

# Chapter 3

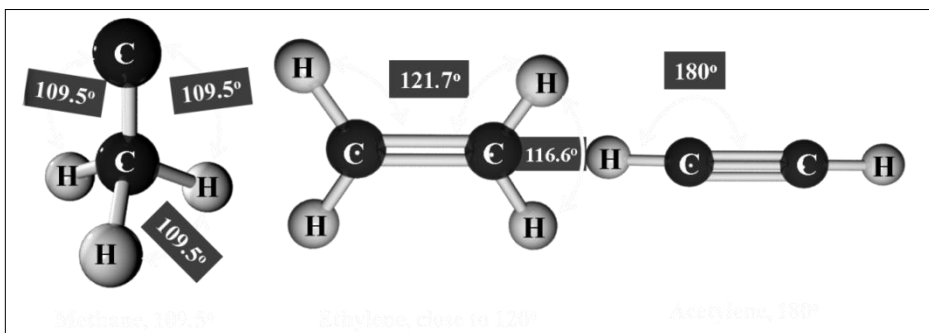
# Hydrocarbon

Day – 1

## Hydrocarbon (Alkanes/Alkanes/Alkanes)

### Introduction

The term ‘hydrocarbon’ means compounds of carbon and hydrogen only. Hydrocarbons play a key role in our daily life. Some examples are ‘LPG’ and ‘CNG’ used as fuels. LPG is the abbreviated form of liquefied petroleum gas whereas CNG stands for compressed natural gas. Petrol, diesel and kerosene oil are obtained by the fractional distillation of petroleum found under the earth’s crust.



Coal gas is obtained by the destructive distillation of coal. The gas after compression is known as compressed natural gas. LPG is used as a domestic fuel with the least pollution. All these fuels contain mixture of hydrocarbons, which are sources of energy. Hydrocarbons are also used for the manufacture of polymers like polythene, polypropene, polystyrene etc. Higher hydrocarbons are used as solvents for paints. They are also used as the starting materials for manufacture of many dyes and drugs.

### Classification

Hydrocarbons are of different types. Depending upon the types of carbon-carbon bonds present, they can be classified into three main categories: –

- (i):- Saturated
- (ii):- Unsaturated and
- (iii):- Aromatic hydrocarbons

Alkanes Saturated Homologous series  $\text{C}_n\text{H}_{2n+2}$  also called paraffins {pare: little, affinis: affinity} Next member differs previous by  $\text{CH}_2$ .

(a):- All C –  $\text{Sp}_3$  hybridized all angle  $109.5^\circ$ .

(b):- Bond Length:- C – C  $\rightarrow 1.54 \text{ \AA}$       C – H  $\rightarrow 1.112 \text{ \AA}$ .

**Isomers:-** Alkanes only form two type of Structural isomers that is Chain Isomers and positional isomers

No of isomers depend on total number of carbon atoms:



They also form Stereo-isomers  $\rightarrow$  Confirmation and optical (already done in isomerism chapter).

### Physical Properties

- (1) State:-**
- $C_1 - C_4 \rightarrow$  colourless odourless gas
  - $C_5 - C_{17} \rightarrow$  colourless odourless liquid
  - $\geq C_{18} \rightarrow$  colourless odourless solid

So why does LPG smell so much – because of Mercaptans (Thiols).

**(2) Density:-** Of liquids increase up from 0.424gm/cc for methane liquid at  $0^\circ\text{C}$  (but higher pressure) to n – hexane 0.6534 and rises to 0.775 for n-haxadecane. In general, more branched paraffin will have less density than normal.

**(3) Solubility:-** Soluble in non Polar solvents like ether, carbontetrachloride. Solubility decreases with increases in molar mass or carbon number.

**(4) Boiling point:-**

(a):- b.p  $\propto$  no. of carbons atom



After this for every carbon b.p. increases approx  $20 - 30^\circ\text{C}$ . (Only for n – compounds).

(b):- bp  $\propto$  Surface area of molecule (for same molar mass). It can be inferred from this that more branched the molecule it will here lower b.p.

Example:-

n–hexane  $\rightarrow 69^\circ\text{C}$  ; 3–methyl pentane  $\rightarrow 63^\circ$  ; 2,3-dimethyl butane  $\rightarrow 58^\circ\text{C}$ ; 2,2 dimethyl butane  $\rightarrow 50^\circ\text{C}$

This can be explained by intermolecular forces. As branching increases the molecular tend to become spherical (i.e. have less surface area per molecule). This decreases intermolecular attraction. This lowers the boiling point

**(5) Melting point:-** Is also proportional to carbon number. This pattern is not so smooth pattern. As can be seen from figure even no. of carbon compounds here higher m.p. than the next member in homologous series. (Which are odd no. of carbon). This is explained as even no. of carbon have better packing efficiency than odd number carbon atoms compounds.

Ex. (1):- Match the following

- |                                  |                 |
|----------------------------------|-----------------|
| 1. Octane                        | A. $-106^\circ$ |
| 2. 2 – methyl heptanes           | B $-116$        |
| 3. 2, 2, 3 ,3-tetramethyl butane | C $-126$        |
| 4. Nonane                        | D $-151$        |

Ans:- 1- C    2 – B    3 – A    4 – D

Ex. (2):- Which has higher b.p. Pentane ( $36.1^\circ\text{C}$ ), 1-Chloropropane ( $47^\circ\text{C}$ ); 2–methyl butane ( $28^\circ\text{C}$ ); 1,2,3,dimethyl propane ( $9.5^\circ\text{C}$ )

**(6) Heat of Combustion:-**

(a):- Heat of comusion  $C_{n+1} > C_n$  Hexane  $>$  Pentane  $>$  isopentane  $>$  neopentane

(b):- Greater the branching, smaller the heat of combustion.

## Alkanes

### Preparation

#### Natural Source – Petroleum & Natural Gas

**Natural Gas:-** Mainly  $C_1 - C_4$ . This comes directly from gas fields. Here  $C_1 - C_2$  fraction relatively higher no it has lower b.p. or high pressure required for it be in liquefied

LPG  $\rightarrow$  First cut in crude distillation  $\rightarrow$  80% ( $C_3 - C_4$ )

**Crude oil:-** Black hardly liquid – complex mixture of alkane. First dewaxed than refined.

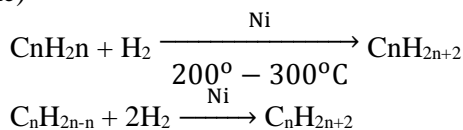
**Wax:-** ( $C_{24} - C_{34}$ )  $\rightarrow$  purified sold as paraffin wax.

Refined:- Fractional distillation

LPG	$< 20^\circ\text{C}$	$C_1 - C_4$ Herly $C_4$
Petroleum ether	$20 - 60^\circ$	$C_5 - C_6$
Light Naphtha	$60 - 100^\circ\text{C}$	$C_6 - C_7 - \text{Petrol}$
Gasoline	$100 - 200^\circ\text{C}$	$C_7 - C_{10}$
Kerosene	$175 - 375$	$C_{12} - C_{18}$
Lube Oil	$> 300^\circ\text{C}$	$C_{18} - C_{22}$
Asphalt or Bitumen	Residue	$> C_{23}$

#### General Methods of Preparation

1. Hydrogenation of Unsaturated Hydrocarbons Sabatier of Sardersens Rxn (Can not prepare Methane)

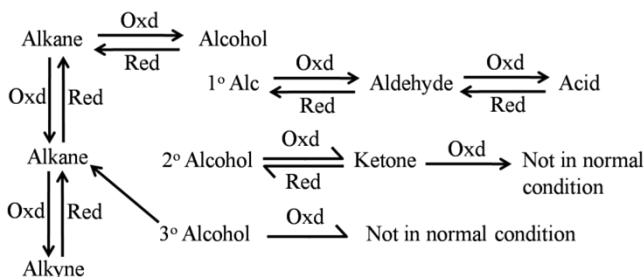


#### **2. Reduction of Alkyl Halide:-**

(a)  $RX + 2H \rightarrow RH + HX$ . Source of nascent Hydrogen can be

1. Zn + dil HCl
2. Zn + Acetic Acid
3. Zn + Cu +  $C_2H_5OH$
4. Red phosph + HI
5. Al + Hg in ethanol.

#### General Oxidation/Reduction



In Vigorous conditions oxidation will produce acids of lower carbon no, after breakage of chain.

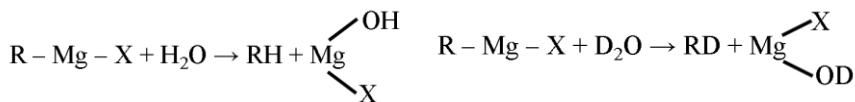
(b) LiAlH<sub>4</sub> can also be used but only for 1° & 2°.

For 3° Alkyl Halide it produces alkene

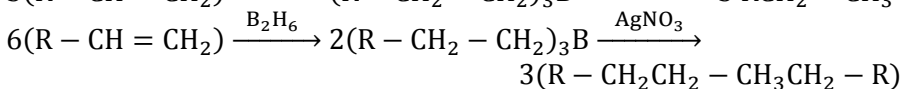
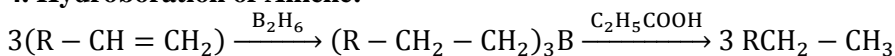
(c) Can also use TPh (Triphenyl tin hydride – Ph<sub>3</sub>SnH)

(d) NaBH<sub>4</sub> on the other hand reduces 2° & 3° halide but not 1°

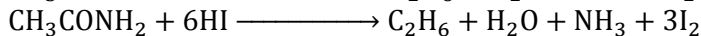
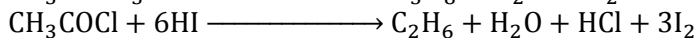
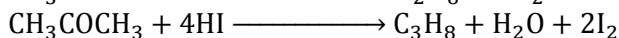
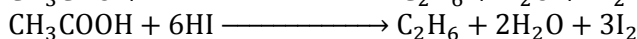
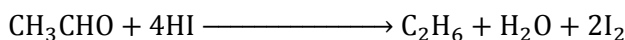
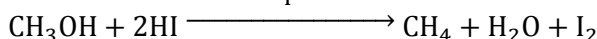
**3. Grignard Reagent:-** If in Grignard reagent is reacted with D<sub>2</sub>O. He get RD



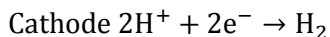
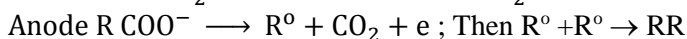
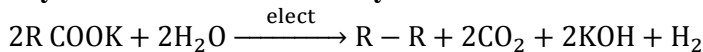
#### 4. Hydroboration of Alkene:-



#### 5. Reduction of Alcohols, Aldehyde, Ketones & Fatty Acids:-



#### 6. Electrolysis of Na or K Salt of Fatty Acids:-



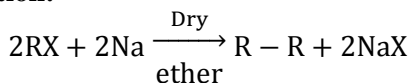
**Note:-** (1):- Methane cannot be formed

(2):- Only even no. carbon chain formed

(3):- Not suitable for odd carbon

(4):- Produces symmetrical hydrocarbons

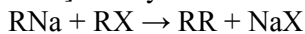
#### 7. Wurtz Reaction:-



#### Mechanism (Most Likely)



This [R – Na] is very reactive & reacts with another RX



(1):- Methane cannot be formed

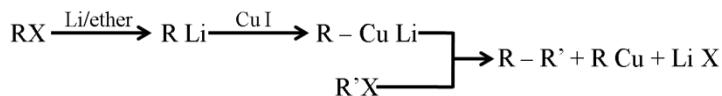
(2):- Only even no. carbon chain formed

(3):- Not suitable for odd carbon

(4):- Produce symmetrical hydrocarbons.

Suppose we use  $R_1$ (even) &  $R_2$ (odd) then we set these compound  $R_1 - R_1$ , (even)  $R_2 - R_2$ (even) &  $R_1 - R_2$ (odd). So not good for odd no.

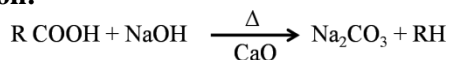
### Another Similar Method Corey House Synthesis



$R - 1^\circ, 2^\circ \text{ \& } 3^\circ$  alkyl

$R' -$  Primary for good yield. or  $CH_3X$  or secondly cycloalkyl

### 8. Decarboxylation:-



If  $R$  is  $CH_3$  then  $CH_4$  good yield

If  $R$  is  $C_2H_5$  than other product formed  $C_2H_6 + CH_4$  etc.

The alkane always contains one carbon less than the original acid. This method is used for reducing carbon atoms in the carbon chain (step down reaction).

