Level-I

Chapter 13

Hydrocarbons

Solutions (Set-1)

Very Short Answer Type Questions :

- 1. What are paraffins?
- **Sol.** The word paraffin has a Latin origin meaning parum, little; affinis, affinity. Those saturated hydrocarbons which are inert under normal conditions and do not react with acids, bases and other reagents are known as paraffins.
- 2. What do you understand by homologous series?
- **Sol.** Those consecutive alkanes which differ by —CH₂ group or by molecular mass 14 are known as homologus series.
- 3. During decarboxylation of sodium salts of carboxylic acid is there any change in the length of the carbon chain.
- **Sol.** Decarboxylation of sodium salts of carboxylic acids gives alkanes containing one carbon atom less than the number of carbon atoms in the carboxylic acid. Example,

$$\begin{array}{c} \mathsf{CH}_3\mathsf{COO}^-\operatorname{Na}^+ + \mathsf{NaOH} \xrightarrow{\operatorname{CaO}} \operatorname{CH}_4 + \mathsf{Na}_2\mathsf{CO}_3 \\ \\ \text{Sodium ethanoate} \end{array}$$

- 4. Name two reagents which can be used to test unsaturation.
- **Sol.** Bromine water and alkaline KMnO₄ can be used to test for the presence of unsaturation.
- 5. What happens when acetylene is passed through dil. H_2SO_4 in presence of $HgSO_4$?
- Sol. Ethanal is obtained.

$$HC \equiv CH \xrightarrow{H_2SO_4, H_2O} HC = CH \xrightarrow{Rearrangement} CH_3 - CHO$$

6. Name any two carcinogenic hydrocarbons.



2 Hydrocarbons

7. In the sulphonation of benzene what acts as an electrophile?

Sol. Sulphur trioxide acts as an electrophile.

8. Of all the conformations in ethane molecule, which one has the greatest and least torsional strain?

Sol. Eclipsed form has the maximum and staggered form has the least torsional strain.

9. Complete the following.

Sol. (A) =
$$\bigcirc$$
 (B) (B)

10. Which concept was given by Kekule to explain the formation of only one ortho disubstituted product?

Sol. The concept of oscillating nature of double bonds in benzene was given by Kekule.



Short Answer Type Questions :

11. Draw the cis- and trans- structure of hex-2-ene. Which isomer will have higher boiling point and why?



cis-hex-2-ene will have higher boiling point because cis form of alkene is found to be more polar than the trans form as a consequence of greater dipole moment.

trans-hex-2-ene

12. Convert propene into 2,3-dimethylbutane.



- 13. What do you understand by aromatization?
- **Sol.** n-Alkanes having six or more carbon atoms on heating to 773 K at 10-20 atmospheric pressure in presence of oxides of vanadium, molybdenum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming.



Which form of geometric isomer has a higher boiling point and why?

- **Sol.** cis-isomer has a greater boiling point than the trans-isomer due to greater polarity and consequent stronger interparticle forces.
- 15. What is polymerisation? Give an example.
- **Sol.** Polymerisation is the process in which small monomers conglomerates to form large molecules called polymers. For example, alkenes undergoes polymerisation at high temperature and pressure to form polymer in presence of catalyst.

$$n(CH_2 = CH_2) \xrightarrow{\text{High temp/Pressure}}_{Catalyst} \leftarrow CH_2 - CH_2 \xrightarrow{}_n$$

$$n(CH_3 - CH = CH_2) \xrightarrow{High temp/Pressure}_{Catalyst} - (CH - CH_2)_n$$

 \downarrow
 CH_3
Polypropene

16. How can you obtain butan-2-one from acetylene?



- 17. Compare the C-H bond lengths and bond dissociation enthalpies of an alkyne, alkene and alkane.
- Sol. As a generalised rule, the more is the s-character in the hybrid orbitals used by an atom, the closer are the bonding electrons to the atom, and the shorter and stronger is the sigma bonds. The decreasing order of C—H bond length is

 $sp^3 > sp^2 > sp$

The decreasing order of bond enthalpies is,



- 18. What is isomerisation reaction? Give an example.
- **Sol.** The process of conversion of one isomer into another isomer is called isomerisation reaction. For example, when butane is heated in presence of anhydrous aluminium chloride and concentrated hydrochloric acid at about 200°C under a pressure of 35 atmospheres, is converted into Isobutane.

$$CH_{3} - CH_{2} - CH_{2} - CH_{3} \xrightarrow{AlCl_{3} + HCl (conc.)}_{200^{\circ}C, 35 \text{ atm}} CH_{3} - CH_{-}CH_{3}$$
Butane

- 19. How can benzene be prepared from sodium benzoate?
- Sol. Lime is heated with coke at very high temperature at which it reacts to form calcium carbide (CaC₂).

$$\begin{array}{c} \mathsf{CaO} + 3\mathsf{C} \xrightarrow{\Delta} \mathsf{CaC}_2 + \mathsf{CO} \\ \mathsf{Lime} & \mathsf{Coke} \end{array}$$

The produced calcium carbide when hydrolysed produces acetylene which is passed through hot iron tube to produce benzene.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$3C_2H_2 \xrightarrow{\text{Fe tube}}{873 \text{ K}} C_6H_6$$

- 20. How will you obtain? Give equation only
 - Ethane from methane (i)
 - Ethane from acetic acid (ii)
- $CH_4 + CI_2 \xrightarrow{hv} CH_3CI + HCI$ **Sol.** (i)

$$CH_3CI + 2Na + CICH_3 \longrightarrow CH_3 - CH_3 + 2NaCI$$

Ethane

(ii)
$$CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$$

$$2CH_{3}COO^{-}Na^{+} \xrightarrow[H_{2}O]{Ethane} CH_{3} - CH_{3} + 2CO_{2} \uparrow + 2NaOH + H_{2} \uparrow Ethane$$

- 21. What is Markovnikov rule? Illustrate with an example.
- Sol. Markovnikov rule states that the negative part of the adding molecule adds to that carbon atom which contains less number of hydrogen atoms. Foundation and a times

$$CH_{3}-CH=CH_{2}+HBr \xrightarrow{H^{+}} CH_{3}-\overset{\oplus}{C}H-CH_{3}$$
Contains less number
of hydrogen atoms
$$CH_{3}-\overset{+}{C}H-CH_{3}+Br^{-} \longrightarrow CH_{3}-CH-CH_{3}$$
(Negative part
of the molecule)

- 22. Can conformational isomers of ethane be separated? Why?
- Sol. No, the conformational isomers of ethane can not be separated. The energy difference between the two extreme forms i.e., staggered and eclipsed form is very small to the order of 12.5 kJ/mol. Even at ordinary temperatures, the ethane molecule gains the thermal or kinetic energy sufficient enough to overcome this energy barrier of 12.5 kJ/mol through intermolecular collisions. So, it can be said that rotation about carbon-carbon single bond in ethane is almost free for all practical purposes and becomes almost impossible to isolate the different conformational isomers of ethane.
- 23. With an example briefly explain pyrolysis.
- Sol. Higher alkanes on heating to high temperatures decompose to lower alkanes or alkenes. Such a decomposition reaction into smaller fragments by the application of heat is called pyrolysis or cracking.

Example :

$$C_{6}H_{14} \xrightarrow{773 \text{ K}} C_{6}H_{12} + H_{2}$$

$$C_{6}H_{14} \xrightarrow{773 \text{ K}} C_{4}H_{8} + C_{2}H_{6}$$

$$C_{3}H_{6} + C_{2}H_{4} + CH_{4}$$

- 24. How many monochlorinated products are possible for
 - (i) neo pentane?
 - (ii) n-pentane?

Sol. (i)
$$H_3C \xrightarrow{CH_3} CH_3 + Cl_2 \xrightarrow{hv} Cl \xrightarrow{CH_2} CH_3$$

 $H_3C \xrightarrow{CH_3} CH_3 + Cl_2 \xrightarrow{hv} Cl \xrightarrow{CH_2} CH_3$
 $H_3C \xrightarrow{CH_3} CH_3$

Only one product 2,2-Dimethylchloropropane can be obtained by monochlorination of neopentane.

(ii) $H_3C - CH_2 - CH_2 - CH_2 - CH_3 \xrightarrow{Cl_2}{h\nu}$

Three products or three monochloro isomeric n-pentane can be obtained *i.e.*,

- (a) $CI CH_2 CH_2 CH_2 CH_3$; 1-chloropentane
- (b) H_3C —CH— CH_2 — CH_2 — CH_3 ; 2-chloropentane ICl
- (c) $H_3C CH_2 CH CH_2 CH_3$; 3-chloropentane
- 25. Draw the structure of ethene showing orbital picture of it to exhibit π -bond, σ -bonds, bond angles and bond length.
- **Sol.** Carbon-carbon bond in alkenes consists of one strong sigma bond formed by the head on overlapping of sp^2 hybridized orbitals and a weak pi-bond obtained by the sideways overlapping of the two 2*p*-orbitals of the two carbon atoms.





(c) Bond angles and bond lengths

- 26. Find the product obtained in the followig cases.
 - (i) C₃H₈ undergoes combustion
 - (ii) Methane undergoes partial oxidation at high pressure in presence of molybdenum oxide.
 - (iii) 2-Methylpropane is subjected to oxidation by KMnO₄

- **Sol.** (i) $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$ Propane Carbon dioxide
 - (ii) Methane forms methanal on partial oxidation at high pressure in presence of molybdenum oxide as catalyst.

$$\begin{array}{c} \mathsf{CH}_4 + \mathsf{O}_2 \xrightarrow{\mathsf{Mo}_2\mathsf{O}_3, \Delta} \\ \text{High pressure} \xrightarrow{\mathsf{MCHO}} \mathsf{HCHO} + \mathsf{H}_2\mathsf{O} \end{array}$$

(iii) Corresponding alcohol is obtained when oxidised by KMnO₄.



- 27. What is Saytzeff rule? Give example.
- **Sol.** Saytzeff rule states that greater is the number of attached alkyl groups, greater is the alkene stability. It shows greater number of hyperconjugative structures raising its stability. Example, the stability order of the alkenes can be given as follows :



Increasing hyperconjugative structures, hence, higher stability

28. Draw the resonance structure of benzaldehyde and tell which position is more prone to electrophilic substitution.



Since electron density decreases at the ortho and para positions, the meta position is having comparatively higher electron density than the ortho and para positions, becoming more prone to electrophilic attack.

- 29. How do structural isomers differ from stereo isomers?
- **Sol.** Structural isomers are the isomers having same molecular formula but different structures *i.e.*, different arrangement of atom or groups of atoms within the molecule. The structure differs due to difference in the attachment positions. This is the reason they are also known as constitutional isomers.

Stereo isomers are the molecules which have same structural formula but have different relative arrangement of atoms or groups of atoms in space. They have the same atomic connectivity but different orientation of atoms or groups in space.

30. Why alkanes and alkynes does not show geometrical isomerism?

Sol. Alkanes : Alkanes do not show geometrical isomerism because :

- (i) These do not possesses carbon-carbon double bond.
- (ii) There is free rotation around C—C single bond.

Alkynes : These does not show geometrical isomerism because :

- (i) The triply bonded carbon atoms are *sp*-hybridized where the bond angle is 180° confirming it to be a linear molecule.
- (ii) Since carbon atoms are triply bounded, only one atom or group can be attached to each carbon atom. So, the different arrangements of atoms or groups in space are not possible.

Long Answer Type Questions :

- 31. Discuss the mechanism of halogenation of methane.
- **Sol.** Halogenation of alkanes takes place either at high temperature or in the presence of diffused sunlight or ultraviolet light. For example, methane undergoes complete replacement of hydrogen by the halogen when allowed to react in excess of halogen.

$$CH_4 + CI_2 \xrightarrow{hv} CH_3CI + HCI$$

Chloromethane

 $CH_3CI + CI_2 \xrightarrow{h\nu} CH_2CI_2 + HCI$ Dichloromethane

 $CH_2CI_2 + CI_2 \xrightarrow{h\nu} CHCI_3 + HCI$ Trichloromethane

$$CHCI_3 + CI_2 \xrightarrow{h\nu} CCI_4 + HCI$$

Tetrachloromethane

The halogenation process is supposed to proceed through the free radical mechanism which involves three steps namely initiation, propagation and termination.

(i) Initiation : Chlorine molecule undergoes homolytic cleavage producing chlorine free radicals in presence of sunlight.

$$CI - CI \xrightarrow{hv} CI^{\bullet} + CI^{\bullet}$$

Homolysis $CI^{\bullet} + CI^{\bullet}$

(ii) **Propagation :** Chlorine free radicals are very reactive and attacks the methane molecule breaking the C—H bond producing a methyl free radical and H—CI.

(a)
$$CH_4 + CI \longrightarrow CH_3 + HCI$$

The methyl radical attack second molecule of chlorine liberating another chlorine radical.

(b)
$$\dot{C}H_3 + CI - CI \longrightarrow CH_3 - CI + \dot{C}I$$

The free radicals produced in the reaction starts a chain reaction.

$$CH_3CI + CI \longrightarrow CH_2CI + HCI$$

$$CH_2CI + CI - CI \longrightarrow CH_2CI_2 + CI$$

(iii) Termination step : The free radicals are consumed and the reaction stops after sometime.

(a)
$$\overset{\bullet}{Cl} + \overset{\bullet}{Cl} \longrightarrow Cl_2$$

- (b) $\dot{CI} + \dot{CH}_3 \longrightarrow CH_3CI$
- (c) $\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3 CH_3$
- 32. Predict the major products of the following reactions with reason.

(i)
$$CH_3 - CH = CH_2 + HBr$$

(ii) 2-Methylpropene + HCl

Sol. The addition will follow the Markovnikov rule which states that negative part of the hydrogen halide will add to the most alkynated carbon of the double bond and hydrogen adds to the less substituted or more hydrogenated carbon atom.



- 33. (i) How will you convert ethanoic acid into benzene?
 - (ii) When 2-pentyne reacts with mercuric sulphate in dilute sulphuric acid, the product obtained is a mixture of two ketone. Show by reaction.
- **Sol.** (i) Ethanoic acid reacts with sodium hydroxide to form salt of sodium ethanoate which is further subjected to decarboxylation method produces methane. Methane is chlorinated in limited quantity of chlorine in presence of diffused sunlight or ultra-violet light which produces methyl chloride. Methyl chloride reacts with sodium in presence of dry ether (Wurtz reaction) to yield ethane, which on limited chlorination gives ethyl chloride. Ethyl chloride undergoes dehydrohalogenation reaction producing ethene which produces vicinal dihalide on reaction to Bromine. The vicinal dihalide produces ethyne when allowed to react with alcoholic KOH followed by reaction with sodamide. Ethyne when passed through red hot iron tube at 873 K undergo cyclisation process to produce benzene.

$$CH_{3}COOH \xrightarrow{NaOH} CH_{3}COO-Na^{+} \xrightarrow{CaO, \Delta} NaOH + CH_{4} \xrightarrow{hv} CH_{3}CI \xrightarrow{Na/dry ether} C_{2}H_{6} \xrightarrow{Cl_{2}} C_{2}H_{5}CI \xrightarrow{+Kcl} alc. KOH$$

$$ightarrow CH_{3}COO-Na^{+} \xrightarrow{CaO, \Delta} NaOH + CH_{4} \xrightarrow{hv} CH_{3}CI \xrightarrow{Na/dry ether} C_{2}H_{6} \xrightarrow{Cl_{2}} C_{2}H_{5}CI \xrightarrow{+Kcl} alc. KOH$$

$$ightarrow CH_{3}COO-Na^{+} \xrightarrow{NaOH} CH_{2} = CH \xrightarrow{hv} CH_{3}CI \xrightarrow{Na/dry ether} C_{2}H_{6} \xrightarrow{-Kcl} C_{2}H_{5}CI \xrightarrow{+Kcl} alc. KOH$$

$$ightarrow CH_{3}OH \xrightarrow{H} CH \equiv CH \xrightarrow{NaNH_{2}} CH_{2} = CH \xrightarrow{Br} \xrightarrow{alc. KOH} \xrightarrow{CH_{2}Br} \xrightarrow{Br_{2}} CH_{2} = CH_{2}$$

$$(ii) CH_{3}-C \equiv C-CH_{2}-CH_{3} + H \xrightarrow{-OH} \xrightarrow{Hg^{2}, H^{+}} CH_{3} \xrightarrow{-C} \equiv C-CH_{2}-CH_{3} + CH_{3} \xrightarrow{-C} = C-CH_{2}-CH_{2} \xrightarrow{-CH_{2}} CH_{2} \xrightarrow{-C} CH_{2} \xrightarrow{-CH_{2}} CH_{3} \xrightarrow{-CH_{3}} CH_{3}$$

- 34. Write the possible isomeric structures of pentene and name them. What are the products obtained when each of it is subjected to reductive ozonolysis?
- Sol. The possible isomeric structures of pentene are :
 - (i) $CH_2 = CH CH_2 CH_2 CH_3$ Pent-1-ene (ii) $CH_3 - CH = CH_2 - CH_2 - CH_3$ Pent-2-ene (iii) $CH_3 - CH = C - CH_3$ 2-Methylbut-2-ene (iv) $CH_2 = CH - CH - CH_3$ 3-Methylbut-1-ene (v) $CH_2 = C - CH_2 - CH_3$ 2-Methylbut-1-ene (v) $CH_2 = C - CH_2 - CH_3$ 2-Methylbut-1-ene

The products obtained when each of it is subjected to reductive ozonolysis are as follows.



- 35. How can the structure of an alkene is determined by ozonolysis?
- **Sol.** Ozonolysis serves one of the best methods to determine the position of double bond in an alkene. When an alkene is treated with ozone in an inert solvent, forms ozonide, which when treated with Zn/H₂O, carbonyl compounds are obtained. The structure of carbonyl compound depends upon the structure of the alkene. Some points should be kept in mind while deciding the structure of the alkene :

н

(i) When formaldehyde O = C - H is obtained, it means the group is $= CH_2$ when O = C - R type of aldehyde is obtained, it means the group is = CHR.

When a keto group, O = C - R is obtained, it means the group is = C - R.

н

- (ii) When only one type of aldehyde or ketone is obtained, it means alkene is symmetrical with respect to the double bond.
- (iii) The structures of carbonyl compounds are written in a way that the carbonyl group faces each other.

$$\begin{array}{ccc} R_{2} & R_{4} \\ I & I \\ R_{1}-C=0 & O=C-R_{3} \\ [A] & [B] \end{array}$$

(iv) The =O of both the compounds are removed and linked through a double bond. This is the structure of unknown alkene.



 R_1 , R_2 , R_3 or R_4 are either hydrogen atoms or alkyl groups or both.

36. What are the steps involved in an electrophilic substitution reaction? Discuss with a general mechanism.

Sol. Electrophilic substitution reactions proceed via three steps

- (i) Generation of an electrophile
- (ii) Attack of electrophile on benzene ring
- (iii) Deprotonation.
- (i) Generation of an electrophile, E[⊕]: During chlorination, alkylation and acylation of benzene, anhydrous FeCl₃, AlCl₃ or FeBr₃, acting as a Lewis acid helps in generation of the electrophile Cl[⊕], R[⊕], RC[⊕]O (acylium ion) respectively by combining with the attacking reagent.

 $E - Nu + AlCl_3 \longrightarrow E^{\oplus} + [AlCl_3Nu]^-$

Where E = Electrophile and Nu = Nucleophile and $[AICl_3Nu]^-$ is the intermediate complex.

(ii) Attack of electrophile on benzene ring (formation of arenium ion) : The attack of electrophile E^{\oplus} results in the formation of a σ (sigma) complex or arenium ion in which one of the carbon is sp^3 hybridized.



The arenium ion gets resonance stabilised.



(iii) **Removal of proton**: To restore the aromatic character, σ -complex releases proton from sp^3 hybridised carbon atom.



- 37. (i) Write the general formula of alkynes.
 - Write down the IUPAC name and structures of all alkynes having the molecular formula C_5H_8 . (ii)
 - (iii) Give any two methods for preparing acetylene.
 - (iv) Discuss any three chemical properties of acetylene.
- **Sol**. (i) The general formula of alkynes is $C_n H_{2n-2}$.
 - C_5H_8 has the following isomers : (ii)

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

pent-1-yne

(b)
$$CH_3 - CH_2 - C \equiv C - CH_3$$

pent-2-yne

(c)
$$CH_3 - CH - C \equiv CH$$

 I
 CH_3
3. Methylput. 1. yrge

3-Methylbut-1-yne

- (iii) Acetylene can be prepared by the following two methods :
 - (a) Hydrolysis of calcium carbide

 $CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$

(b) By dehydrohalogenation of vicinal dihalides of alkanes

$$CH - C \equiv CH$$

$$CH_{3}$$
ethylbut-1-yne
an be prepared by the following two methods :
ysis of calcium carbide
$$C_{2} + 2H_{2}O \longrightarrow C_{2}H_{2} + Ca(OH)_{2}$$
ydrohalogenation of vicinal dihalides of alkanes
$$CH_{2} - Br + 2KOH \longrightarrow CH \equiv CH + 2KBr + 2H_{2}O$$

$$H_{2} - Br + 2KOH \longrightarrow CH \equiv CH + 2KBr + 2H_{2}O$$

1-2-dibromoethane

- (iv) The three chemical properties of acetylene are as follows :
 - (a) Addition of hydrogen :

$$HC \equiv CH + 2H_2 \xrightarrow{\text{Ni/Pd/Pt}} H_3C \xrightarrow{\text{CH}_3}$$

(b) Addition of halogens :



(c) Cyclic polymerisation : When acetylene is passed through red hot iron tube at 873 K. Cyclic polymerisation takes place forming benzene.

38. Predict the major product in the following reactions. Give mechanism as well.

(i)
$$C_6H_6 + CH_3CH_2CH_2 - OH \xrightarrow{H_2SO_4} ?$$

(ii) $C_6H_6 + CH_3 - CH_3 + AICI_3 \xrightarrow{\Delta} ?$

Sol. (i) In the presence of H₂SO₄ propanol first gives 1° carbocation which then rearranges by hydride shift to give 2°carbocation. The carbocation then reacts with benzene to form Isopropyl benzene.



39. Explain the following.

- (i) Why alkenes are more reactive than alkanes?
- (ii) Acetylene reacts with Sodamide to form an acetylide while ethylene does not?
- (iii) But-2-ene shows geometrical isomerism but but-1-ene does not?
- **Sol.** (i) Alkenes contains π -bond which is weaker than sigma bond and can be easily broken. Whereas in alkanes, all the bonds are strong σ (sigma) bonds which are difficult to break. So alkenes show greater reactivity in comparison to alkanes.

(ii) Acetylene reacts with sodamide (NaNH₂) that is a strong base, due to its acidic nature. It contains acidic hydrogen in it.

$$H - C \equiv C - H + NaNH_{2} \longrightarrow H - C \equiv C^{-}Na^{+} + NH_{3}$$

Sodium acetylide

(iii) In but-1-ene, the carbon atom is linked by double bond which is attached with two hydrogen atoms and thus it will not show geometrical isomerism.



While But-2-yne can show geometrical isomerism being the doubly bonded carbon atom is linked by different groups.



41. Give the structural formulae for the seven alkynes of the formula C₆H₁₀. Which of these isomers are terminal alkynes? Which of these on partial hydrogenation followed by reductive ozonolysis will produce only one type of compound?



Terminal alkynes are those which have a triple bond at the end of the carbon chain. Here in the isomers given (A), (E), (F) and (G) are the terminal alkynes.

Hex-3-yne when subjected to partial hydrogenation followed by reductive ozonolysis will produce same carbonyl compound.



- 42. What are the conditions necessary for exhibiting geometric isomerism in open chain compounds? Why cisisomer is more polar than trans-isomer?
- Sol. (i) The conditions necessary for geometric isomerism
 - (a) There should be a double bond in the molecule.
 - (b) The two atoms or groups attached to each doubly bonded carbon atom should be different. If one of the two double bonded carbon atoms carries two identical groups or atoms then the molecule does not exhibit geometrical isomerism. For example :



16 Hydrocarbons

(ii) Cis-isomer is more polar than the trans-isomer because in it the individual bond dipoles do not cancel out each other. For example, dipole moment of cis-but-2-ene is 0.33 D whereas that of trans-but-2-ene is almost zero.



- 43. (i) What is Huckel rule? Give example to explain.
 - (ii) Why benzene prefer to undergo substituion reaction rather than addition reaction?
- **Sol.** (i) Huckel rule defines the aromaticity of a compound. If a following set of characteristics are followed, the compound will be aromatic.
 - (a) It should be planar.
 - (b) It should have complete delocalisation of π -electrons in the ring.
 - (c) It should have $(4n + 2)\pi$ electrons in the ring where 'n' is whole number 0, 1, 2, 3,

Example :

Benzene has six π -electrons and behaves as an aromatic compound



 (ii) Despite of being highly unsaturated, benzene prefer to undergo substitution rather than addition because in addition reaction, the resonance stabilised benzene ring is destroyed, destroying its aromatic character. On the other hand, aromaticity is maintained during substitution since delocalisation of electron remains intact.

6



- 44. Explain the orbital structure of benzene with the reason for its extra stability.
- **Sol.** According to the orbital structure, each carbon atom in benzene is sp^2 hybridized with three orbitals lying in one plane at an angle of 120°. There is one unhybrid orbital lying perpendicular to the hybrid orbitals plane. Each carbon atom uses two hybrid orbitals for axial overlaing with the two other carbon atom orbitals on the

either side, whereas the third one is used to overlap axially with 1s orbital of hydrogen forming six C–H sigma bonds. From given figure C–C and C–H sigma bonds can be depicted.



The unhybridized p-orbital undergoes sideways overlapping forming weak π -bonds.



The molecular orbital containing π -electrons spreads uniformly over the entire carbon skeleton forming a doughnut structure. This delocalisation of π -electrons, results in decrease of energy and hence accounts for its extra stability of benzene.



Orbital picture of benzene

45. With a suitable mechanism show how benzene can be converted to Styrene (C_6H_5 —CH= CH_2).

Sol. Benzene undergo Friedel Craft's reaction to be alkylated.



Mechanism :



Level-I

Chapter 13

Hydrocarbons

Solutions (Set-2)

	[Alka	anes (Nome	enclature,	Classification	, Preparatio	on, Properties	5)]
1.	The minimum number of carbon atoms in alkane molecule to show chain isomerism is						
	(1) 2	(2)	3	(3)	4	(4)	5
Sol.	Answer (3)					io'	
	Butane can form n	-butane and	isobutane.			13.00	
2.	Alkanes can be iodinated in the presence of						
	(1) HI	(2)	I_2 and P	(3)	$I_2 + HIO_3$	i ^{ce5} (4)	Pl ₃
Sol.	Answer (3)				Se ales	5	
	HIO ₃ and HNO ₃ being oxidants oxidize HI and prevent the backward reduction of RI.						
3.	(CH ₃) ₃ CMgCl on re	action with D	2O produces		4 guilt		
	(1) (CH ₃) ₃ CD	(2)	$(CH_3)_3COD$	(3)	(CD ₃) ₃ CD	(4)	(CD ₃) ₃ COD
Sol.	I. Answer (1) (CH ₃) ₃ CMgCl + D ₂ O \rightarrow (CH ₃) ₃ CD + MgODCl						
4.	In the given reaction	on	4	(Or			
	O II						
	$CH_{3} - \overset{H}{C} - C_{2}H_{5} \xrightarrow{x} CH_{3} - CH_{2} - C_{2}H_{5}$						
	'X' will be						
	(1) LiAlH ₄			(2)	NaBH ₄		
	(3) BCl ₃ SnH			(4)	$NH_2 - NH_2 /$	OH [—] , glycol	
Sol.	Answer (4)						
	It is Wolff-Kishner	reduction.					

- 5. In the complete combustion of hydrocarbon (C_nH_{2n + 2}) the number of oxygen molecules required per mole of hydrocarbon is
 - (1) $\frac{n}{2}$ (2) $\frac{(n+1)}{2}$ (3) $\frac{(3n+1)}{2}$ (4) $\left(n+\frac{1}{2}\right)$

Sol. Answer (3)

$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \rightarrow nCO_2 + nH_2O$$
 (Eudiometric equation)

6. Highest boiling point is expected for

Sol. Answer (4)

Due to largest surface area.

7. Consider the following reaction

$$CH_{3} - CH - CH - CH_{3} + Br \rightarrow \dot{X} + HBr$$

$$D CH_{3} - \dot{X} + HBr$$

Identify the structure of the (X)

(1)
$$CH_3 - CH - CH - CH - CH_2$$

 $D CH_3$
(3) $CH_3 - CH - CH_3$
 $H - CH_3$

(2)
$$CH_3 - CH - CH_3 - CH_3$$

 $D CH_3$
(4) $CH_3 - CH - CH_3$
 $CH_3 - CH - CH_3$

Sol. Answer (2)

The reaction proceeds in a direction to give most stable free radical as reaction intermediate.

[Alkenes (Nomenclature, Classification, Preparation, Properties)]

- 8. Consider the following statements : a hydrocarbon of molecular formula C₅H₁₀ may be
 - (I) Mono-substituted alkene
 - (II) di-substituted alkene
 - (III) tri-substituted alkene

Which of the above statements are correct?

(1) I, II and III (2) I and II but not III (3) II and III but not I (4) I and III but not II

Sol. Answer (1)

$$\begin{array}{c} \mathsf{CH}_3-\mathsf{CH}_2-\mathsf{CH}_2-\mathsf{CH}=\mathsf{CH}_2 \\ \text{monosubstituted} \end{array} \quad \begin{array}{c} \mathsf{CH}_3-\mathsf{CH}=\mathsf{CH}-\mathsf{CH}_2-\mathsf{CH}_3 \\ \text{disubstituted} \end{array}$$

with respect to presence of alkyl groups.

9.
$$\begin{bmatrix} & Me \\ & N^{\oplus} \\ & I \\ & Et \end{bmatrix} OH^{-} \xrightarrow{\Delta}$$

The alkene formed as a major product in the above elimination reaction is



Sol. Answer (2)



10. 2.8 g of pure alkene containing only one double bond per molecule, reacts completely with 8 g of bromine in an inert solvent. The molecular formula of alkene is

Foundation

(1) C_2H_4 (2) C_4H_8 (3) C_3H_4 (4) C_6H_{12}

Sol. Answer (2)

$$\begin{array}{c} C_4H_8 + Br_2 \rightarrow C_4H_8Br_2 \\ \scriptstyle 2.8 \text{ gram} & 8 \text{ gram} & 10.8 \text{ gram} \end{array}$$

 \therefore 8 g Br₂ reacts with 2.8 g alkene

:. 160 g Br₂ reacts with = $\frac{2.8 \times 160 \text{ g}}{8}$ g alkene = 56 g alkene

Hence alkene is C₄H₈

11.
$$() \rightarrow ()$$

The most suitable sequence of reagents to perform this conversion is

- (1) HBr then $(CH_3)_3COK/(CH_3)_3C-OH$
- (2) NBS then alcoholic KOH
- (3) HBr-peroxide then CH₃CH₂OK/CH₃CH₂OH
- (4) HBr-peroxide then $(CH_3)_3 COK/(CH_3)_3 COH$

Sol. Answer (4)



12. The compound having only primary hydrogen atoms is

Sol. Answer (2)

$$CH_3$$
 $C = C$ CH_3 It contains only primary hydrogen





14. Arrange the following compounds in increasing order of reactivity towards the addition of HBr

$$RCH = CHR, \prod_{CH_2}^{CH_2}, R_2C = CHR, R_2C = CR_2$$

$$(1) \prod_{CH_2}^{CH_2} < RCH = CHR < R_2C = CHR < R_2C = CR_2$$

$$(2) R_2C = CHR < RCH = CHR < CH_2 = CH_2 < R_2C = CR_2$$

$$(3) R_2C = CR_2 < R_2C = CHR < RCH = CHR < CH_2 = CH_2 < CH_2 = CH_2$$

$$(4) R_2C = CR_2 < CH_2 = CH_2 < RCH = CHR < R_2C = CHR$$
Sol. Answer (1)
Due to formation of most stable carbocation.
15. HBr reacts with CH_2 at room temperature to give

- 15. II CH—OCH₃
 - (1) CH₃CHO and CH₃OH
 - (3) $BrCH_2 CH_2 O CH_3$

- (2) BrCH₂CHO and CH₃OH
 (4) H₃C—CHBr—OCH₃

Sol. Answer (4)



16. Colouration of Br₂ / CCl₄ will be discharged by









19. Most probable product of the addition of one molecule of Br_2 on Hexa-1, 3, 5-triene is

(1)
$$Br-CH_2-CH=CH-CH=CH-CH_2Br$$

(2) $CH_2=CH-CH-CH-CH=CH_2$
(3) $CH_2-CH-CH=CH-CH=CH_2$
 Br
 Br
 Br
 Br
 $CH-CH_2-CH=CH-CH=CH$

Sol. Answer (1)

Conjugated diene is more stable than isolated or cumulated dienes.

20. The intermediate during the addition of HCI to propene in the presence of peroxide is

(1)
$$CH_3 - \dot{C}H - CH_2CI$$

(2) $CH_3 - \ddot{C}H - CH_3$
(3) $CH_3 - CH_2 - \ddot{C}H_2$
(4) $CH_3 - CH_2 - \dot{C}H_2$

Sol. Answer (2)

As HCI does not give peroxide effect the reaction of HCI even under the presence of peroxide proceeds through ionic mechanism.

$$CH_3 - CH = CH_2 \longrightarrow CH_3 - CH - CH_3 \longrightarrow CH_3 - CH - CH_3$$

 $H = CH_2 \longrightarrow CH_3 - CH - CH_3 \longrightarrow CH_3 - CH - CH_3$
reactive
intermediate

- 21. Compound A (i) decolourises Baeyer's reagent (ii) on hydroxylation and further oxidation with KMnO₄ gave formic acid and acetone (iii) on ozonolysis gave one molecule of acetone and one molecule of formaldehyde. A is
 - (1) Propylene (2) Ethylene (3) n-Butylene (4) Iso-Butylene
- Sol. Answer (4)



- 22. Which of the following alkene on acid catalysed hydration form 2-methyl propan-2-ol ?
 - (1) $(CH_3)_2C = CH_2$ (3) $CH_3 - CH = CH - CH_3$ (2) $CH_3 - CH = CH_2$ (4) $CH_3 - CH_2 - CH = CH_2$

Sol. Answer (1)



- 23. The reaction of chlorine water with propene gives
 - (1) $CICH_2 CH(OH)CH_3$

Sol. Answer (1)

$$CH_{3} - CH = CH_{2} \xrightarrow{CI_{2}/H_{2}O} CH_{3} - CH - CI_{2}$$

(2) CH₂(OH)CH(CI)CH₃

(4) CICH(OH)CH₂CH₃

24. Point out (A) in the given reaction sequence



Sol. Answer (3)

$$\bigcup_{H_2O_2} O_3 \rightarrow 2CH_2 \xrightarrow{COOH} \Delta \rightarrow 2CH_3COOH + 2CO_2$$

[Alkynes (Nomenclature, Classification, Preparation, Properties)]

25. Consider the following reaction



The reactive intermediate involved in this reaction is

(3) Free radical anion (2) Carbocation (4) Free radical cation (1) Carbanion Sol. Answer (3)



(Radical anion) - a reactive intermediate Divisions of Aakas

26. The reaction

 $CH_3CHBr - CH_2Br + 2KOH(alc)$

 $\xrightarrow{\Delta}$ CH₃C \equiv CH + 2KBr + 2H₂O is called

- (1) Dehalogenation (2) Dehydrohalogenation (3) Decarboxylation (4) Dehydration
- Sol. Answer (2)

Removal of Br and H from α & β carbon is called dehydrohalogenation

- The reaction of one equivalent of HBr with $H_2C = CH C \equiv CH$ at relatively high temperature gives which 27. of the following as major product?
 - (1) $CH_2 = CH CBr = CH_2$

3)
$$CH_2 = CH - CH = CHBr$$

- Sol. Answer (1)

 $CH_2 = CH - C \equiv CH \xrightarrow{HBr} CH_2 = CH - C = CH_2$ Conjugated diene

- (2) $CH_3 CHBr C \equiv CH$
- (4) $CH_3 CH_2 C \equiv C Br$

[Aromatic Hydrocarbons (Preparation, Properties)]

28. Which equation does not represent an example of Friedel-Crafts reaction?

(1)
$$C_6H_6 + C_2H_5CI \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCI$$

(2)
$$C_2H_5OH + HCI \xrightarrow{ZnCl_2} C_2H_5CI + H_2O$$

(3)
$$C_6H_6 + CHCI_3 \xrightarrow{AICI_3} (C_6H_5)_3 CH$$

 $(4) \quad C_{6}H_{6} + CH_{3}CH_{2}COCI \xrightarrow{Anhy}{AlCl_{3}} C_{6}H_{5}COCH_{2}CH_{3} + HCI$

Sol. Answer (2)

Friedel Crafts alkylation involve conversion of Arene into alkyl arene in the presence of acids (Lewis acid as mineral acid). But in example (2). Alkyl halide is obtained from alcohol.

29. Among the following compounds, the decreasing order of reactivity towards electrophilic substitution is



Other unsaturated compounds give less stable reactive intermediate when treated with electrophile.

