

GRIGNARD'S REAGENT, REDUCTION & ALKANE

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Syllabus

Grignard's reagent : Nucleophilic substitution reactions, nucleophilic addition reactions (grignard addition)

Reduction : Reduction of alkenes and alkynes, Carbonyl compounds etc.

Alkane : Preparation, properties and reactions of alkanes. Combustion and halogenation of alkanes preparation of alkanes by Wurtz reaction and decarboxylation reactions.

Name : _____ Contact No. _____

GRIGNARD REAGENT, REDUCTION & ALKANES

Introduction of Organometallic compounds

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



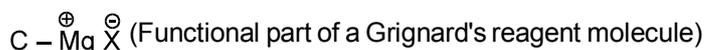
(Where C is a carbon atom of an organic molecule and M is a metal atom)

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-Alkylpotassamide), $(CH_3COO)_4Pb$ (Lead tetraacetate), etc.

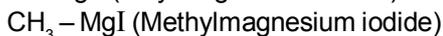
Note : It should be noted that $(CH_3)_4Si$ (Tetramethylsilane, TMS) is also not an organometallic compound because silicon is a nonmetal.

Most important examples of organometallic compounds are Grignard's reagents. In Grignard's 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.



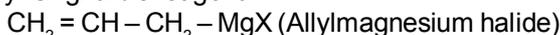
In organometallic compounds, the metal atom can be bonded to carbon atom of a hydrocarbon radical (Saturated, unsaturated, aliphatic, alicyclic or aromatic) or carbon atom of a heterocyclic radical. Some examples are given below.

1. Saturated Aliphatic Grignard's reagent



2. Unsaturated Aliphatic Grignard's reagent

(i) Alkenyl Grignard's reagent



(ii) Alkynyl Grignard's reagent



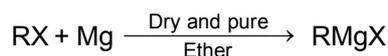
3. Alicyclic Grignard's reagent



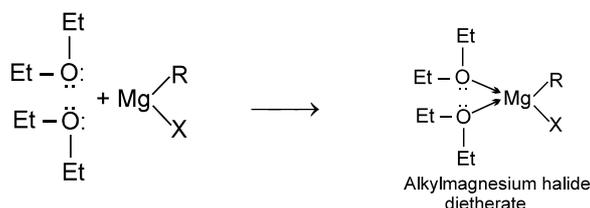
4. Aromatic Grignard's reagent



Preparation



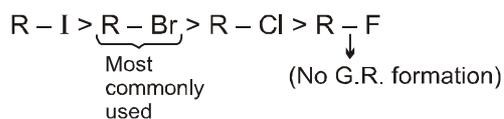
Ether is used as a solvent because it is a Lewis base that donates its lone pair of electrons to electron-deficient magnesium atom, therefore providing stability to the Grignard's reagent by completing the octet on magnesium atom.



Process : To an etherial solution of alkyl halide Mg metal is added at very low temp. (0 – 5°C). A vigorous reaction takes place , and a solution of G.R. is obtained. It cannot be evaporated to get it in solid state. The reaction will be explosive. It is stable only in solution state.

Reactivity order with respect to X (For preparation of RMgX)

R – X :



Iodides forms organometallic compounds at the fastest rate.

Structural stability of G.R.

If the alkyl part has more stable negative charge, then RMgX is more stable. It will be less reactive

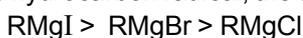
e.g. $CH_3 - CH_2 - MgX$; $CH_2 = CH - MgX$; $CH_3C \equiv C - MgX$

Reactivity order : 1 > 2 > 3

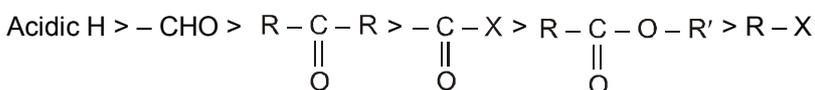
Stability order : 1 < 2 < 3

Reactivity order of Grignard's reagent

On having same hydrocarbon radical, the order of reactivity of Grignard's reagents will be as follows :



Reactivity order with respect to active H

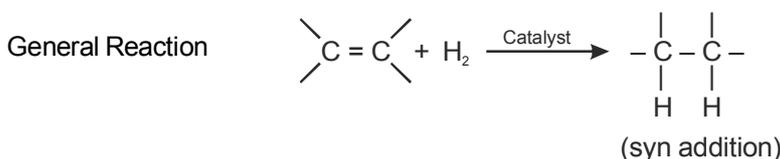


Except X (halogen) all other functional groups must be absent in the alkyl group otherwise. G.R. will be destroyed by internal reactions.

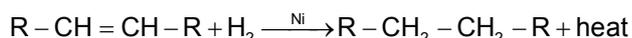
[– NO₂, – CN must also be absent]

Reduction

Catalytic Hydrogenation :



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

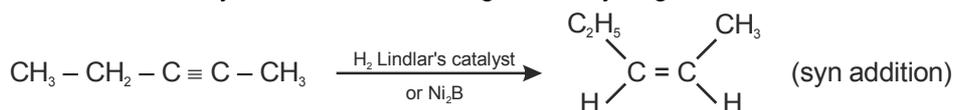


Partial Reduction

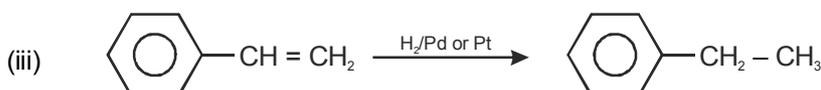
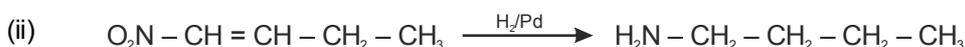
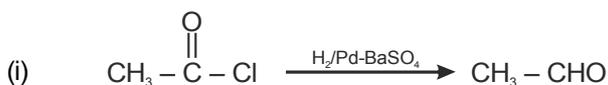
(a) Lindlar's catalyst :

It is a poisoned palladium catalyst (composed of powdered barium sulphate coated with palladium) poisoned with quinoline or sulphur. Nickel boride Ni₂B (P-2 catalyst) (made from sodium acetate and sodium borohidride) 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 is called **Rosenmund Reduction**.

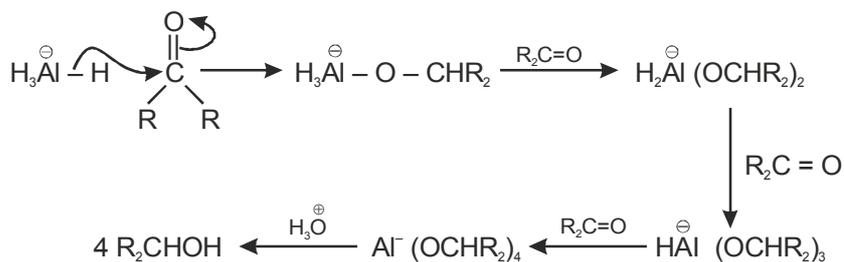


Reduction by metal hydrides and alkoxides :

LiAlH_4 (LAH) Lithium aluminium hydride (strong reducing agent) :

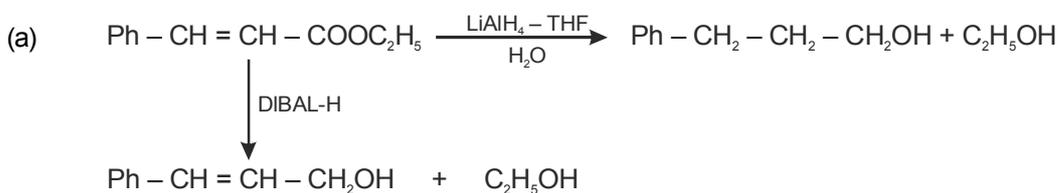
NaBH_4 Sodium borohydride (Mild reducing agent) :

Mechanism :

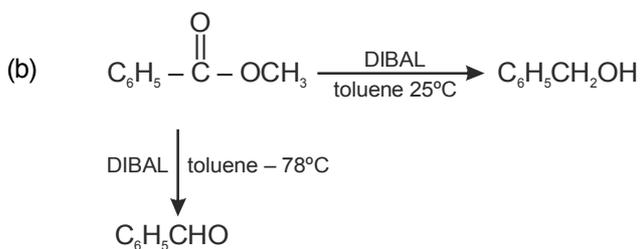


DIBAL-H (Diisobutyl Aluminium Hydride) (ALANE)

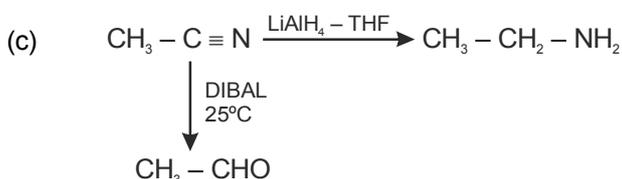
Most important alane is diisobutyl aluminium hydride. It runs parallel to LAH (Lithium aluminium hydride) as a reducing agent but it is more selective.



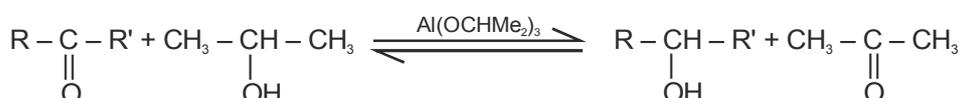
By DIBAL at ordinary temperature esters are reduced to alcohols but at low temperature esters are reduced to aldehyde.



LAH reduce RCN to amine but DIBAL is found to be reduce it to aldehyde.

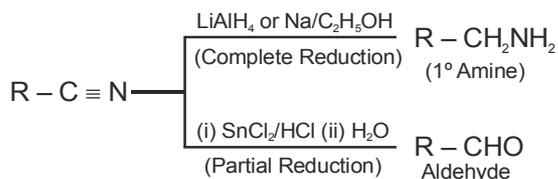


MPV Reduction (by isopropyl alcohol and aluminium isopropoxide)



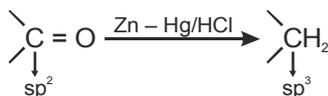
Stephen's Reduction :

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.



Clemmensen's Reduction

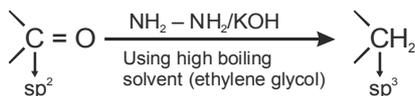
Used to get alkane from carbonyl compounds :



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

Wolff-kishner reduction ($\text{NH}_2\text{NH}_2/\text{KOH}$) :

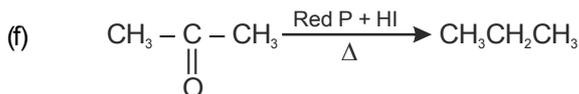
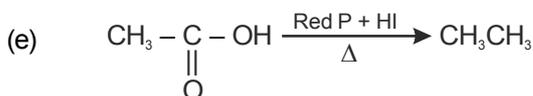
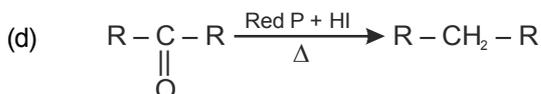
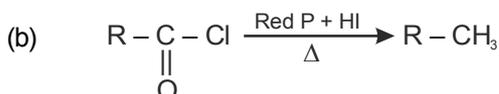
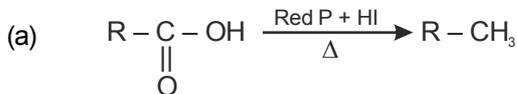
Used to get alkane from carbonyl compounds



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

By Red P & HI :

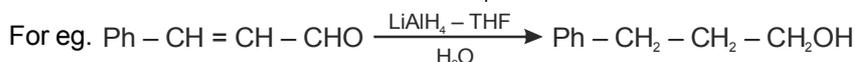
All the functional groups reduced into corresponding hydrocarbon.



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

S. No.	Group	Product	H ₂ + Catalyst	LiAlH ₄ in ether	NaBH ₄ in EtOH	LiAlH(OBu ^t) ₃ in THF
1	- CHO	- CH ₂ OH	+	+	+	+
2	$\begin{array}{c} \diagup \\ \text{C} = \text{O} \\ \diagdown \end{array}$	$\begin{array}{c} \diagup \\ \text{CHOH} \\ \diagdown \end{array}$	+	+	+	+
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	$\begin{array}{c} \diagup \\ \text{C} = \text{C} \\ \diagdown \end{array}$	$\begin{array}{c} \diagup \\ \text{CH} - \text{CH} \\ \diagdown \end{array}$	+	-	-	-

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



ALKANE

INTRODUCTION :

- * Saturated hydrocarbons are known as alkanes or paraffins (Less reactive).
- * Alkanes with carbon chains that are unbranched are called normal alkanes. Each member of the series differ from the next higher and next lower member by >CH₂ group.
- * General formula : $\text{C}_n\text{H}_{2n+2}$
- * All the carbon atoms in alkanes are in sp³ state of hybridization and geometry is tetrahedral.
- * All the bond angles are tetrahedral angles i.e., H-C-H or H-C-C bond angle is 109°28'



Properties

(i) Overlapping

(ii) Bond length

(iii) Bond energy

C-C

sp³ - sp³

1.54 Å

80 - 85 kcal

C-H

sp³ - s

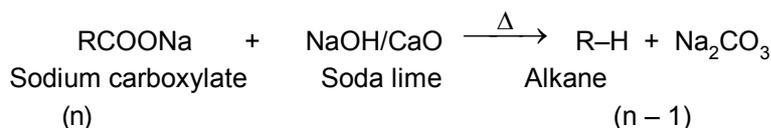
1.112 Å

98.6 kcal

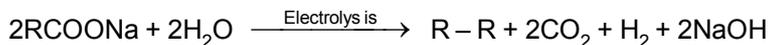
METHODS OF PREPARATION :

(i) From Carboxylic acids :

(a) By de-carboxylation :



[b] Kolbe's electrolytic synthesis :



* Methane cannot be prepared by this method.



Anode

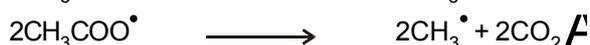
Cathode

Mechanism :

Ionic free radical :



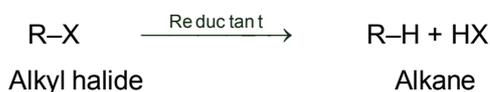
At anode :



At cathode :

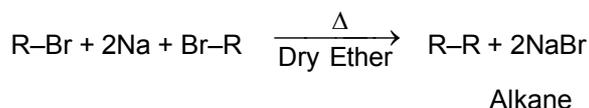


(ii) Reduction of Alkyl Halides :



Reductants : Zn-Cu couple/EtOH, Na-EtOH, Zn-HCl, Pt or Pd or Ni/H₂ Al-Hg/EtOH, LiAlH₄ etc.

(iii) Wurtz Reaction :



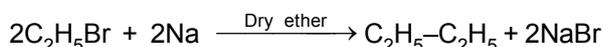
* Methane cannot be prepared by this method.

* The alkane produced is higher and symmetrical i.e., it contains double in the number of carbon atoms present in the alkyl halide taken.

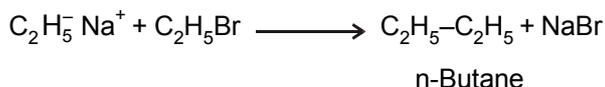
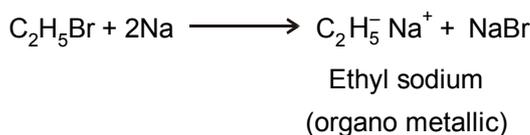
* When the two reacting alkyl halides are different, a mixture of three different alkanes is obtained. So the Wurtz reaction is not useful for preparing alkanes containing odd no. of C atoms.



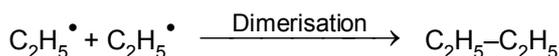
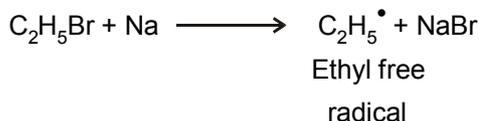
* **Mechanism :** Wurtz reaction may proceed via the formation of organometallic compound or alkyl free radicals. [i.e. Both ionic and free radical mechanisms are proposed]



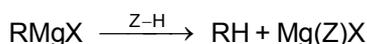
(A) Ionic Reaction Mechanism :



(B) Free radical Reaction Mechanism :



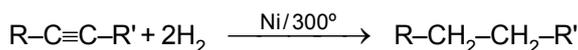
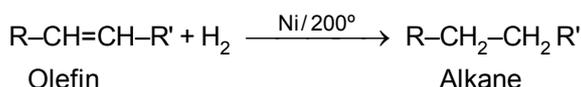
(iv) From Grignard reagent :



Z-H [compound containing active hydrogen]

HOH, NH₃, RC≡CH, C₆H₅OH, CH₃COOH, RNH₂, R₂NH, Pyrrole, C₂H₅OH etc.

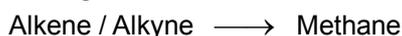
(v) From Alkenes and Alkynes (Hydrogenation) :



- * When the catalyst are Pt or Pd, hydrogenation proceeds smoothly at ordinary temperature and pressure.
- * With Nickel catalyst, higher temperature (200° – 300°C) and pressure are needed. (In this case the reaction is known as Sabatier Senderen's reaction)
- * With Raney Nickel, the reaction takes place at room temperature.



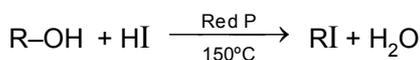
In this reaction following alkanes are not formed from unsaturated hydrocarbons



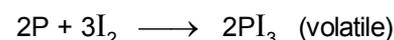
- * The reaction is exothermic. The heat released in the reaction is known as heat of hydrogenation.

(vi) Reduction of Alcohols, Aldehydes, Ketones and Acids by Red P and HI (150°C) :

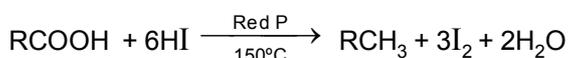
(a) By the reduction of alcohols :



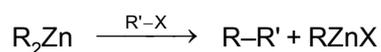
*Since iodine is produced during the reaction, it may react with the resulting alkane, so it is removed by adding red phosphorus.



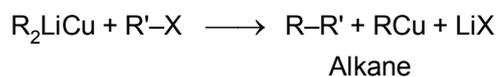
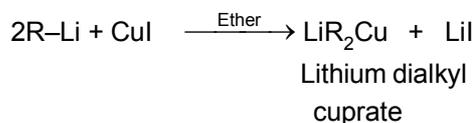
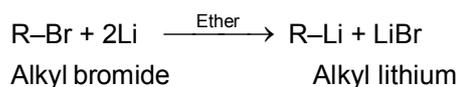
(b) By reduction of acid :



(viii) From dialkyl zinc :

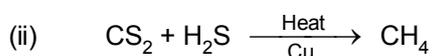
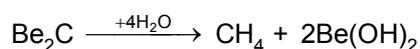
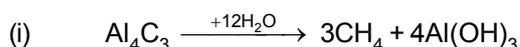


(ix) Corey-House Synthesis :

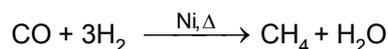


* This method is useful for preparation of alkanes containing odd no. of c-atoms.

Specific methods of preparation of CH₄ :



(iii) **Sabatier Senderen's :**



PHYSICAL PROPERTIES :

(i) Alkanes from C₁-C₄ are gases.
C₅-C₁₇ are liquids, C₁₈ - onwards are waxy, white solids.

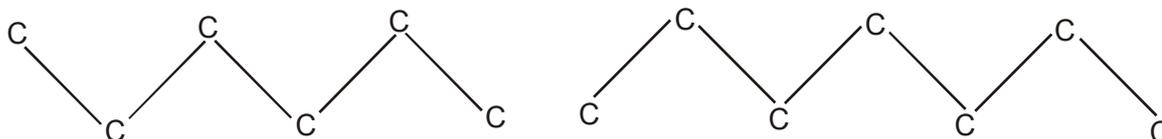
Note : Neopentane is a gas.

(ii) **Boiling point :**

☞ Boiling point \propto molecular weight (for homologes) $\propto \frac{1}{\text{Branches}}$ (for isomers)

e.g. order of boiling point
n-pentane > isopentane > neopentane

(iii) **Melting point :** Alkanes containing even no. of carbon atoms have higher melting points than it's next higher or next lower homologue having odd no. of carbon atoms. It is because of more symmetry of alkane molecules with even no. of carbon atoms as compared to alkanes with odd no. of carbon atoms.



(Both methyl groups are directed in opposite direction) (Both methyl groups are on the same side)

* Alkanes are colourless, odourless and tasteless.

* Alkanes are lighter than water. These are insoluble in water and soluble in organic solvents.

CHEMICAL REACTIONS

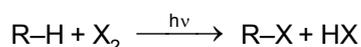
1. Stability
2. Substitution reactions :-
 - (a) Halogenation
 - (b) Nitration
 - (c) Sulphonation
 - (d) Chlorosulphonation (Reed reaction)
3. Oxidation :
4. Cracking / Pyrolysis :
5. Isomerisation
6. Aromatization
7. Addition of CH_2

1. Stability

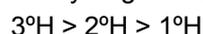
Although alkanes are chemically unreactive under ordinary conditions due to the presence of strong C–C and C–H sigma (σ) bonds, yet they give following reactions under special conditions

2. Substitution Reaction

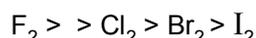
(a) Halogenation :



* Reactivity order of hydrogen atoms in alkanes is



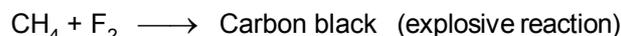
* Reactivity order of halogens is



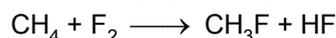
Fluorine can react in dark. Cl_2 and Br_2 require light energy. I_2 does not show any reaction at room temperature, on heating it shows iodination.

☞ Fluorination –

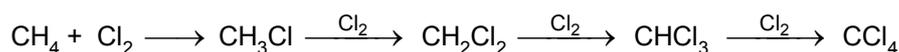
* Direct-fluorination of alkanes is usually explosive.



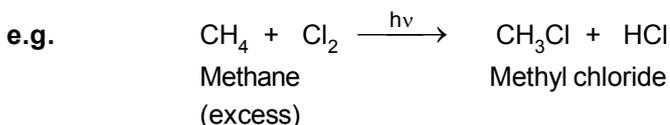
* It is carried out successfully by diluting fluorine with nitrogen (Inert gas).



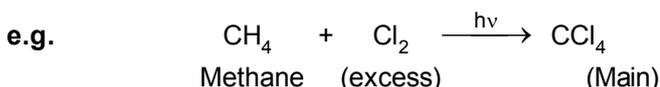
☞ Chlorination –



★ The monochloro derivative of alkane is obtained as a major product by taking alkane in excess.



* When chlorine is in excess, carbon tetrachloride will be the major product.



Chlorination of alkanes takes place in the following conditions.

* No reaction at room temperature in darkness.

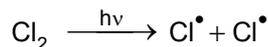
* At 300°C in darkness.

* At 100°C in the presence of organic peroxides.

* At 150°C in the presence of Tetra ethyl lead

⇒ Chlorination of methane is based on free radical mechanism and it completes in the following three steps :

(a) Chain initiating (first) step



(b) Chain propagating (second) step



(c) Chain terminating (third) step



☞ **Bromination** : Bromination of alkanes is similar to chlorination but not so vigorous.

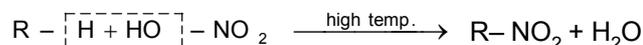
☞ **Iodination** : Iodination of alkanes is slow and reversible.



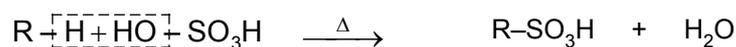
* Iodination may be carried out in the presence of an oxidising agent such as HIO_3 , HNO_3 , HgO , etc. which destroys the HI as it is formed and so drives the reaction to the right.



(b) **Nitration** : When a mixture of vapour of alkane nitric acid is heated at high temperature ($400^\circ\text{C} - 450^\circ\text{C}$) a mixture of all possible nitroalkanes is obtained (The reaction involves both C–C and C–H bond cleavage).



(c) **Sulphonation** : In this reaction, hydrogen atom of the C–H bond is replaced by $-\text{SO}_3\text{H}$ group.



(Fuming)

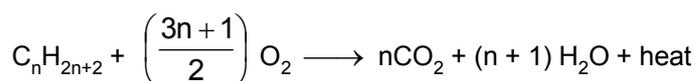
Alkane sulphonic acid

* Fuming H_2SO_4 = mixture of SO_3 + Conc. $\text{H}_2\text{SO}_4 = \text{H}_2\text{S}_2\text{O}_7$ (Oleum)

* Alkanes containing 6 or more carbon atom and lower branched alkenes (not lower unbranched) can be sulphonated).

Oxidation

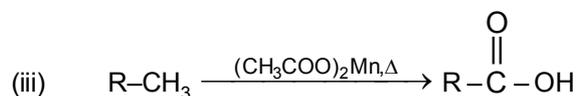
(a) **Complete oxidation or combustion** : All alkanes readily burn in excess of air or oxygen to form CO_2 and H_2O .



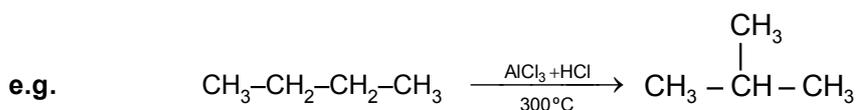
☞

$$\frac{\text{Volume of alkane}}{\text{Volume of oxygen}} = \frac{2}{3n+1}$$

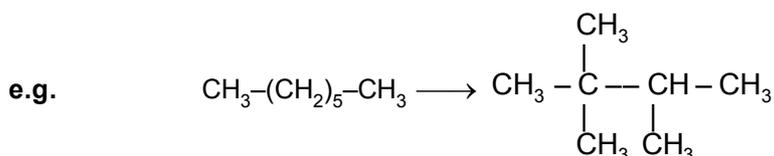
(b) Catalytic oxidation :



(5) Isomerisation : Straight chain alkanes are converted into their branched chain isomers when heated in the presence of $\text{AlCl}_3 + \text{HCl}$ at 300°C .



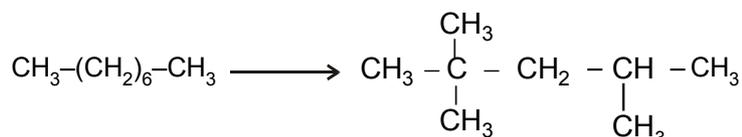
*If we take n-heptane then it converts into highly branched alkane (triptane).



n-heptane

Triptane [2,2,3-Trimethyl butane]

*If we take n-octane then it converts into most stable form iso-octane.

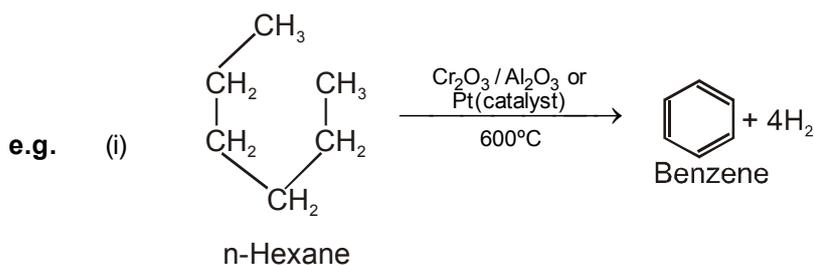


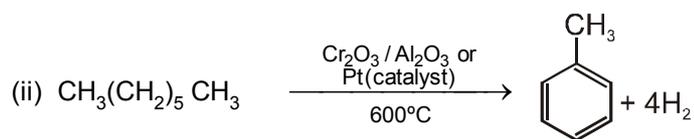
n-Octane

iso-octane [2,2,4-Trimethyl pentane]

*Isomerisation of alkanes is of great importance in petroleum industry to increase the octane number of petrol (gasoline).

(6) Aromatization, hydroforming or catalytic reforming : The conversion of aliphatic compounds into aromatic compound is referred to as aromatization. Alkanes having six or more carbon atoms are heated at 600°C in the presence of a catalyst such as Cr_2O_3 supported over alumina or Pt, an aromatic hydrocarbon results.



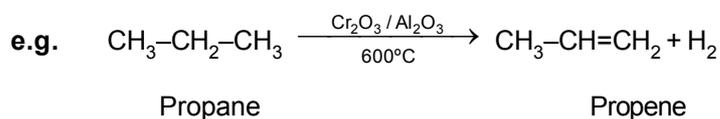


n-Heptane

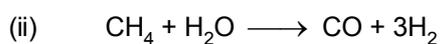
Toluene

* Aromatization involves cyclization and dehydrogenation.

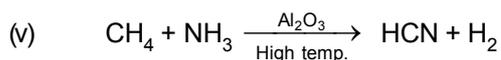
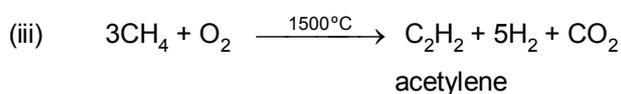
Dehydrogenation :



Special properties of CH₄



Synthetic gas



Important points :

*Methan is also called marsh gas or damp fire.

*CNG (Compressed naturel gas) \Rightarrow CH₄ + propane + butane + Higher alkane. 84%

*LPG is called as liquified petroleum gas or kitchen gas or domestic gas.(Mixture of liquid propane + liquid butane and other liquid paraffines)

*The mixture of n-butane and isobutane called calor gas.

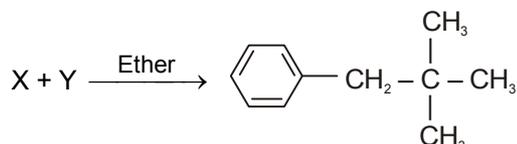
EXERCISE # 1

PART - I : OBJECTIVE QUESTIONS

* Marked Questions are having more than one correct option.

Section (A) : Grignard's Reagents

A-1. The best yield of given product can be obtained by using which set of reactants X and Y respectively :



- (A) PhLi + Neopentyl chloride
 (B) PhMgBr + Neopentyl bromide
 (C) t-Bu - MgBr + Benzyl bromide
 (D) Benzylchloride + t-Butyl chloride $\xrightarrow{\text{Na}}$

A-2. The order of reactivity of alkyl halide in the reaction $R - X + \text{Mg} \longrightarrow \text{RMgX}$ is :

- (A) RI > RBr > RCl (B) RCl > RBr > RI (C) RBr > RCl > RI (D) RBr > RI > RCl

A-3. On conversion into Grignard followed by treatment with ethanol, how many alkyl halides (excluding stereoisomers) would yield 2-methyl butane.

- (A) 2 (B) 3 (C) 4 (D) 5

A-4*. Which of the following reacts with Grignard reagent to give alkane?

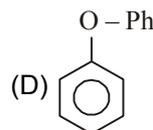
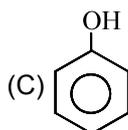
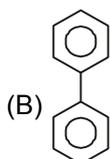
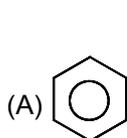
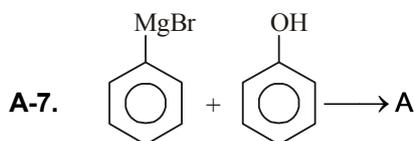
- (A) nitro ethane (B) acetyl acetone (C) acetaldehyde (D) acetone

A-5. How many litres of methane would be produced when 0.595 g of CH_3MgBr is treated with excess of $\text{C}_4\text{H}_9\text{NH}_2$

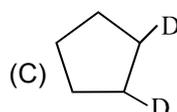
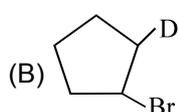
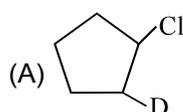
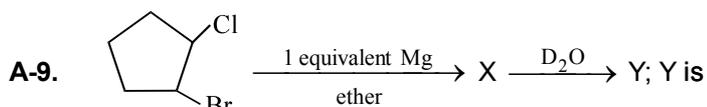
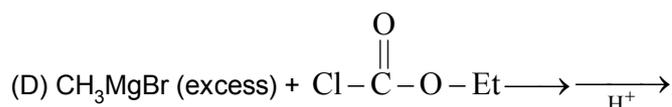
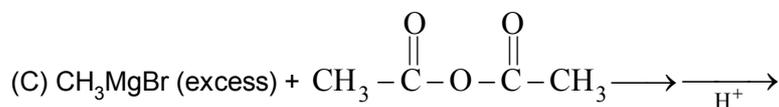
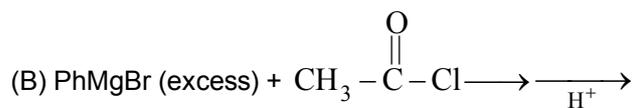
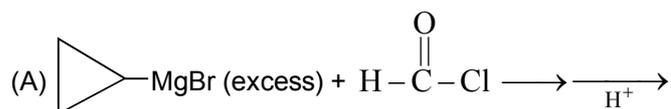
- (A) 0.8 litre (B) 0.08 litre (C) 0.112 litre (D) 1.12 litre

A-6. How many litres of ethene would be produced when 2.62 g of vinyl magnesium bromide is treated with 224 mL of ethyne at STP.

- (A) 0.224 litre (B) 0.08 litre (C) 0.448 litre (D) 1.12 litre

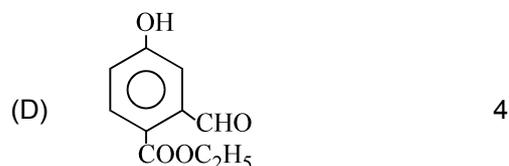
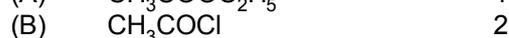
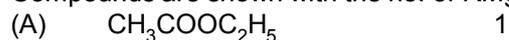


A-8*. In which of the following reactions 3° alcohol will be obtained as a product.

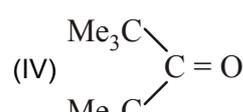
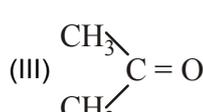
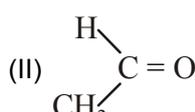
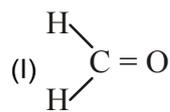


(D) None of these

A-10. Compounds are shown with the no. of RMgX required for complete reaction, select the incorrect option



A-11. What will be the order of reactivity of the following carbonyl compounds with Grignard's reagent?



(A) I > II > III > IV

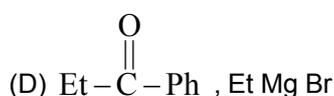
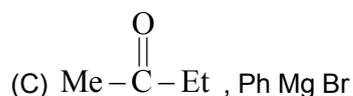
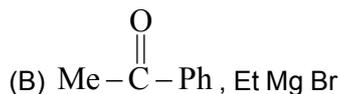
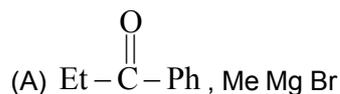
(B) IV > III > II > I

(C) II > I > IV > III

(D) III > II > I > IV

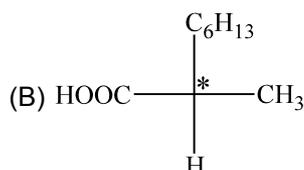
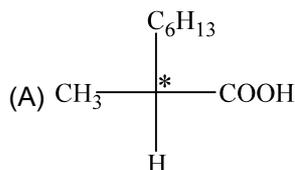


X, Y will be :





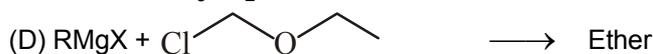
X is :



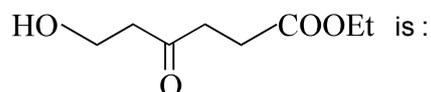
(C) A and B both

(D) None of these

A-14. In which one of the following reaction products are not correctly matched in :



A-15. The number of moles of grignard reagent consumed per mole of the compound



(A) 4

(B) 2

(C) 3

(D) 1

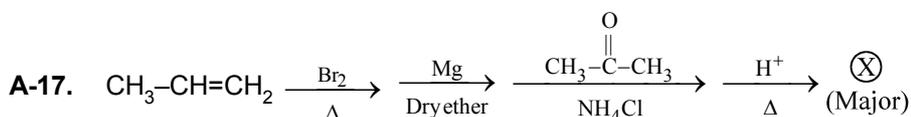
A-16*. Select the correct statement :

(A) 1,4-dibromobutane react with excess of magnesium in ether to generate di-Grignard reagent.

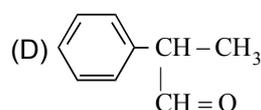
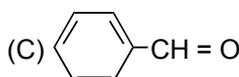
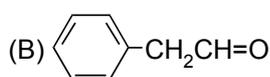
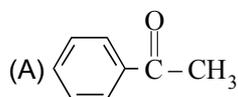
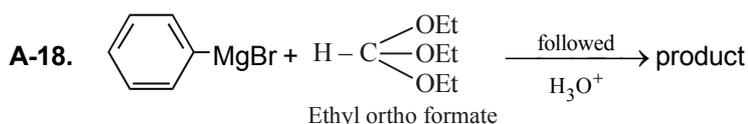
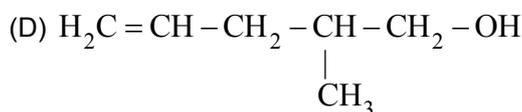
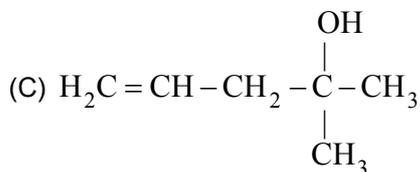
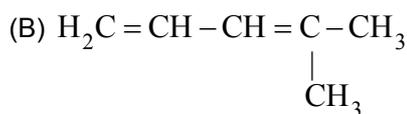
(B) 1,2-dichlorocyclohexane treated with excess of Mg in ether produces cyclohexene.

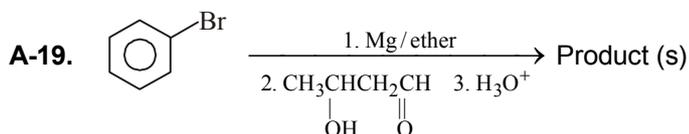
(C) Vicinal dihalides undergo dehalogenation to give alkene when heated with Zn dust or Mg.

(D) 1,3-dichloropropane by treatment with Zn dust or Mg forms cyclopropane.

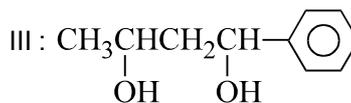
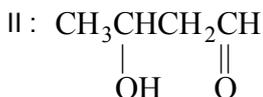
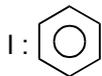


End product of above reaction is :





Select the product from the following :

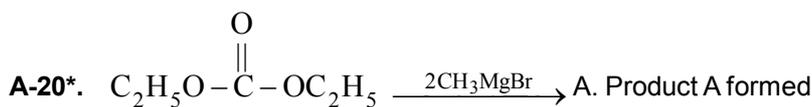


(A) III

(B) I, III

(C) I, II

(D) II, III



(A) is ethyl acetate

(B) further react with $\text{CH}_3\text{MgBr}/\text{H}_2\text{O}^+$ to give acetone

(C) further react with $\text{CH}_3\text{MgBr}/\text{H}_2\text{O}^+$ to give t-butyl alcohol

(D) Can give pinacol when treated with Mg followed by H_2O

Section (B) : Reduction



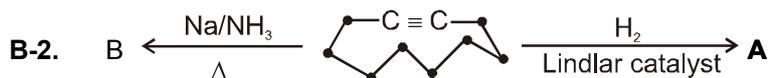
A and B are geometrical isomers ($\text{R}-\text{CH}=\text{CH}-\text{R}$) :

(A) A is trans, B is cis

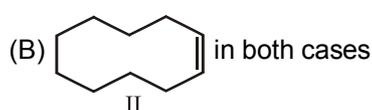
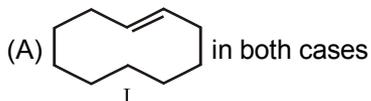
(B) A and B both are cis

(C) A and B both are trans

(D) A is cis, B is trans

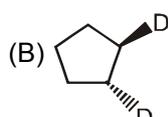
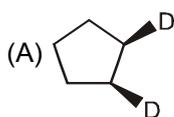
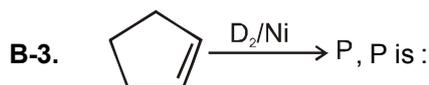


A and B are :



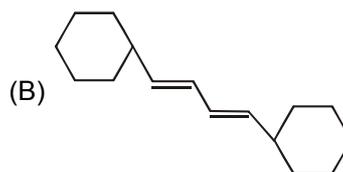
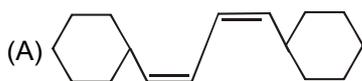
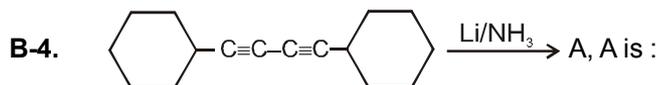
(C) A is I, B is II

(D) A is II, B is I



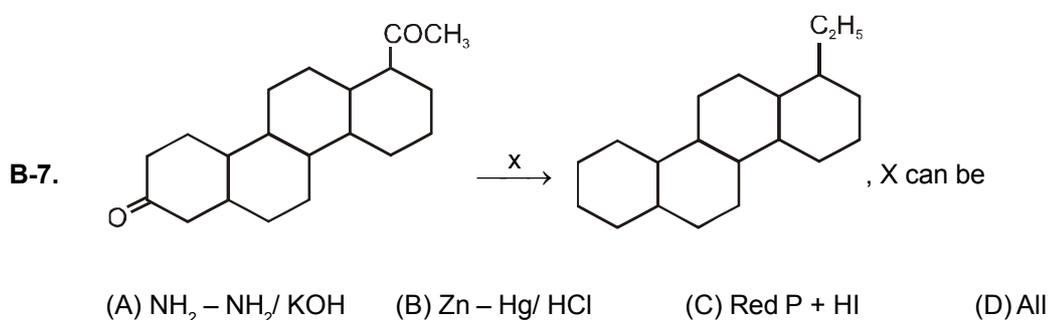
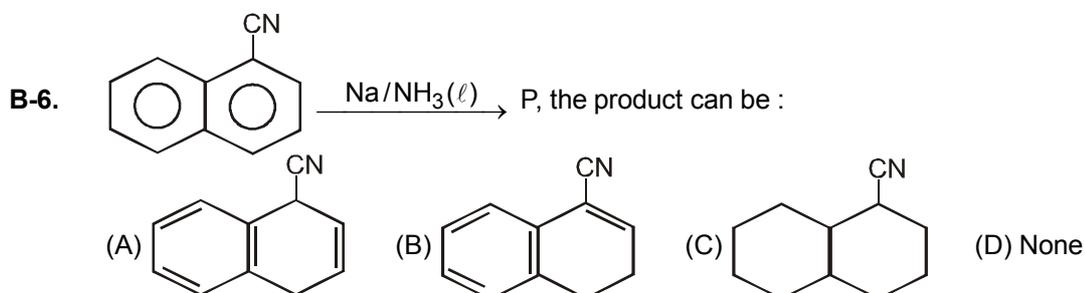
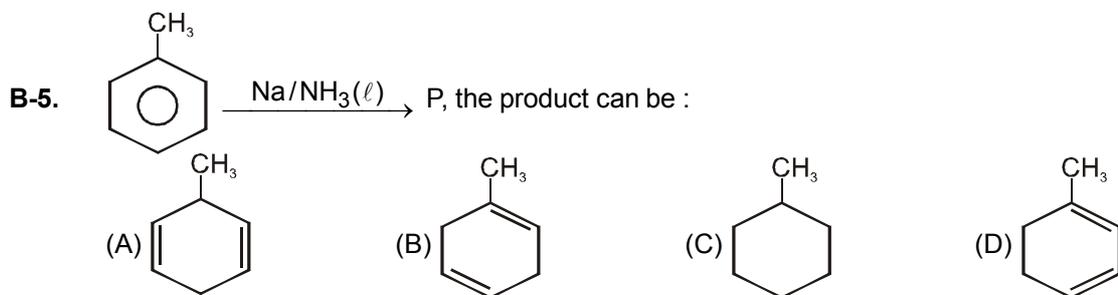
(C) both are correct

(D) None



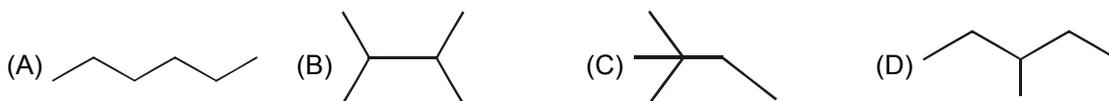
(C) Both (A) and (B)

(D) None of these

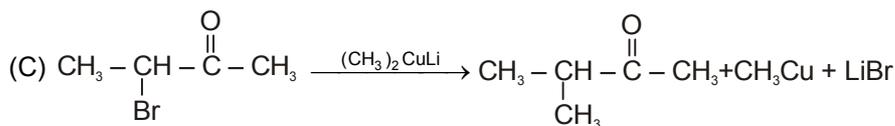
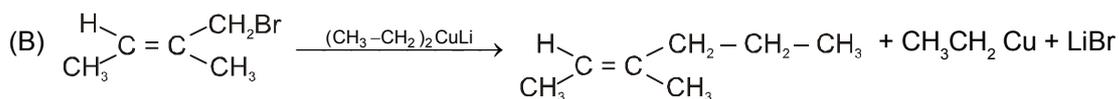
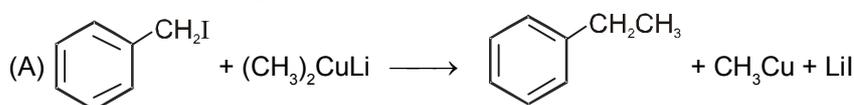


Section (C) : Preparation of alkane

C-1. C_6H_{12} (A) has two types of alkenes that can be reduced to one type of C_6H_{14} (B). B is:



C-2. Which of the following reaction is correct ?



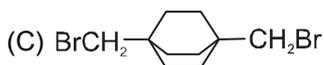
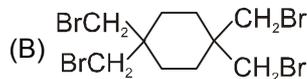
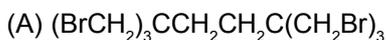
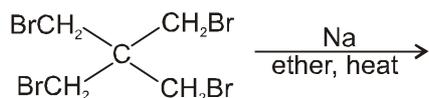
(D) All of these

C-3. Which of the following alkanes can be synthesized by the Wurtz reaction in good yield ?

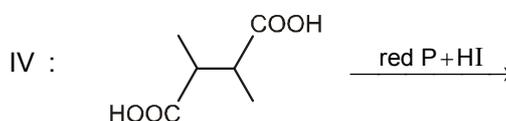
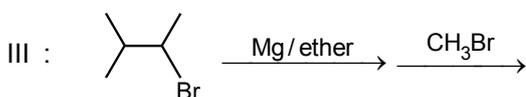
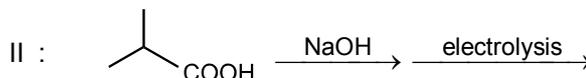
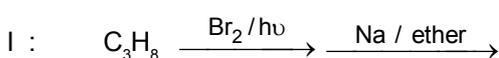
- (A) $(\text{CH}_3)_2\text{CH} - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$
 (C) $\text{CH}_3 - \text{CH}_2 - \text{C}(\text{CH}_3)_2\text{CH}_2 - \text{CH}_3$

- (B) $(\text{CH}_3)_2\text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$
 (D) $(\text{CH}_3)_3\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$

C-4. The product formed in the reaction



C-5. Which of the following reaction produces the same product :



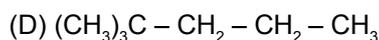
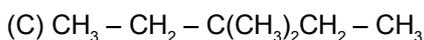
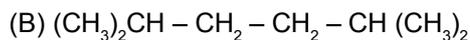
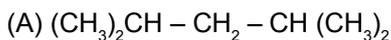
(A) I, & II

(B) I, II, III & IV

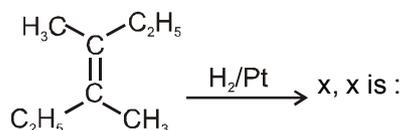
(C) I, III & IV

(D) II, III & IV

C-6. Which of the following alkanes can be synthesized by the Wurtz reaction in good yield ?



C-7.



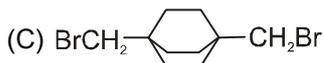
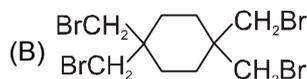
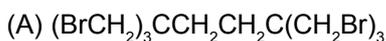
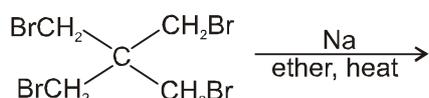
(A) Only (R,R) product

(B) Only (S,S) product

(C) Meso compound

(D) Racemic mixture

C-8. The product formed in the reaction



C-9. During the preparation of ethane by Kolbe's electrolytic method using inert electrodes the pH of the electrolyte:

(A) Increases progressively as the reaction proceeds

(B) Decreases progressively as the reaction proceeds

- (C) Remains constant throughout the reaction
 (D) May decrease of the the concentration of the electrolyte is not very high

C-10. $\text{BrCH}_2\text{-CH}_2\text{-CH}_2\text{Br}$ reacts with Na in the presence of ether at 100°C to produce :

- (A) $\text{BrCH}_2\text{-CH=CH}_2$ (B) $\text{CH}_2=\text{C=CH}_2$ (C) $\begin{array}{c} \text{CH}_2\text{-CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$ (D) All of these

Section (D) : Reactions of Alkane

D-1. Which statement is incorrect about free radical halogenation of alkanes –

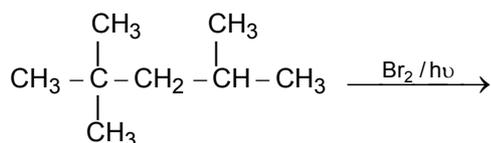
- (A) The number of product molecules formed by one photon is very high
 (B) If O_2 is added, initially the rate of reaction decreases, then it increases
 (C) Inhibitors combine with free radical and terminate the chain reaction
 (D) presence of $\text{C}_6\text{H}_5\text{-CO-OC-C}_6\text{H}_5$ inhibits the free radical reaction.



D-2. The number of possible enantiomer pairs that can be produced during monochlorination of 2-methylbutane is :

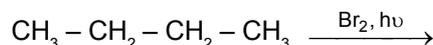
- (A) 2 (B) 3 (C) 4 (D) 1

D-3. For the given reaction how many products are optically active (all isomers) :



- (A) 1 (B) 2 (C) 3 (D) 4

D-4. Which statement is correct about photochemical bromination of Butane



- (A) 1-Bromobutane and 2-Bromobutanes are formed in equal amounts.
 (B) 2-Bromobutane is formed with faster rate than 2-chlorobutane in the other experiment of chlorination.
 (C) The major product is an equimolar mixture of two compounds
 (D) Homolysis of C – H bond has lower activation energy than homolysis of Br – Br bond.

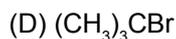
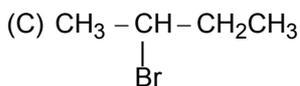
D-5. Write correct reactivity order towards photochemical chlorination.



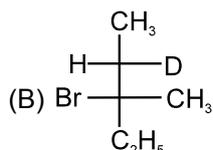
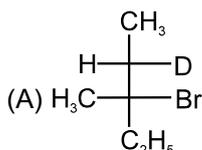
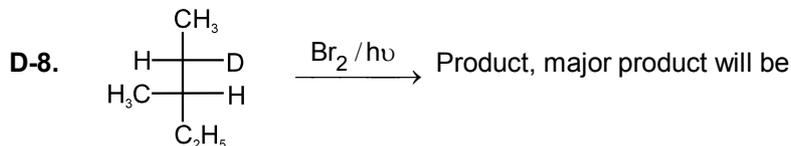
- (A) $X > Y > Z > W$ (B) $Y > X > Z > W$ (C) $X > Z > W > Y$ (D) $Z > W > Y > X$

D-6. Formation of free radical takes place with absorption of minimum energy in the case of :

- (A) $\text{CH}_3\text{-(CH}_2\text{)}_2\text{-CH}_2\text{Br}$ (B) $(\text{CH}_3\text{)}_2\text{CHCH}_2\text{Br}$

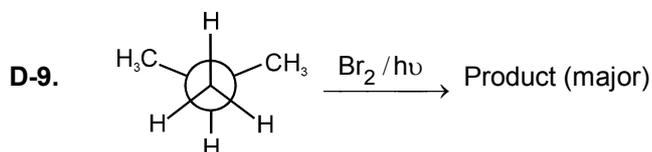


- D-7.** What is the chief product obtained when n-butane is treated with Br_2 in the presence of light at 130°C ?
 (A) $\text{CH}_3 - \text{CH}_2 - \text{CHBr} - \text{CH}_3$ (B) $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$
 (C) $(\text{CH}_3)_3\text{CBr}$ (D) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Br}$

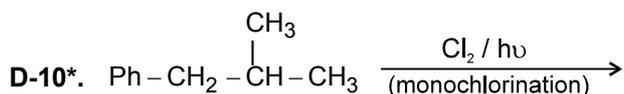
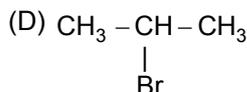
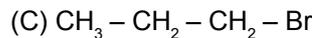
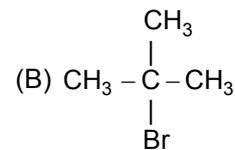
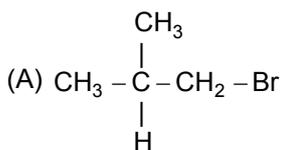


(C) Both A and B

(D) none of above



Identify the major product.



Which statements is/are correct about photochemical chlorination of the above compound

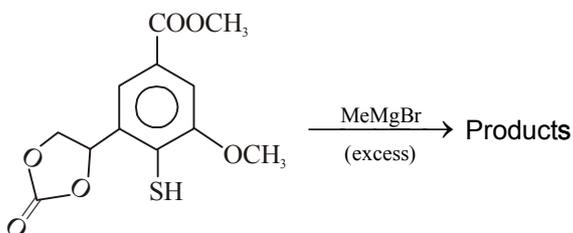
- (A) The major product will have chiral carbon atom but is optically inactive.
 (B) The intermediate free radical of the major product is resonance stabilised.
 (C) The intermediate free radical is tertiary for major product.
 (D) The intermediate free radical is planar, and stabilised by only hyperconjugation.

PART - II : MISLLANEOUS QUESTIONS

COMPREHENSION

Comprehension # 1

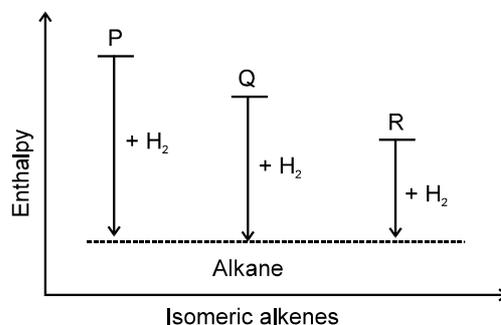
Consider the given reaction and answer the following questions.



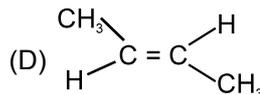
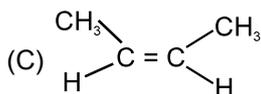
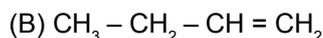
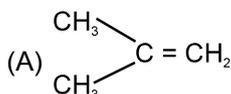
- Number of RMgX consumed in the reaction is :
 (A) 4 (B) 5 (C) 6 (D) 7
- How many product will be formed in given reaction (excluding stereo) :
 (A) 2 (B) 3 (C) 4 (D) 5
- Which of the following reaction will give the same Hydrocarbon formed as one of the product in the above reaction.
 (A) $\text{EtMgBr} + \text{Me} - \text{OH} \longrightarrow$ (B) $\text{PhMgBr} + \text{Me} - \text{OH} \longrightarrow$
 (C) $\text{MeMgBr} + \text{Ph} - \text{OH} \longrightarrow$ (D) $\text{MeMgBr} + \text{CH}_3 - \text{CHO} \longrightarrow$

Comprehension-2

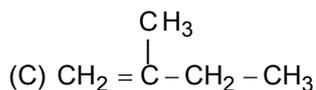
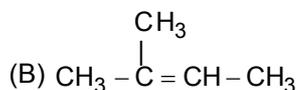
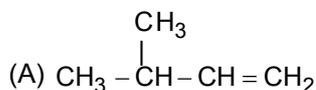
The addition of hydrogen to an alkene is an exothermic reaction & the enthalpy change is called the heat of hydrogenation. More branched alkenes are more stable and have less potential energy. The alkene having higher potential energy releases more heat on hydrogenation. In the figure the enthalpy changes of three isomeric alkenes has been shown.



- From the above statement & graph identify P if P, Q & R are the isomers of butene.



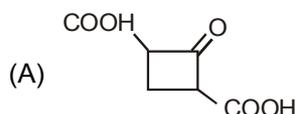
- Which of the following can be R if P, Q and R are isomeric pentenes ?



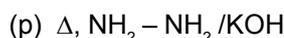
Match the column

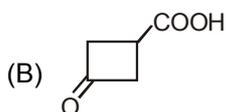
- Match the reactants given in Column-I with the reagent given in Column-II of reagent in the preparation of cyclobutane

Column-I

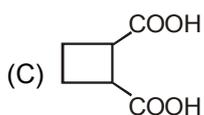


Column-II

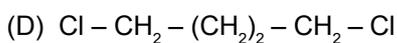




(q) Na/ ether



(r) NaOH/CaO/ Δ , Zn-Hg/HCl

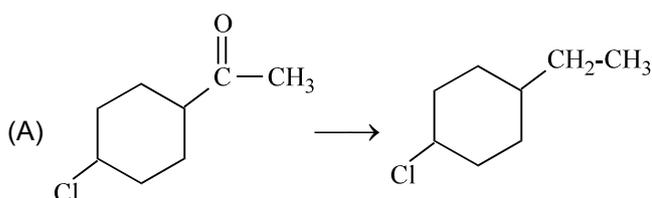


(s) Electrolysis, H_2/Ni

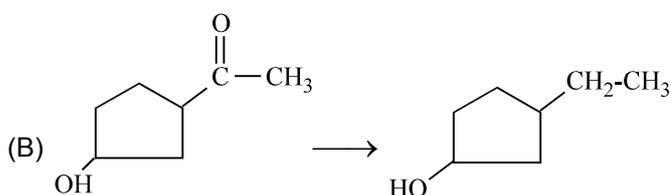
7. Match the column

Column I

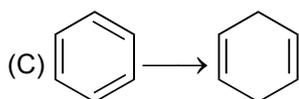
Column II



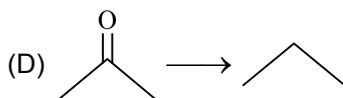
(P) Birch reduction



(Q) Stephen's reduction



(R) Wolf-Kishner reduction

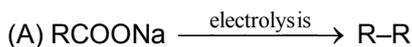


(S) Clemmensen reduction

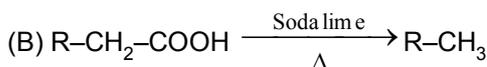
8. Match the column

Column I

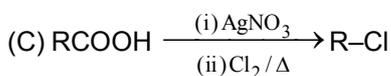
Column II



(P) Corey-House reaction



(Q) Kolbe electrolysis



(R) Oakwood degradation



(S) Hunsdiecker reaction

Assertion / Reasoning

DIRECTIONS :

Each question has 5 choices (A), (B), (C), (D) and (E) out of which ONLY ONE is correct.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False.

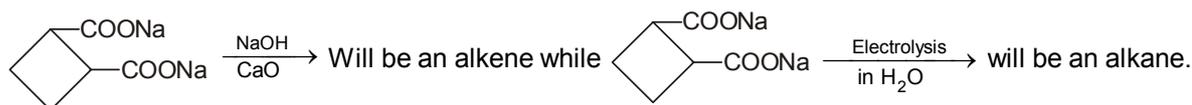
(D) Statement-1 is False, Statement-2 is True.

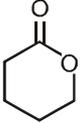
(E) Statement-1 and Statement-2 both are False.

9. **Statement-1:** In the bromination of propane and 2-Methyl propane. 2-Methyl propane gives more stable transition state.
Statement-2: 3° C–H bond is weaker than 2° C – H bond.
10. **Statement-1 :** In the free radical reaction, reaction slow down for the peroid of time during which inhibitor exists and after which the reaction proceed normally.
Statement-2 : Oxygen as inhibitor slow down the reaction for some times.
11. **Statement-1 :** The melting point of neopentane is higher than n-pentane but boiling point of neopentane is lower than n-pentane
Statement- 2 : Melting point depends upon packing of molecules whereas boiling point depends upon surface area. Neopentane fits into crystal lattice readily but has minimum surface area.
12. **Statement-1 :** $\dot{\text{Cl}} + \text{CH}_4 \longrightarrow \dot{\text{C}}\text{H}_3 + \text{H} - \text{Cl}$ step (1)
 $\dot{\text{C}}\text{H}_3 + \text{Cl}_2 \longrightarrow \text{CH}_3 - \text{Cl} + \dot{\text{Cl}}$ step (2)
 Step (1) is more difficult than step (2)
Statement-2 : Once formed, methyl radicals react easily with any of the halogen; it is how fast methyl radicals are formed that limit the rate of overall reaction.
13. **Statement-1 :** Grignard reagent can be prepared in all nonpolar solvent.
Statement-2 : Diethyl ether solvates the Grignard reagent.
14. **Statement-1:** In the bromination of propane and 2-Methyl propane. 2-Methyl propane gives more stable transition state.
Statement-2: 3° C–H bond is weaker than 2° C – H bond.
15. **Statement-1 :** The preparation of G.R. occurs in solution phase.
Statement-2 : The reaction will be explosive in solid phase. G.R. is stable only in solution phase.
16. **Statement-1 :** n-butane on heating in presence of AlCl_3 gives Isobutane
Statement-2 : n-butane and isobutane are isomers.
17. **Statement-1 :** Alkanes undergo free radicals substitution reaction
Statement-2 : Alkanes undergo homolytic fission.
18. **Statement-1 :** CH_3MgBr is prepared in cold aqueous solution.
Statement-2 : Water molecule stabilise grignard molecule by H–Bonding.

TRUE I FALSE

19. The product of reaction



20.  can be reduced by, NaBH_4/THF .
21. Reactivity order of different grignard reagent is $\text{CH}_3\text{MgI} > \text{CH}_3\text{MgBr} > \text{CH}_3\text{MgCl}$.
22. Cis alkenes are formed by the reduction of alkyne by use of lindlar's catalyst.
23. H^- attacks on carbon of $\text{>C}=\text{O}$ during reduction by $\text{LiAlH}_4/\text{H}_2\text{O}$.

FILL IN THE BLANKS

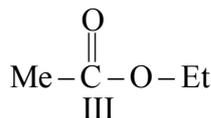
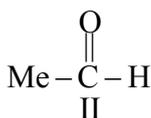
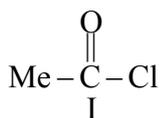
24. R_2CuLi is formed in
25. Reaction of $\text{>C}=\text{O}$ and grignard reagent is addition reaction.
26. Ni_2B is called catalyst.
27. Reaction of H_2 with Ni/Pd/Pt on alkene is
28. Paraffin wax is mixture of
29. In Bouveault Blanc **reduction** reducing species is an

EXERCISE # 2

PART - I : MIXED OBJECTIVE

Single Correct Answer Type

1. Order of rate of reaction of following compound with phenyl magnesium bromide is :



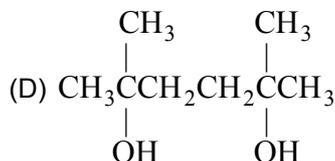
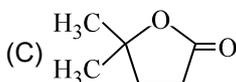
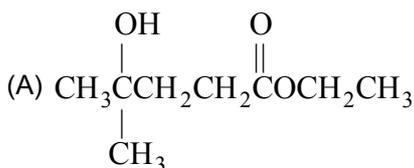
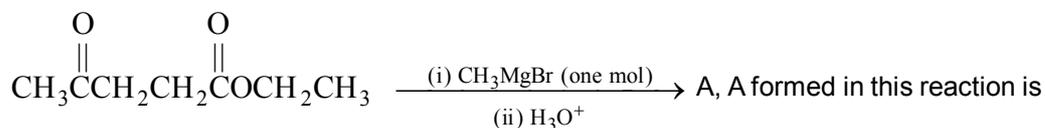
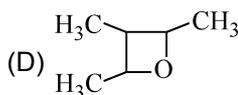
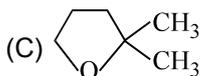
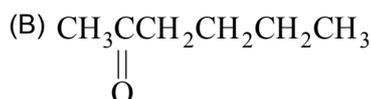
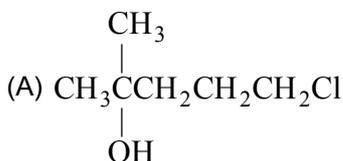
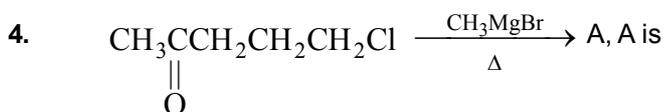
- (A) I > II > III (B) II > III > I (C) III > I > II (D) II > I > III

2. Select the correct order of decreasing reactivity of the following compounds towards the attack of Grignard reagent :

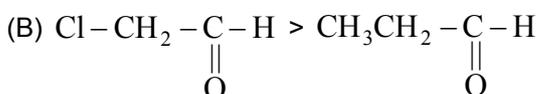
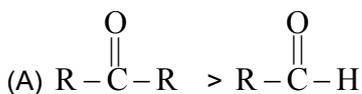
- (I) Methyl benzoate (II) Benzaldehyde (III) Benzoylchloride (IV) Acetophenone
 (A) II > III > I > IV (B) I > II > III > IV (C) III > II > IV > I (D) II > IV > I > III

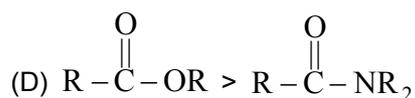
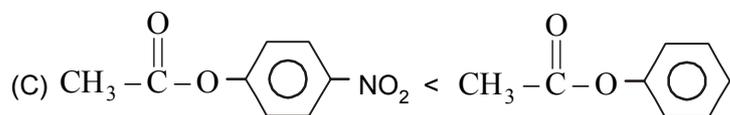


- (A) Enantiomer (B) Diastereomers (C) Meso (D) Achiral

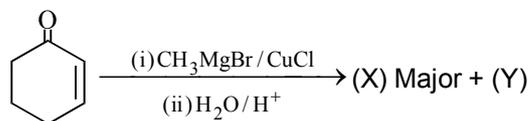


6. Select the correct order of reactivity towards Grignard reagent for nucleophilic attack.

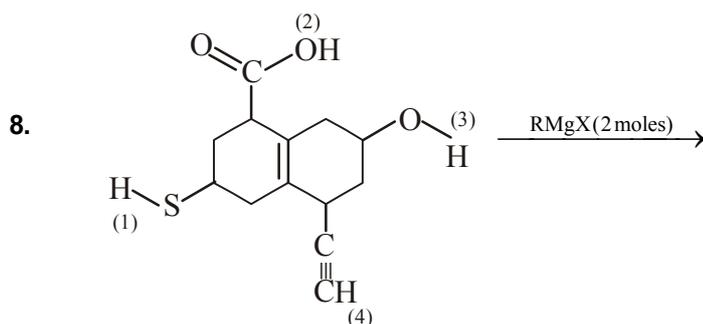
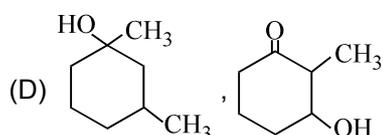
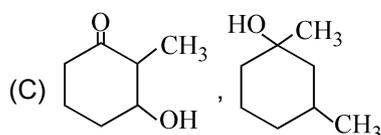
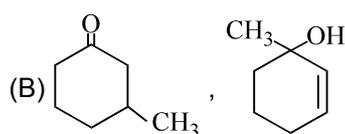
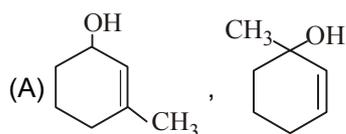




7. In the reaction sequence :

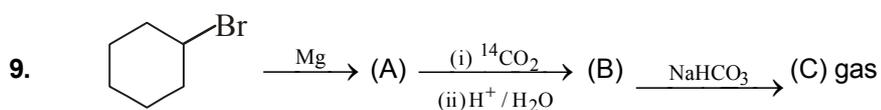


(X) & (Y) respectively are



Deprotonation will occur from the following positions :

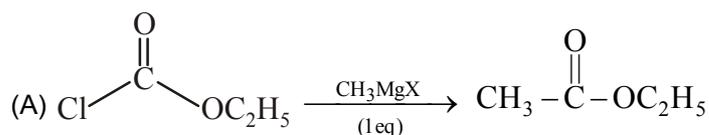
- (A) 1,2 (B) 1,3 (C) any two positions (D) 1,4

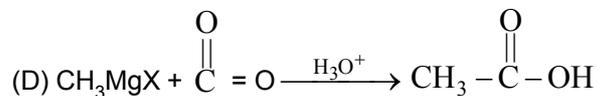
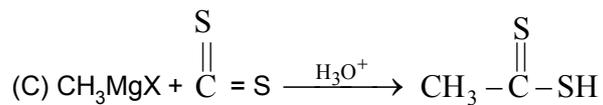
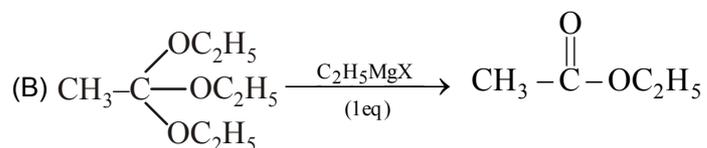


Product C is :

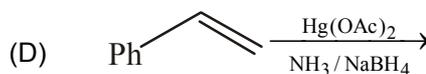
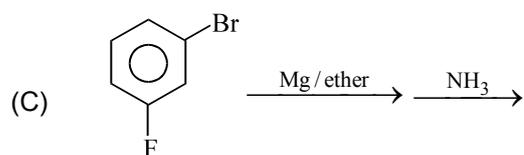
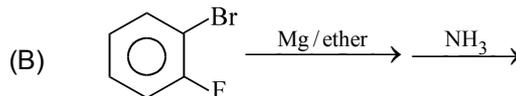
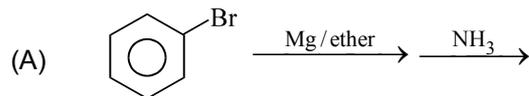
- (A) CO (B) $^{14}\text{CO}_2$
 (C) CO_2 (D) A mixture of $^{14}\text{CO}_2$ and CO_2

10. Which of the following is incorrect.

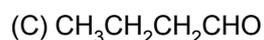
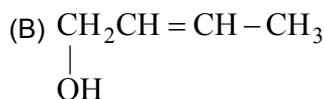
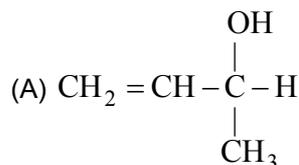




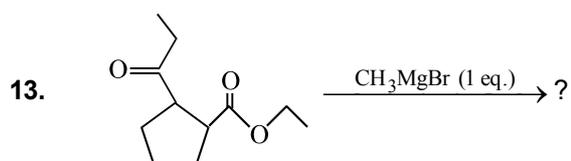
11. Which reaction gives 1° aromatic amine as major product.



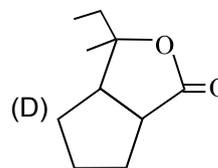
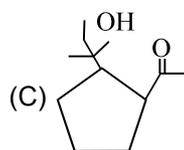
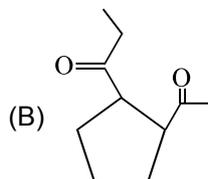
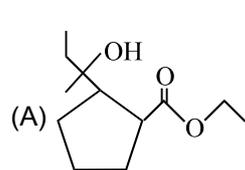
12. $\text{CH}_3\text{MgBr} + \text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \xrightarrow{\text{H}_3\text{O}^+}$ Product (1, 4 addition). It is :



(D) none



The product is :



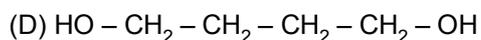
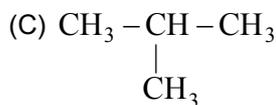
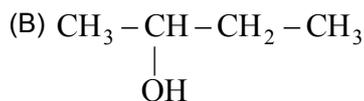
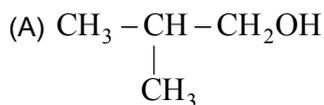
14. $\text{RMgX} \xrightarrow[\text{(ii)NH}_4\text{Cl}]{\text{(i)CH}_3\text{CN}}$ (A) $\xrightarrow[\text{NH}_4\text{Cl}]{\text{RMgX}}$ (B) will be :

(A) 1° ROH

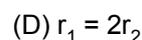
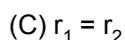
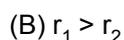
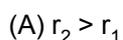
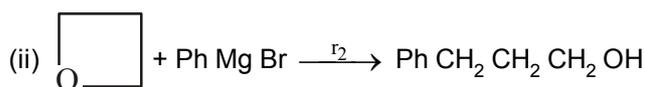
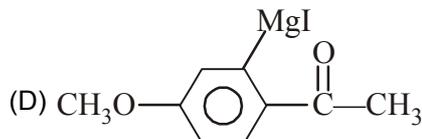
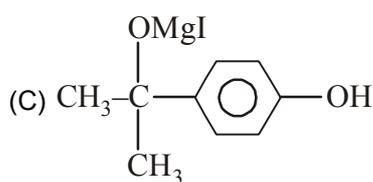
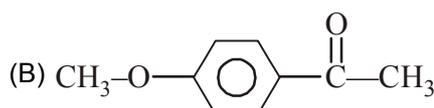
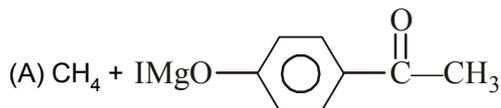
(B) 2° ROH

(C) 3° ROH

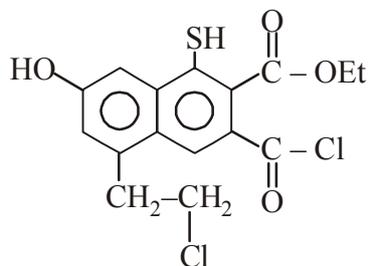
(D) Alkene



16. The reaction of 1 mole each of p-hydroxy acetophenone and methyl magnesium iodide will give :



18. How many moles of Grignard reagent will be required by one mole of given compound?



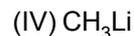
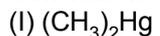
(A) 7

(B) 6

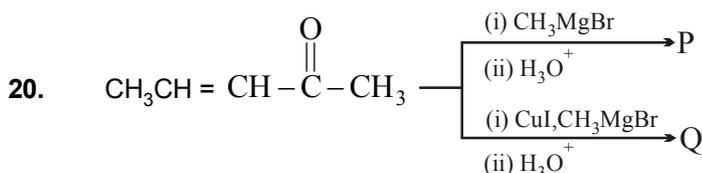
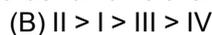
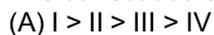
(C) 8

(D) 5

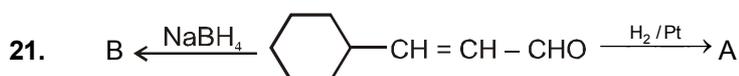
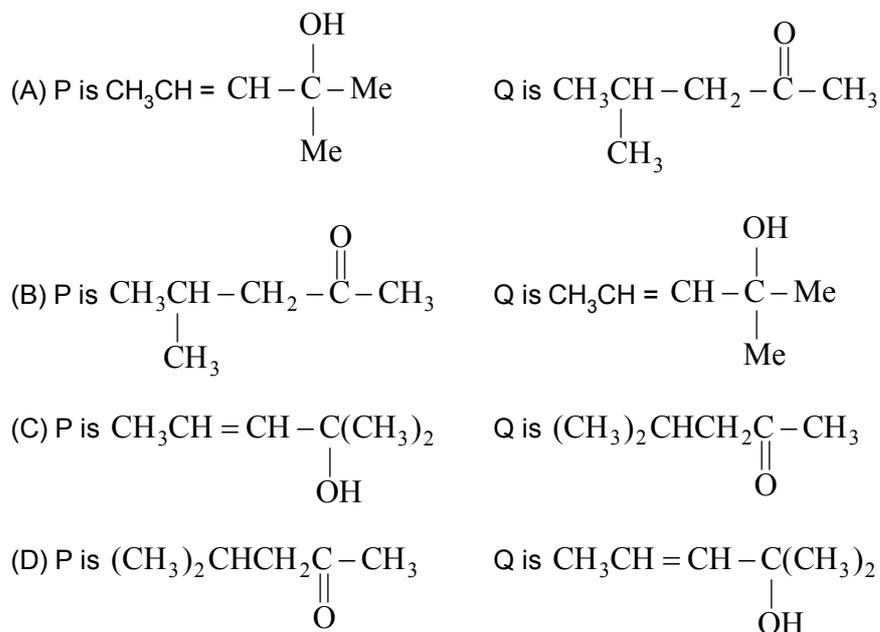
19. Consider the given organometallic compound.



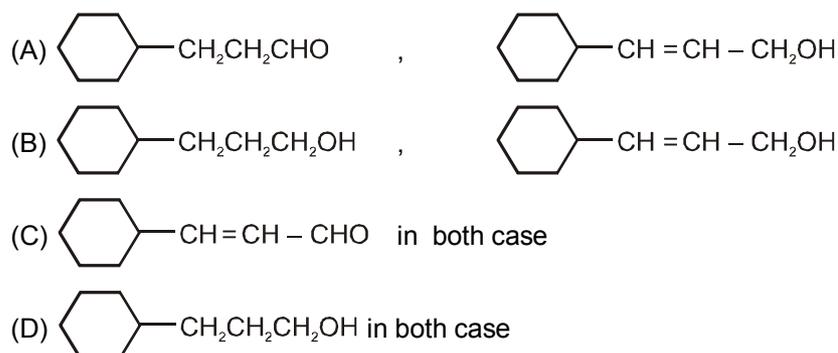
The correct decreasing order of ionic character is :



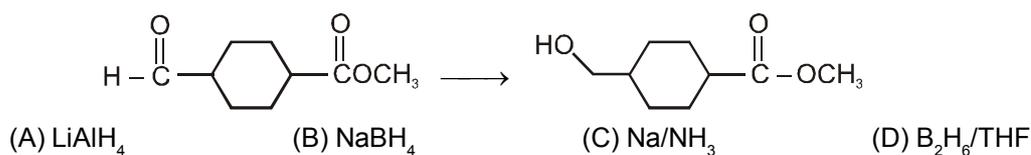
P & Q are respectively :



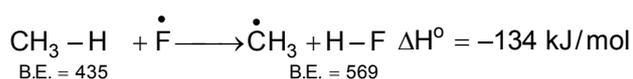
A and B are respectively :

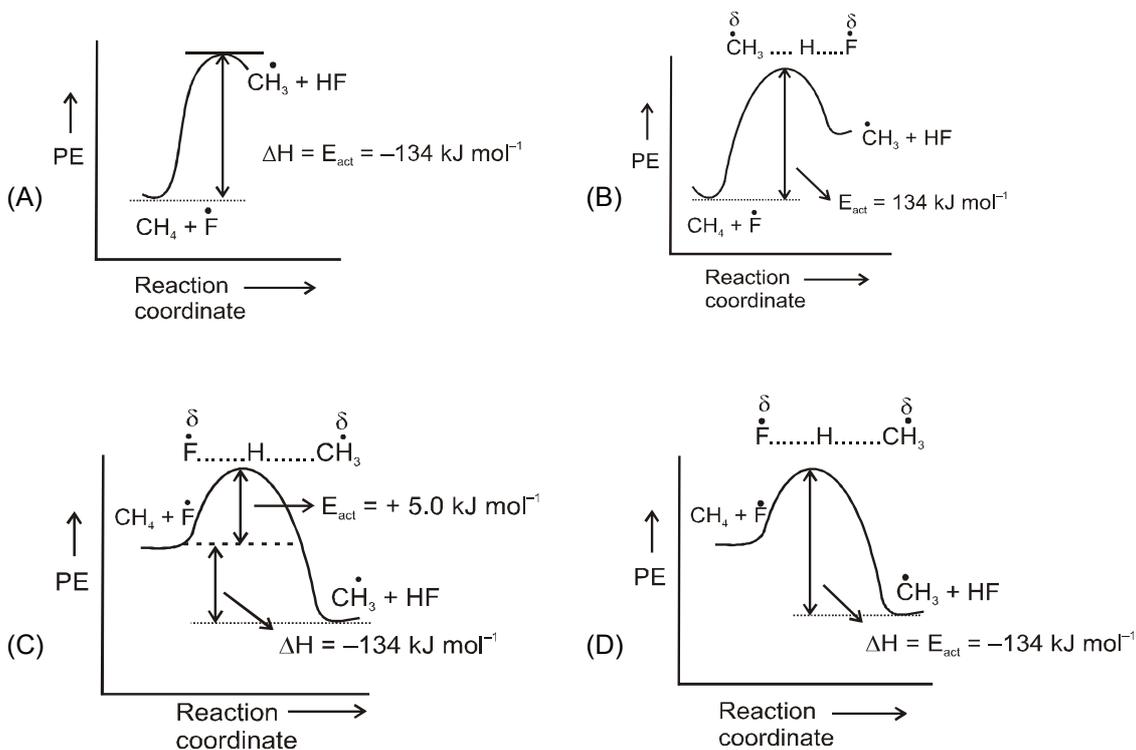


22. Which reducing agent, would you use to carry out the following transformation.



23. Which of the following is correct potential energy diagram for the given chain propagating step.



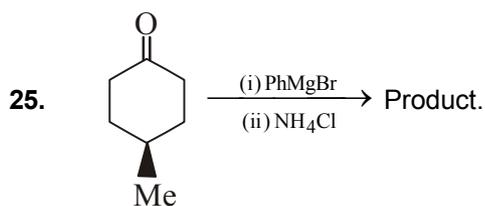


24. An isomer of C_5H_{12} gives total six isomeric products on monochlorination. Calculate the percentage yield of the primary monochloride which is chiral. Consider the following relative reactivity of C – H bonds for chlorination.

Degree of C – H	1° C – H	2° C – H	3° C – H
Relative reactivity for chlorination (RR)	1	3	5

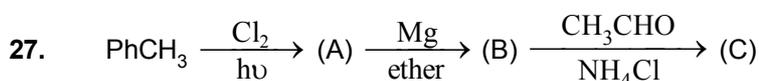
- (A) 26.8% (B) 25% (C) 30% (D) 50%

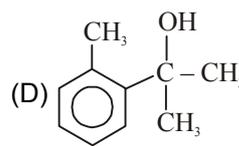
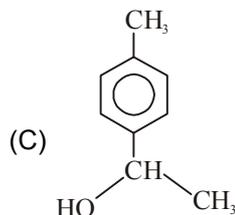
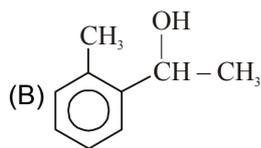
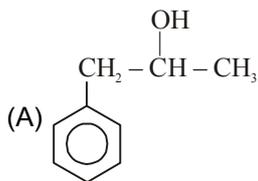
More than one choice type



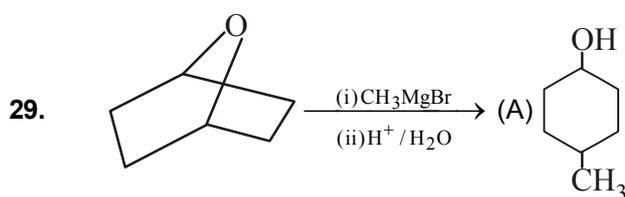
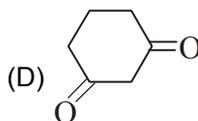
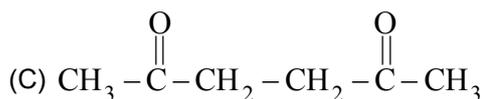
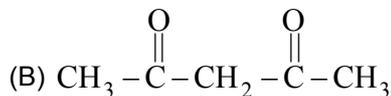
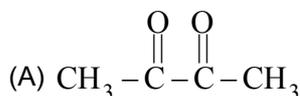
Products in this reaction will be

- (A) Stereoisomers (B) Enantiomer (C) Diastereomers (D) Geometrical isomers
26. $2CH_3MgBr \xrightarrow[\text{(ii) H}^+]{\text{(i) CH}_3\text{ONH}_2}$
- (A) $CH_3-O-NH-CH_3$ (B) $CH_3-NH-CH_3$ (C) CH_3-NH_2 (D) CH_3-OH





28. Nucleophilic addition of Grignard reagent cannot occur in :



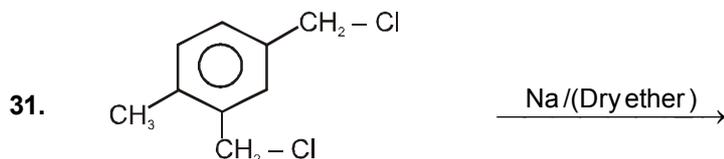
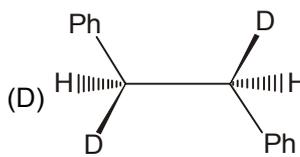
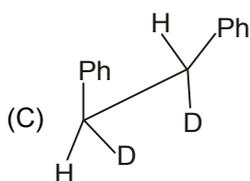
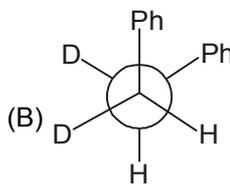
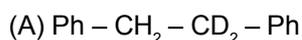
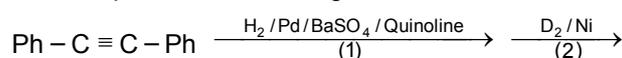
(A) The product is optically active

(B) The product contains plane of symmetry

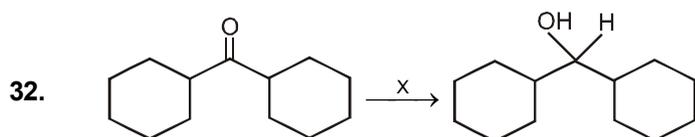
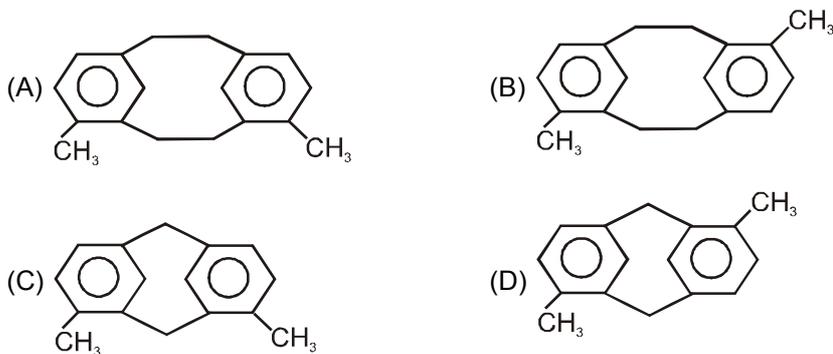
(C) The product shows geometrical isomerism.

(D) The product shows optical isomerism.

30. The end product of following reaction is :



Products obtained in above Wurtz reaction is :



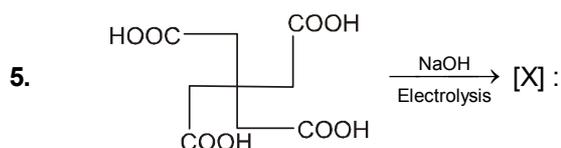
X is / are ?

- (A) $\text{NaBH}_4/\text{EtOH}$ (B) $\text{LiAlH}_4/\text{THF}$ (C) $\text{Al}(\text{OPr}^i)_3/\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$ (D) Red P + HI

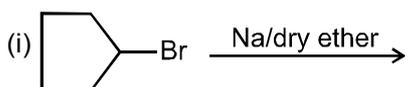
33. Photochemical fluorination is explosive while iodination is too slow to occur. The reason for this is
 (A) Bond dissociation energy of I_2 is minimum
 (B) Formation of CH_3-F is most exothermic
 (C) Formation of $\text{H}-\text{F}$ is most exothermic while formation of $\text{H}-\text{I}$ is endothermic
 (D) F_2 has lower bond dissociation energy than Cl_2 or Br_2

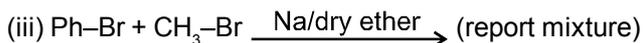
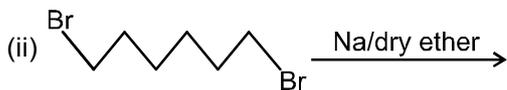
PART - II : SUBJECTIVE QUESTIONS

- How do you account for formation of ethane during chlorination of methane.
- How many alkanes of molecular weight 100 are chiral ?
- Sodium salt of which acid will be needed for preparation of propane ? Write chemical equation for the reaction.
- Prepare butane from chloroethane using the Corey-House synthesis.

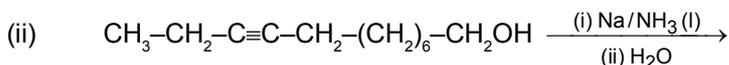
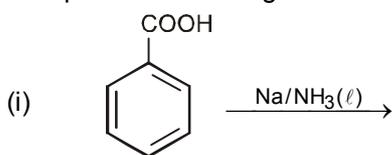


6. Write the major product of following reactions.

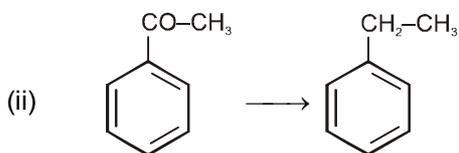
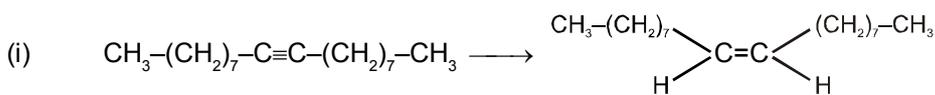




7. Sodium salt of which acid will be needed for preparation of propane ? Write chemical equation for the reaction.
8. Prepare butane from chloroethane using the Corey-House synthesis.
9. How is the following conversion carried out ?
Propanoic acid to 1-propanol
10. How will you convert
(i) Benzoyl chloride to benzaldehyde
(ii) Propanone to 2-propanol
11. Complete the following reactions :

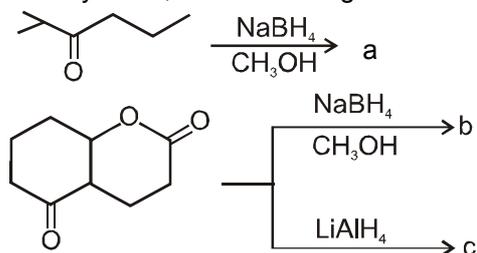


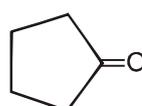
12. Give reaction conditions (reagents and/or catalyst) for effecting the following conversions :



13. An organic compound (A) which have molecular formula $\text{C}_2\text{H}_4\text{O}$ and reduced by Zn-Hg / HCl to give an hydrocarbon (B) C_2H_6 . Identify (A) and (B).

14. Identify a to c, in the following reaction :



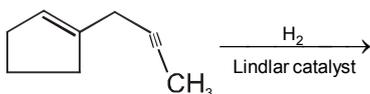
15.  $\xrightarrow{\text{Zn-Hg/HCl}}$ A, A is ?

EXERCISE # 3

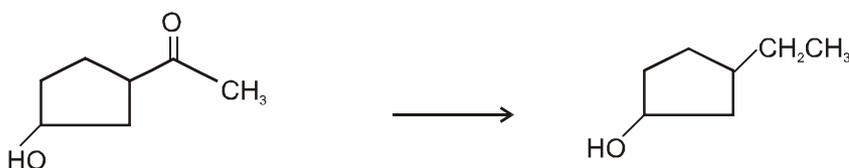
PART - I : IIT-JEE PROBLEMS (PREVIOUS YEARS)

* Marked Questions are more than one correct options.

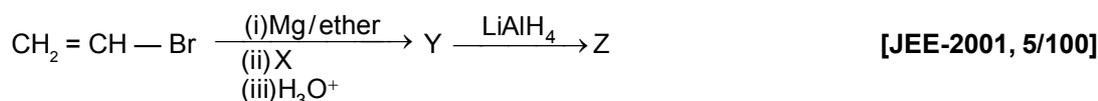
1. What would be the major product in the following reaction ? [JEE-2000, 1/100]



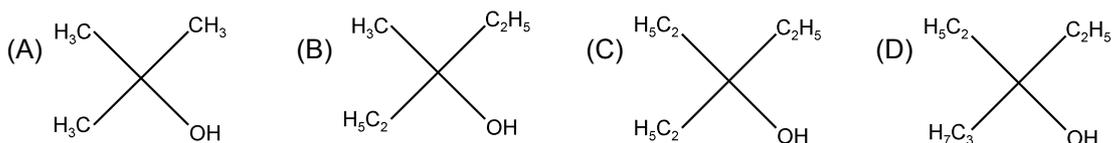
2. The appropriate reagent for the following transformation: [JEE-2000, 1/100]



- (A) Zn (Hg), HCl (B) $\text{NH}_2\text{NH}_2, \text{OH}^-$ (C) H_2/Ni (D) NaBH_4
3. Identify X and Y in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde ($\text{H}_2\text{C}^*\text{O}$) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the radioactive carbon in the entire scheme. X is obtained by heating of BaCO_3^* with H_2SO_4 .

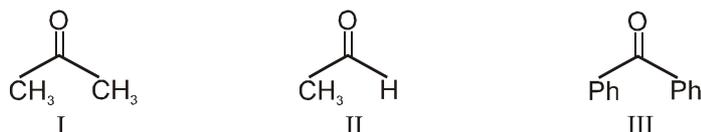


4. Ethylester $\xrightarrow[\text{excess}]{\text{CH}_3\text{MgBr}}$ P. The product P will be [JEE-2003, 3/84]

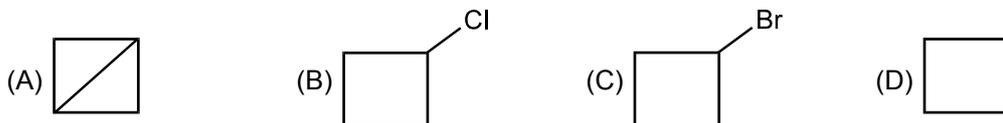


5. The number of chiral compounds produced upon monochlorination of 2-methylbutane is : [JEE-2004, 3/84]
- (A) 2 (B) 4 (C) 6 (D) 8

6. The order of reactivity of phenyl magnesium bromide with the following compounds is : [JEE-2004, 3/84]



- (A) (II) > (III) > (I) (B) (I) > (III) > (II) (C) (II) > (I) > (III) (D) all react with the same rate
7. 1-Bromo-3-chlorocyclobutane will react with two moles of Na in ether producing [JEE-2005, 3/60]



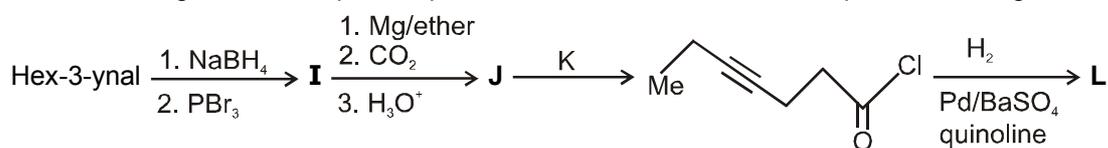
8. Phenyl magnesium bromide reacting with t-Butyl alcohol gives [JEE-2005, 3/60]



9. $(\text{CH}_3)_2\text{CH} - \text{CH}_2\text{CH}_3 \xrightarrow{\text{Cl}_2/h\nu} [\text{N}] \xrightarrow{\text{Fractional distillation}} [\text{P}]$ [JEE-2006, 5/184]
The number of possible isomers [N] and number of fractions [P] are
(A) (6, 6) (B) (6, 4) (C) (4, 4) (D) (3, 3)

Comprehension -1

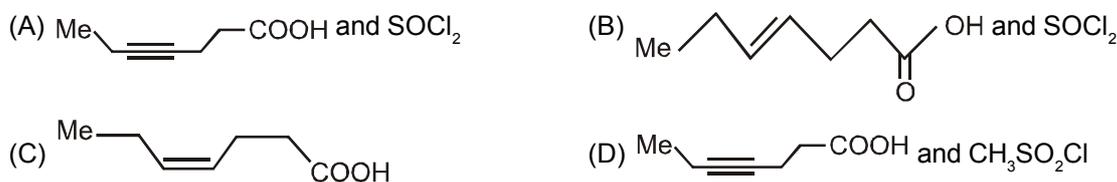
In the following reaction sequence, product **I**, **J** and **L** are formed. **K** represents a reagent.



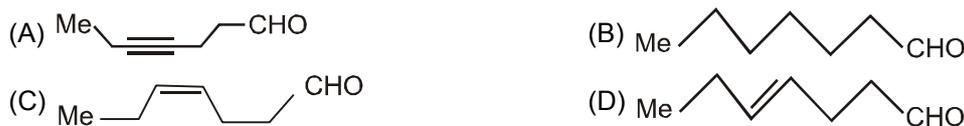
10. The structure of the product **I** is ; [JEE-2008, 4/163]



11. The structures of compound **J** and **K**, respectively, are : [JEE-2008, 4/163]



12. The structure of product **L** is : [JEE-2008, 4/163]



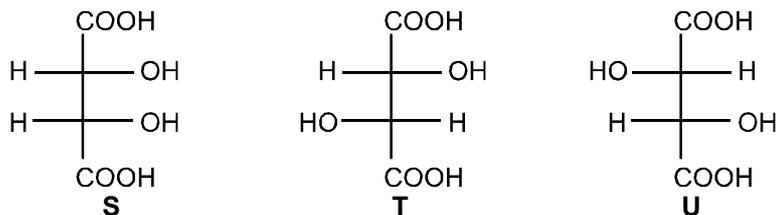
13. Match each of the compounds in **Column I** with its characteristic reaction(s) in **Column II**. [JEE-2009, 8/160]

Column I	Column II
(A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$	(p) Reduction with Pd-C/ H_2
(B) $\text{CH}_3\text{CH}_2\text{OCOCH}_3$	(q) Reduction with SnCl_2/HCl
(C) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$	(r) Development of foul smell on treatment with chloroform and alcoholic KOH.
(D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	(s) Reduction with diisobutylaluminium hydride (DIBAL-H)
	(t) Alkaline hydrolysis

Paragraph for Question Nos. 14 to 15

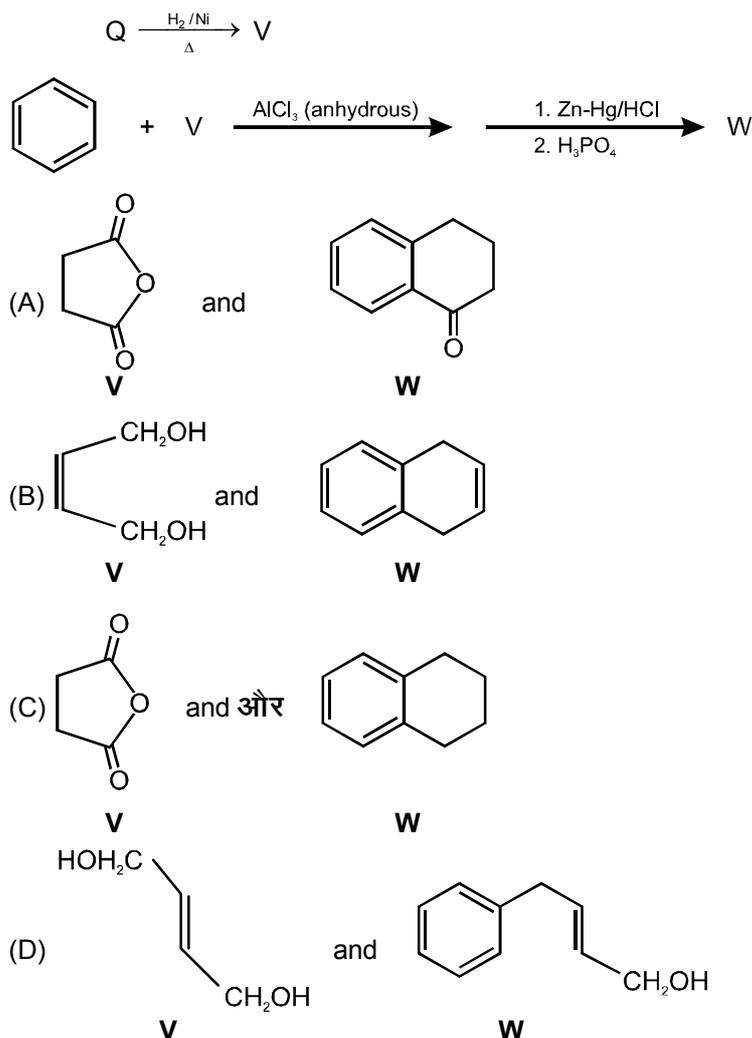
P and **Q** are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorize Br_2/H_2O . On heating, **P** forms the cyclic anhydride.

Upon treatment with dilute alkaline $KMnO_4$, **P** as well as **Q** could produce one or more than one from **S**, **T** and **U**.



14. In the following reaction sequences **V** and **W** are, respectively :

[JEE Advanced_2013]



15. Compounds formed from **P** and **Q** are, respectively :

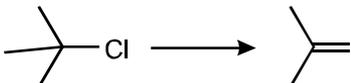
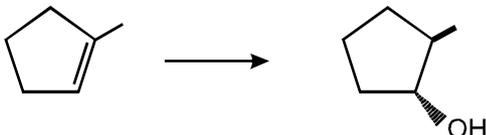
[JEE Advanced_2013]

- (A) Optically active **S** and optically active pair (**T**, **U**)
- (B) Optically inactive **S** and optically inactive pair (**T**, **U**)
- (C) Optically active pair (**T**, **U**) and optically active **S**
- (D) Optically inactive pair (**T**, **U**) and optically inactive **S**

16. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct

answer using the code given below the lists :

[JEE Advanced_2013]

- P.  1. (i) $\text{Hg}(\text{OAc})_2$; (ii) NaBH_4
- Q.  2. NaOEt
- R.  3. Et-Br
- S.  4. (i) BH_3 ; (ii) $\text{H}_2\text{O}_2/\text{NaOH}$

Codes :

	P	Q	R	S
(A)	2	3	1	4
(B)	3	2	1	4
(C)	2	3	4	1
(D)	3	2	4	1

PART - II : AIEEE PROBLEMS (PREVIOUS YEARS)

1. CH_3MgI is an organometallic compound due to : [AIEEE-2002]
 (1) $\text{Mg} - \text{I}$ bond (2) $\text{C} - \text{I}$ bond (3) $\text{C} - \text{Mg}$ bond (4) $\text{C} - \text{H}$ bond
2. But-1-ene may be converted to butane by reaction with : [AIEEE-2003]
 (1) $\text{Zn} - \text{HCl}$ (2) $\text{Sn} - \text{HCl}$ (3) $\text{Zn} - \text{Hg}$ (4) Pd / H_2
3. Which one of the following is reduced with Zn/Hg and hydrochloric acid to give the corresponding hydrocarbon [AIEEE-2004]
 (1) Ethyl acetate (2) Acetic acid (3) Acetamide (4) Butanone
4. 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly [AIEEE-2005]
 (1) 1-Bromo-3-methylbutane (2) 1-Bromo-2-methylbutane
 (3) 2-Bromo-3-methylbutane (4) 2-Bromo-2-methylbutane
5. The treatment of CH_3MgX with $\text{CH}_3\text{C}\equiv\text{C}-\text{H}$ produces [AIEEE-2008]
 (1) $\text{CH}_3\text{C}\equiv\text{C}-\text{CH}_3$ (2) $\text{CH}_3-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{C}-\text{CH}_3$ (3) CH_4 (4) $\text{CH}_3-\text{CH}=\text{CH}_2$
6. 2-Hexyne gives trans - 2 - Hexene on treatment with : [AIEEE-2012, 4/120]
 (1) Pt/H_2 (2) Li/NH_3 (3) Pd/BaSO_4 (4) LiAlH_4
7. In the given transformation, which of the following is the most appropriate reagent ? [AIEEE-2012, 4/120]
- 
- (1) $\text{NH}_2\text{NH}_2, \text{OH}^-$ (2) $\text{Zn} - \text{Hg}/\text{HCl}$ (3) $\text{Na}, \text{Liq. HCl}$ (4) NaBH_4

EXERCISE # 4

NCERT QUESTIONS

1. Sodium salt of which acid will be needed for the preparation of propane ? Write chemical equation for the reaction.
2. How will you convert ethanoic acid into benzene?
3. Write chemical equations for combustion reaction of the following hydrocarbons :
 - (i) Butane
 - (ii) Pentene
 - (iii) Hexyne
 - (iv) Toluene
4. In the alkane $\text{H}_3\text{C} - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$, identify $1^\circ, 2^\circ, 3^\circ$ carbon atoms and give the number of H atoms bonded to each one of these.
5. Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.

ANSWERS

Exercise # 1

PART - I

A-1. (C)	A-2. (A)	A-3. (C)	A-4*. (AB)	A-5. (C)	A-6. (C)	A-7. (A)
A-8*. (BCD)	A-9. (D)	A-10. (A)	A-11. (A)	A-12*. (ABC)	A-13. (C)	A-14. (C)
A-15. (A)	A-16*. (ACD)	A-17. (B)	A-18. (C)	A-19. (C)	A-20*. (CD)	B-1. (A)
B-2. (D)	B-3. (A)	B-4. (B)	B-5. (B)	B-6. (A)	B-7. (D)	B-8. (A)
B-9. (A)	C-1. (B)	C-2. (D)	C-3. (B)	C-4. (D)	C-5. (B)	C-6. (B)
C-7. (D)	C-8. (D)	C-9. (A)	C-10. (C)	D-1. (D)	D-2. (A)	D-3. (D)
D-4. (C)	D-5. (B)	D-6. (D)	D-7. (A)	D-8. (C)	D-9. (B)	D-10*. (AB)

PART - II

1. (C)	2. (C)	3. (C)	4. (B)	5. (B)		
6. (A) - (p, r) ; (B) - (r) ; (C) - (r) ; (D) - (q)						
7. (A) S; (B) R; (C) P; (D) R,S						
8. (A) Q, (B) R, (C) S, (D) P						
9. (A)	10. (B)	11. (A)	12. (A)	13. (D)	14. (A)	15. (A)
16. (B)	17. (B)	18. (E)	19. F	20. F	21. T	22. T
23. T	24. corey house alkane synthesis	25. nucleophilic	26. P-2 catalyst			
27. syn addition.	28. hydrocarbons	29. electron				

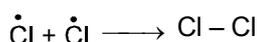
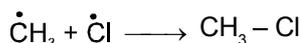
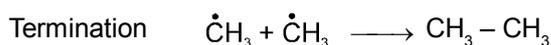
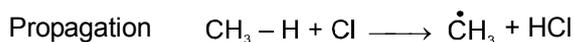
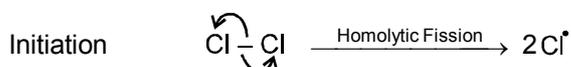
Exercise # 2

PART - I

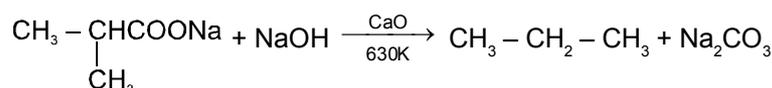
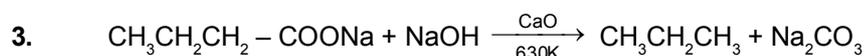
1. (A)	2. (C)	3. (A)	4. (C)	5. (C)	6. (B)	7. (B)
8. (A)	9. (C)	10. (B)	11. (B)	12. (C)	13. (D)	14. (C)
15. (B)	16. (A)	17. (B)	18. (A)	19. (D)	20. (C)	21. (B)
22. (B)	23. (C)	24. (C)	25. (ACD)	26. (CD)	27. (ABC)	28. (BD)
29. (BC)	30. (BC)	31. (AB)	32. (ABC)	33. (BC)		

PART - II

1. Chlorination of methane is a free radical reaction which occurs by the following mechanism

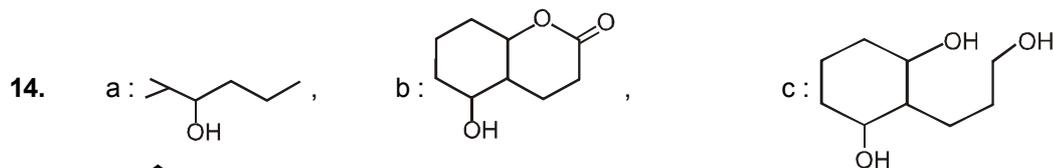
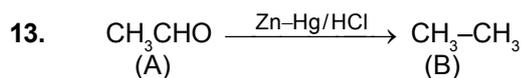
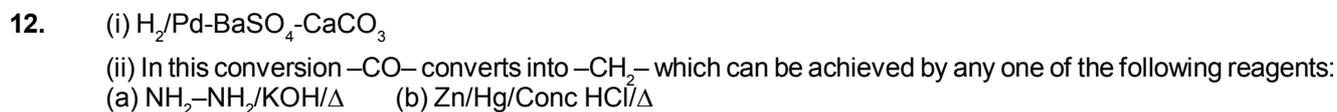
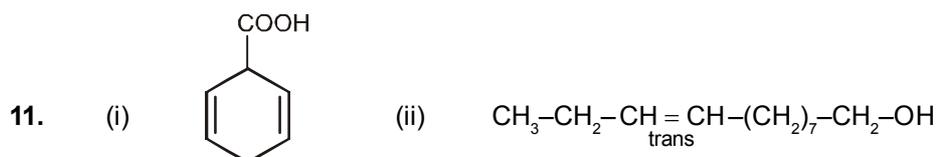
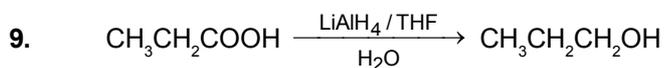
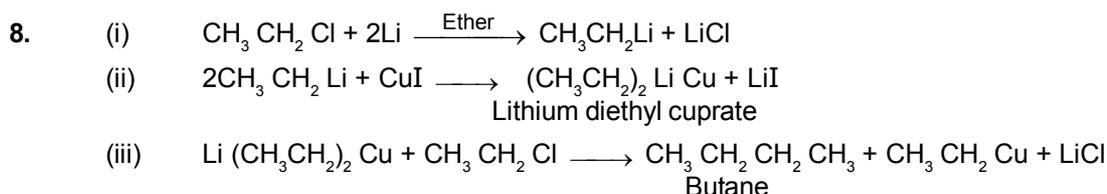
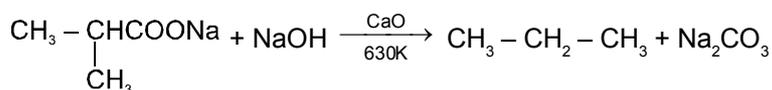
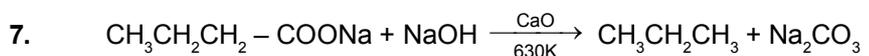
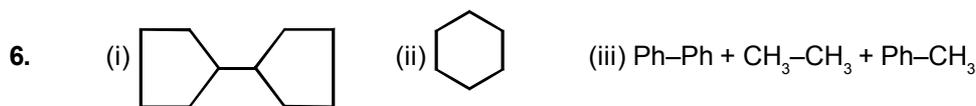
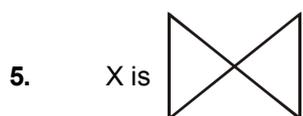


2. 4



4. (i) $\text{CH}_3\text{CH}_2\text{Cl} + 2\text{Li} \xrightarrow{\text{Ether}} \text{CH}_3\text{CH}_2\text{Li} + \text{LiCl}$
 (ii) $2\text{CH}_3\text{CH}_2\text{Li} + \text{CuI} \longrightarrow (\text{CH}_3\text{CH}_2)_2\text{LiCu} + \text{LiI}$
 Lithium diethyl cuprate
 (iii) $\text{Li}(\text{CH}_3\text{CH}_2)_2\text{Cu} + \text{CH}_3\text{CH}_2\text{Cl} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{Cu} + \text{LiCl}$

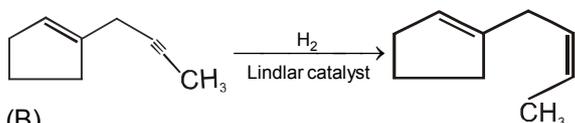
Butane

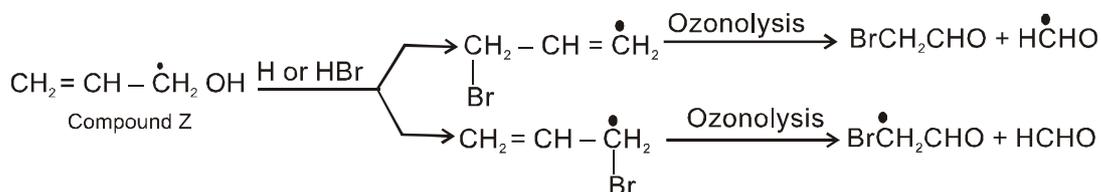
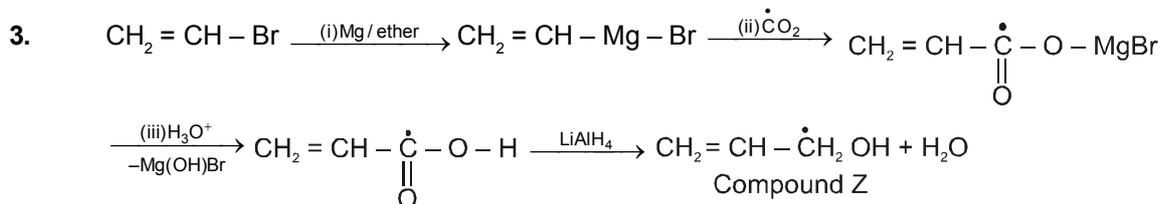


Exercise # 3

PART - I

1. In presence of lindlar's catalyst (Pd and CaCO₃) in quinoline) partial hydrogenation takes place and give cis-isomer.





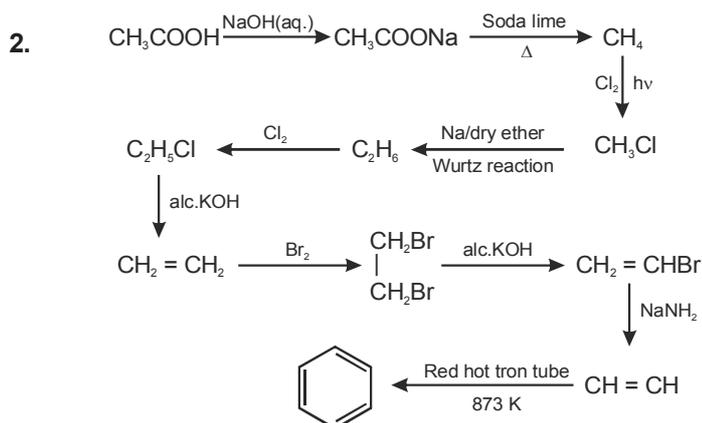
4. (A) 5. (B) 6. (C) 7. (A) 8. (B) 9. (B)
 10. (D) 11. (A) 12. (C) 13. (A) - p, q, s, t ; (B) - s, t ; (C) - p ; (D) - r

PART - II

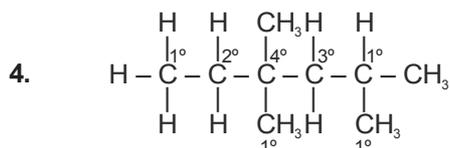
1. (3) 2. (4) 3. (4) 4. (4) 5. (3) 6. (2) 7. (1)

Exercise # 4

1. Butanoic acid,



3. (i) $\text{C}_4\text{H}_{10}(\text{g}) + 13/2\text{O}_2(\text{g}) \xrightarrow{\Delta} 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{g})$
 (ii) $\text{C}_5\text{H}_{10}(\text{g}) + 15/2\text{O}_2(\text{g}) \xrightarrow{\Delta} 5\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{g})$
 (iii) $\text{C}_6\text{H}_{10}(\text{g}) + 17/2\text{O}_2(\text{g}) \xrightarrow{\Delta} 6\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{g})$
 (iv) $\text{C}_7\text{H}_8(\text{g}) + 9\text{O}_2(\text{g}) \xrightarrow{\Delta} 7\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$



15 H attached to 1° carbons
 4 H attached to 2° carbons
 1 H attached to 3° carbons

5. Due to the formation of side products. For example, by starting with 1-bromopropane and 1-bromobutane, hexane and octane are the side products besides heptane.