CONCEPT MAP

ACYCLIC HYDROCARBONS

(Open chain structures containing C and H only)

Although hydrocarbons are primarily consumed in fuels, nonfuel applications of hydrocarbons are of great importance to society and the economy. Certain hydrocarbons can be found in lubricating oils, greases, solvents, fuels, wax, asphalts, cosmetics and plastics.



Saturated

C—C single bonds present

Alkanes

General formula, C_nH_{2n+2}

Preparation

• From alkyl halides:

$$2R$$
—Br + $2Na$ $\xrightarrow{Dry \text{ ether}} R$ — R + $2NaBr$ (Wurtz reaction)

R-X can be converted to alkane using Zn + CH₃COOH, Zn + dil. HCl, Zn-Cu + C₂H₅OH,LiAlH₄, Zn + NaOH, NaBH₄ and Ph₃SnH reducing agents.

• From carboxylic acids:

$$RCOOH \xrightarrow{Red P/HI} RCH_3 + H_2O + I_2$$
 $2RCOONa + NaOH \xrightarrow{\Delta} Na_2CO_3 + RH$
 $2RCOOK + 2H_2O \xrightarrow{Electrolysis}$
 $R-R + 2CO_2 + H_2 + 2KOH$
(Kolbe's electrolysis method)

• From carbonyl compounds:

$$RCOCH_3 \xrightarrow{NH_2NH_2} R-CH_2CH_3$$
 $(Wolff-Kishner reduction)$
 $RCOCH_3 \xrightarrow{Zn/Hg} RCH_2CH_3 + H_2O$
 $(Clemmensen reduction)$

Properties

Substitution reaction:

Order of reactivity:

Alkanes: $3^{\circ} > 2^{\circ} > 1^{\circ} > CH_{4}$ Halogens: $F_2 > Cl_2 > Br_2 > I_2$

Oxidation:

(a) Combustion or complete oxidation:

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow$$

$$nCO_2 + (n+1)H_2O + heat$$

(b) Catalytic oxidation:

$$2CH_4 + O_2 \xrightarrow{Cu-tube} 2CH_3OH_9 : 1$$

Unsaturated

C—C multiple bonds present

Alkenes (>C=C<)

General formula, C,H2n

Preparation

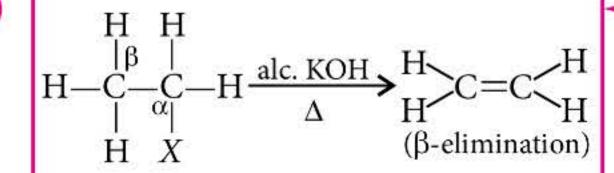
Hydrogenation of alkynes:

(a)
$$R-C \equiv C-R' + H_2$$

$$\frac{Pd/C}{\text{(Lindlar's catalyst)}} \xrightarrow{R} C = C \xrightarrow{R'} H$$
(b) $R-C \equiv C-R' + H_2$

$$\frac{Na/liq. NH_3}{or LiAlH_4} \xrightarrow{R} C = C \xrightarrow{R'} H$$
(trans-alkene)

• Dehydrohalogenation:



• Dehalogenation:

$$X-CH_2-CH_2-X+Zn \xrightarrow{\text{Methanol}} \Sigma$$
(vic. dihalides)
$$CH_2=CH_2+ZnX_2$$

• Dehydration of alcohols:

CH₃CH₂—OH
$$\xrightarrow{\text{Conc. H}_2\text{SO}_4}$$
 CH₂=CH₂

Properties

Addition of halogen:

$$CH_{2} = CH_{2} + Br_{2} \xrightarrow{CCl_{4}} CH_{2} - Br$$

$$(Brown CH_{2} - Br$$

$$colour) (Colourless)$$

Addition of halogen acid:

$$CH_3$$
— CH = CH_2 + $HBr \xrightarrow{Markownikoff's}$ rule

 Br
 CH_3 — CH — CH_3

HBr addition in presence of peroxide follows anti-Markownikoff's rule, known as Kharasch effect or peroxide effect.

Oxidation:

$$CH_2 = CH_2 + H_2O + O_2 \frac{alk. KMnO_4}{298-303 K}$$

 $HO-CH_2-CH_2-OH$

Alkynes (—C≡C—)

General formula, C_nH_{2n-2}

Preparation

• From calcium carbide:

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

• Dehalogenation:

$$\begin{array}{ccc} CH_2-CH_2 & \xrightarrow{KOH} & CH_2=CHBr \\ | & | & \\ Br & Br & \xrightarrow{NaNH_2} & CH \equiv CH \end{array}$$

Properties

• Acidic nature:

$$CH \equiv CH + Na \xrightarrow{liq. NH_3} CH \equiv \bar{C}Na + \frac{1}{2}H_2$$

• Addition reactions:

$$CH \equiv CH \xrightarrow{Pt/Pd/Ni} CH_3 - CH_3$$

$$CH_3 - C \equiv CH \xrightarrow{Br_2} CCl_4$$

$$CH_3 - CBr_2 - CHBr_2$$

$$CH_3 - C \equiv CH \xrightarrow{H_2O} CH_3 - C \equiv CH_2$$

$$OH$$

$$Isomerisation OH$$

$$O$$

Commercial Uses

- Alkanes : Ethane is used for making hexachloroethane which is an artificial camphor. Higher alkanes in the form of gasoline, kerosene oil, diesel, lubricating oils and paraffin wax are widely used.
- Alkenes : Ethene is used as a general anaesthetic. It is a starting material for a large number of compounds such as glycol, ethyl halides, ethyl alcohol, ethylene oxide, etc.
- Alkynes : Acetylene is used as a general anaesthetic under the name naracylene. Acetylene is used as an illuminant.