HYDROCARBONS

ALKANES C_nH_{2n-2}

PREPARATION

From unsaturated hydrocarbons

- $CH_2=CH_2 \xrightarrow[H_2]{Pt/Pd/Ni} CH_3-CH_3$

From alkyl halides

- $CH_3-CH_2-Cl \xrightarrow[H^+]{Zn} CH_3CH_3 + NaI$
- $2CH_3-I \xrightarrow[\text{dry ether}]{Na} CH_3CH_3$ (Wurtz RX)

From carboxylic acids (Kolbe's Electrolytic Method)

- $CH_3-CH_2-Cl \xrightarrow[H^+]{Zn} CH_3CH_3 + NaI$
- $2CH_3-I \xrightarrow[\text{dry ether}]{Na} CH_3CH_3$ (Wurtz RX)

CHEMICAL PROPERTIES

Substitution Reaction — Halogenation

1. Initiation: $Cl_2 \xrightarrow{hv} \dot{C}l + \dot{C}l$
2. Propagation: $Cl_4 + \dot{C}l \rightarrow \dot{C}H_3 + HCl$; $\dot{C}H_3 + Cl-Cl \rightarrow \dot{C}H_3 + \dot{C}l$
3. Termination: $\dot{C}l + \dot{C}l \rightarrow Cl_2$; $\dot{C}H_3 + \dot{C}l \rightarrow CH_3Cl$

Combustion

- $C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + y/2H_2O$

Controlled Oxidation

- $CH_4 + O_2 \xrightarrow[\text{10 atoms}]{Cu/523\ K} 2CH_3OH$
- $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$

Isomerization

- $2CH_3(CH_2)_4CH_3 \xrightarrow[HCl]{\text{Anhyd. } AlCl_3}$

Aromatic Reforming

- $\xrightarrow[\text{10-20 atm, 773 K}]{Cr_2O_3}$

Reaction with Steam

- $CH_4 + H_2O \xrightarrow{Ni} CO + 3H_2$

Pyrolysis

- $C_6H_{14} \xrightarrow{773\ K} C_6H_{12} + H_2$
- $\rightarrow C_4H_8 + C_2H_6 + H_2$
- $\rightarrow C_3H_6 + C_2H_4 + CH_4$

CONFORMERS

Sawhorse Projection

Eclipsed, Staggered

Newman Projection

Staggered, Eclipsed

PHYSICAL PROPERTIES

- Alkanes are hydrophobic
- Generally non-polar in nature
- Boiling point increases with increase in
- Boiling point decreases with increase in branching

ALKENES

PREPARATION

Electrophilic reactions

- $CH_3-CH=CH_2 \xrightarrow{\text{cold conc.}} CH_3-CH(OSO_3H)-CH_3$
- $CH_3-CH=CH_2 \xrightarrow[H^+]{H_2O} CH_3-CH(OH)-CH_3$

From acidic dehydration of alcohols

- $HO-CH_2-CH_3 \xrightarrow{\text{conc. } H_2SO_4} CH_2=CH_2 + H_2O$

From vicinal dihalides

- $Br-CH_2-CH_2-Br \xrightarrow{Zn} CH_2=CH_2 + ZnBr_2$

From alkyl halides

- $CH_3-CH_2-X \xrightarrow{\text{alc. KOH}} CH_2=CH_2 + HX$

From alkynes

- $R_2C=CR_2 + H_2 \xrightarrow{Pd/C}$

CHEMICAL PROPERTIES

Ozonolysis

- $CH_2=CH_2 + O_3 \rightarrow$ ozonide $\xrightarrow[H_2O]{Zn}$ $HCHO + HCHO$

Oxidation

- $CH_2=CH_2 + H_2O \xrightarrow[\text{273 K}]{\text{dil. } KMnO_4} CH_2(OH)-CH_2(OH)$

Polymerization

- $n\,CH_2=CH_2 \xrightarrow[\text{High pressure, catalyst}]{\text{High temp.}} (CH_2-CH_2)_n$

Aromatic reforming

- $CH_2=CH_2 + Br_2 \rightarrow CH_2(Br)-CH_2(Br)$

Addition of hydrogen halides

- **Markovnikov's rule:** "Negative part of the addendum gets attached to the carbon containing lesser number of hydrogens". (I) is major product.
- **Anti-Markovnikov effect / Kharash effect / Anti-peroxide effect:** This mechanism proceeds via free radical mechanism and the minor product via Markovnikov effect becomes major product. (II) is major product.
  - Symmetrical alkene: $CH_2=CH_2 + HBr \rightarrow BrCH_2-CH_3$
  - Asymmetrical alkene: $CH_3-CH=CH_2 + HBr$ → (I) $CH_3CH_2BrCH_3$ (II) $CH_3CH_2CH_2Br$

PHYSICAL PROPERTIES

- Alkenes have a short odour
- Increase in branching leads to decrease in boiling point
- First few members are gases and rest are liquids & solids.
- Alkenes are insoluble in water but soluble non-polar solvents

ALKYNES C_nH_{2n-2}

$HC\equiv CH$

PHYSICAL PROPERTIES

- First few members of alkynes are gases
- Boiling point of alkene increases as the chain length increases
- Boiling point decreases with increase in the branching
- Soluble in non-polar solvents and insoluble in water
- Most of them are odourless except for thyne

PREPARATION

- From calcium carbide: $CaO + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$
- From vicinal dihalides: $BrCH_2-CH_2Br \xrightarrow[\Delta]{\text{alc. KOH}} CH\equiv CH + 2H_2O + KBr$

CHEMICAL PROPERTIES

$HC\equiv CH$

- $\xrightarrow[\text{Pt, Pd, Ni}]{H_2} CH_2=CH_2 \xrightarrow{H_2} CH_2-CH_2$
- $\xrightarrow{Br_2} CH(Br)=CH(Br)$
- $\xrightarrow[Hg^{2+},\ H^+]{H_2O} CH_2=C(OH)-H$
- $\xrightarrow{HCl/CH_3COOH} CH_2=CHCl$

Polymerisation

- Cyclic polymerisation: Iron tube, Red hot 873 K
- Linear polymerisation: High temp./High pressure → $-(CH=CH-CH=CH)-$

ARENES

PREPARATION

Decarboxylation of carboxylic acids

- $C_6H_5COONa \xrightarrow[\Delta]{NaOH} C_6H_6 + Na_2CO_3$

Reduction of phenol using Zn dust

- $C_6H_5OH \xrightarrow[\Delta]{Zn} C_6H_6 + ZnO$

CHEMICAL PROPERTIES

Electrophilic substitution reaction

- Conc. HNO_3, Conc. H_2SO_4 (323-333 K) → $C_6H_5NO_2$
- Conc. $H_2SO_4 + SO_3$ → $C_6H_5HSO_3$
- Anhyd. $AlCl_3 + Cl_2$ → C_6H_5Cl
- Anhyd. $AlCl_3 + CH_3Cl$ → $C_6H_5CH_3$
- Anhyd. $AlCl_3$ + CH_3COCl → $C_6H_5-C(=O)-CH_3$

Addition reaction

- Δ, $3H_2$, Ni → C_6H_{12}
- $3Cl_2$, UV, 500 K → $C_6H_6Cl_6$

PHYSICAL PROPERTIES

- Immiscibel in water but completely soluble in polar
- Characteristic smell
- Highly notatile in nature
- Burn with a sooty flame

Huckel's rule of aromaticity

1. Planarity
2. Delocalisation of of π-electrons
3. Presence of (4n + 2)-π electrons

Carcinogenicity and toxicity

1. 2-benzanthracene
1. 2-benzpyrene

Aromatics are toxic in nature and most of them are classified as carcinogens.

ANAND MANI