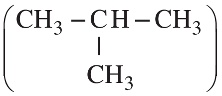
Hydrocarbons

ALKANES Section - 1

Hydrocarbons are the binary compounds of carbon and hydrogen only. Hydrocarbons occur in nature in the form of coal, natural gas and petroleum. All the organic compounds (other than hydrocarbons) are derived from hydrocarbons, by substituting hydrogen with a functional group or by adding a functional group. Hydrocarbons are classified into two categories: Aliphatic hydrocarbons (open chains) and Cyclic hydrocarbons (closed chains). Here, we will first study aliphatic type, which are further divided into Saturated hydrocarbons (Alkanes) and Unsaturated hydrocarbons (Alkenes, Alkynes), and then cyclic hydrocarbons, which are further divided into Cycloalkanes, Cycloalkenes and Aromatic Hydrocarbons.

ALKANES : [C_nH_{2n+2}]

Alkanes form a homologous series, represented by a general formula : C_nH_{2n+2}. These have a tetrahedral structure around carbon atom or one can say that all the carbon atoms in alkanes show sp^3 type of hybridisation. The important members of alkanes are: Methane (CH_4), Ethane (CH_3CH_3), Propane ($CH_3CH_2CH_3$), n-Butane ($CH_3CH_2CH_2CH_3$) and its isomer, Iso-butane



$$\left(\begin{array}{c}CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3\end{array}\right).$$

Generally, alkanes are also represented as : RH, RCH_3, R-R, R-R′ (where R and R′ are alkyl radical)

Preparation of Alkanes :

1. Reduction of Alkenes and Alkynes :

$$C_nH_{2n} \xrightarrow[Ni/573K]{H_2} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

$$C_nH_{2n-2} \xrightarrow[Pt \text{ or } Ni/573K]{2H_2} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

This is known as Sabatier-Sandern's reaction.

Note : For the reduction of alkenes, and alkynes Pd – carbon/Ethanol at 25°C (50 atm) is generally used.

$$(CH_3)_2C=CH_2 \xrightarrow[25^\circ C,\ 50\ atm]{Pd\text{–}C/C_2H_5OH} \underset{\text{Isobutane}}{(CH_3)_2\,CHCH_3}$$

2. From Alkyl Halides :

(a) By reducing Alkyl Halides :

Reducing agents : Zn + CH_3COOH ; Zn + HCl ; Zn + NaOH ; Zn–Cu Couple ; Al – Hg amalgam.

$$RX + H_2 \longrightarrow RH + HX$$

Alkyl iodides are reduced by HI in red P under high temperature and pressure.

$$RI + HI \xrightarrow[150^\circ C,\ \text{high pressure}]{\text{Red P}} RH + I_2 \quad (I_2 \text{ is removed by P as : } 2P + 3I_2 \longrightarrow 2PI_3)$$

(b) Wurtz Reaction :

It involves the condensation of two molecules of alkyl halide with Na and dry ether, to give symmetric alkanes.

$$2RI + Na \xrightarrow[\text{ether}]{\text{dry}} R-R + NaI$$

If we start with R′I and RI, we get mixture of alkanes. Hence it is not good method for unsymmetric alkanes.

Note : Methane cannot be formed by this method.
Order of reactivity of alkyl halides RI > RBr > RCl > RF.

(c) Frankland Reaction :

$$RI + Zn + RI \longrightarrow R-R + ZnI_2$$

3. Reduction of Alcohols :

$$ROH + 2HI \xrightarrow[150^\circ C,\ \text{high Pressure}]{\text{Red P}} RH + I_2 + H_2O$$

4. Reduction of Aldehyde and Ketones :

$$RCHO + 2H_2 \xrightarrow[\text{HCl}]{\text{Zn-Hg}} RCH_3 + H_2O$$

$$RCOR + 2H_2 \xrightarrow[\text{HCl}]{\text{Zn-Hg}} RCH_2R + H_2O$$

This is known as Clemmensen’s Reduction.

$$RCHO \xrightarrow[\text{alc. KOH}]{NH_2NH_2} RCH_3 + H_2O$$

$$RCOR \xrightarrow[\text{alc. KOH}]{NH_2NH_2} RCH_2R + H_2O$$

This is known as Wolf-Kishner's Reduction.

5. From Carboxylic Acids :

(a) Reduction :

$$RCOOH + 6HI \xrightarrow{\text{Red P}} RCH_3 + 2H_2O + 3I_2$$

(b) Decarboxylation :

It is obtained by heating sodium salts of carboxylic acids with sodalime (NaOH - CaO).

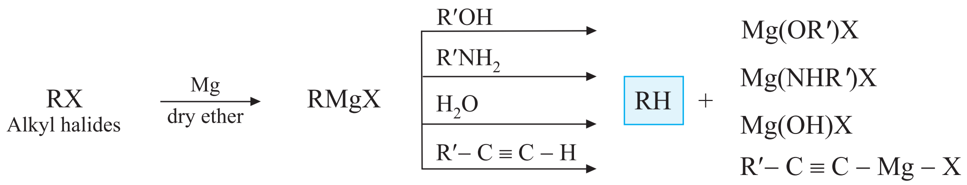
$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$$

Note : In the product there is one carbon less than parent compound. So this reaction is an important method to reduce a carbon atom in organic synthesis (known as Step-down method).

(c) Kolbe's Electrolysis :

$$2CH_3COONa + 2H_2O \xrightarrow{\text{electrolysis}} \underbrace{CH_3-CH_3+2CO_2}_{\text{(At Anode)}} + 2NaOH + \underbrace{H_2}_{\text{(At Cathode)}}$$

6. From Grignard Reagent (Alkyl magnesium halides, RMgX) :



Note : Any compound having acidic H atom(s), decomposes Grignard reagent.

7. By action of water on Aluminium and Beryllium Carbide :

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$

$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2$$

Note : Only Methane is formed by this reaction.

8. Through formation of Lithium Dialkylcuprates :

$$RX + 2Li \xrightarrow[\text{ether}]{\text{diethyl}} RLi + LiX$$

$$2RLi + CuI \longrightarrow \underset{\substack{\text{Lithium dialkyl}\\ \text{cuprate}\\ \text{[Gilman's Reagent]}}}{R_2CuLi} + LiI$$

$$R_2CuLi + R'X \longrightarrow R—R' + RCu + LiX$$

This is known as Corey House Synthesis

Note : **(i)** R can be 1°, 2°, 3° alkyl or aromatic group.
(ii) R′ should be 1° alkyl, 2° cycloalkyl or aromatic group.

Physical Properties of Alkanes :

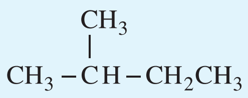
The physical properties of alkanes such as boiling point, density and solubility depend upon the intermolecular forces of attraction. The magnitude of these forces of attraction depend upon the surface area of contact between adjacent molecules. Greater the surface area, stronger are the forces of attraction.

1. **Physical State :** The normal alkanes C_1 to C_4 are colourless gases, C_5 to C_{17} are colourless liquids and from C_{18} onwards are colourless waxy solids.

2. **Boiling Point :** The boiling points of the unbranched alkanes show a regular increase with increasing molecular weight. The increase is by 20 – 30°C for each $-CH_2$ unit added to the chain. Branching of the alkane chain, however, lowers the boiling point.

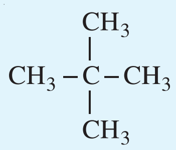
$CH_3CH_2CH_2CH_2\text{-}CH_3$

n-Pentane
B.P. = 309 K



$CH_3-\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{C}}H-CH_2CH_3$

Isopentane
B.P. = 301 K

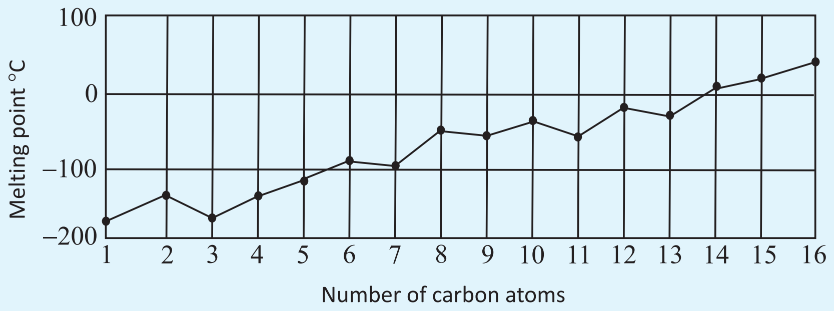


$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$

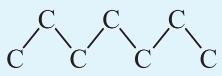
Neopentane
B.P. = 282.5 K

The explanation for these effects lies in the van der Waals forces. With unbranched alkanes, as molecular weight increases, so does molecular surface areas. With increasing surface area, the van der Waals forces between molecules increase, therefore more energy is required to separate molecule from one another. Branching in the chain, on the other hand, makes a molecule more compact, reducing its surface area. As a result, the strength of the van der Waals forces operating between the molecules decreases. This results in the lowering the boiling point. (Observe the boiling points of isomericpentanes above)

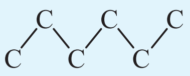
3. **Melting point :** The melting points of alkanes do not follow a very smooth gradation with the increase of molecular size. Alkanes with even number of carbon atoms have higher melting point than the next lower and next higher alkanes having odd number of carbon atoms.



It is explained by the fact that alkanes with an odd number of carbon atoms have their end-carbon atoms on the same side of the molecule and the even numbered carbon atoms alkanes have their end-carbon atoms on the opposite sides of the molecules. Thus, alkanes with even number of carbon atoms pack closely in such a manner as to permit greater inter molecular attraction and therefore have slightly higher melting point.



Odd number of carbon atoms



Even number of carbon atoms

The more compact molecule, the more is the packing efficiency of a molecular solid. This results in higher melting point. For example, neopentane when packed (in solid form) has a higher melting point as compared to n-pentane (less effective packing due to open chain structure).

Name	Formula	B.P. (K)	M.P. (K)	Density (as liquids)
Methane	CH_4	111.0	90.5	0.4240
Ethane	CH_3CH_3	184.4	101.0	0.5462
Propane	$CH_3CH_2CH_3$	230.9	85.3	0.5824
n-Butane	$CH_3(CH_2)_2CH_3$	272.4	134.6	0.5788
Isobutane	$(CH_3)_2CH-CH_3$	261.0	114.7	-
n-Pentane	$CH_3(CH_2)_3CH_3$	309.1	143.3	0.6264
Isopentane	$(CH_3)_2CH-CH_2-CH_3$	300.9	113.1	-
Neopentane	$(CH_3)_3C-CH_3$	282.5	256.4	-

3. **Solubility :** 'Like dissolves like' is the general rule of solubility. In the light of this rule, alkanes which are predominantly non-polar are insoluble in polar solvents such as water, alcohol, etc. but are highly soluble in non-polar solvents such as Petroleum ether, Benzene, Carbon tetrachloride, etc.

4. **Density :** The density of alkanes increases with the increase in the molecular masses till the limiting value of about $0.8\ g\ cm^{-3}$ is reached. This means that all alkanes are lighter than water.

Reaction of Alkanes :

Alkanes being saturated compounds undergo only substitution reactions, at $C-H$ bond. The hydrogen atom is replaced by other atom(s) such as : X-(halogens), NO_2(nitro), etc.

1. Halogenation :

Replacement of H-atom by X-atom (X = Cl, Br, I) in presence of UV light. The substitution reaction is explained by free radical mechanism.

$$CH_4 \xrightarrow{Cl_2/h\nu} CH_3Cl \xrightarrow{Cl_2/h\nu} CH_2Cl_2 \xrightarrow{Cl_2/h\nu} CHCl_3 \xrightarrow{Cl_2/h\nu} CCl_4$$

The bromination is same as chlorination but it is relatively slow and high temperature favours it.

The iodination is reversible reaction : $CH_4 + I_2 \rightleftharpoons CH_3I + HI$

Note : HI is a reducing agent, so oxidising agents, such as HIO_3, HNO_3, HgO are used to oxidise HI.

$$5HI + HIO_3 \longrightarrow 3H_2O + 3\,I_2$$

Fluorination of alkanes is too vigorous to be controlled under ordinary conditions. Further-more, fluorination brings about extensive rupture of $C-C$ and $C-H$ bonds leading to a mixture of product. Alkyl fluorides are more conveniently prepared indirectly by heating suitable chloroalkanes with inorganic fluorides such as AsF_3, SbF_3, AgF, Hg_2F_2 etc. For example,

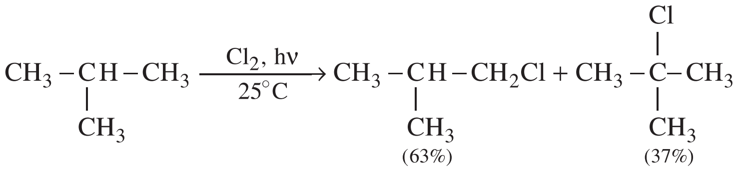
$$2\,CH_3CH_2-Cl + Hg_2F_2 \longrightarrow 2\,CH_3CH_2-F + Hg_2Cl_2$$

The above reaction is known as *Swarts reaction*.

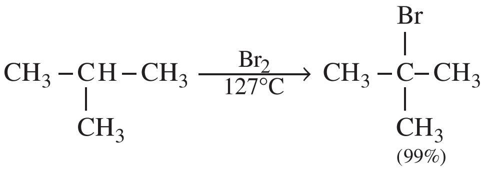
Ease of halogenation :	$3^\circ H > 2^\circ H > 1^\circ H > CH_4$
Reactivity of X_2 *:*	$F_2 > Cl_2 > Br_2 > I_2$

The reactivity decreases with the electronegativity of the halogens.

Consider halogenation in Isobutane.



$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{C}H-CH_3} \xrightarrow[25^\circ C]{Cl_2,\ h\nu} \underset{(63\%)}{\underset{\displaystyle CH_3}{CH_3-\underset{|}{C}H-CH_2Cl}} + \underset{(37\%)}{\underset{\displaystyle CH_3}{CH_3-\overset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}-CH_3}}$$



$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{C}H-CH_3} \xrightarrow[127^\circ C]{Br_2} \underset{(99\%)}{\underset{\displaystyle CH_3}{CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{|}{C}}}-CH_3}}$$

The above reactions show that Bromine is *less reactive* toward alkanes (in general) than chlorine. But bromine shows greater ability to identify among different types of hydrogen atom (i.e., primary, secondary and tertiary). It gives exclusive replacement of tertiary hydrogen atom. Chlorine, on the other hand is less selective than Bromine. Fluorine is even *less selective* than Chlorine and gives equal percentage of substituted products. (*We will discuss mechanism of this reaction later*).

Note :
- Laboratory chlorination of alkanes is often done with SO_2Cl_2 (sulphuryl chloride), instead of Cl_2 and an organic peroxide, ROOR is used as an indicator.
- During monochlorination, number of monochlorinated products formed are equal to number of different types of hydrogen atoms in the alkane.

2. Nitration :

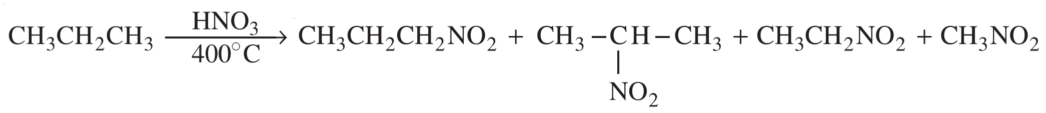
Lower members do not react with conc. HNO_3 at ordinary temperatures but long chain members on heating with HNO_3 yield nitro-alkanes.

$$C_6H_{13}-H + \underset{\text{(vapour)}}{HONO_2} \xrightarrow{400^\circ C} C_6H_{13}NO_2 + H_2O$$

However, when a mixture of vapour of an alkane and nitric acid is heated at 400 - 450°C, nitroalkane is formed readily. By this process lower as well as higher alkanes can be converted into nitroalkanes.

$$\underbrace{CH_3-H + HONO_2}_{\text{(vapour)}} \xrightarrow{450^\circ C} CH_3NO_2 + H_2O$$

In alkanes having two or more carbon atoms, there is always a possibility that the C - C bonds may break at high temperature and a mixture of nitro alkanes is formed.



$$CH_3CH_2CH_3 \xrightarrow[400^\circ C]{HNO_3} CH_3CH_2CH_2NO_2 + \underset{\displaystyle NO_2}{CH_3-\underset{|}{C}H-CH_3} + CH_3CH_2NO_2 + CH_3NO_2$$

3. Sulphonation :

Lower alkanes do not undergo sulphonation but higher member (from hexane onwards) are sulphonated slowly when treated with fuming sulphuric acid at about 400°C.

$$C_6H_{13}-H + HOSO_3H \xrightarrow{SO_3} \underset{\text{Hexane sulphonic acid}}{C_6H_{13}SO_3H} + H_2O$$

However lower members such as Propane, Butane, Pentane, etc., react with SO_3 in vapour phase to form Sulphonic acids.

4. Cracking : (Pyrolysis)

The decomposition of a compound by heat is called pyrolysis. The alkanes, on heating under high temperature in absence of air, are broken down into lower alkanes, alkenes and hydrogen during cracking of alkanes,either rupture of carbon-hydrogen bonds or rupture of carbon-carbon bonds take place resulting in the formation of mixture of lower alkanes, alkenes and hydrogen. The rupture of C – H bonds is catalysed by oxide of Chromium, Vandium, Molybednum, etc., and the rupture of C – C bonds is catalysed by Silica, Alumina, Zinc oxide, etc.

$$C_2H_6 \xrightarrow[Cr_2O_3]{500°C} CH_2=CH_2 + H_2$$

$$C_3H_8 \xrightarrow[Cr_2O_3]{500°C} CH_3CH=CH_2 + H_2$$

$$C_3H_8 \xrightarrow[Al_2O_3]{500°C} CH_2=CH_2 + CH_4$$

5. Reaction with Steam :

$$CH_4 + H_2O \xrightarrow[1273\ K]{Ni} CO + 3H_2$$

6. Combustion :

(a) Complete Combustion :

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O + \text{heat}$$

Note : Enthalpy of combustion increases with increase in number of carbon atoms in alkane. For isomeric alkane, enthalpy of combustion decreases with increase in branching

(b) Incomplete Combustion :

If the combustion of alkanes is carried out in limited supply of air or oxygen, CO is produced along with unburnt carbon in the form of carbon black or soot.

$$2CH_4 + \underset{\text{(limited)}}{3O_2} \longrightarrow 2CO + 4H_2O$$

$$CH_4 + \underset{\text{(limited)}}{O_2} \longrightarrow \underset{\text{Carbonblack}}{C} + 2H_2O$$

Carbon black is used in the preparation of black inks, paints, polishes etc.

(c) **Catalyst Oxidation :** Different products are formed under different conditions.

(i) When a mixture of methane and oxygen (9 : 1 by volume) at a pressure of 100 atm. is passed through a copper tube at 573 K, methanol is formed.

$$\underset{\text{Methane}}{2CH_4} + O_2 \xrightarrow[\text{Cu tube}]{\text{100 atm. 573 K}} \underset{\text{Methanol}}{2CH_3OH}$$

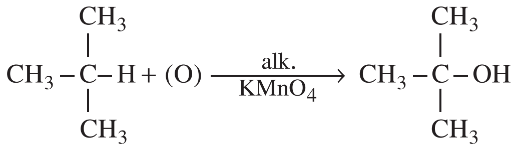
(ii) When a mixture of methane and oxygen under pressure is passed over heated molybdenum oxide, it is oxidised to methanal.

$$\underset{\text{Methane}}{CH_4} + O_2 \xrightarrow[\Delta,\ \text{pressure}]{Mo_2O_3} \underset{\text{Methanal}}{HCHO} + H_2O$$

(iii) Higher alkanes on oxidation in presence of silver oxide give carboxylic acids.

$$\underset{\text{Alkane}}{2\ R-CH_3} + 3O_2 \xrightarrow[\Delta]{Ag_2O} \underset{\text{Carboxylic acid}}{2\ RCOOH} + 2\ H_2O$$

(iv) In presence of oxidising agents such as $KMnO_4$, $K_2Cr_2O_7$ etc.



$$CH_3-\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}-H + (O) \xrightarrow[KMnO_4]{\text{alk.}} CH_3-\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}-OH$$

Isobutane tert-Butyl alcohol

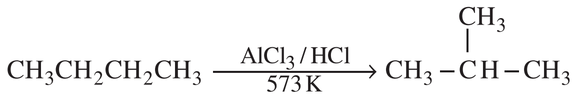
7. Aromatisation :

$$CH_3-(CH_2)_4-CH_3 \xrightarrow[600^\circ C/15\,atm]{Cr_2O_3-Al_2O_3} C_6H_6\ (\text{Benzene}) + 4H_2$$

8. Isomerization :

When n-alkanes are heated with anhydrous aluminium chloride and hydrogen chloride at 573 K under a pressure of about 35 atm, they are converted into branched chain alkanes. For example,

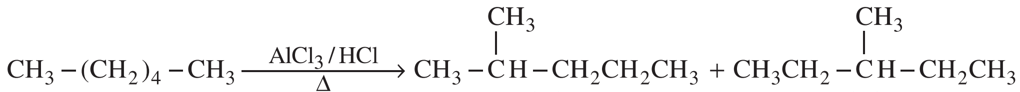
(i)



$$CH_3CH_2CH_2CH_3 \xrightarrow[573\,K]{AlCl_3/HCl} CH_3-\overset{\substack{CH_3\\ |}}{C}H-CH_3$$

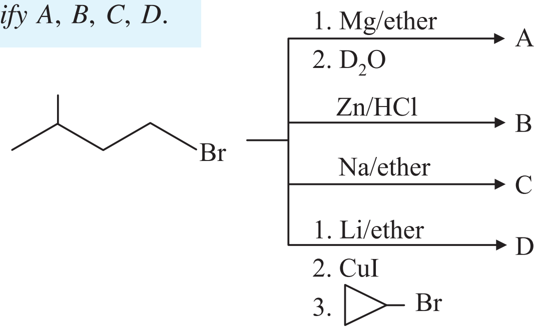
Isobutane

(ii)

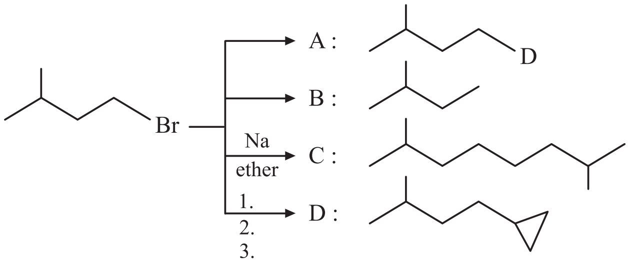


$$\underset{\text{n-Hexane}}{CH_3-(CH_2)_4-CH_3} \xrightarrow[\Delta]{AlCl_3/HCl} \underset{\text{2-Methylpentane}}{CH_3-\overset{\substack{CH_3\\ |}}{C}H-CH_2CH_2CH_3} + \underset{\text{3-Methylpentane}}{CH_3CH_2-\overset{\substack{CH_3\\ |}}{C}H-CH_2CH_3}$$

Illustration - 1 *Identify A, B, C, D.*



SOLUTION :



[RMgBr + DOD → RD + Mg(Br)OD]

(Reduction)

(Wurtz Reaction)

(Corey-House synthesis)

IN-CHAPTER EXERCISE-A

1. *Identify the compounds A, B, C . . . .*

(i) $(CH_3)_3C-MgI + CH_3NH_2 \longrightarrow A$ **(ii)** $Neopentane + Cl_2 \xrightarrow{h\nu} B$

(iii) $(CH_3)_2\,CHMgBr + cyclopentanol \longrightarrow C$ **(iv)** $Isobutyl\ chloride \xrightarrow[Red\ P]{HI} D$

Choose the correct alternative. Only one choice is correct.

2. *Which of the following has highest percentage of hydrogen :*

(A) CH_4 **(B)** C_2H_4 **(C)** C_6H_6 **(D)** C_2H_2

3. *Ethane is obtained from Ethyl iodide :*

(A) *By its reduction with ethanol and Zn-Cu couple* **(B)** *By reacting it with Na in ether*

(C) *By heating it with alcoholic KOH* **(D)** *By reacting it with AgCN*

4. *Condition for maximum yield of C_2H_5Cl is :*

(A) $C_2H_6\ (excess) + Cl_2 \xrightarrow{UV\ Light}$ **(B)** $C_2H_6 + Cl_2 \xrightarrow{Dark}$

(C) $C_2H_6 + Cl_2\ (excess) \xrightarrow{UV\ Light}$ **(D)** $C_2H_6 + Cl_2 \xrightarrow{UV\ Light}$

5. *Action of Heavy water (D_2O) on Methylmagnesium bromide gives :*

(A) CD_4 **(B)** CH_3D **(C)** CH_2D_2 **(D)** CHD_3

***6.** *Which of the following will produce Ethane at high temperature ?*

(A) *Reduction of CH_3COOH with HI and red P* **(B)** *Reduction of CH_3COCH_3 with HI and red P*

(C) *Soda-lime decarboxylation of Sodium propionate* **(D)** *Hydrogenation of Ethene in presence of Ni*