c) 38. (d) 39. 40. (b) (a) 41. (c) 42. (d) 43. (b) 44. (a) 45. (d) 46. (b) **47.** (b) 48. (b) 49. (b) **50**. (a) 51. 57. **52.** (b) 53. 54. 55. **56.** (d) **58. 59**. 60. (a) (c) (a) (c) (a) (a) (a) (a) 61. (c) **62.** (d) **63**. (b) 64. (c) **65.** (a) 66. (b) **67.** (c) **68**. (d) 69. (d) 70. (d) 71. 73. (c) **74.** (c) 75. (a) **76.** (d) 77. (d) **78.** (c)



EXPLANATIONS

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

$$sp sp sp sp^2 sp^2 sp^3 sp^3$$

HC\(\equiv CH > H_2C\(\equiv CH_2 > CH_3\)\(-CH_3\)

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:

$$HC \equiv CH > CH_3 - C \equiv CH >> CH_3 - C \equiv C - CH_3$$

This is due to $+I$ effect of $-CH_3$ group.

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

$$CH_{3}-C \stackrel{\delta^{+}}{=} CH + H \stackrel{\delta^{+}}{-} OH \stackrel{\delta^{+}}{\underset{333 \text{ K}}{\longrightarrow}} \underbrace{\begin{bmatrix}OH\\\\CH_{3}-C = CH_{2}\\\\(A)\end{bmatrix}}_{Tautomerises} CH_{3} \stackrel{C}{=} CH_{2}$$

$$CH_{3}-C = CH_{3}$$

3. (c) : Conformers of ethane have different dihedral angles.

4. (d): Friedel–Crafts reaction :

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_4 \\ \text{CH}_3 \\ \text{CH}_5 \\ \text{CH}_5 \\ \text{CH}_3 \\ \text{CH}_4 \\ \text{CH}_3 \\ \text{Cumene} \\ \text{Cumene} \\ \end{array}$$

Chlorobenzene, bromobenzene and chloroethene are not suitable halide components as C-X bond acquires some double bond character due to resonance of lone pair of electrons with π bond.

- **5.** (a): Biphenyl is coplanar as all C-atoms are sp^2 hybridised.
- **6. (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 by only two.

7. (c):

$$\begin{array}{c} \operatorname{Br} & \operatorname{O} \\ \operatorname{H}_2\operatorname{C}=\operatorname{C}-\operatorname{OH} \Longrightarrow \operatorname{H}_3\operatorname{C}-\operatorname{C}-\operatorname{Br} \\ \operatorname{CH}_3\operatorname{CH}_2\operatorname{CH}_2\operatorname{Br} & \underline{\operatorname{Elimination}} \operatorname{CH}_3\operatorname{CH}=\operatorname{CH}_2 \end{array}$$

9. (a)

Newman's projections of ethane

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.

11. (d): Mechanism of nitration is: $HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$



If a large amount of KHSO₄ is added then conc. of HSO₄ ions increases and the reaction will be shifted in backward direction hence, the rate of nitration will be slower.

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

HC
$$\equiv$$
CH $\xrightarrow{\text{NaNH}_2/\text{liq.NH}_3}$ HC \equiv CNa $\xrightarrow{\text{CH}_3\text{CH}_2\text{Br}}$ CH $_3\text{CH}_2\text{C}\equiv$ CNa $\xleftarrow{\text{NaNH}_2/\text{liq. NH}_3}$ CH $_3\text{CH}_2\text{C}\equiv$ CH $\xrightarrow{\text{1-Butyne }(X)}$ CH $_3\text{CH}_2\text{Br}$ CH $_3\text{CH}_2\text{C}\equiv$ CCH $_2\text{CH}_3$

14. (c):

$$(A) \begin{tabular}{|c|c|c|c|} \hline CH_2 & CH_3 & CH_2 \\ \hline \hline HCl & Cl & HCl \\ \hline \hline $Markovnikov's$ & $addition$ & $addition$ \\ \hline $1\text{-}Chloro-1\text{-}methylcyclohexane} \end{tabular}$$

15. (a):

$$\begin{array}{c} CH_3 \\ + C - C - CH = CH_2 \xrightarrow{H^+} H_3C \xrightarrow{C} - CH - CH_3 \\ CH_3 \\ \end{array}$$

2,3-Dimethylbut-2-ene

16. (c):

$$\begin{array}{c|c} H_3C & \xrightarrow{\text{(i) O}_3} \\ \hline \\ \text{CH}_3 & \xrightarrow{\text{(ii) Zn/H}_2O} \\ \hline \\ \text{OHC} & \xrightarrow{\text{CH}_3} & \xrightarrow{\text{CH}_3} \\ \hline \\ \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\ \hline \end{array}$$

17. (d): Enthalpy of hydrogenation is inversely proportional to the stability of alkenes.

Stability of alkenes : I > II > IIIEnthalpy of hydrogenation : $I \le II \le III$

18. (c): $-CH_3$ 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

$$\begin{array}{c} CH_{3} \\ \hline \\ CH_{3} \\ \hline \\ CH_{3} \end{array} \xrightarrow{\text{(no substitution occurs here)}} \begin{array}{c} Br_{2} \\ \hline \\ FeBr_{3} \\ \hline \end{array}$$

1,3-Dimethylbenzene (m-Xylene)

19. (a): CH₃CH₂CH=CH₂ HBr/H₂O₂ (peroxide or anti-markovnikov's effect)

$$\begin{array}{c} \text{Br} \\ \begin{array}{c} \text{Br} \\ \\ \end{array} \\ \begin{array}{c} \text{C}_2\text{H}_5\text{ONa} \\ \end{array} \\ \text{CH}_3\text{CH}_2\text{CH} - \text{CH}_2\text{CH} \\ \\ \text{H} \\ \text{1-Bromobutane} \\ \\ \text{(Y)} \end{array}$$

20. (b):
$$C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O$$

$$0 = \stackrel{sp}{C} = 0$$
 $\stackrel{sp}{HC} = \stackrel{sp}{C} + \stackrel{sp}{C} +$

- 21. (a): Nitrobenzene is strongly deactivated, hence will not undergo Friedel-Craft's reaction.
- 22. (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) rule. So it is non-aromatic compound. All other compounds (a, b, c) are planar and have $6\pi e^-$, so they are aromatic.

23. (c):
$$HC \equiv CH \xrightarrow{H_2SO_4} Hg^{2+} \rightarrow$$

$$\begin{bmatrix} CH_2 \\ || \\ CHOH \\ Vinyl \ al \ cohol \end{bmatrix} \xrightarrow{Tautomerises} CHO \\ \xrightarrow{P} Acetal \ deh \ vde$$

Acetaldehyde does not give Victor Meyer test.



24. (a):
$$CH_3 - C - CH = CH_2 \xrightarrow{H_3O^{\oplus}}$$

$$CH_3 - C - CH = CH_3 \xrightarrow{OH^-} CH_3 - C - CH - CH_3$$

$$CH_3 - C - CH - CH_3 \xrightarrow{OH^-} CH_3 - C - CH - CH_3$$

$$CH_3 \xrightarrow{1^{\circ} \text{ carbocation (less stable)}} (Minor product)$$

$$Methyl shift$$

$$CH_3 - \overset{\oplus}{C} - CH - CH_3 \xrightarrow{OH^-} CH_3 - \overset{OH^-}{C} - CH - CH_3$$

$$CH_3 - \overset{\oplus}{C} - CH - CH_3 \xrightarrow{OH^-} CH_3 - \overset{OH^-}{C} - CH - CH_3$$

$$CH_3 - \overset{\oplus}{C} - CH - CH_3 \xrightarrow{OH^-} CH_3 - \overset{OH^-}{C} - CH - CH_3$$

25. (a): Maleic acid shows geometrical isomerism and not optical isomerism.

$$H$$
 $C = C$
 H
 $HOOC$
 $Maleic acid$
 H

- 26. (a): Terminal alkynes (1-butyne) react with NaNH2 to form sodium acetylide and evolve hydrogen but 2-butyne do not.
- 27. (b): The anti-conformation is the most stable conformation of *n*-butane. In this, the bulky methyl groups are as far apart as possible thereby keeping steric repulsion at a minimum.
- 28. (b): Cracking: The process of cracking converts higher alkanes into smaller alkanes and alkenes. This process can be used for production of natural gas.
- **29.** (c): The reaction of Cl₂, in presence of FeCl₃, with benzene yields a ring substitution product.

$$CH_3$$
 $+ Cl_2/FeCl_3$ CH_3 CH_3 CH_3 CI CI CI CI

In presence of sunlight, free radical reaction takes place.

30. (d):
$$\bigcirc$$
 Br

The given reaction sequence can be delineated as:

$$CH_{2}CH_{3} \xrightarrow{KMnO_{4}} COOH$$

$$COOH$$

$$COOH$$

$$Br_{2}$$

$$FeCl_{3}$$

$$COOH$$

$$COOC_{2}H_{5}$$

$$COOH$$

$$COOC_{2}H_{5}$$

$$COOH$$

$$COOC_{2}H_{5}$$

$$COOH$$

$$COOC_{2}H_{5}$$

$$COOH$$

$$COOC_{2}H_{5}$$

$$COOC_{2}H_{5}$$

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

 \therefore C₂ - sp, C₃ - sp³, C₅ - sp² and C₆ - sp³

33. (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 qualifies to exhibit geometrical isomerism.

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

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

35. (d):
$$CH_3 - CH - CH = CH_2 \xrightarrow{\delta_+ \delta_- H - Br} A$$



$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 - \text{C} - \text{CH} = \text{CH}_2 + \text{H}^{\perp} \longrightarrow \text{CH}_3 - \text{C} - \text{CH} - \text{CH}_3 \\ \text{H} \\ & & & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & &$$

36. (d):
$$\begin{array}{c} sp^3 \\ \text{CH}_3 - \text{CH} = \begin{array}{c} sp^2 \\ \text{CH} - \text{CH}_2 - \text{C} = \begin{array}{c} sp \\ \text{CH} \end{array}$$

The state of hybridisation of carbon in 1, 3 and 5 position are sp, $sp^3 sp^2$

37. (c):
$$CH_3 - CH_2 - C \equiv CH + HCI \xrightarrow{I}$$

$$CH_3 - CH_2 - C = CH_2 \xrightarrow{HI} CH_3 - CH_2 - C - CH_3$$

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

$$H_3C - CH - CH = CH_2$$
 $\xrightarrow{\text{(i) } O_3}$ $\xrightarrow{\text{(ii) } Zn/H_2O_2}$ $\xrightarrow{\text{CH}_3}$

3-Methyl-1-butene

$$\begin{array}{ccc} \mathrm{H_{3}C-CH-CH} = \mathrm{O} & + & \mathrm{CH_{2}O} \\ \mathrm{CH_{3}} & & \mathrm{Formaldehyde} \end{array}$$

2-Methylpropanal

(b)
$$\overbrace{(ii) \text{ Zn/H}_2\text{O}_2}$$
 no reaction

$$H_3C - CH_2 - C = O + CH_2O$$
 CH_3 Formaldehydd

(d)
$$H_3C - C = CH - CH_3 \xrightarrow{(i) O_3} CH_3$$
2-Methyl-2-butene

$$\begin{array}{c} O \\ \parallel \\ H_3C - C \\ \parallel \\ CH_3 \end{array} + \begin{array}{c} CH_3CHO \\ Acetaldehyde \\ \end{array}$$

39. (a): The relative rates of hydrogenation decrease with the increase of steric hindrance. In order of stability of alkene, most stable the alkene slowly it gives the product.

$$R \subset C$$
 $R > R \subset C$
 $R > R \subset C$

$$R$$
 $C = C$ R R $C = C$ H R H $C = C$ H

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

$$R = C + H_2/Pt \xrightarrow{\text{fast}} R - CH_2 - CH_2 - R$$

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

$$CH_{3}C \equiv C-CH_{2}CH_{3} + O_{3} \longrightarrow CH_{3} - C \longrightarrow C-CH_{2}CH_{3}$$

$$0 \longrightarrow 0$$

$$0 \longrightarrow 0$$

$$0 \longrightarrow 0$$

$$CH_{3}COOH + CH_{3}CH_{2}COOH$$
41. (c): $C_{6}H_{5}H + H_{2}C \equiv CH_{2} \xrightarrow{AlCl_{3}, HCl}$

$$C_{6}H_{5}CH_{2}CH_{3}$$

41. (c) :
$$C_6H_5H + H_2C = CH_2 \xrightarrow{AlCl_3, HCl} C_6H_5CH_2CH_2$$

42. (d): The formation of *n*-propyl bromide in presence of peroxide can be explained as follows: Step 1: Peroxide undergoes fission to give free radicals.

$$R - O - O - R \longrightarrow 2R - \dot{O}$$

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.

$$CH_{3}CH = CH_{2} + \dot{B}r$$

$$CH_{3}CH - \dot{C}H_{2} \text{ (less stable)}$$

$$CH_{3}CH - CH_{2}Br \text{ (more stable)}$$



Step 4: More stable free radical attacks on HBr. $CH_3\dot{C}HCH_2Br + HBr \longrightarrow CH_3CH_2CH_2Br + \dot{B}r$ *n*-propyl bromide

Step 5: $\dot{Br} + \dot{Br} \longrightarrow Br_2$

43. (b):

$$\begin{array}{c} CH_3 \\ CH_3C = CH - CH_3 & \xrightarrow{NaIO_4} & CH_3 - C = O \\ + & CH_3COOH \end{array}$$

$$Cl_{2} \xrightarrow{\text{Energy}} 2Cl$$

$$cl_{2} \xrightarrow{\text{sunlight}} 2Cl$$

$$cH_{2} \xrightarrow{\text{CH}_{2}Cl}$$

$$hCl \longrightarrow hCl \longrightarrow hCl$$

$$hCl \longrightarrow hCl$$

$$hCl$$

 $-\mathrm{NH}_2$ group is electron donating hence increases electron density on ring. Benzene is also electron rich due to delocalisation of electrons. $-\mathrm{NO}_2$ group is electron withdrawing hence, decreases electron density on ring. Thus, correct order for electrophilic substitution is I > II > III.

46. (b):

$$\begin{array}{c} MgBr \\ + O = C & \longrightarrow O = C & - OMgBr \\ O & \longrightarrow O = C & \longrightarrow OH \\ &$$

The product is benzoic acid.

48. (b) : Alcohols may be dehydrated to the corresponding olefins. The order of ease of dehydration is

 3° alcohol > 2° alcohol > 1° alcohol.

$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Al}_2\text{O}_3, 620 \text{ K}} \text{CH}_2 \text{=CH}_2$$

49. (b): Phenol exists as a resonance hybrid of the

following structures.

Thus, due to resonance the oxygen atom of the – OH group acquires a positive charge and hence attracts electron pair of the O – H bond leading to the release of hydrogen atom as proton.

Once the phenoxide ion is formed it stabilises itself by resonance which is more stable than the parent phenol as there is no charge separation.

Effect of substituent \rightarrow Presence of electron withdrawing groups ($-NO_2$, -X, -CN) increase the acidity of phenols while the presence of electron releasing groups ($-NH_2$, $-CH_3$) decrease the acidity of phenols. This explains the following order of acidity.

p-nitrophenol > phenol > p-cresol.

50. (a): Due to -I effect of F atom, CF_3 in benzene ring deactivates the ring and does not favour electrophilic substitution. While $-CH_3$ and $-OCH_3$ are '+I group' which favours electrophilic substitution in the benzene ring at 'ortho' and 'para' positions. The +I effect of $-OCH_3$ is more than $-CH_3$, therefore the correct order for electrophilic substitution is

51. (a): In Friedel-Crafts reaction toluene is obtained by the action of CH₃Cl on benzene in presence of AlCl₃.

$$\begin{array}{c} & & \text{CH}_3 \\ \hline \\ & + \text{CH}_3\text{Cl} & \xrightarrow{\text{AlCl}_3} & \hline \\ & & + \text{HCl} \end{array}$$



52. (b): Propene adds to diborane (B₂H₆) giving an addition product. The addition compound on oxidation gives 1-propanol. Here addition of water takes place according to anti-Markownikoff's rule.

53. (c):
$$H_3C$$
 $C = C$ H (trans-2-butene)

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

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

$$H_3C$$
 $C = C$
 CH_3
 H_3C
 $C = C$
 CH_3
 $C = C$
 CH_3
 $C = C$
 CH_3

55. (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.

$$\begin{array}{c} H \\ H \\ \end{array}$$

56. (d):

CH=CH + H₂O
$$\xrightarrow{\text{dil. H}_2\text{SO}_4}$$
 CH₂=CH—OH

Acetylene (unstable)

CH₃—C—H

O

Acetaldehyde

57. (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

- **58.** (a): -OH, -Cl and $-CH_3$ groups in benzene are *ortho-para* directing groups and activate the ring towards electrophilic substitution reaction. But among these -OH group is strongly activating while $-CH_3$ is weakly activating and -Cl is deactivating. Thus, phenol will be most easily attacked by an electrophile.
- **59.** (a): Arenes undergo nucleophilic substitution reaction and are resistant to addition reactions, due to delocalisation of π -electrons. These are also stabilized by resonance.

60. (a):

$$CH_3 - CH_2 - CH_2 - CH_3 + C_2H_5 - CH_5$$
Br

2-Bromopentane

 $CH_3 - CH = CH - CH_2 - CH_3 + KBr + C_2H_5 - CH_5$

trans-(2-Pentene)

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

62. (d)

$$CH_2=CH_2 + HOC1 \longrightarrow CH_2OH \xrightarrow{aq. NaHCO_3} CH_2OH \xrightarrow{CH_2OH} CH_2OH$$

Therefore, $M = CH_2Cl-CH_2OH$ and $R = aq.NaHCO_3$

- **63. (b)**: In alkyne, two carbon atoms constituting the triple bond are sp-hybridised. Carbon undergoes sp-hybridisation 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.
- **64. (c)**: The branching of chain increases the octane number of a fuel. High octane number means better fuel.
- 65. (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.
- **66. (b)** : $CH_3CH_2CH_2CH_3$ *n*-butane Newman projection for *n*-butane is

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

- **67.** (c) : $Cl_2 + FeCl_3 \rightarrow FeCl_4^- + Cl^+$
- **68.** (d): In this reaction, HBr undergoes heterolytic fission as HBr \rightarrow H⁺ + Br⁻

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



69. (d): H
$$C = CH_3$$
 CH_3 CH_3 CH_3 CH_4 CH_4 CH_5 CH_5

Both methyl group cancel each other. So net zero dipole moment exists.

70. (d):
$$6(R - CH = CH_2) \xrightarrow{B_2H_6} 2R(CH_2CH_2)_3B$$

$$\xrightarrow{\text{H}_2\text{O}_2} R\text{CH}_2\text{CH}_2\text{OH} + 2\text{H}_3\text{BO}_3$$

- **71.** (c): In the case of but-2-ene (CH₃-CH=CH-CH₃) both double bonded carbons are identical. Therefore, it does not observe the anti-Markownikoff's addition of HBr.
- **72.** (c): Nitronium ion (NO_2^+) is an electrophile that actually attacks the benzene ring.
- **73.** (c): KOH in C₂H₅OH, when reacts with 1,1-dihaloalkanes form alkynes.
- **74. (c)**: Reduction of non-terminal alkynes with Na in liq. NH₃ at 195 200 K gives *trans* alkene.

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

$$H \longrightarrow C = C \longrightarrow CH_3$$

$$trans-But-2-ene$$

(Birch reduction)

75. (a): Alkynes react with strong bases like NaNH₂ to form sodium acetylide derivative known as acetylides.

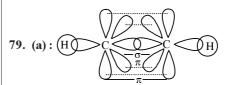
$$H - C \equiv C - H + NaNH_2 \longrightarrow$$

 $H - C \equiv \overline{C} - Na^{\dagger} + 1/2H_2$

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

$$3^{\circ} > 2^{\circ} > 1^{\circ}$$

- 77. (d): Benzene shows kekule structures which are resonating structures and these structures are separated by a double headed arrow (\leftrightarrow) .
- 78. (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.



The formation of C-H bond in acetylene involves sp-hybridised 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 ($\equiv C-H$) can be easily removed.

80. (d): All the three reagents except ammoniacal $AgNO_3$ reacts with 1, 2 and 4 compounds. The compound 3 possessing the terminal alkyne only reacts with ammoniacal $AgNO_3$ and thus can be distinguished from 1, 2 and 4 compounds.

