



Chapter - 13

# Hydro Carbons

#### • Preparation of Alkanes:

(1) From unsaturated hydrocarbons:

(2) Wurtz reaction 
$$\left[ \text{Alkyl Halide} + \text{Na} \xrightarrow{\text{Dry}} \text{Higher alkane} \right]$$

$$R-X + 2Na + X-R$$
 Dry ether  $R-R + 2NaX$ 

(3) Sodalime decarboxylation method:

[Sodium salt of carboxylic acid + NaOH + CaO  $\rightarrow$  Alkane [ $n_c = 1$  less]

$$R$$
— $CH_2COONa^+ + NaOH \xrightarrow{CaO} ?$ 

$$R - CH_{2} \xrightarrow{O} C - O Na^{+} + NaOH \xrightarrow{CaO} R - CH_{3} + Na_{2}CO_{3}$$
Alkene

## • Koble's electrolytic method:

Potassium salt of carboxylic acid (aq) — Current → Higher alkane

$$R{\rm -\!CH_2COO\!K^+\ (aq)} \xrightarrow{\rm Electrolysis}?$$

$$R - CH_{2} \xrightarrow{\searrow} C - OK^{+}$$

$$\downarrow \qquad \qquad Current \\ R - CH_{2} \xrightarrow{\searrow} C - OK^{+}$$

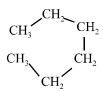
$$R - CH_{2} \xrightarrow{\searrow} C - OK^{+}$$

## • Chemical Properties of Alkanes:

(1) **Halogenation**: One (H) atm is replaced by halogen at a time.

$$CH_4(g) + Cl_2(g) \xrightarrow{hv} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

(2) Aromatisation: n-Hexane  $\xrightarrow{\text{Cr}_2\text{O}_3 \text{ or } \text{V}_2\text{O}_5}$  or or



#### **Alkenes**

## • Preparation of alkenes:

(1) From alkynes [Alkyne +  $H_2 \longrightarrow$  Alkene]

$$R - C \equiv C - R$$

$$R - C \equiv C - R$$

$$Na + liq.NH_3$$

$$R - C = C$$

$$R$$

$$C = C$$

$$H$$

$$R - C \equiv C - R$$

(2) From alkyl halide by (dehydrohalognation)

Alkyl Halides + alc.KOH 
$$\xrightarrow{\Delta}$$
 Alkene

Carbon attached with halogen is  $\alpha$ -carbons

Carbon attached with  $\alpha$ -carbons is  $\beta$ -carbons

Halogen is removed and 'H'-atom is removed from  $\beta$ -carbon to form (C=C) double bond.

(3) By Dehydration of alcohols (Ion of water molecule)

[Alcohol + Conc.H<sub>2</sub>SO<sub>4</sub>
$$\xrightarrow{\Delta}$$
Alkene]

Carbon attached to alcohoic group is  $\alpha$ -carbon.

Carbon attached to  $\alpha$ -carbon is  $\beta$ -carbon.

(4) From vicinal dihalides [Compounds in which halogen atom are attached with adjacent carbons]

$$\begin{bmatrix} \text{Vicinal dihalide} + \text{Zn} \xrightarrow{\Delta} \text{Alkene} \end{bmatrix}$$

$$\begin{bmatrix} X & X \\ & | \\ & C \\ & | \end{bmatrix}$$

$$- C - C - C - + Zn \xrightarrow{\Delta} - C = C - + ZnX_{2}$$

$$- C = C - + E \xrightarrow{N_{u}} \xrightarrow{N_{u}} - C - C - C - C$$

$$| N_{u} = E$$

# **Chemical Properties of Alkenes:**

(1) Addition of Halogens :  $\begin{bmatrix} Alkene + X_2 \longrightarrow Vicinal \ dihalide \end{bmatrix}$ 

- (2) Addition of H—X :  $\begin{bmatrix} Alkene + HX \longrightarrow Alkyl \ halide \end{bmatrix}$
- (A) **Markownikoff's rule (M.R.)**: During electrophillic addition of hydrogen halide, the electron deficient electrophile (E<sup>+</sup>) always attack

on that doubly/triply bounded carbon atom. which already has greater number of hydrogen atoms.

$$CH_{3}-CH = CH_{2} + H \xrightarrow{ \ \ \ \ \ \ \ } Br \xrightarrow{ \ \ \ \ \ \ \ } CH_{3}-CH-CH_{2}$$

$$Br \xrightarrow{ \ \ \ \ \ \ \ \ } Br \xrightarrow{ \ \ \ \ \ } H$$

(B) **Peroxide/Kharasch effect (Anti M.Rule) :** This effect takes place in presence of peroxides when the hydrogen free radical (H) attacks on that doubly bonded carbon which has lesser number of hydrogen atoms.

$$CH_{3}-CH = CH_{2} + H \xrightarrow{\text{OP}} Br \xrightarrow{\text{Benzoyl}} CH_{3}-CH-CH_{2} + CH_{3}COOH \xrightarrow{\text{Peroxide}} CH_{3}-CH-CH_{2} + CH_{3}COOH \xrightarrow{\text{Perox}} H \xrightarrow{\text{Br}} Br$$

(C) Ozonolysis

$$C = C + O_3 \xrightarrow{Zn/H_2O} C = O + O = C$$

In this reaction all those carbons which form double bonds get findly converted into carbonyl carbons.

If alkenes are symmetrical then both carbonyl compounds are same.

If more than two double bonds are present then we get at least one compound which has two carbonyl groups at the end. Such bifunctional compounds are formed from that part of alkene which is in between the double bonds.

For cyclic alkenes:

- (D) With potassium paramagnate:
- (i) Cold dilute alkaline KMnO<sub>4</sub> = Baeyer's reagent.

$$-\begin{array}{c|c} & & & \\ \hline -C & -C & -\end{array} = -\begin{array}{c|c} & & \\ \hline \end{array} \begin{array}{c} & & \\ \end{array} \begin{array}{c} & & \\ \hline \end{array} \begin{array}{c} & & \\ \end{array}$$

[Alkene + cold dil.  $KMnO_4 \rightarrow Diol$ ]

Baeyer's test for the presence of (C = C) bond

Compound + cold dil. alk.  $KMnO_4 \longrightarrow Purple$  colour decolourised  $\therefore$  Compound is alkene.

#### (ii) Hot KMnO<sub>4</sub>

Case (1): 
$$H = \frac{\text{KMnO}_4}{100^{\circ}\text{C}} \cdot \text{CO}_2 + \text{H}_2\text{O}$$

Case (2): 
$$R = \frac{\text{KMnO}_4}{100^{\circ}\text{C}} \xrightarrow{\text{R}-\text{COOH}}$$

Case (3): 
$$\underset{R}{\overset{R}{\nearrow}} C = \frac{KMnO_4}{100^{\circ}C} \xrightarrow{R} \overset{O}{\overset{\parallel}{\longrightarrow}} R \xrightarrow{\qquad C - R}$$

$$\begin{array}{c} \text{CH}_3 & \text{O} \\ \text{CH}_3 - \text{C} - \text{CH} - \text{CH}_3 + \text{hot KMnO}_4 \xrightarrow{100^{\circ}\text{C}} \text{CH}_3 - \text{C} - \text{CH}_3 \\ \text{Ketone} \\ + \begin{array}{c} \text{CH}_3 - \text{COOH} \\ \text{Carboxylic acid} \end{array}$$

# **Alkynes**

#### • Preparation:

(1) 
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + HC \equiv CH$$

Calcium carbide

Acetylene

(2) From Vicinal dihalides 
$$\left[ \text{Vicinal dihalide} + \frac{\text{(i) alc. KOH}}{\text{(ii) Na/NH}_3} \rightarrow \text{Alkyne} \right]$$

# • Chemical properties:

(1) Hydration [Addition of water]

$$\left[\text{Alkyne} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{Carbonyl compound}\right]$$

$$R - C \equiv C - H + H_2O \xrightarrow{\text{dil } H_2SO_4} \xrightarrow{\text{H}} \xrightarrow{\text{R-C}} \xrightarrow{\text{C}} \xrightarrow{\text{H}} \xrightarrow{\text{H}} \xrightarrow{\text{R-C}} - CH_3$$

(2) Addition of Halogen molecule : [Alkyne +  $2X_2 \longrightarrow Tetra$  halides]

$$-C \equiv C - +X_2 \longrightarrow -C = C - \xrightarrow{X_2} - \xrightarrow{X_1} \xrightarrow{X_2} - C - C - C$$

(3) Ozonolysis : [Alkyne  $+O_3 \longrightarrow$  Dicarbonyl compound]

$$-C \equiv C - +O_3 \xrightarrow{Zn} -C = C -$$
(4) 3HC = CH Fe red hot tube/873K

#### Benzene

• Preparation:

(2) 
$$3HC \equiv CH \xrightarrow{\text{Fe red hot tube}} 873K$$

Chemical proprtics

(1) Nitration:

$$+ \frac{\text{conc. HNO}_3 + \text{conc. H}_2\text{SO}_4}{\text{NO}_2^+}$$
Nitrobenzene

(2) Halogenation:

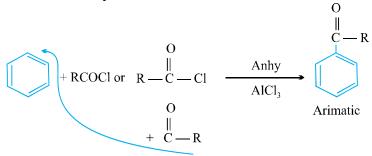


Chlorobenzene Bromobenzene

(3) Friedal-Craft Alkylation:

$$\begin{array}{c|c} & & & R \\ + R - X & & & Anhydrous \\ & & Alkyl \ halide \\ & (R^{+}) & & Alkyl \ Benzene \end{array}$$

(4) Friedal-Craft Acylation:

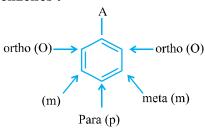


#### Huckel's Rule:

Conditions: (i) Compound most be planar.

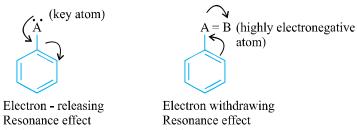
- (ii) Complete delocalisation of  $\pi e^-$
- (iii) Presence of  $(4n + 2) \pi e^{-1}$ . (n = 1, 2, 3, ...)

#### **Derivatives of Benzenes:**

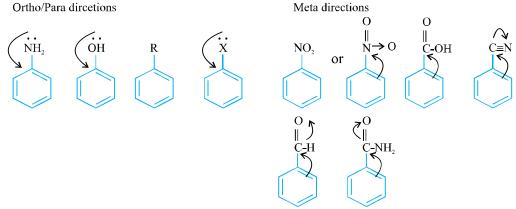


Ortho/Para directors: Group which direct the incoming electrophile to attach at ortho/para positions.

Meta directors: Groups which direct the incoming electrophile to attack at meta position.



(+R) (-R)



# **Hydrocarbons**

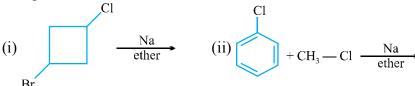
#### 1-Mark Questions

1. Give IUPAC name of 
$$CH (CH_3) - (CH_2)_4 - CH_3$$

- 2. Five the IUPAC name of
- 3. Give the standard formula of 5-sec-butyl, 4-isopropyldecane.
- 4. Give the standard formula of 4-tert-butyl, 4-ethyl-2, 2, 5, 5-tetra methyl hexane.
- **5.** Obtain isobutane from *n*-butane.
- **6.** *n*-Hexane

#### 2-Mark Questions

- 7. Out of 2-Methylpentane and 2, 3-Dimethylpentane which has greater boiling point and Why?
- 8. Give the structure of alkyl halide which when treated with sodium metal in presence of ether gives (CH<sub>3</sub>)<sub>2</sub>CH.CH(CH<sub>3</sub>)<sub>2</sub>.
- **9.** Complete:



- 10. Explain:
  - (i) Staggered form of ethane is more stable than eclipsed form.
  - (ii) Wurtz reaction is carried out in dry ether.

# Chemistry Class XI

#### **Alkenes**

#### 1-Mark Questions

11. Give IUPAC name of



- 12. Give hybridisation of central carbon in allene (CH<sub>2</sub>=C=CH<sub>2</sub>)
- 13. Name the effect which decide the stability of alkenes.
- 14. Complete the reaction :  $CH_3$ — $CH=CH_2 + HC1$  Peroxide ?
- **15.** Which gas is produced during addition of HBr in alkenes is presence of peroxides?

#### 2-Mark Questions

17. Arrange the alkenes in decreasing order of stability.  $CH_3$ — $CH = CH(CH_3)$ ,  $CH_2 = CH_2$ ,  $CH_3$ — $CH = CH_2$ 

18. Complete the reaction 
$$CH_2 = CH - C = CH_2 + O_3 \xrightarrow{CH_3COOH} ?$$

$$CH_3$$

**19.** Complete the reaction :

$$+ HBr \longrightarrow ?$$

$$+ O_3 \xrightarrow{Zn} ?$$

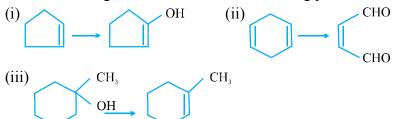
- 21. Name the alkene which will yield a mixture of cyclopentanone and propanal on treatment with  $O_3$  followed by reduction with  $Z_1$ .
- 22. An alkene on treatment with H—Br in presence of peroxide can generate

# 23. Explain:

- (i) Melting point of cis-2-Butene is lower than that of trans-2-Butene.
- (ii) Kharasch/peroxide effect is spontaneous with HBr only.

#### 3 Mark Questions

- **24.** Complete the reactions :
  - (i)  $(CH_3)_2C = CH CH_3 + hot KMnO_4 \longrightarrow$
  - (ii)  $(CH_3)_2C = CH.CH_3 + cold dil. KMnO_4 \longrightarrow$
  - (iii)  $(CH_3)_2C = CH.CH_3 + HBr \xrightarrow{Peroxide}$
- 25. Indicate the reagents used to form the following products:



- **26.** (i) Convert: iso-propylbromide  $\longrightarrow$  *n*-propyl bromide.
  - (ii) Give IUPAC name of Vinyl chloride.

# **Alkyn**es

#### 1 Mark Questions

- **27.** Give IUPAC name of acetylene.
- **28.** Which alkyne would you start with to prepare  $CH_3$ — $CH_2$ — $CH_2$ —CO— $CH_3$ ?
- **29.** Name the reagent used in the following changes:

$$CH_{3}$$
  $CH_{2}$   $CH_{2}$   $CH_{3}$   $C$ 

30. Give the alkyne which produce acetic acid and proponoic acid on treatment with alkaline  $KMnO_4$  at 100°C.

#### 2 Mark Questions

- **31.** Convert : Acetylene  $\rightarrow$  Propylene.
- **32.** Convert : Ethylene  $\rightarrow$  Acetylene.
- 33. Obtain:  $C \equiv C CH_3$  from
- **34.** Give the product when 1-methylcyclohexane reacts with:
  - (i) aq. acidic  $KMnO_4$  (ii)  $O_3$  followed by  $Zn/CH_3COOH$ .

# 42 Chemistry Class XI

35. Pent-1-yne 
$$\xrightarrow{\text{(i) NaNH}_2/\text{NH}_3}$$
 (A)  $\xrightarrow{\text{H}_2}$  (B)  $\xrightarrow{\text{Br}_2}$  (C) Catalyst

Identity A, B and C compounds and give their reactions.

### Benzene

1 Mark Questions

- **36.** Who discovered benzene?
- **37.** Give reason whether is aromatic or not.
- 38. Is pyrrole  $\binom{N}{H}$  an aromatic compound or not ? Give reason.

39. 
$$+ \text{CH}_3\text{COCl} \xrightarrow{\text{anhy. AlCl}_3}$$
?

**40.** Give major product only  $CH_3(o/p)$ 

$$NO_2(m)$$
 + conc.  $HNO_3$  + conc.  $H_2SO_4 \longrightarrow ?$ 

**41.** Give major product only

$$+ Br_2 \xrightarrow{\text{FeBr}_3} 5$$

**42.** (i) Convert Acetylene → Benzene

(ii) 
$$+ \text{Cl}_2 \xrightarrow{\text{U.V.}} ?$$

- 43. Distinguish chemically butyne and but-2-yne.
- **44.** (i) Planar, cyclic, conjugated compounds with  $(4n + 2) \pi e^-$  are knows as ......
  - (ii) Planar, cyclic, conjugated compounds with (4n)  $\pi e^-$  are knows as ......

3 Mark Questions

2 Mark Questions

**45.** Convert: Ethylene → Nitrobenzene.

46. Give chemical tests to distinguish the following:

- (i) Pent-1-yne and pent-2-yne
- (ii) Ethylene and Acetylene
- (iii) Ethane and Ethylene

**47.** Complete the following reactions :

- (i) CH<sub>3</sub>COONa + NaOH →
- (ii) iso-butyl bromide + alc. KOH →
- (iii) iso-butyl alcohol + conc.  $H_2SO_4 \xrightarrow{\Delta}$

(iv) 
$$(CH_3)_2C = CH.CH_3 + HBr \xrightarrow{Peroxide}$$

(v) 
$$CH_3$$
— $C$ = $CH_2 + H_2O$   $\xrightarrow{H^+}$   $CH_3$ 

(vi) 
$$(CH_3)_2C = CH_2 + cold dil. KMnO_4 \longrightarrow$$

(vii) 
$$(CH_3)_2C==CH.CH_3 + hot KMnO_4 \longrightarrow$$

(viii) 
$$(CH_3)_2C == CH.CH_3 + O_3 \xrightarrow{CH_3COOH}$$

(ix) CH<sub>3</sub>—CH—CH<sub>3</sub> + 2 alc. KOH 
$$\longrightarrow$$
 | | Br Br

$$(x) CaC_2 + H_2O \longrightarrow$$

(xi) 
$$CHCl_3 + Ag \longrightarrow$$

(xii) 
$$CH_3$$
— $C \equiv CH + H_2O \xrightarrow{H^+} Hg^{2+}$ 

(xiii) 
$$CH_3$$
— $C \equiv CH_2CH_3 + O_3 \xrightarrow{H_2O}$ 

(xiv) CH<sub>3</sub>C=CH + alc. KMnO<sub>4</sub> 
$$\xrightarrow{100^{\circ}\text{C}}$$

(xv) 
$$C_6H_6 + H_2 \xrightarrow{\text{Ni}} 473 \text{ K}$$

**48.** Conversions:

- (i) Ethane  $\rightarrow$  Ethyne
- (ii) Acetylene → But-2-yne
- (iii) Propene → Propanol

- (iv) Acetic acid  $\rightarrow$  Methane
- (v) Acetylene  $\rightarrow$  Acetone (CH<sub>3</sub>COCH<sub>3</sub>)
- (vi) Acetylene → Cyclohexane
- **49.** A hydrocarbon (X) on treatment with ammonical AgNO<sub>3</sub> gave white precipitate. On treatment with water in dil. H<sub>2</sub>SO<sub>4</sub> and HgSO<sub>4</sub>, it gave CH<sub>3</sub>—CHO. When (X) is treated with 1mol of NaNH<sub>2</sub>/NH<sub>3</sub>, along with *n*-propyl bromide, gave compound (Y), which on treatment with Lindlar's catalyst gave (Z) compound (Z) on treatment with O<sub>3</sub> along with Zn gave HCHO and butanol. Identify X, Y, Z and givel all the reactions.
- **50.** An alkyl halide C<sub>5</sub>H<sub>11</sub>Br(A) reacts with alc. KOH to give on alkene (B) which reacts with Br<sub>2</sub> to give compound (C), which on dehydrobromination gives an alkyne (D). On treatment with sodium metal in liquid ammonia, one mole of (D) Give one mole of sodium salt of (D) and half mole of H<sub>2</sub>(g). Complete hydrogenation of (D) yields a straight chain alkane. Identify A, B, C and D. Give the reaction involved.
- **51.** The sex attractant pheromme of codling moth has the molecular formula  $C_{13}H_{24}O$ . On catalytic reaction this compound gives 3-Ethyl-7-methyl-1-decanol having molecular formula  $C_{13}H_{28}O$ . On reduction ozonolysis the pheromme produces 2-pentane, 4-ketohexanal and 2-Hydroxyethanal. On the basis of these information, Write the structure of this pheromme.
- **52.** 896 ml of a hydrocarbon (A) having 87.80% C and 12.19% H weights 3.28 g at STP. Hydrogenation of (A) gives 2-methylpentane. Also compound (A) on hydration in presence of H<sub>2</sub>SO<sub>4</sub> and HgSO<sub>4</sub> gives Ketone (B) having molecular formula C<sub>6</sub>H<sub>12</sub>O. The ketone (B) gives a positive iodoform test. Find the structure of (A) give all reactions.

[**Hint :** (i) 1 mole of a compound at STP contains 22400 mL volume (ii) Ketones having CH<sub>3</sub>—C—structures gives positive iodoform test]

- 53. (a) Compound A{ $C_{10}H_{18}O$ } undergo reaction with  $H_2SO_4$  at 250°C to yield a mixture of two alkenes { $C_{10}H_{16}$ }. The major alkene product (B) gives only cyclopentanone after ozone treatment followed by reduction with Zn in CH<sub>3</sub>COOH. Identify (A) and (B) give the reactions involved.
  - (b) Convert  $PhC = CH \longrightarrow PhC = C.CH_3$
  - (c) Benzene does not give addition reactions under normal conditions.