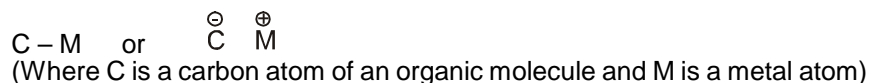


GRIGNARD REAGENT, REDUCTION & ALKANE

1. GRIGNARD REAGENT

1.1 Organometallic compounds

Organometallic compounds are the organic compounds in which a metal atom is directly attached to carbon of organic moiety through covalent bond or ionic bond. For example



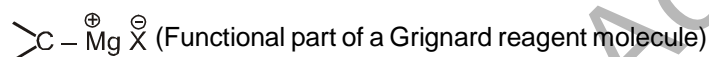
If the metal atom is attached to oxygen, nitrogen, sulphur, etc., then such an organic compound is not regarded as an organometallic compound. The following structural formula do not belong to the family of organometallic compounds.

RONa (Sodium alkoxide), CH_3COONa (Sodium acetate), CH_3COOAg (Silver acetate), RSK (Potassium mercaptide) RNHK

(N-Alkylpotassiumamide), $(\text{CH}_3\text{COO})_4\text{Pb}$ (Lead tetraacetate), etc.

Note : It should be noted that $(\text{CH}_3)_4\text{Si}$ (Tetramethylsilane, TMS) is also not an organometallic compound because silicon is a nonmetal.

Most important examples of organometallic compounds are Grignard reagents. In Grignard reagent, the carbon and magnesium atoms are bonded with each other through polar covalent bond and magnesium atom is attached to halogen by ionic bond.




In organometallic compounds, the metal atom can be bonded to carbon atom of a hydrocarbon parts (Saturated, unsaturated, aliphatic, alicyclic or aromatic) or carbon atom of a heterocyclic part. Some examples are given below.

Saturated Aliphatic Grignard reagent :- $\text{CH}_3 - \text{MgI}$
(Methylmagnesium iodide)


Unsaturated Aliphatic Grignard reagent :-


(i) Alkenyl Grignard reagent :- $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{MgX}$ (Allylmagnesium halide)

(ii) Alkynyl Grignard reagent :- $\text{CH} \equiv \text{C} - \text{CH}_2 - \text{MgX}$ (Propargylmagnesium halide)

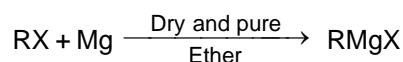
Alicyclic Grignard reagent :-  MgX (Cyclohexylmagnesium halide)

Aromatic Grignard reagent :-  MgX (Phenylmagnesium halide)

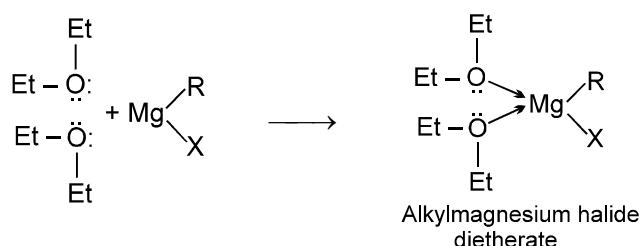
Heterocyclic Aromatic Grignard reagent :-  MgX (Pyridine-4-magnesium halide)

Heterocyclic Nonaromatic Grignard reagent :-  MgX (Piperidine-4-magnesium halide)

1.2 Preparation of Grignard Reagent

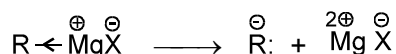


Ether is used as a solvent because it is a Lewis base that donates its lone pair of electrons to electron-deficient magnesium atom, therefore providing stability to the Grignard reagent by completing the octet on magnesium atom.

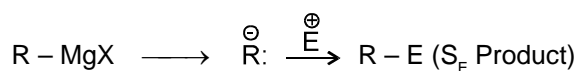


1.3 Reactions of Grignard reagents

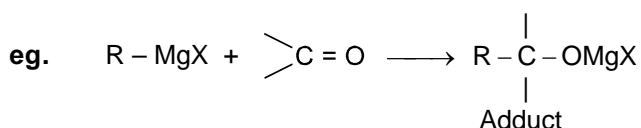
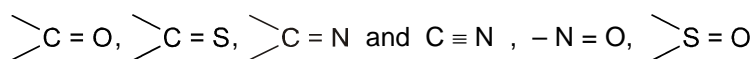
It has been found out by estimation that there is 35% ionic character in carbon-magnesium bond of Grignard reagent. Therefore, there is a tendency of forming carbanion by heterolysis of this polar coordinate bond as follows.



The carbanion (a nucleophile) formed as shown above, attacks the positively charged electrophilic centre of other compound. Therefore, it can be said that if a Grignard reagent is regarded as the substrate, then electrophile displaces MgX, i.e. electrophilic substitution (S_E) reaction takes place.



Grignard reagents form adducts by addition on the following types of pi bonds.



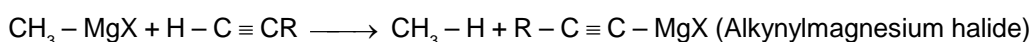
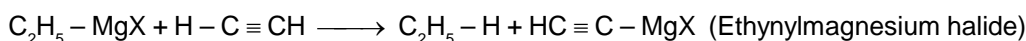
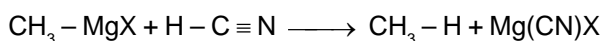
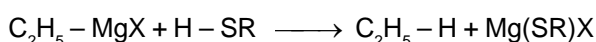
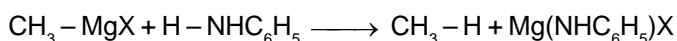
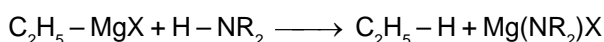
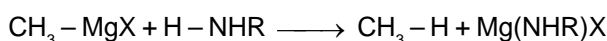
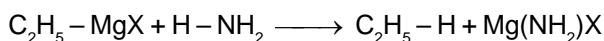
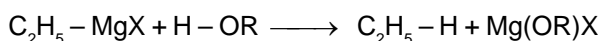
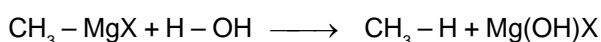
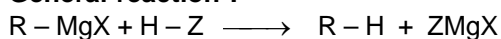
On having same hydrocarbon radical, the order of reactivity of Grignard reagents will be as follows :
 $RMgI > RMgBr > RMgCl$

1.4 Synthetic importance of Grignard reagents

1.4.1 Synthesis of Alkanes

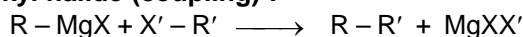
(i) With compounds having reactive hydrogen atom

General reaction :

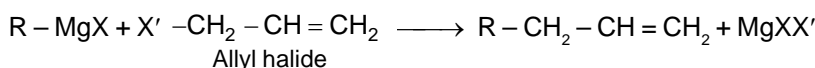


Methane gas is released on reacting methylmagnesium iodide with a compound containing reactive hydrogen atom. The reaction is used for estimation of reactive hydrogen atoms present in a molecule. This method is called **Zerewitinoff** method of estimation of reactive hydrogen atoms.

(ii) With alkyl halide (coupling) :

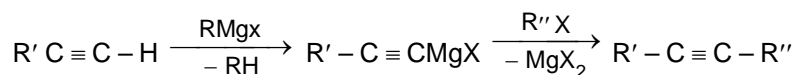


1.4.2 Synthesis of alkenes

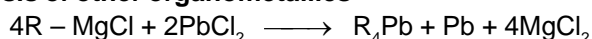


1.4.3 Synthesis of higher alkynes

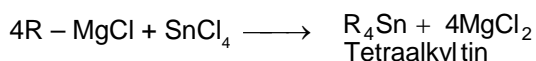
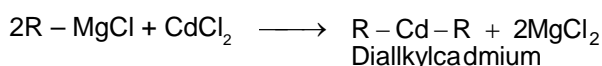
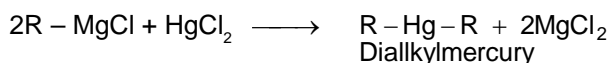
Non-terminal alkynes



1.4.4 Synthesis of other organometallics



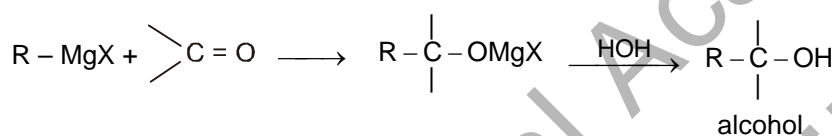
Two important antiknocking compounds, tetraethyllead (T.E.L.) and tetramethyllead (T.M.L.) are manufactured by the above reaction.



1.4.5 Synthesis of Alcohols

There are following methods to obtain alcohols from Grignard reagent.

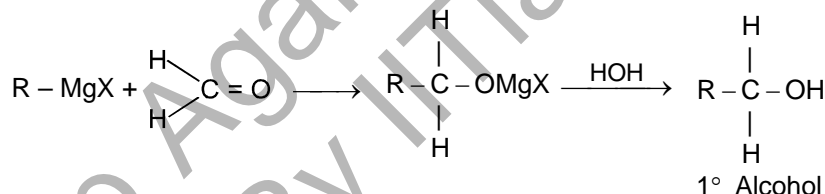
(i) From carbonyl compounds



This is nucleophilic addition reaction

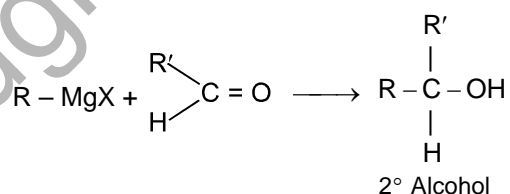
(a) Primary or 1° Alcohols

Primary alcohols are formed on taking formaldehyde



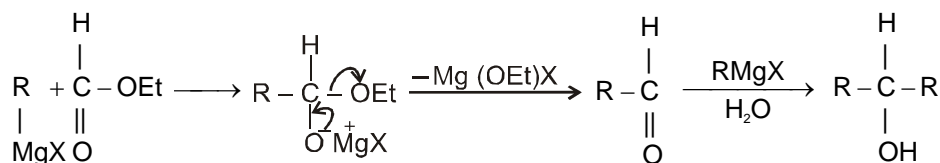
(b) Secondary or 2° alcohols

(1) From RCHO Secondary alcohols are formed by the reaction of any aldehyde other than formaldehyde.



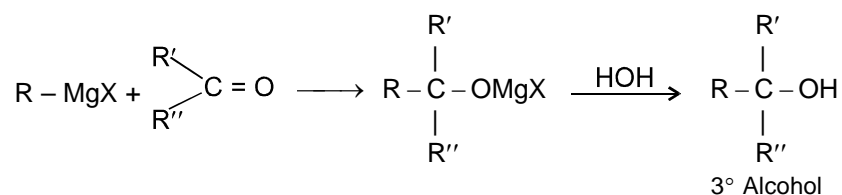
(2) From Formic Ester :

Secondary alcohols are obtained on hydrolysis of the product obtained by taking excess of Grignard reagent and adding formic ester to it.

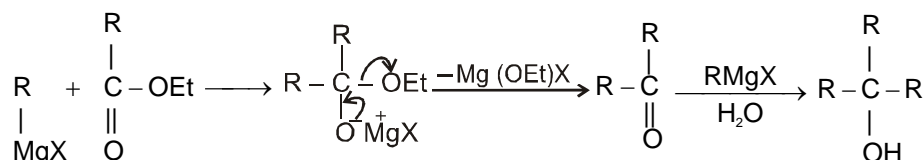


(c) **Tertiary or 3° alcohols**

(1) Tertiary alcohols are formed by taking any ketone

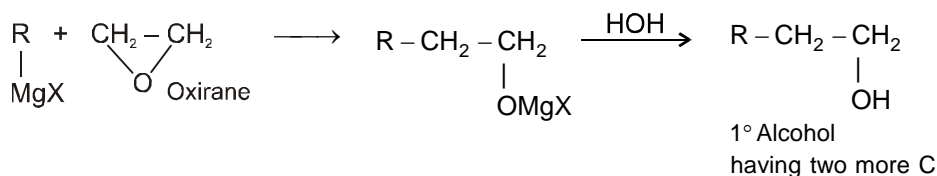


(2) Tertiary alcohols are also obtained on hydrolysis of the product obtained by taking excess of Grignard reagent and an ester of a higher homologue of formic acid.



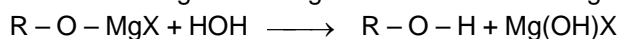
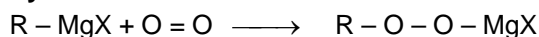
Various alcohols can be prepared by changing R in the above synthesis.

(iii) **From Epoxides**



(iv) **From Oxygen**

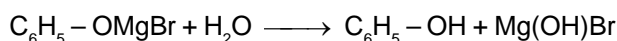
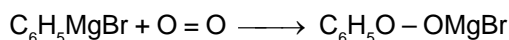
(a) **Synthesis of alcohol**



Primary, secondary and tertiary alcohols can be obtained by above reaction

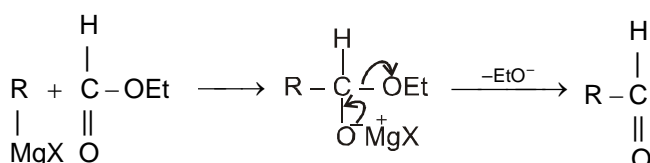
(b) **Synthesis of phenols**

Phenol is obtained on hydrolysis of the product obtained by reaction of arylmagnesium bromide with oxygen.



1.4.6 **Synthesis of Aldehydes**

Corresponding aldehyde is obtained on hydrolysis of the product obtained by reacting of formic ester and Grignard reagent in equimolar ratio.

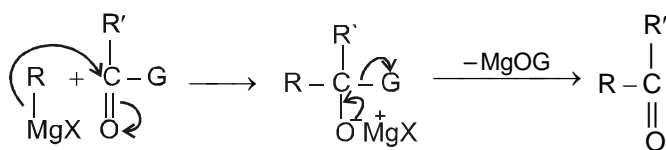


Tetrahedral intermediate

In this reaction tetrahedral intermediate is formed so this mechanism is called **S_N2 Th mechanism**

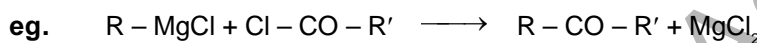
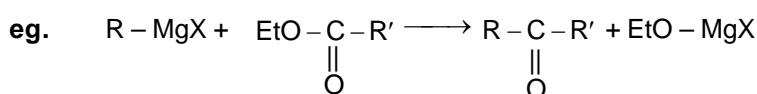
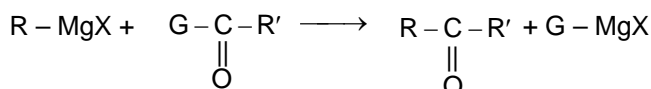
1.4.7 Synthesis of Ketones

(i) From Acid derivative



Where G = -OEt, -Cl

The above reaction sequence can be simplified as follows for convenience.



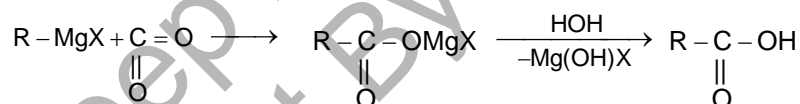
(ii) From Alkyl Cyanides

A ketimine is formed on hydrolysis of the adduct obtained by the reaction of Grignard reagent and an alkyl cyanide, which gives ketone on further hydrolysis.



1.4.8 Synthesis of Carboxylic acids

A carboxylic acid is formed on hydrolysis of the adduct formed by passing carbon dioxide in the ethereal solution of a Grignard reagent.



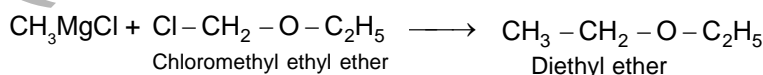
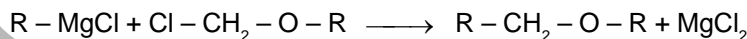
1.4.9 Synthesis of Carboxylic acid esters

Esters are formed on reacting the ethylchloroformate with Grignard reagent.



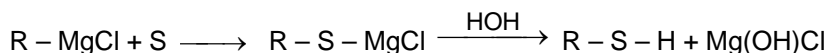
1.4.10 Synthesis of Ethers

Higher ethers can be synthesised by reacting a lower chlorinated ether with Grignard reagent.



1.4.11 Synthesis of Mercaptans

Alkanethiols, i.e. mercaptan is formed on hydrolysis of the product obtained by adding sulphur to the ethereal solution of Grignard reagent.



2. REDUCTION

Introduction

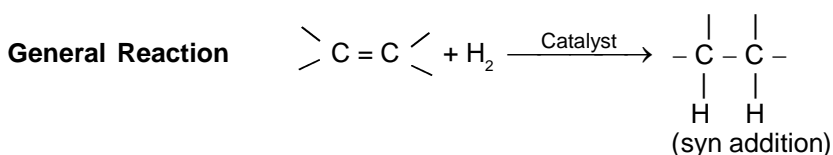
Reduction covers both the addition of hydrogen (or deuterium) to a double bond and the replacement of an atom or group by hydrogen (or deuterium). In other words, reduction means hydrogenation or hydrogenolysis.

Methods of Reduction :

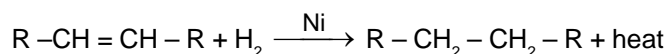
2.1 Catalytic hydrogenation : The catalysts used can be divided into two broad classes, both of which mainly consist of transition metals and their compounds :

2.1.1 Heterogeneous catalysts : (catalysts insoluble in the reaction medium)

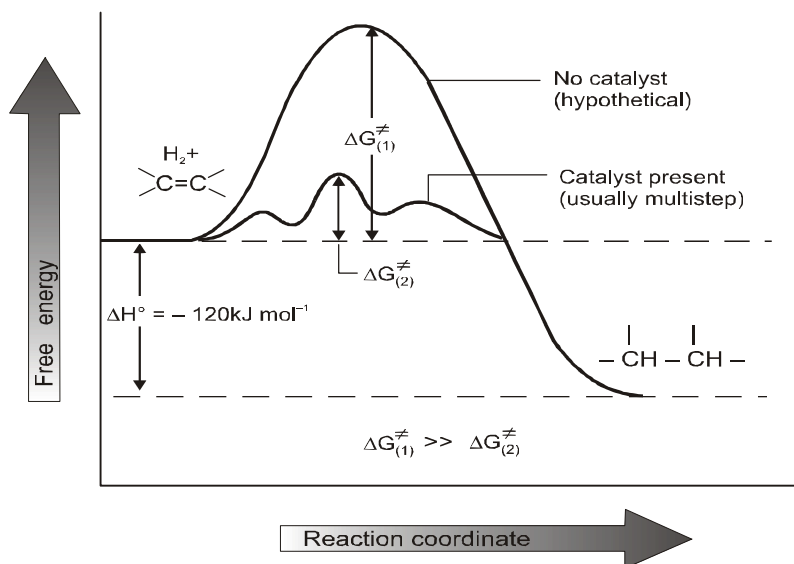
In heterogeneous catalytic hydrogenation catalysts are used in powdered form (Raney nickel (Ni), Palladium on charcoal (Pd/C), Platinum metal or its oxide). Substrate molecules are assumed to undergo homolysis into atoms which are chemisorbed at the surface of the catalyst. The substrate is also chemisorbed on the surface of the catalyst.



Hydrogenation of an alkene is an exothermic reaction ($\Delta H^\circ \cong -120 \text{ kJ mol}^{-1}$):



The process is exothermic, there is usually a high free energy of activation for uncatalyzed alkene hydrogenation, therefore, the uncatalyzed reaction does not take place at room temperature. Hydrogenation will take place readily at room temperature in the presence of a catalyst because the catalyst provides a new pathway for the reaction that involves lower free energy of activation.



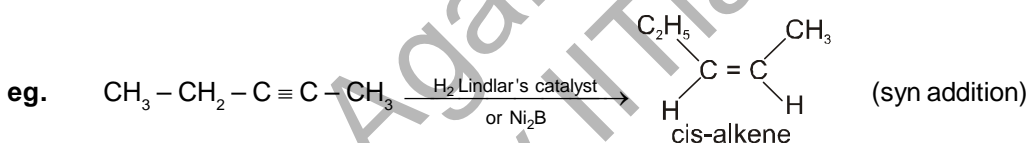
Heterogeneous hydrogenation catalysts typically involve finely divided platinum, palladium, nickel, or rhodium deposition on the surface of powdered carbon (charcoal). Hydrogenation actually takes place at the surface of the metal, where the liquid solution of the alkene comes in contact with hydrogen and the catalyst. Hydrogen gas is adsorbed into the surface of these metal catalysts and the catalyst weakens the H – H bond. In fact, if H_2 and D_2 are mixed in the presence of a Pt catalyst, the two isotopes quickly scramble to produce a random mixture of HD, H_2 and D_2 . (No scrambling occurs in the absence of the catalyst.) Hydrogenation is an example of heterogeneous catalysis, because the (solid) catalyst is in a different phase from the reactant solution. In contrast, homogeneous catalysis involves reactants and catalyst in the same phase, as in the acid-catalyzed dehydration of an alcohol.

Both hydrogen atoms usually add from the same side of the molecule. This mode of addition is called a **syn** addition.

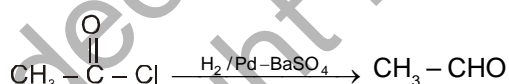
The ease of reduction of various functional groups toward catalytic hydrogenation (Ni/Pd/Pt)

Substrate	Product
RCOCl	RCH ₂ OH
RNO ₂	RNH ₂
RC≡CR	RCH ₂ CH ₂ R
RCHO	RCH ₂ OH
RCH=CHR	RCH ₂ CH ₂ R
RCOR	RCHOHR
RC≡N	RCH ₂ NH ₂
RCOOR'	RCH ₂ OH + R'OH
RCONHR'	RCH ₂ NHR'

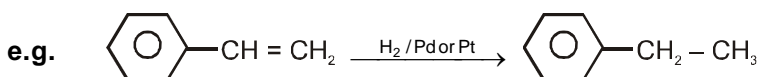
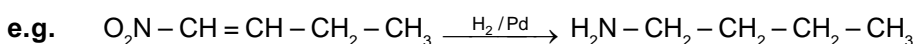
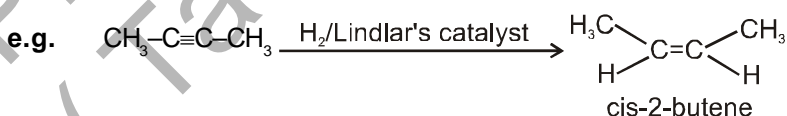
Lindlar's catalyst : is a poisoned palladium catalyst, composed of powdered barium sulphate coated with palladium, poisoned with quinoline. Nickel boride Ni₂B (**P-2 catalyst**) (made from sodium acetate and sodium borohydride) is an excellent alternative catalyst for the conversion of alkyne into alkene. (syn addition)
The partial reduction of alkyne to alkene is heterogeneous hydrogenation with Lindlar's catalyst.



Acid chloride reduced to aldehyde by using Pd /BaSO₄ catalyst

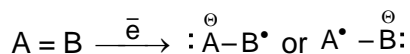
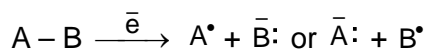


This reaction is called **Rosenmund Reduction**



2.2 Reduction by Dissolving Metals

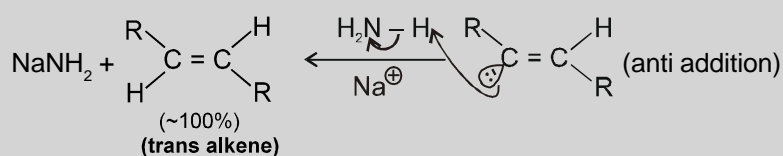
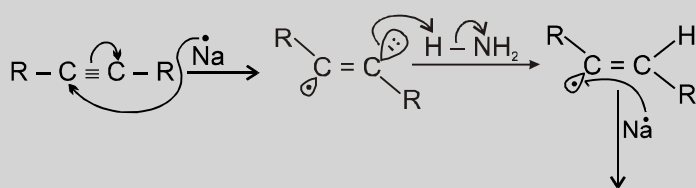
The general mechanism of reduction by dissolving metals is based on the fact that the metal acts as a source of electrons first an electron adds to the substrate causing fission of a single bond into a free radical and an anion or it can add to a double bond forming a resonance - stabilized radical ion.



2.2.1 Reduction by Na or Li/NH₃ (Birch reduction)

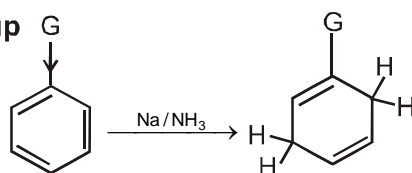
Mechanism :

Reagents Na(or Li,K) + liq NH₃ \longrightarrow Na⁺ + e⁻ (solvated electron)

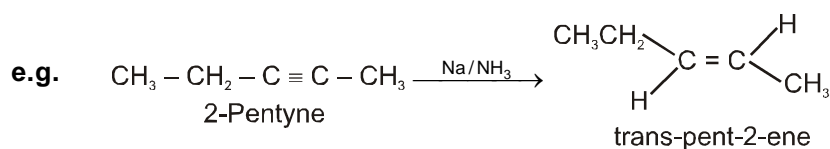
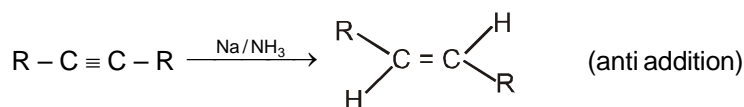
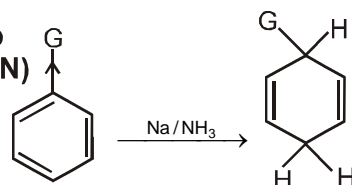


Typical example of reduction for aromatic system :-

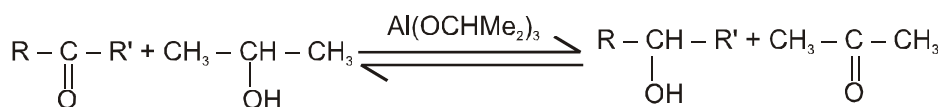
(electron releasing group
- R, - OR, - NH₂)



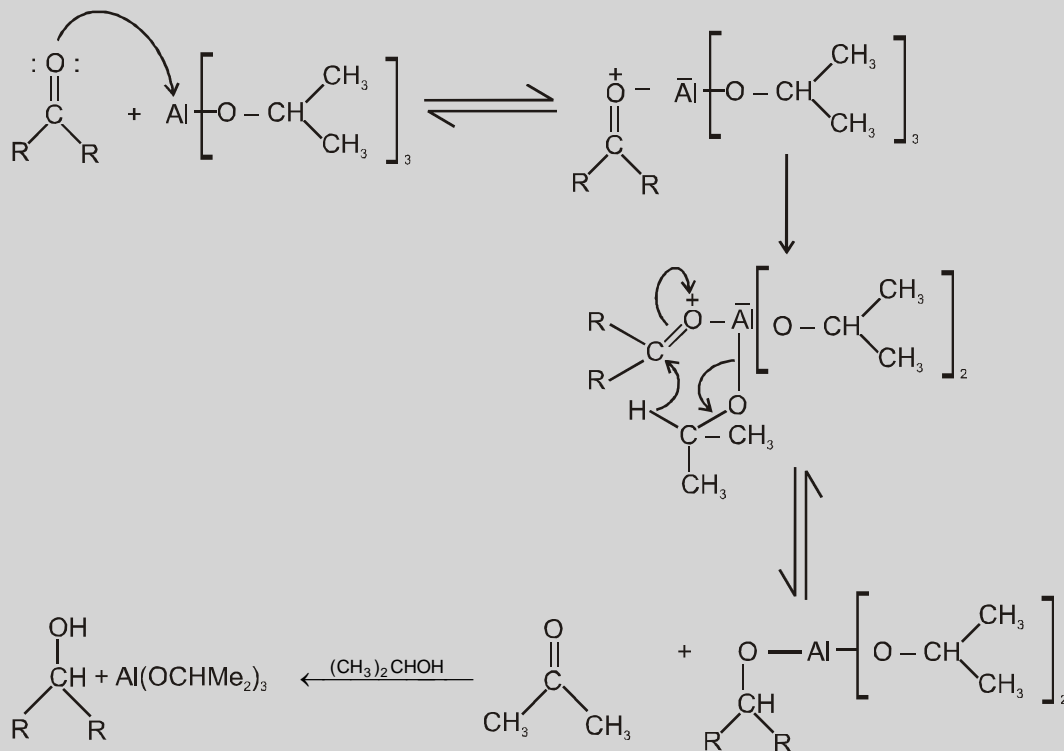
(electron withdrawing group
- NO₂, - COOH, - CHO, - CN)



2.3.4 Reduction by isopropyl alcohol and aluminium isopropoxide. This is called the **Meerwein-Ponndorf-Verley reduction**



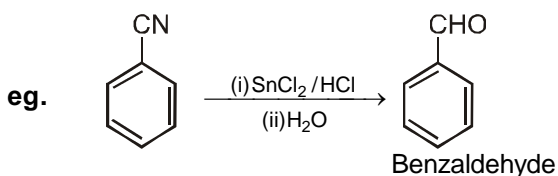
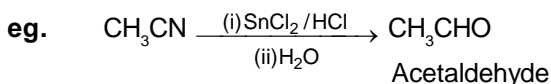
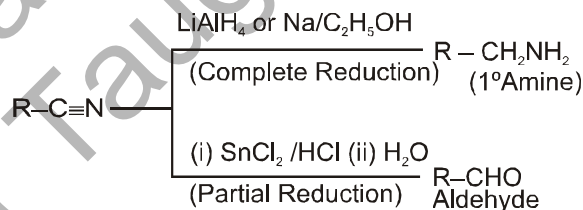
Mechanism :



2.4 Miscellaneous Reductions

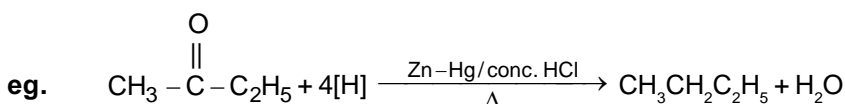
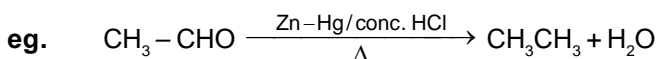
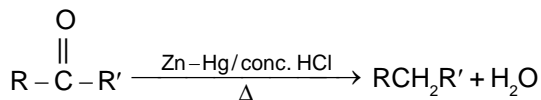
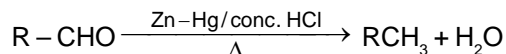
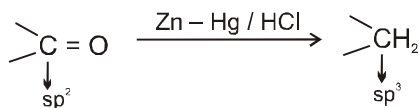
2.4.1 Stephen's Reductions

When reduction of compounds is carried out with acidified stannous chloride (SnCl_2/HCl) at room temperature, imine hydrochloride is obtained which on subsequent hydrolysis with boiling water gives aldehyde. This specific type of reduction of nitrile is called stephen's reduction.



2.4.2 Clemmensen's Reduction :

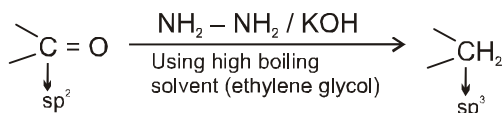
Used to get alkane from carbonyl compounds.



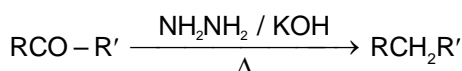
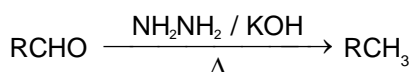
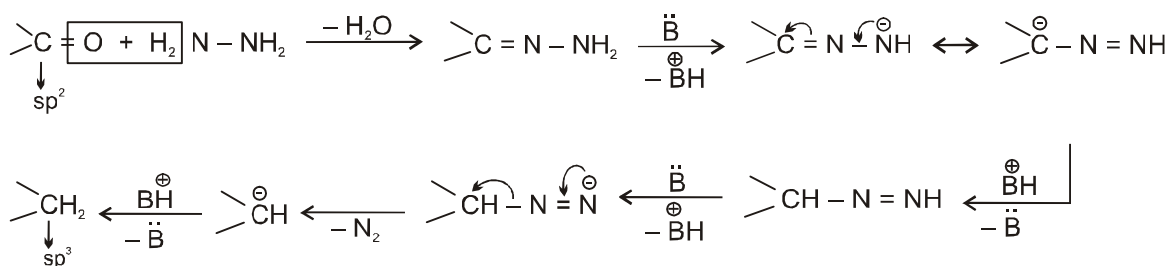
Clemmensen reduction is not used for compounds which have **acid sensitive** group.

2.4.3 Wolff-kishner reduction with $\text{NH}_2\text{NH}_2 / \text{KOH}$

Used to get alkane from carbonyl compounds

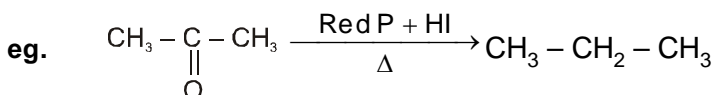
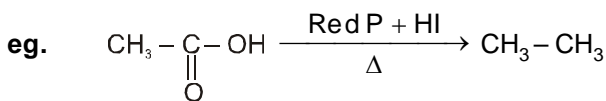
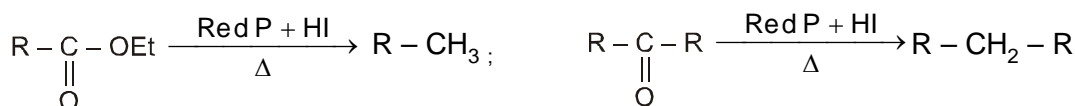
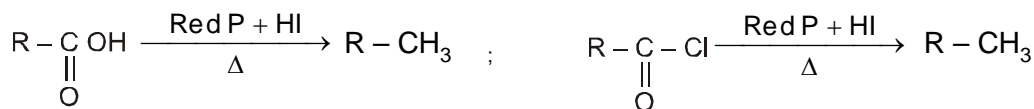


Mechanism :



Wolff-kishner reduction is not used for compounds which have **base sensitive** groups.

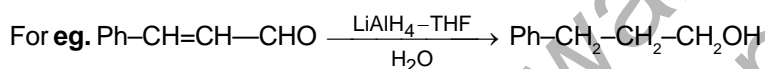
2.4.4 By Red P & HI



Various functional groups and their products by the use of different reducing agents

S.No.	Group	Product	H ₂ + Catalyst	LiAlH ₄ in ether	(i-Bu) ₂ AlH (DIBALH)	NaBH ₄ in EtOH	LiAlH(OBu ^t) ₃ in THF
1	-CHO	-CH ₂ OH	+	+	+	+	+
2	>C=O	>CHOH	+	+	+	+	+
3	-CO ₂ H	-CH ₂ OH	+	+	+	-	-
4	-COOR'	-CH ₂ OH	+	+	+	-	-
5	-CONH ₂	-CH ₂ NH ₂	+	+	+	-	-
6	-COCl	RCH ₂ OH	+	+	+	+	+
7	epoxide	alcohol	+	+	+	-	-
8	-CN	-CH ₂ NH ₂	+	+	+	-	-
9	RNO ₂	RNH ₂	+	+	+	-	-
10	>C=C<	>CH-CH<	+	-	-	-	-

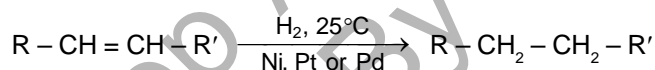
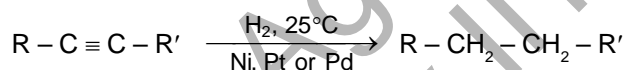
(*) double bond can be reduced by LiAlH₄ / THF only in cinnamic system.



3. ALKANE

3.1 General method of preparation

3.1.1. By catalytic reduction of alkenes and alkynes



Hydrogenation → Addition of H₂ to unsaturated bond.

Hydrogenation is of two kinds

- (a) Heterogeneous (b) Homogeneous

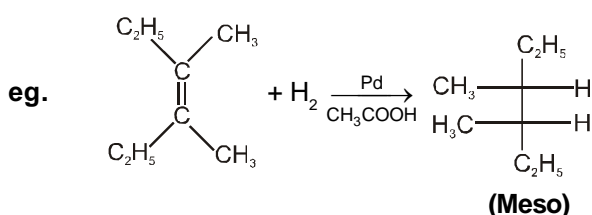
(a) Heterogeneous : It is two phase hydrogenation the catalyst is finely divided metal like Ni, Pt or Pd and a solution of alkene.

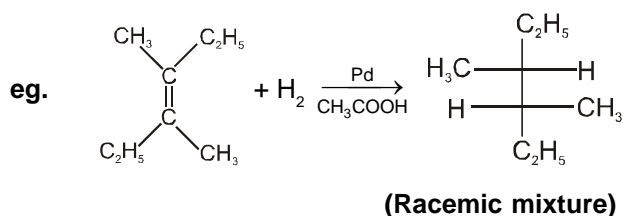
(b) Homogeneous : It is one phase hydrogenation both catalyst and alkenes are in solution. In this hydrogenation catalyst are organic complex of transition metal like Rh or Ir.

Hydrogenation is exothermic, quantitative and during the hydrogenation, total heat evolved to hydrogenate one mole of unsaturated compound is called **heat of hydrogenation**. Heat of hydrogenation is the measurement of stability of isomeric alkenes.

$$\text{stability of alkene} \propto \frac{1}{\text{Heat of hydrogenation}}$$

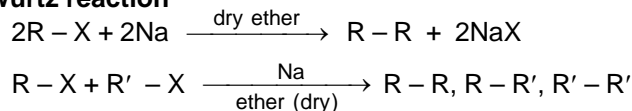
Note : Hydrogenation of alkene or alkyne in presence of metal catalyst is syn addition





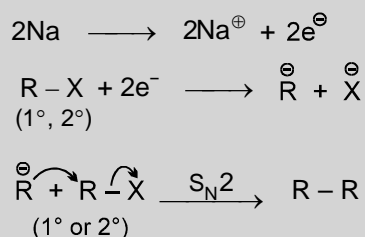
3.1.2. From alkyl halide

(i) By wurtz reaction

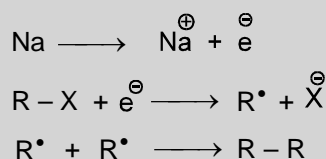


Mechanism \longrightarrow Two mechanisms are suggested

(a) Ionic mechanism

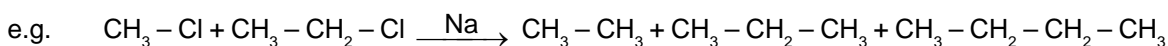
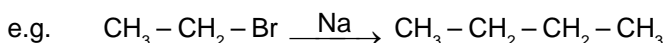


(b) Free radical mechanism



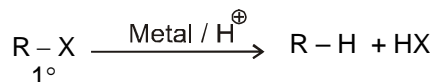
Note : The alkyl halide should be 1° or 2°, with 3° R-X S_N2 and free radical coupling is not possible due to steric hindrance so in that case elimination or disproportionation is possible.

In the ionic mechanism alkyl sodium ($\overset{\ominus}{\text{R}}\text{Na}^{\oplus}$) gives $\overset{\ominus}{\text{R}}$ strong base as well as nucleophile which gives S_N2 with R-X, ether should be dry otherwise if moisture is present than $\overset{\ominus}{\text{R}}$ forms R-H instead of R-R with H₂O.



(ii) By reduction of alkyl halides

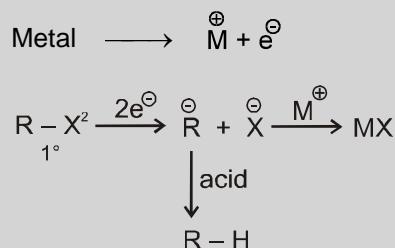
(A) with metal-acid

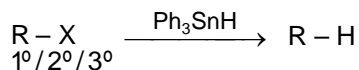
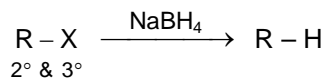
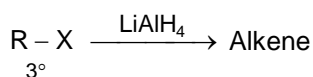
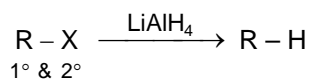
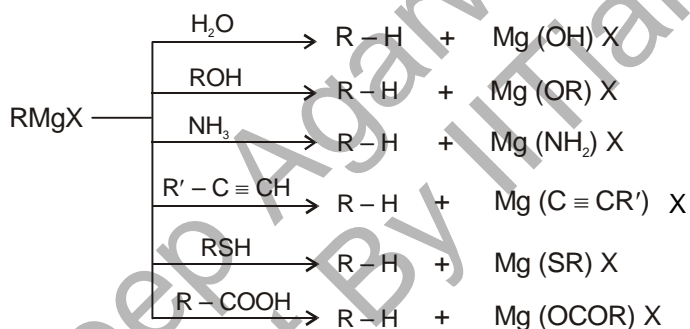
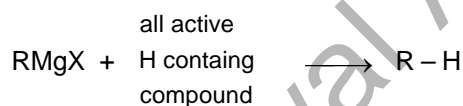
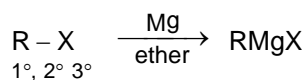
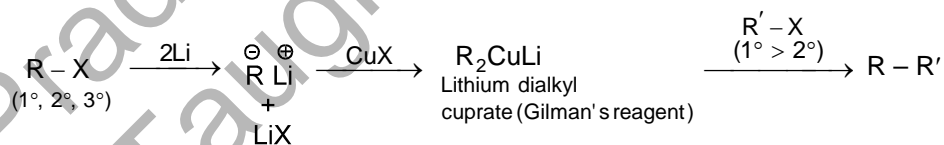
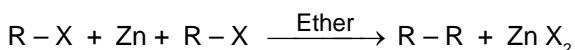


Reducing agent

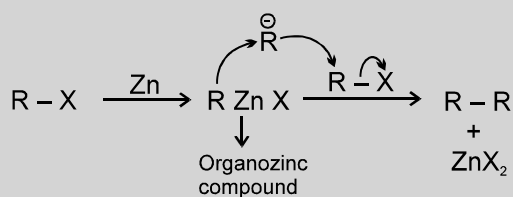
Zn / HCl, Zn-Cu / H₂O or Zn-Cu + CH₃COOH
 Zn-Cu / C₂H₅OH, Na-Hg / HCl, Al-Hg / H₂O etc.

Mechanism



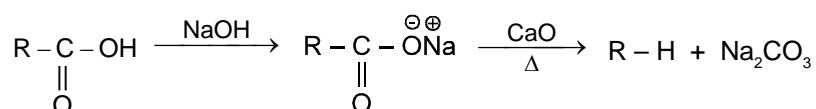
(B) With metal hydrides(a) **TPH** (Ph_3SnH) Triphenyltin hydride : It reduces 1° , 2° & 3° R-X (b) **NaBH_4** :(c) **LiAlH_4** :**3.1.3 From organometallic compound****(i) By Grignard Reagent.****(ii) By corey house alkane synthesis****Mechanism** R_2CuLi is the source of R^\ominus  R_2CuLi does not react with $-\text{NO}_2$, $-\text{CN}$, $>\text{C}=\text{O}$ etc.**(iii) By Franklands reagent**

Mechanism

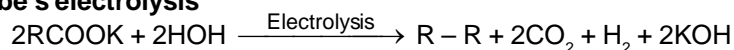


3.1.4 From carboxylic acids: -

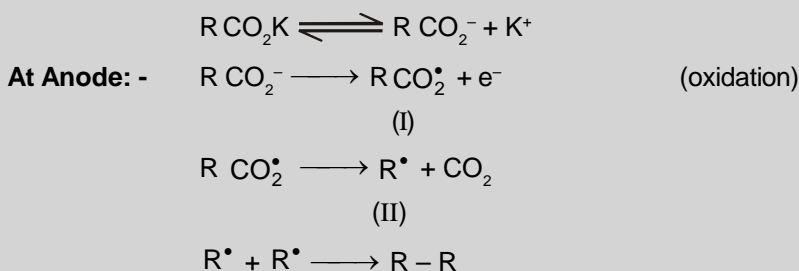
- (i) **By soda lime** : Fatty acids are good source of hydrocarbon, continuous heating of sodium salt of carboxylic acid (R – COONa) with soda lime (NaOH – CaO) gives hydrocarbon, this process is known as decarboxylation (e.g. replacement of – COOH group by – H) decarboxylation also takes place on heating only, when compound is gem dicarboxylic acid or there is keto group or double bond on β carbon.



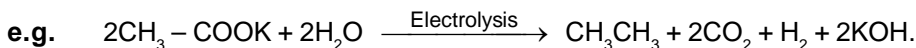
- (ii) **By Kolbe's electrolysis**



Mechanism

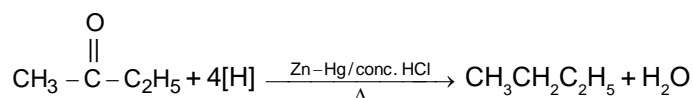
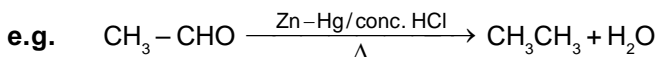
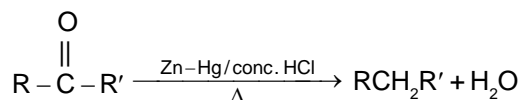
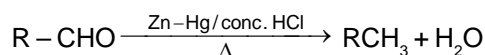


If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has 2(n-1) carbon atoms.



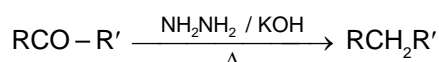
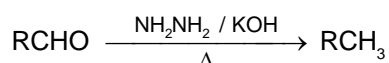
3.1.5 By Reduction

- (i) **By Clemmensen's reduction : with Zn – Hg / conc. HCl**

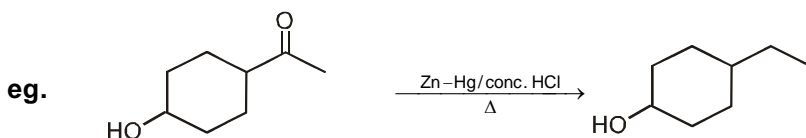


Clemmensen reduction is not used for compounds which have **acid sensitive** group.

- (ii) **By Wolff-kishner reduction with NH₂NH₂ / KOH**



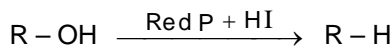
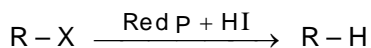
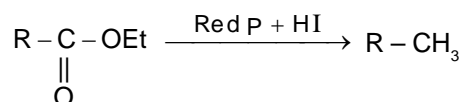
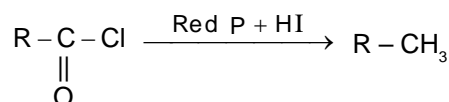
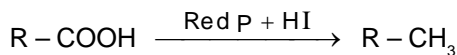
Wolff-kishner reduction is not used for compounds which have **base sensitive** groups.



Clemmensen's reduction can be used to reduce the given compounds.

(iii) **By red P & HI**

Red P & HI is strong reducing agent



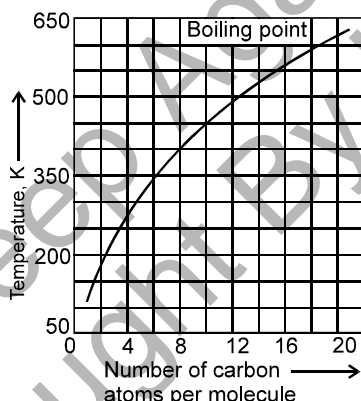
3.2 Physical Properties of Alkanes :

3.2.1 Physical state :

The first four members (C_1 to C_4) are gases ; the next thirteen members, (C_5 to C_{17}) are liquids while the higher members are **waxy solids**.

3.2.2. Boiling points :

The boiling points of n-alkanes increase regularly with the increase in the number of carbon atoms.

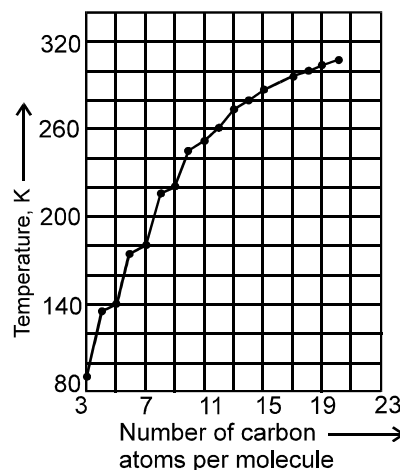


Among the isomeric alkanes, the branched chain isomers have relatively low boiling points as compared to their corresponding straight chain isomers. Greater the branching of the chain, lower is the boiling point. This is due to the fact that branching of the chain makes the molecule more compact and brings it close to a sphere, so the magnitude of vander wall forces decreases.

3.2.3. Melting Points

It is evident that the increase in melting point is relatively more in moving from an alkane having odd number of carbon atoms to the higher alkane with even no. of 'C' while it is relatively less in moving from an alkane with even number of carbon atoms to the higher alkane.

Explanation : The alkanes with even no. of 'C' atoms are more closely packed.



3.2.4. Solubility

In keeping with the popular rule "like dissolves like" hydrocarbons are insoluble in polar solvent like water because they are predominantly non-polar in nature.

3.2.5. Density

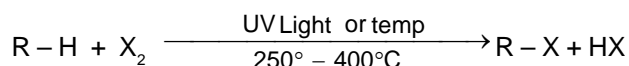
The densities of alkanes increase with increasing molecular weight but become constant at about 0.8 g cm^{-3} . This means that all alkanes are lighter than water.

3.3 Chemical Reactions of Alkanes :

Characteristic reaction of alkanes are **free radical substitution** reaction, these reactions are generally chain reactions which are completed in three steps.

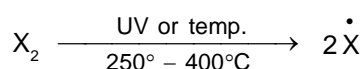
(i) chain initiation (ii) chain propagation. (iii) chain termination

3.3.1. Halogenation :

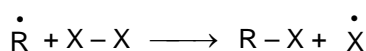


Mechanism of halogenation of alkane \longrightarrow

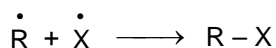
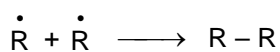
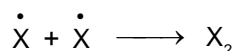
(i) Chain initiation \rightarrow it is an endothermic step.



(ii) Chain propagation \rightarrow



(iii) Chain termination \rightarrow it is always **exothermic**



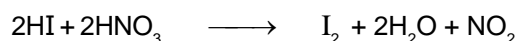
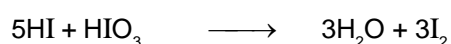
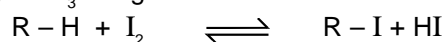
Steps of halogenation, Value of ΔH for each step. (Kcal/mole)

	F	Cl	Br	I
(i) $\text{X}_2 \longrightarrow 2\dot{\text{X}}$	+ 38	+ 58	+46	+36
(ii) $\dot{\text{X}} + \text{CH}_4 \longrightarrow \dot{\text{C}}\text{H}_3 + \text{HX}$	- 32	+ 1	+ 16	+ 33
(iii) $\dot{\text{C}}\text{H}_3 + \text{X}_2 \longrightarrow \text{CH}_3\text{X} + \dot{\text{X}}$	- 70	- 26	- 24	- 20

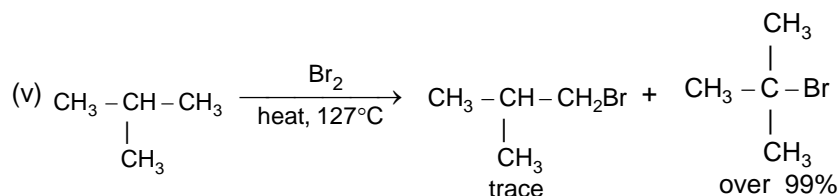
Reactivity of X_2 : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

Reactivity of H : $3^\circ\text{H} > 2^\circ\text{H} > 1^\circ\text{H}$

With F_2 alkanes react so vigorously that even in the dark and at room temperature, reactant is diluted with an Inert gas. Iodination is reversible reaction, since HI formed as a by product and It is a strong reducing agent and reduces alkyl iodide back to alkane. Hence iodination can be done only in presence of strong oxidising agent like HIO_3 , HNO_3 or HgO .



Formation of alkyl free radical is rate determining step.



Relative amounts of the various isomers differ remarkably depending upon the halogen used. From the above reaction, it is observed that chlorination gives mixture in which no isomer greatly dominates while, in bromination gives a mixture in which one isomer dominates greatly (97% – 99%),

Factors affecting the relative yields :-

Factors determining the relative yields of the isomeric products.

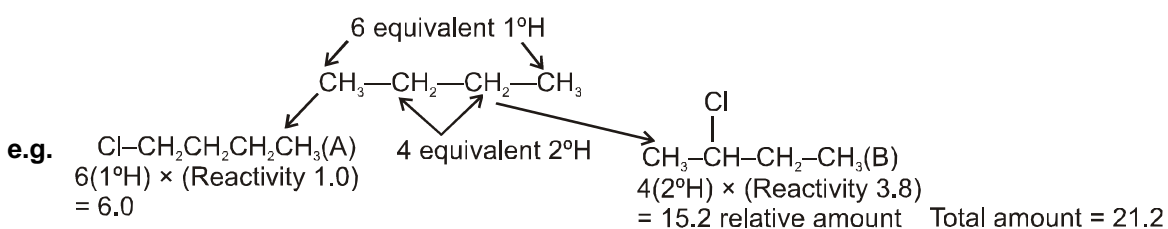
(i) **Probability factor** : This factor is based on the number of each kind of H atom in the molecule.

(ii) **Reactivity of hydrogen** : The order of reactivity is $3^\circ > 2^\circ > 1^\circ$ the relative rate per hydrogen atom is found to be

Primary	Secondary	tertiary	
1	: 3.8	: 5	For chlorination at 25°C
1	: 82	: 1600	For bromination at 127°C

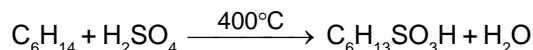
(iii) **Reactivity v/s selectivity principle** → The more reactive is halogen less selective it will be, so the more reactive chlorine free radical is less selective and more influenced by the probability factor and the less reactive $\dot{\text{B}}\text{r}$ is more selective and less influenced by the probability factors.

Based on relative reactivity of different types of H, percentage of each in the product mixture can be calculated.

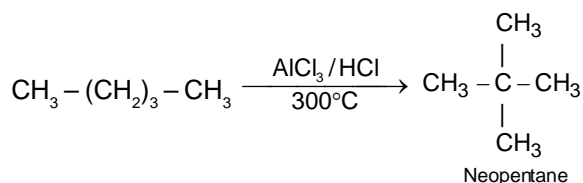
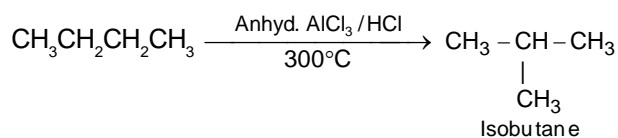


$$\% \text{ yield A} = \frac{6}{21.2} \times 100 = 28.3 \% \quad ; \quad \% \text{ yield B} = \frac{15.2}{21.2} \times 100 = 71.1\%$$

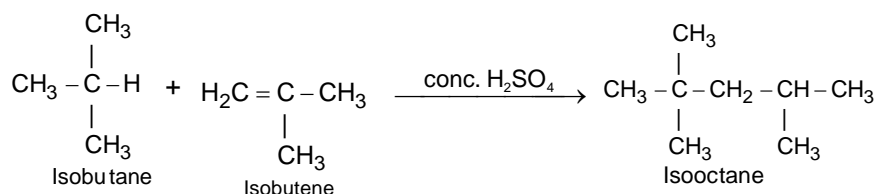
3.3.2. Sulphonation : Lower alkanes are not easily sulphonated but hexane & higher members are sulphonated on heating with oleum (conc. $\text{H}_2\text{SO}_4 + \text{SO}_3$) at 400°C



3.3.3. Isomerisation :

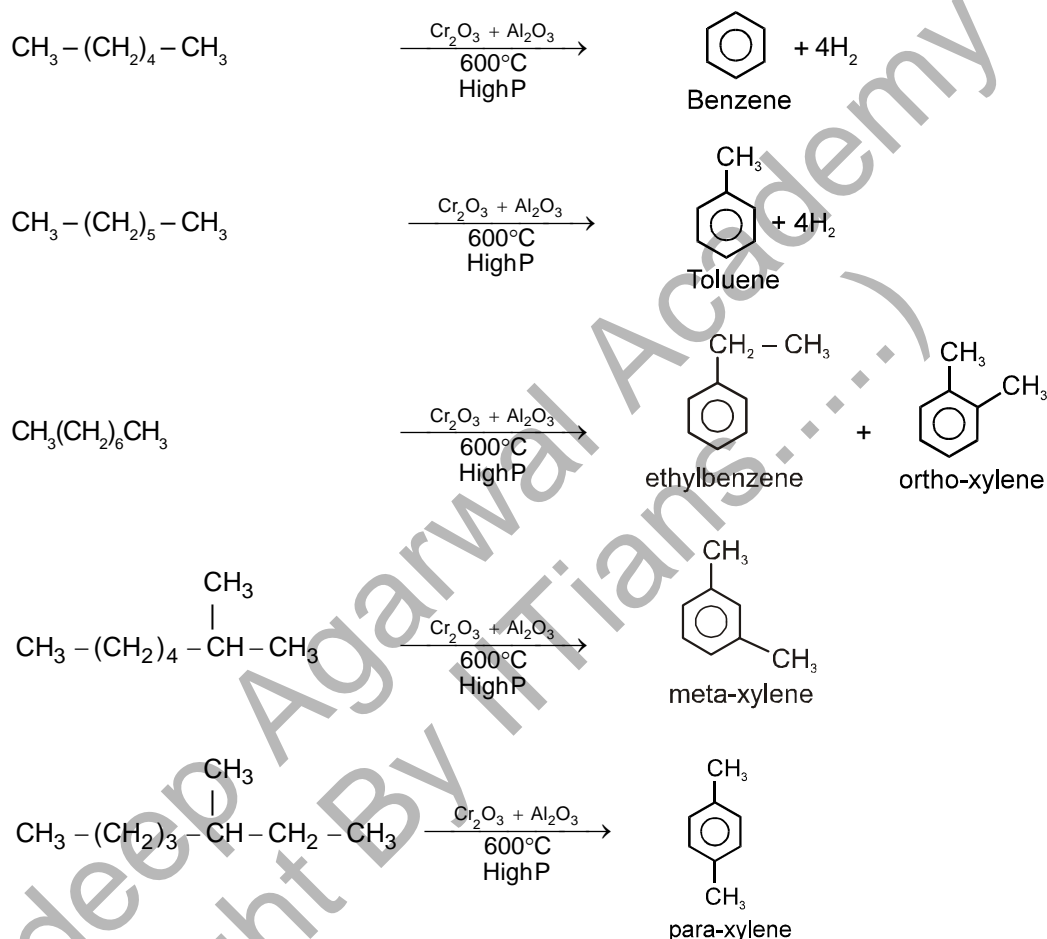


3.3.4. Alkylation : Isoalkanes add to isoalkenes in presence of conc. H_2SO_4 or HF to give higher branched alkane

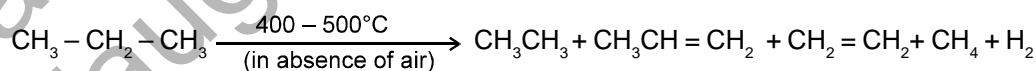


3.3.5. Aromatisation :

Alkanes containing 6 or more number of C atoms are oxidised (dehydrogenate & cyclised) in presence of oxidising agent at higher temperature and form benzene or its derivatives.

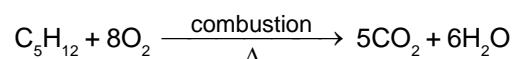
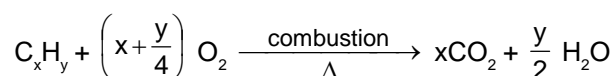
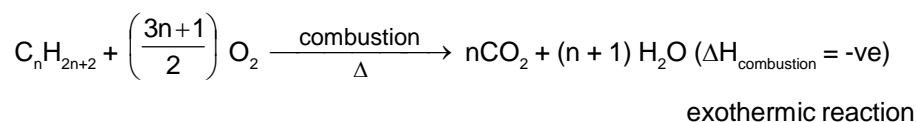


3.3.6 Pyrolysis / Cracking



Higher alkanes are heated in absence of air so these compounds break down into smaller alkanes which are better fuel. Mixture of products contains all lower alkanes, alkenes & hydrogens.

3.3.7. Combustion :

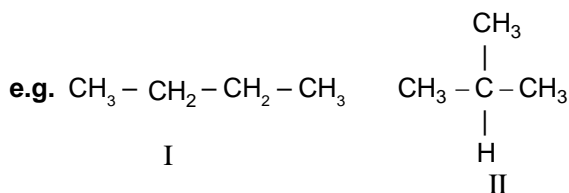


Heat of combustion : Amount of heat liberated when 1 mole of hydrocarbon is completely burnt into CO_2 & H_2O .

ΔH of combustion is a measurement of stability of alkane :

Combustion is used as a measurement of stability.

More branched alkanes are more stable and have lower heat of combustion.

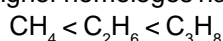


$$\Delta H_{\text{comb.}} : \text{I} > \text{II}$$

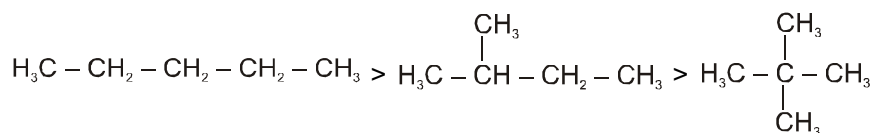
$$\text{Stability} : \text{II} > \text{I}$$

Points to remember for ΔH of combustion

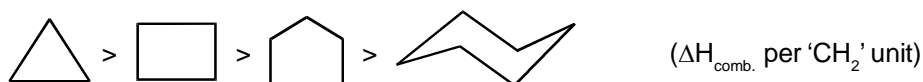
Homologes : Higher homologes have higher heat of combustion.



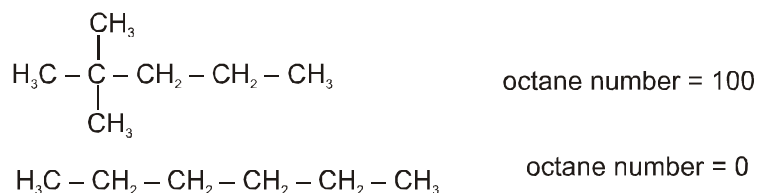
Isomers : Branched isomer has lower heat of combustion. More branched alkane has more no. of primary C-H bonds. (therefore it has more bond energy).



Cyclo-alkanes : More strained ring has higher heat of combustion per $-\text{CH}_2-$ unit.



3.3.8 Octane Number : It is a scale of fuel efficiency when the fuel burns during combustion, more branched alkanes have lower knocking (cracking sound). so are better fuels. On commercial scale iso-octane has been allotted a rating i.e. octane no. of Isooctane is 100 & n-heptane is - '0'



If the octane no. of a fuel is 80, it means that the efficiency of the fuel is equivalent to the efficiency of mixture of 80% isooctane and 20% n-heptane.

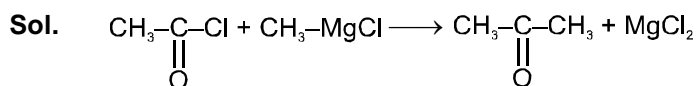
MISCELLANEOUS SOLVED PROBLEMS

1. Which of the following formula represents Grignard reagent ?
(A) H_2NMgX (B) $HC \equiv CMgX$ (C) R_2Mg (D) $Mg(OH)Br$
Ans. B
Sol. Grignard reagent is represented by $RMgX$.
2. Which of the following is not a Grignard reagent ?
(A) $(CH_3)_2CHMgCl$ (B) $CH_3COOMgI$ (C) $C_6H_{11}MgBr$ (D) C_2H_5MgCl
Ans. B
Grignard reagent is represented by $RMgX$. Where R = Carbon.
3. What is the motive of adding iodine in small amount during preparation of methylmagnesium iodide ?
(A) It acts as a catalyst (B) It converts ether into alkyl iodide
(C) It decreases the violence of the reaction (D) It acts as an electrophilic
Ans. A
Sol. It acts as a catalyst
4. The reaction of an alkyl halide and magnesium is initially very slow, but later becomes very fast, because
(A) The reaction is autocatalytic (B) The Grignard reagent formed is ether-soluble
(C) The reaction is endothermic (D) The reaction is exothermic
Ans. D
 $R-X + Mg \longrightarrow R-MgX \quad \Delta H = -ve$
5. A Grignard reagent is formed on reacting magnesium with
(A) Alkyl halide in the presence of dry ether
(B) Alkyl halide in the presence of phenol
(C) Alkyl halide in the presence of alcohol
(D) Alkyl halide in the presence of alcoholic ether
Ans. A
Sol. $R-X + Mg \longrightarrow R-MgX$ (Grignard Reagent)
6. Zerewitinoff's method is used for
(A) the estimation of reactive hydrogen atom (B) the estimation of alkoxy group
(C) the preparation of a higher ether (D) the preparation of a Grignard reagent
Ans. A
Sol. $Z-H + R-MgX \longrightarrow R-H + MgXZ$
This is estimation of reactive hydrogen atom.
7. Primary alcohol cannot be obtained by the reaction of a Grignard reagent with
(A) The simplest alkanal (B) Dimethylene oxide
(C) Ethylene glycol (D) Oxygen
Ans. C
Sol. $RMgX + HCHO \longrightarrow R-CH_2OH$
 $RMgX + (CH_2)_2O \longrightarrow R-CH_2-CH_2-OH$
 $R-MgX + (CH_2OH)_2 \longrightarrow R-H + MgXOCH_2CH_2OH$
 $RMgX + O_2 \longrightarrow ROH$
8. Primary, secondary and tertiary alcohols can be obtained by hydrolysis of the products formed on reaction of a Grignard reagent with
(A) Isobutyraldehyde (B) Butanone (C) Oxygen (D) Oxirane
Ans. C
Sol. $R-MgX + O_2 \longrightarrow ROMgX \xrightarrow{H_3O^+} ROH$
(1°, 2°, 3°) (1°, 2°, 3°)

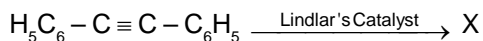
9. Which of the following is formed on the reaction of one mole of acetyl chloride with one mole of methylmagnesium chloride ?

- (A) 2-Butanol (B) Acetone (C) Isobutyl alcohol (D) t-Butyl alcohol

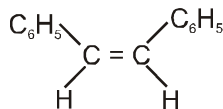
Ans. B



10. Identify the product - X

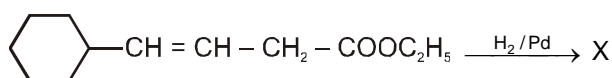


Sol.

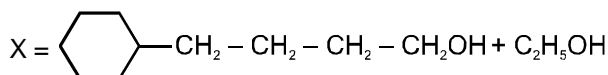


Cis-stilbene

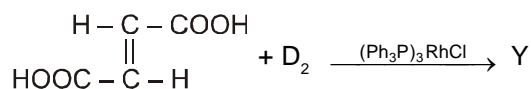
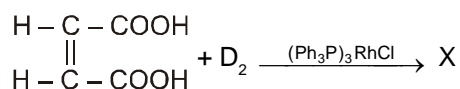
11. Identify X



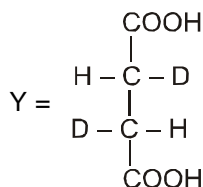
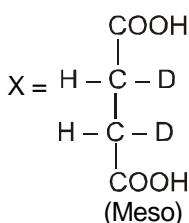
Sol.



12. Identify the product x and y

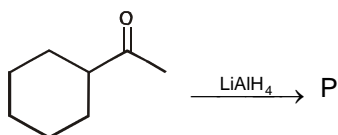


Sol.

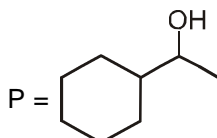


(dl) Racemic mixture

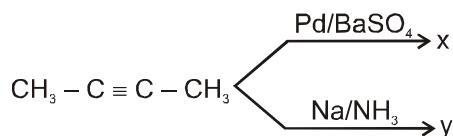
13. Identify product ?



Sol.

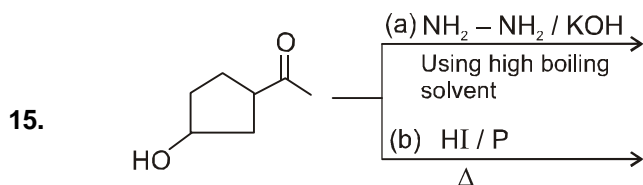


14.

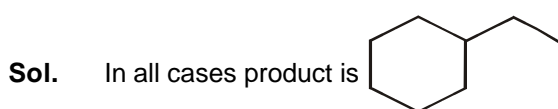
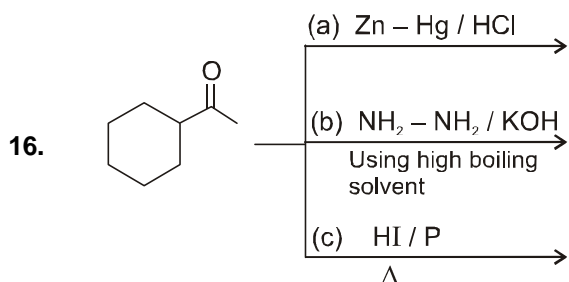
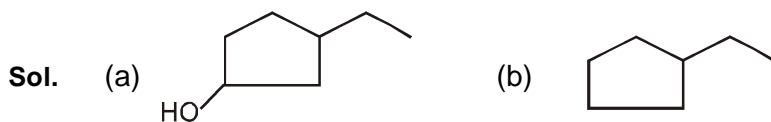


Where x and y ?

Sol. x = Cis 2 butene , y = trans 2 butene



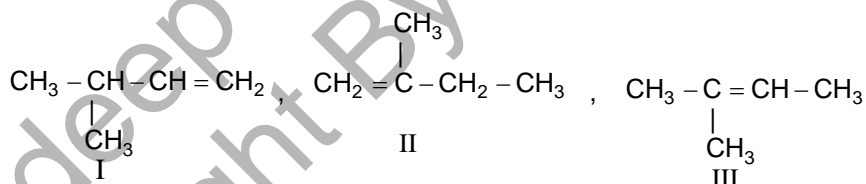
Write the products.



17. Arrange the following alkenes in decreasing order of their stability
 $R_2C=CR_2$, $CH_2=CH_2$, $R_2C=CH_2$, $R-CH=CH-R$ (cis, trans), $R_2C=CHR$, $RCH=CH_2$

Sol. $R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > R-CH=CH-R > RCH=CHR > R-CH=CH_2 > CH_2=CH_2$
trans cis

18. What is the order of stability of following alkene

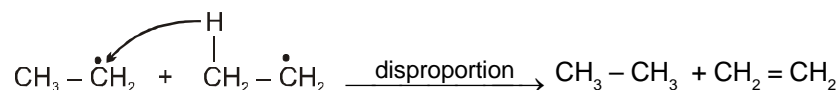
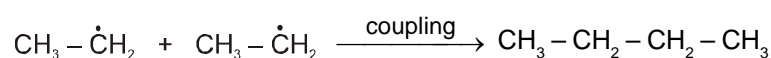
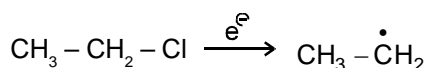
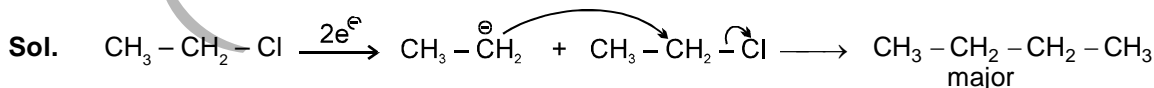


Ans. III > II > I

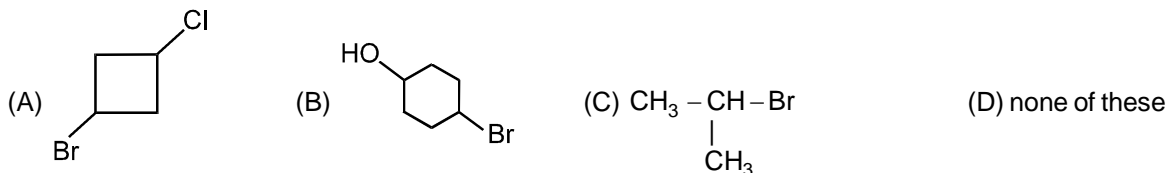
Sol. Stability of alkene \propto Hyperconjugative Structure.

19. $C_2H_5Cl \xrightarrow[\text{Ether}]{Na}$ products

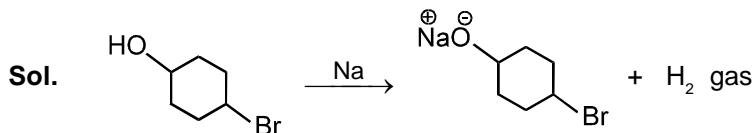
Write all possible product



20. Wurtz reaction will not be observed in

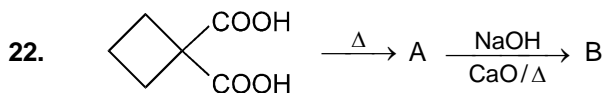


Ans. B

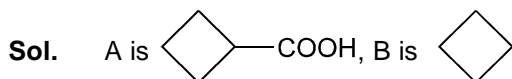


21. $\text{CH}_3 - \text{Br} \xrightarrow{\text{Li}} \text{A} \xrightarrow{\text{CuI}} \text{B} \xrightarrow{\text{Y}} \text{C}$
if C is $\text{CH}_3 - \text{CH}_2 - (\text{CH}_2)_5 - \text{CH}_3$, than what is Y.

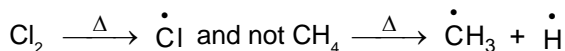
Ans. $\text{CH}_3 - (\text{CH}_2)_6 - \text{Br}$



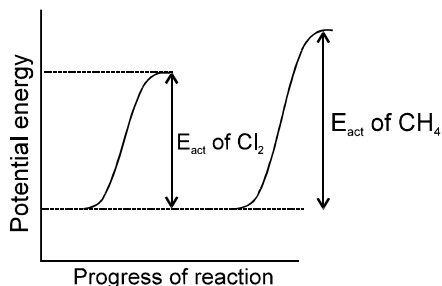
What are A and B



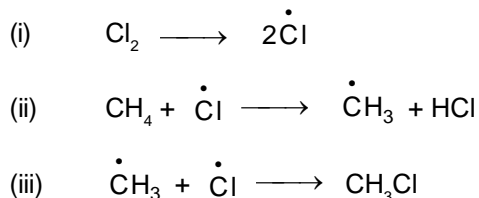
23. Explain why the chain initiating step in thermal chlorination of CH_4 is



Sol. Because E_{act} of Cl_2 is less than E_{act} of CH_4



24. Chlorination of CH_4 involves following steps :



Which of the following is rate determining ?

(A) Step (i) (B) Step (ii) (C) Step (iii) (D) Step (ii) and (iii) both

Ans. B

Sol. Formation of alkyl free radical is Rds step.