#### Chapter

# 13

## Hydrocarbons

#### TYPE A: MULTIPLE CHOICE QUESTIONS

- Which is not aromatic compound? [1997]
  - (a) Cyclohexane
- (b) Trinitrotoluene
- (c) Picric acid
- (d) Xylene
- 2. 1-Butyne and cold alkaline KMnO<sub>4</sub> react to produce: [1997]
  - (a) CH<sub>2</sub>CH<sub>2</sub>COOH
  - (b) CH<sub>3</sub> CH<sub>2</sub>COOH+ CO<sub>2</sub>
  - (c) CH<sub>3</sub> CH<sub>2</sub>COOH+HCOOH
  - (d) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH
- 3. Which is used as antiknock in petrol? [1997]
  - (a) Tetraethyl lead
- (b) Tetramethyl lead
- (c) Tetrapropyl lead (d) Tetrabutyl lead
- 4. In the following reaction, Z is identified as

$$CH \equiv CH \xrightarrow{Z} CH_3CHO$$

(a) concentrated H<sub>2</sub>SO<sub>4</sub>

- (b) CH<sub>3</sub>COCl
- (c)  $20 \% H_2SO_4 + HgSO_4$
- (d) CH<sub>2</sub>OH
- 5. The number of  $\sigma$  and  $\pi$  bonds present in ethene is :

[1997]

[1997]

- (a) 6σ
- (b)  $3\sigma$
- (c)  $4\sigma$ ,  $2\pi$
- (d)  $5\sigma$ ,  $1\pi$
- **6.** Glycerol contains

[1997]

- (a) one primary and two secondary alcoholic groups
- (b) two primary and one secondary alcoholic groups
- (c) one primary, one secondary and one tertiary alcoholic groups
- (d) one secondary and two tertiary alcoholic groups
- **7.** Prestone is a mixture of:

[1998]

- (a) Glycol + H<sub>2</sub>O
- (b) Glycerol + H<sub>2</sub>O
- (c) Acetone + H<sub>2</sub>O
- (d)  $propanal + H_2O$

8.  $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$ Benzene Methyl chloride Toluene

The above reaction is:

[1998]

- (a) Wurtz Fittig reaction
- (b) Grignard reaction
- (c) Friedel-Craft's reaction
- (d) Ullmann reaction
- **9.** Geometrical isomerism is possible in case of :
  - (a) tartaric acid
- (b) 1-butene [1999]
- (c) 2-butene
- (d) propene
- **10.** Alkynes usually show which type of reaction? [1999]
  - (a) Substitution
- (b) Elimination
- (c) Addition
- (d) Replacement
- **11.** The product obtained by treating benzene with chlorine in presence of ultraviolet light is:

[1999]

- (a)  $CCl_4$
- (b)  $C_6H_5Cl$
- (c)  $C_6H_6Cl_6$
- (d)  $C_6Cl_6$
- **12.** The natural gas mainly contains:
- [1999]

- (a) methane
- (b) propane
- (c) butane
- (d) pentane
- **13.** Which compound can be sulphonated easily?
  - (a) benzene
- (b) toluene [1999]
- (c) nitrobenzene
- (d) chlorobenzene
- **14.** With ammonical cuprous chloride solution, a reddish brown precipitate is obtained on treating with:
  - (a) CH<sub>4</sub>
- (b) C<sub>2</sub>H<sub>4</sub> [2001]
- (c) C<sub>2</sub>H<sub>2</sub>
- (d)  $C_3H_6$
- 5. The boiling points of four saturated hydrocarbons are given below. Which boiling point suggests maximum number of carbon atoms in its molecule: [2001]
  - (a)  $-162^{\circ}$  C
- (b)  $-88.6^{\circ}$  C
- (c)  $-0.5^{\circ}$  C
- (d)  $-42.2^{\circ}$  C

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- **16.** The size of C C bond in benzene is [2002]
  - (a) 1.22 Å
- (b) 1.54 Å
- (c) 1.39 Å
- (d) 1.56 Å
- 17. Thermite is a mixture of iron oxide and [2002]
  - (a) zinc powder
  - (b) potassium metal
  - (c) sodium shavings
  - (d) aluminium powder
- **18.** The treatment of benzene with isobutene in the presence of sulphuric acid gives: [2003]
  - (a) iso-butylbenzene (b) tert-butylbenzene
  - (c) *n*-butylbenzene
- (d) no reaction
- **19.** The compund having only primary hydrogen atoms is : *[2004]* 
  - (a) isobutene
- (b) 2, 3-dimethylbutene-1
- (c) cyclohexane
- (d) propane
- **20.** Among the following, the aromatic compund is:









- **21.** Which of the following gives propyne on hydrolysis? [2005]
  - (a)  $Al_4C_3$
- (b)  $Mg_2C_3$
- (c)  $B_4C$
- (d)  $La_4C_3$
- **22.** The major product obtained on treatment of CH<sub>3</sub>CH<sub>2</sub>CH(F)CH<sub>3</sub> with CH<sub>3</sub>O<sup>-</sup>/CH<sub>3</sub>OH is:
  - (a) CH<sub>2</sub>CH<sub>2</sub>CH(OCH<sub>2</sub>)CH<sub>2</sub>
- [2005]

[2004]

- (b)  $CH_3CH = CHCH_3$
- (c)  $CH_3CH_2CH = CH_2$
- (d) CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>
- **23.** 3-Phenylpropene on reaction with HBr gives (as a major product): [2005]
  - (a)  $C_6H_5CH_2CH(Br)CH_3$
  - (b) C<sub>6</sub>H<sub>5</sub>CH(Br)CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>
  - (c) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br
  - (d)  $C_6H_5CH(Br)CH=CH_2$
- **24.** Below, some catalysts and corresponding proceses/reactions are matched. The mismatch is:
  - (a)  $[RhCl(PPh_3)_2]$ : Hydrogenation [2006]
  - (b)  $TiCl_4 + Al(C_2H_5)_3$ : Polymerization
  - (c) V<sub>2</sub>O<sub>5</sub>: Haber-Bosch process
  - (d) Nickel-Hydrogenation

- **25.** Which of the following sequence of reactions (reagents) can be used for the conversion of
  - $C_6H_5CH_2CH_3$  into  $C_6H_5CH = CH_2$  ?[2006]

[2007]

- (a)  $SOCl_2: H_2O$  (b)  $SO_2Cl_2: alc KOH$
- (c)  $Cl_2/hv: H_2O$  (d)  $SOCl_2: alc KOH$
- **26.** Propene on hydroboration and oxidation produces
  - (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH
  - (b) CH<sub>3</sub>CHOHCH<sub>3</sub>
  - (c) CH<sub>3</sub>CHOHCH<sub>2</sub>OH
  - (d) CH<sub>3</sub>CH<sub>2</sub>CHO.

27. 
$$CH_2CH = CH_2$$
 [2007]

on mercuration and demercuration produces

- (d) none of these.
- **28.** Which of the following species participate in sulphonation of benzene ring? [2007]
  - (a)  $H_2SO_4$
- (b)  $SO_2$
- (c) HSO<sub>3</sub>
- (d)  $SO_2^-$
- **29.** The most important method of preparation of hydrocarbons of lower carbon number is *[2009]* 
  - (a) Pyrolysis of higher carbon number of hydrocarbons
  - (b) Electrolysis of salts of fatty acids
  - (c) Sabatier and Senderen's reaction
  - (d) Direct synthesis
- 30. The alkene  $R CH = CH_2$  reacts readily with  $B_2H_6$  and formed the product B which on oxidation with alkaline hydrogen peroxide produces [2010]
  - (a)  $R CH_2 CHO$
  - (b)  $R CH_2 CH_2 OH$
  - (c) R C = O $CH_3$
  - $\begin{array}{ccc} \text{(d)} & \text{R}-\text{CH}-\text{CH}_2 \\ & | & | \\ & \text{OH} & \text{OH} \end{array}$

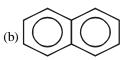
Hydrocarbons————

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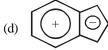
- **31.** 1-Butyne can be distinguished most easily from 2-butyne by *[2011]* 
  - (a) bromine water
- (b) ozonolysis
- (c) Tollen's reagent
- (d) KMnO<sub>4</sub> solution
- 32. Compound X of molecular formula  $C_4H_6$  takes up one equivalent of hydrogen in presence of Pt to form another compound Y which on ozonolysis gives only ethanoic acid. The compound X can be [2011]
  - (a)  $CH_2 = CH CH = CH_2$
  - (b)  $CH_2 = C = CHCH_3$
  - (c)  $CH_3C \equiv CCH_3$
  - (d) All the three
- **33.** The chemical system that is non-aromatic is



[2012]







- **34.** Consider the following statements: A hydrocarbon of molecular formula C<sub>5</sub>H<sub>10</sub> is a
  - I. monosubstituted alkene
  - II. disubstituted alkene
  - III. trisubstituted alkene

Which of the following statement(s) is(are) correct? [2012]

- (a) I, II and III
- (b) I and II
- (c) II and III
- (d) I and III
- **35.** Which one of the following cannot be prepared by Wurtz reaction? [2012]
  - (a) CH<sub>4</sub>
- (b)  $C_2H_6$
- (c)  $C_3H_8$
- (d)  $C_4 H_{10}$
- **36.** Which of the following has the lowest dipole moment? [2013]

(a) 
$$CH_3 \rightarrow C = C \leftarrow H_3$$

- (b)  $CH_3C \equiv CCH_3$
- (c)  $CH_3CH_2C \equiv CH$
- (d)  $CH_2 = CH C \equiv CH$
- 7. Predict the nature of P in the following reaction

$$CH_3C \equiv CCH_3 \xrightarrow{\text{NaNH}_2 / \text{inert solvent}} F$$

[2014]

- (a) CH<sub>2</sub>=CHCH=CH<sub>2</sub>
- (b)  $CH_2=C=CH-CH_3$
- (c) CH<sub>3</sub>CH<sub>2</sub>C≡CH
- (d) No reaction
- **38.** Which of the following would not give 2-phenylbutane as the major product in a Friedel-Crafts alkylation reaction? [2014]
  - (a) 1-butene + HF
  - (b) 2-butanol +  $H_2SO_4$
  - (c) Butanoyl chloride + AlCl<sub>3</sub> then Zn, HCl
  - (d) Butyl chloride + AlCl<sub>3</sub>
- **39.** Which is the most suitable reagent among the following to distinguish compound (3) from rest of the compounds? [2015]
  - 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 KMnO<sub>4</sub>
  - (d) Ammonical silver nitrate.
- **40.** The alkene that will give the same product with HBr in the absence as well as in the presence of peroxide is

[2016]

- (a) 2-butene
- (b) 1-butene
- (c) propene
- (d) 1-hexene
- **41.** The end product (C) in the following sequence of reactions is [2017]

$$HC \equiv CH \xrightarrow{1\% \text{ HgSO}_4} A \xrightarrow{CH_3MgX} B \xrightarrow{[O]} (C)$$

- (a) acetic acid
- (b) isopropyl alcohol
- (c) acetone
- (d) ethanol

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**42.** In the given reaction

 $CH_3CH_2CH = CHCH_3 \xrightarrow{X}$ 

CH<sub>3</sub>CH<sub>2</sub>COOH +CH<sub>3</sub>COOH

The X is

[2017]

- (a)  $C_2H_5ONa$
- (b) Conc. HCl +Anhy.ZnCl<sub>2</sub>
- (c) Anh. AlCl<sub>3</sub>
- (d)  $KMnO_4/OH^-$

#### TYPE B: ASSERTION REASON QUESTIONS

**Directions for (Qs. 43-53):** These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) If the Assertion is incorrect but the Reason is correct.
- **43. Assertion :** CH<sub>4</sub> does not react with Cl<sub>2</sub> in dark. **Reason :** Chlorination of CH<sub>4</sub> takes place in sunlight. [2001]
- **44. Assertion :** Alkylbenzene is not prepared by Friedel-Craft alkylation of benzene.

**Reason :** Alkyl halides are less reactive than acyl halides. [2003]

**45. Assertion :** *trans*-2-Butene on reaction with Br<sub>2</sub> gives *meso*-2, 3-dibromobutane.

**Reason :** The reaction involves *syn*-addition of bromine. [2003]

**46. Assertion :** 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 1-butene as a major product.

**Reason:** 1-Butene is more stable than 2-butene [2004]

According to Saytzeff's rule, 2-butene should be the product which is more branched or substituted compound and hence, more stable than butene-1 **47. Assertion :** Rates of nitration of benzene and hexadeuterobenzene are different.

**Reason :** C–H bond is stronger than C–D bond. [2005]

**48. Assertion :** Cyclopentadienyl anion is much more stable than allyl anion.

**Reason:** Cyclopentadienyl anion is aromatic in character. [2005]

**49. Assertion :** 1, 3-Butadiene is the monomer for natural rubber.

**Reason :** Natural rubber is formed through anionic addition polymerization. [2006]

**50. Assertion :** Addition of HBr on 2-butene gives two isomeric products.

**Reason :** Addition of HBr on 2-butene follows Markovnikov rule. [2006]

**51. Assertion :** *trans*-butene-2 on reaction with bromine forms racemic mixture.

**Reason:** *trans*-Compound in *trans* addition forms two types of stereoisomers. [2007]

**52. Assertion :** Acetylene on reacting with sodamide gives sodium acetylide and ammonia. **Reason :** *sp* hybridised carbon atoms of acetylene are considerably electronegative.

[2007]

**53. Assertion :**Friedel-Craft's reaction is used to introduce an alkyl or acyl group in benzene nucleus.

**Reason :** Benzene is a solvent for the Friedel-Craft's alkylation of bromobenzene. [2008]

**Directions for (Qs.54-61):** Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- **54. Assertion :** 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.

**Reason:** It involves the free radical mechanism. [2009]

**55. Assertion**: Benzene removes a butter stain from a table cloth.

**Reason:** Butter has an affinity towards benzene. [2010]

**56. Assertion :** Trans-2-butene on reaction with Br<sub>2</sub> gives meso-2, 3-dibromobutane.

**Reason:** The reaction involves syn-addition of bromine. [2009, 2014]

**57. Assertion :** 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane. [2015]

**Reason:** It involves the formation of a primary radical.

58. Assertion: Nitrating mixture used for carrying out nitration of benzene consists of conc. HNO<sub>3</sub> + conc. H<sub>2</sub>SO<sub>4</sub>. [2015]
 Reason: In presence of H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> acts as a base and produces NO<sub>2</sub><sup>+</sup> ions.

59. Assertion: Energy of resonance hybrid is equal to the average of energies of all canonical forms.Reason: Resonance hybrid cannot be presented by a single structure. [2016]

**60. Assertion :** Tropylium cation is aromatic in nature

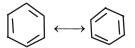


**Reason :** The only property that determines its aromatic behaviour is its planar structure.

[2014, 2016]

**61. Assertion :** Benzene exhibit two different bond lengths, due to C – C single and C = C double bonds. [2017]

**Reason :** Actual structure of benzene is a hybrid of following two structures.



### **HINTS & SOLUTIONS**

#### Type A: Multiple Choice Questions

- 1. (a) Aromatic compounds are closed chain planar compunds with  $(4n + 2)\pi$  electrons and show delocalization of  $\pi$  electrons. Cyclohexane does not coincide with this definition as it does not have benzene ring, while other three have benzene ring.
- 2. **(b)**  $CH_3 CH_2 C \equiv CH + \xrightarrow{KMnO_4} CH_2COOH + CO_2$
- 3. (a) Tetraethyl lead (TEL) is used as antiknock in petrol.
- 4. (c)  $C_2H_2 \xrightarrow{HgSO_4/H_2SO_4} CH_3CHO$

So, z is 20% H<sub>2</sub>SO<sub>4</sub> + HgSO<sub>4</sub>

5. (d) C = C

No. of  $\sigma$  bonds 5 and no. of  $\pi$  bond = 1

**6. (b)** The structure of glycerol is

$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

It contains two primary and one secondary alcoholic groups.

- 7. (a) Prestone is a mixture of glycol & H<sub>2</sub>O. It has freezing point much below 0°C, hence it is used as an antifreeze for automobile radiators.
- **8. (c)** The given reaction is known as Friedel-Craft reaction.
- 9. (c) Geometrical isomerism is shown by molecules containing double bond having unlike groups on each of the doubly bonded carbon atom.
- 10. (c) In most cases, alkynes show addition reactions as they contain two double bonds. In some cases, it undergoes substitution reaction.

$$\begin{array}{c} {\rm C_2H_2 + AgNO_3 + 2NH_4OH} \longrightarrow \\ {\rm C_2Ag_2 + 2NH_3 + 2H_2O} \\ {\rm Silver} \\ {\rm acetylide} \end{array}$$

This reaction occurs only in terminal alkynes.

**11. (c)** In presence of sunlight, benzene reacts with chlorine to form addition product.

$$+3Cl_2 \longrightarrow \begin{matrix} Cl \\ H \\ Cl \\ H \end{matrix} \qquad \begin{matrix} H \\ Cl \\ H \\ Cl \end{matrix}$$

Benzene hexachloride

- 12. (a) Natural gas contains mainly methane
- **13. (b)** Sulphonation is electrophilic substitution reaction of benzene. This reaction is facilitated by any group having +I effect (inductive effect). As CH<sub>3</sub> has +I effect, toluene facilitates this reaction most.
- **14. (c)** Acetylene forms brown copper acetylide with ammonical cuprous chloride solution.

$$Cu_2Cl_2 + C_2H_2 \longrightarrow Cu_2C_2 + 2HCl$$

$$2HCl + 2NH_4OH \longrightarrow 2NH_4Cl + 2H_2O$$

- 15. (c) The heavier the molecule, greater is the boiling point. So molecule with boiling point -0.5°C will have maximum number of carbon atoms.
- **16.** (c) The size of C C bond in benzene is 1.39 Å which lies between 1.34 Å (bond length of C C) and 1.54 Å (bond length of C = C).
- **17. (d)** Thermite is a mixture of iron oxide and Al powder. Al reduces iron oxide to iron giving out enormouns heat.

$$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3 + Heat$$

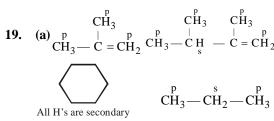
18. **(b)** 
$$CH_2 = C - CH_3 + H^+ \longrightarrow CH_3 - C^+ - CH_3$$

$$CH_3 \qquad CH_3$$
Highly stable

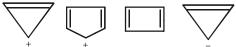
$$CH_{3}$$

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

$$+ (CH_{3})_{3}C^{+} \longrightarrow$$



20. (a) According to Huckel's rule, the cyclic planar conjugated system having  $(4n + 2) \pi$  electrons show aromaticity.



 $2\pi$  electrons  $4\pi$  electrons  $4\pi$  electrons

21. **(b)**  $Mg_2C_3$  gives propyne.  $Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + CH_3 - C \equiv CH$ 

**22. (b)** CH<sub>3</sub>CH<sub>2</sub> - CH(F) - CH<sub>3</sub> is a secondary halide. So, it will undergo dehydrohalogenation to form alkene.

$$\label{eq:ch3ch2} \begin{split} \text{CH}_3\text{CH}_2-\text{CH}(\text{F})-\text{CH}_3 & \xrightarrow{\text{CH}_3\text{O}^-} \\ \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 \\ & \text{(Saytzeff product)} \end{split}$$

23. (a) 
$$CH_2 - CH = CH_2 + H^+ \text{from HBr}$$
3-Phenylpropene

$$\begin{array}{c} \text{CH}_2\overset{+}{\text{CH}}\text{CH}_3\\ \\ \longrightarrow & \begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_3\\ \\ \end{array}\\ \\ \xrightarrow{\text{more stable 2°carbocation}} \end{array}$$

- 24. (c) V<sub>2</sub>O<sub>5</sub> is used as a catalyst in contact process for the manufacture of SO<sub>3</sub> and hence H<sub>2</sub>SO<sub>4</sub>. In Haber-Bosch process for the manufacture of NH<sub>3</sub>, finely divided Fe + molybdenum are used.
- **25. (b)** SO<sub>2</sub>Cl<sub>2</sub> causes free radical substitution at benzylic position.

$$\begin{array}{c} {\rm C_6H_5CH_2CH_3} \xrightarrow{{\rm SO_2Cl_2}} {\rm C_6H_5CHClCH_3} \\ \xrightarrow{{\rm alc}} {\rm C_6H_5CH} = {\rm CH_2} \end{array}$$

**26.** (a) Propene on hydroboration and oxidation produces propanol.

$$3CH_{3}-CH = CH_{2} + BH_{3} \xrightarrow{\text{(Hydroboration)}}$$

$$(CH_{3}CH_{2}CH_{2})_{3}B \xrightarrow{\text{(Oxidation)}}$$

$$3CH_{3}CH_{2}CH_{2}OH$$

27. (a) 
$$CH_2CH=CH_2 \xrightarrow{(CH_3COO)_2Hg \text{ (mercuration)}}$$

$$\begin{array}{|c|c|c|}\hline & CH_2CH-CH_2-Hg & \xrightarrow{(NaBH_4/NaOH)} \\ \hline & I & THF \\ & OCOCH_3 & \end{array}$$

- **28. (b)** SO<sub>3</sub> participates in sulphonation of benzene.
- 29. (a)  $C_6H_{14} \xrightarrow{\text{Pyrolysis}} C_2H_4 + C_4H_{10}$ Hexane Ethene Butane
- 30. (b)  $6R CH = CH_2 \xrightarrow{B_2H_6} 2(RCH_2CH_2)_3 B$   $\xrightarrow{\text{H}_2O_2} 6RCH_2CH_2OH + 2H_3BO_3.$ 
  - 1. (c) Tollen's reagent is ammonical silver nitrate which reacts with 1-alkynes to form white percipitate of silver alkynide.

$$CH_3CH_2C \equiv CH + \underbrace{AgNO_3 + NH_4OH} \rightarrow$$

$$CH_3CH_2C \equiv CAg \downarrow + NH_4NO_3 + H_2O$$
white ppt.

**32. (d)** Formation of only CH<sub>3</sub>COOH by ozonolysis indicates that the compound Y should be CH<sub>3</sub>CH = CHCH<sub>3</sub> which can be formed by all of the three given compounds

$$CH_2 = CH - CH = CH_2 \xrightarrow{-1H_2/Pt}$$

$$CH_3 - CH = CH - CH_3$$

$$CH_3C = CCH_3 \xrightarrow{-1H_2/Pt} CH_3CH = CHCH_3$$

$$X$$

$$CH_2 = C = CHCH_3 \xrightarrow{-1H_2/Pt}$$

$$X$$

$$CH_3CH = CHCH_3 \xrightarrow{-O_3} 2CH_3COOH$$

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- 33. (c) 34. (a)
- **35.** (a) CH<sub>4</sub> has only one carbon atom, hence it can't be prepared by Wurtz reaction, which involves two molecules of alkyl halide.
- **36. (b)**  $CH_3C \equiv CCH_3$ , being symmetrical, has the lowest dipole moment
- 37. (c) When non-terminal alkynes are heated with NaNH<sub>2</sub> in an inert solvent, the triple bond migrates to the end carbon atom.
- **38.** (c) The Friedal-crafts alkylation reaction will give propyl phenyl ketone which further on Clemmenson's reduction will give butyl beggene
- **39.** (d) Br<sub>2</sub> in CCl<sub>4</sub> (a), Br<sub>2</sub> in CH<sub>3</sub>COOH (b) and alk. KMnO<sub>4</sub> (c) will react with all unsaturated compounds, i.e., 1, 3 and 4 while ammonical AgNO<sub>3</sub> (d) reacts only with terminal alkynes, i.e., 3 and hence 3 can be distinguished from 1, 2 and 4 by. ammonical AgNO<sub>3</sub> (d).
- 40. (a) The addition of HBr takes place according to anti-Markovnikoff's rule in presence of peroxide for unsymmetrical alkenes.

  The addition of HBr to symmetrical alkenes is not affected by the presence or absence of peroxide.
- **41.** (c)

$$\begin{split} HC \equiv CH & \xrightarrow{1\% \text{HgSO}_4} CH_3 \text{CHO} \xrightarrow{CH_3 \text{MgX}} \\ & \xrightarrow{20\% \text{H}_2 \text{SO}_4} CH_3 \xrightarrow{[A]} CH_3 \text{COCH}_3 \\ & CH_3 \text{CHOHCH}_3 \xrightarrow{[O]} CH_3 \text{COCH}_3 \\ & \text{[B]} & \text{Acetone} \text{[C]} \end{split}$$

**42. (d)** A doubly bonded carbon atom having an alkyl group is oxidised to aldehyde which is further oxidised to carboxylic acid.

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH} = \text{CH}\,\text{CH}_3 & \xrightarrow{(i)\,\text{KMnO}_4,\,\text{OH}^-} \\ & \xrightarrow{(ii)\,\text{H}^+} & \\ \text{CH}_3\text{CHO} & + & \text{CH}_3\text{CH}_2\text{CHO} \\ \downarrow & & \downarrow \\ \text{CH}_3\text{COOH} & & \text{CH}_3\text{CH}_2\text{COOH} \end{array}$$

#### Type B: Assertion Reason Questions

- **43. (b)** Chlorination of CH<sub>4</sub> takes place either in presence of light or at high temperature, and not in dark because in darkness, Cl free radicals are not produced.
- **44. (b)** Alkylbenzene is not prepared by Friedel-Craft alkylation because monoalkyl product

undergoes alkylation to produce polyalkylated benzene. Further the reason that "acyl halides are more reactive than alkyl halides" although not correct explanation of the assertion it is true because acyl halides are more electron deficient than alkyl halides

The reaction is trans addition of  $Br_2$  and not syn addition.

46. (d) 
$$CH_3 - CH_2 - CH - CH_3 \longrightarrow CH_3 - CH = CH - CH_3$$

$$2-Butene$$

**47. (d)** Rates of nitration of benzene and hexadeuterobenzene are same because the rate determining step (formation of carbocation) is same in both the cases, i.e.,

it does not involve the cleavage of C—H/C—D bond which takes in the second step.

Cyclopentadienyl anion contains  $6\pi$  electrons, so it is aromatic and stabilised

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by reasonance. Thus it is more stable than allyl anion which is not aromatic, although it is also stabilised by resonance.

- **49. (d)** Natural rubber is polymer of isoprene. Thus assertion is false. Further the reason is also false because 1, 3- butadiene undergoes free radical polymeration rather than anionic.
- **50.** (c)  $CH_3-CH=CH-CH_3$  on reaction with HBr gives

$$CH_3-CH_2-C-C-CH_3\\Br$$

which contains one chiral carbon. So, it will give two optical isomers. Hence A is correct. Since 2-butene is symmetrical molecule so it will not follow Markownikov rule. Thus R is false.

**51. (d)** On *anti* addition of Br<sub>2</sub> to *trans*-butene-2, we get *meso* compounds

$$\begin{array}{c} \text{H-C-CH}_3 \\ \text{H-Br} \\ \text{CH}_3\text{-C-H} \end{array} + \text{Br}_2 \Longrightarrow \begin{array}{c} \text{CH}_3 \\ \text{H-Br} \\ \text{H-Br} \\ \text{CH}_3 \end{array} + \begin{array}{c} \text{CH}_3 \\ \text{Br-H} \\ \text{Br-H} \\ \text{CH}_3 \end{array}$$

While *syn* addition gives a racemic mixture. Hence both assertion and reason are false.

**52. (a)** Acetylene on reaction with sodamide gives sodium acetylide and ammonia.

$$CH = CH \xrightarrow{NaNH_2} HC = \overline{C} \stackrel{+}{Na} + NH_3$$
monosodium
acetylide

Here formation of sodium acetylide can be explained by *sp*-hybridisation of carbon atom. As we know that an electron in *s*-orbital is more tightly held than in a *p*-orbital. In *sp* hybridisation, *s*-character is 50% as compared to  $sp^2$  (33%) or  $sp^3$ (25%). So, due to large s-character the carbon atom is quite electronegative and hence Na of NaNH<sub>2</sub> can replace H<sup>+</sup> of C–H bond.

Hence assertion and reason both are true and reason is the correct explanation of assertion.

53. (c) Yes, we use Friedel-Crafts reaction for introducing an alkyl or acyl group in benzene nucleus. Thus, assertion is true. However, the reason is not true because if benzene is used as a solvent, during

alkylation of bromobenzene, benzene will be alkylated in preference to bromobenzene because benzene is more reactive for  $\boldsymbol{S}_{\boldsymbol{E}}$  than bromobenzene.

**54.** (a) This reaction takes place against Markovnikoff's srule

H H H H

$$H - C - C - C = C$$
 $H + H + H$ 
 $H - C - C - C = C$ 
 $H + H + H$ 
 $H + H + H$ 

In this reaction *anti*-Markovnikoff's addition is explained on the basis of the fact that in the presence of peroxide the addition takes place via a free radical mechanism.

- **55. (b)** Benzene is a non-polar solvent. Butter is composed of organic compounds of low polarity. So, it gets dissolved in benzene.
- 56. (c) The assertion that trans-2 butene reacts with Br<sub>2</sub> to product meso-2, 3-dibromobutane is correct but it does not involve syn-addition of Br<sub>2</sub>.
- 57. (c) Here assertion is correct but reasoning is incorect. In presence of peroxide, addition of HBr on alkenes takes place via free radicals; here two free radical are formed, 2° free radical, being more stable, governs the product.

$$\text{CH}_3\text{CH}_2\text{CHBr}\,\mathring{\text{C}}\text{H}_2 \xleftarrow{\text{Br}^{\bullet}} \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$$

$$\stackrel{1^{\circ} \text{ free radical}}{\text{(less stable)}}$$

$$\begin{array}{c} \stackrel{\text{Br}^{\bullet}}{\longrightarrow} \text{CH}_{3}\text{CH}_{2} \, \mathring{\text{C}} \, \text{HCH}_{2}\text{Br} \, \text{CH}_{3}\text{CH}_{2} \, \mathring{\text{C}} \, \text{HCH}_{2}\text{Br} \\ \text{2° free radical} & \text{2° free radical} \\ \text{(more stable)} & \text{(more stable)} \end{array}$$

58. (a) 
$$HNO_3 + 2H_2SO_4 \rightleftharpoons$$
  
 $2HSO_4^- + NO_2^+ + H_3O^+$ 

- **59.** (d)
- **60.** (c)  $(4n+2)\pi$  electrons and planar structure are the essential conditions for aromaticity.
- 61. (c) Benzene has a uniform C C bond distance of 139 pm, a value intermediate between the C C single. (154 pm) and C = C double (134 pm) bonds.