

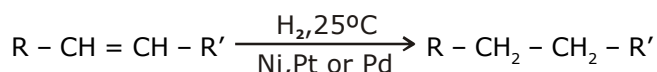
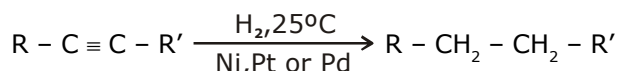
ALKANE

Alkane are the saturated non polar hydrocarbon having general formula C_nH_{2n+2} .

Hydrocarbon – Those organic compounds which contain only carbon and hydrogen atoms are known as hydrocarbons.

1.2 General method of preparation

1.2.1 By catalytic reduction of alkenes and alkynes



Hydrogenation \rightarrow Addition of H_2 to unsaturated bond.

Hydrogenation is of two kind

(a) Heterogeneous and (b) Homogeneous

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

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

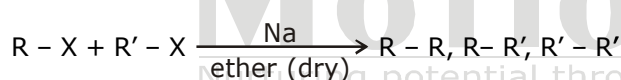
Hydrogenation is exothermic, qualitative and during the hydrogenation, total heat evolved to hydrogenate one mole of unsaturated compound is called heat of hydrogenation. Heat of hydrogenation is the measurement of stability of isomeric alkenes.

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

1.2.2 From alkyl halide

(A) From organometallic compound \rightarrow compound having $C - M$ bond. ($M \rightarrow$ metal)

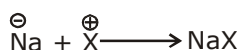
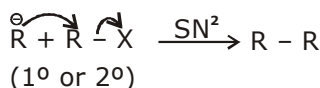
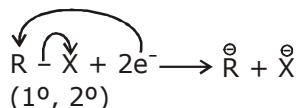
(i) By wurtz reaction



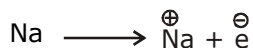
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Mechanism \longrightarrow Two mechanisms are suggested

(a) Ionic mechanism

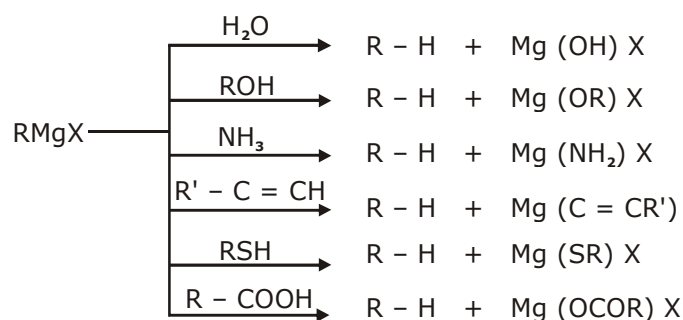
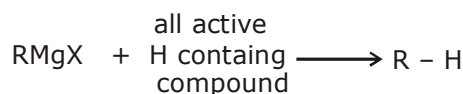
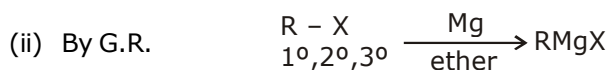


(b) Free radical mechanism

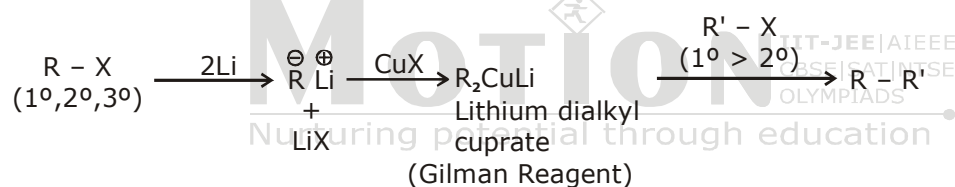


Note : The alkyl halide should be 1° or 2° , with $3^{\circ} \text{R} - \text{X}$ SN^2 and free radical coupling is not possible due to steric hinderance so in that case elimination or disproportionation is possible.

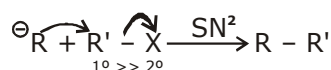
In the ionic mechanism alkyl sodium ($\text{R}^{\oplus} \text{Na}^{\ominus}$) gives R^{\ominus} strong base as well as nucleophile which gives SN^2 with $\text{R} - \text{X}$, ether should be dry otherwise, if moisture is present then R^{\ominus} forms $\text{R} - \text{H}$ instead of $\text{R} - \text{R}$ with H_2O .



(iii) By corey house alkane synthesis

**Mechanism**

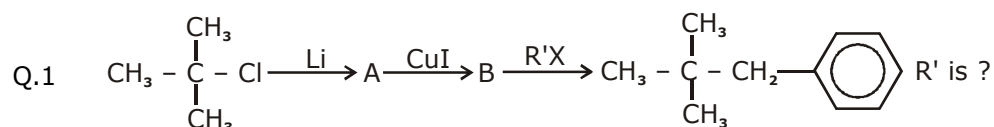
R_2CuLi is the source of R^{\ominus}



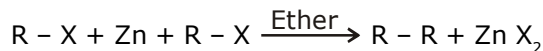
R_2CuLi do not reacts with $-\text{NO}_2$, $-\text{CN}$, $> \text{C} = \text{O}$ etc.

Ex.1 $\text{CH}_3 - \text{Br} \xrightarrow{\text{Li}} \text{A} \xrightarrow{\text{CuI}} \text{B} \xrightarrow{\text{Y}} \text{C}$
 if C is $\text{CH}_3 - \text{CH}_2 - (\text{CH}_2)_5 - \text{CH}_3$, than what is Y.

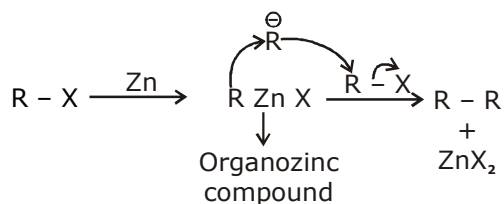
Ans. $\text{CH}_3 - (\text{CH}_2)_6 - \text{Br}$



(iv) By Frankland's reagent

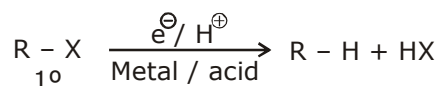


Mechanism



(B) By reduction of alkyl halides

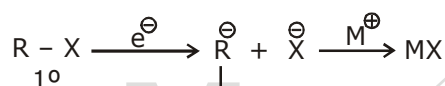
(i) with metal-acid



Reducing agent

Zn / acid, Zn - Cu / H_2O or Zn - Cu + acid
Zn - Cu / $\text{C}_2\text{H}_5\text{OH}$, Na - Hg / acid, Al - Hg / H_2O etc.

Mechanism



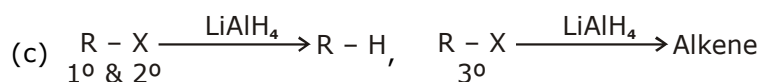
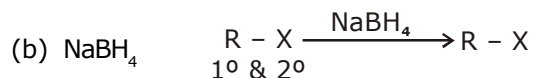
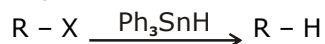
acid

$\text{R} - \text{H}$

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Nurturing potential through education

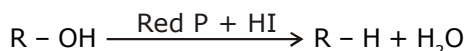
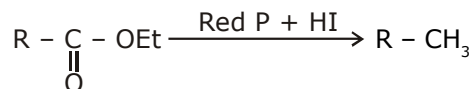
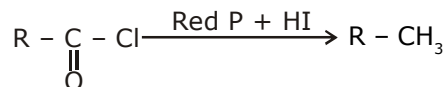
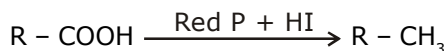
(ii) With Metal hydrides

(a) TPH (Ph_3SnH) : It reduces 1° , 2° & 3° $\text{R} - \text{X}$

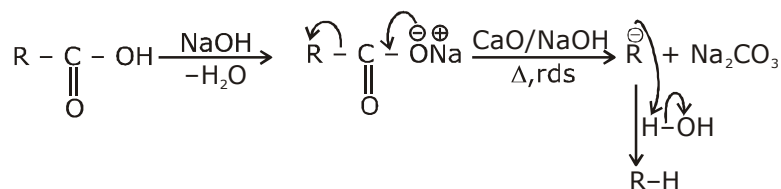
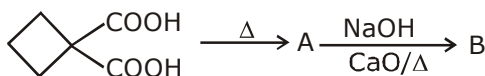


1.2.3 By red P & HI

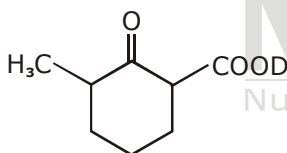
Red P & HI is strong reducing agent



1.2.4 By soda lime → Fatty acids are good source of hydrocarbon, correction, heating of sodium salt of carboxylic acid ($R - \text{COONa}$) with soda lime ($\text{NaOH} - \text{CaO}$) gives hydrocarbon, which is known as decarboxylation (e.g. replacement of $-\text{COOH}$ group by $-\text{H}$) decarboxylation also takes place on heating only, when compound is gem dicarboxylic acid or there is keto group or double bond on β carbon.

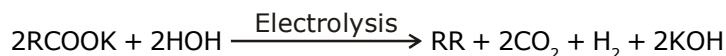
**Ex.2**

What are A and B

Ans.

Optically active

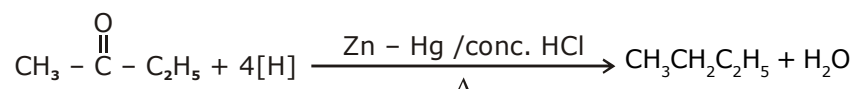
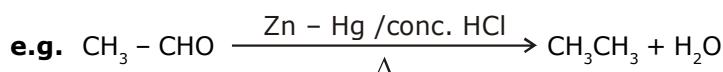
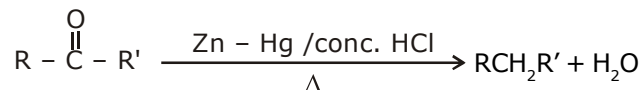
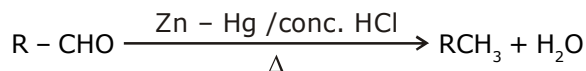
Write the structure of A and mention its stereochemistry

1.2.5 By Kolbe's electrolysis

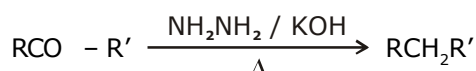
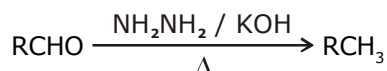
If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has $2(n - 1)$ carbon atoms.

1.2.6 Reduction of aldehydes, ketones :

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



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

(b) By Wolff-kishner reduction with NH_2NH_2 / KOH

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

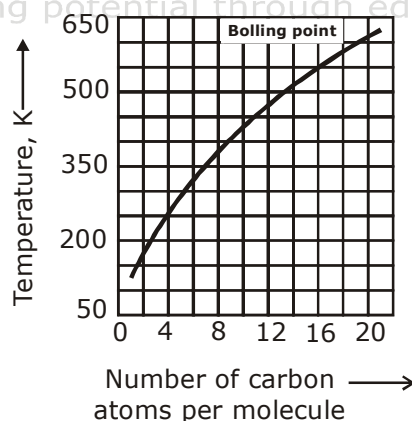
1.3 Physical Properties of Alkanes :

3.3.1 Physical State :

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

1.3.2 Boiling points :

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

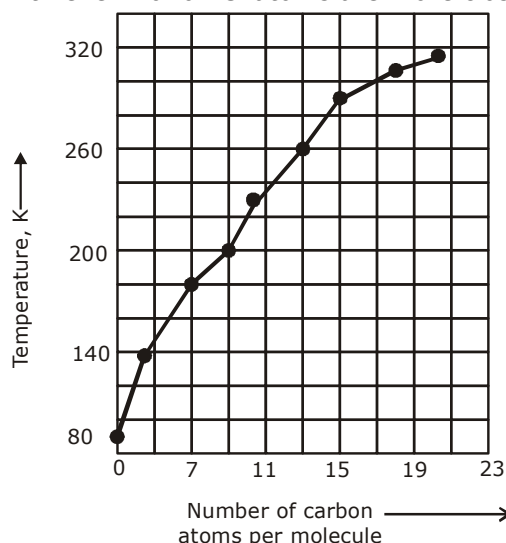


Among the isomeric alkanes, the branched chain isomers have relatively low boiling points as compared to their corresponding straight chain isomers. Greater the branching of the chain, lower is the boiling point. This is due to the fact that branching of the chain makes the molecules more compact and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

1.3.3. Melting Points

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

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



1.3.4 Solubility

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

1.3.5 Density

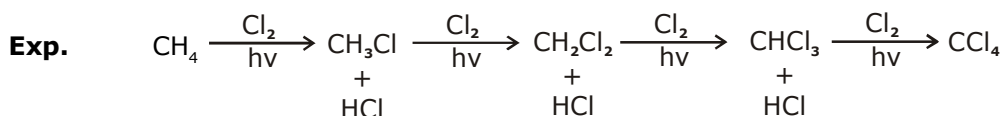
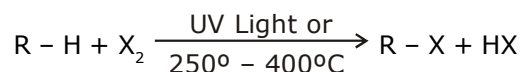
The densities of alkanes increase with increasing molecular weight but become constant at about 0.8 g cm^{-3} . This means that all alkanes are lighter than water so they float over water.

1.4 Chemical Reaction of Alkanes :

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

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

Examples of free radical substitution reaction →



When equimolar amount of methane and Cl_2 are taken, a mixture of four possible products are formed,

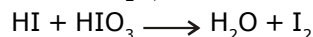
but if we take excess of CH_4 then yield of CH_3Cl will be the major product.

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

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

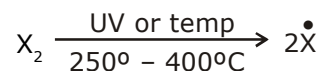
with F_2 alkanes reacts so vigorously that, even in the dark and at room temp, reactant diluted with an inert gas.

Iodination is reversible reaction, since HI formed as a by-product is a strong reducing agent and reduces alkyl iodide back to alkane. Hence iodination can be done only in presence of strong oxidizing agent like HIO_3 , HNO_3 or HgO

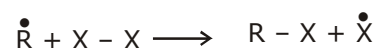


Mechanism of halogenation of $\text{CH}_4 \longrightarrow$

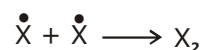
(i) Chain initiation \rightarrow it is an endothermic step



(ii) Chain propagation \rightarrow



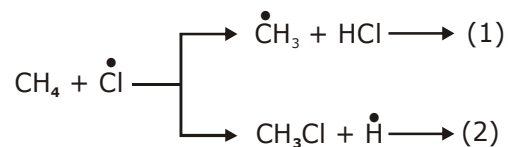
(iii) Chain termination \rightarrow it is always exothermic



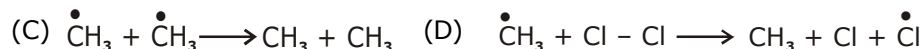
Each photon of light cleaves one chlorine molecule to form two chlorine radicals, each chlorine atom starts a chain and on an average each chain contains 5000 repetitions of the chain propagating cycle so about 10,000 molecules of CH_3Cl are formed by one photon of light.

Some reagent affects the rate of halogenation : For example

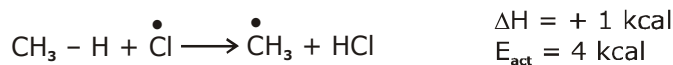
Q.3 In the given ways which is feasible



Q.4 Which of the following reaction has zero activation energy



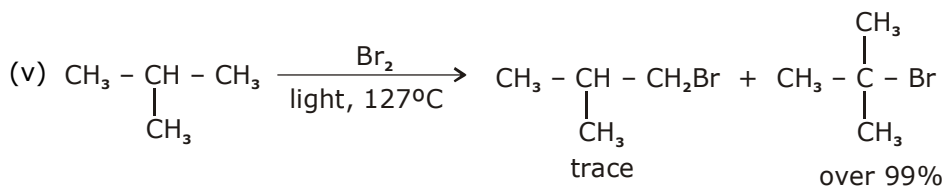
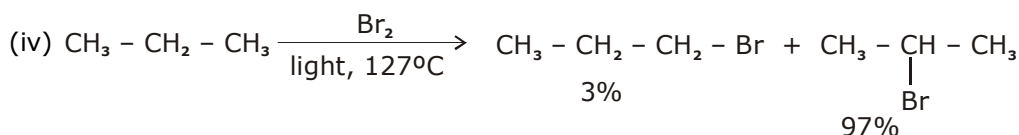
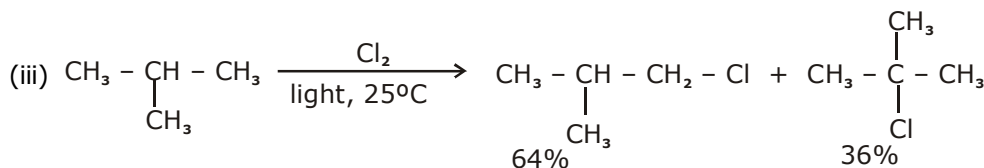
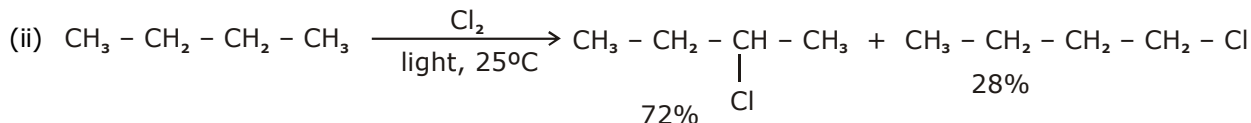
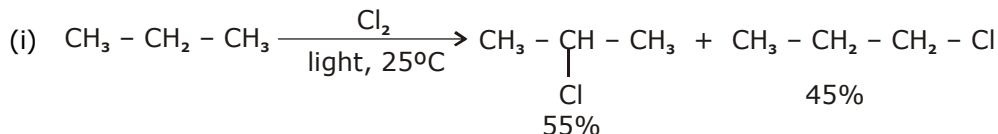
Q.5 If the E_{act} for a forward reaction is given



the E_{act} for backward reaction will be

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

Halogenations of higher alkane :

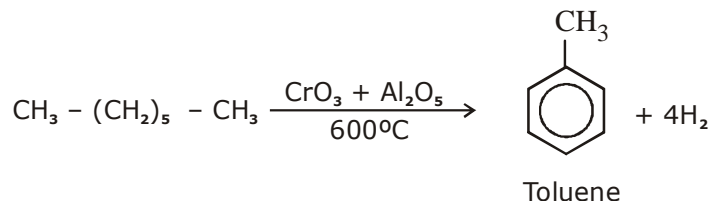


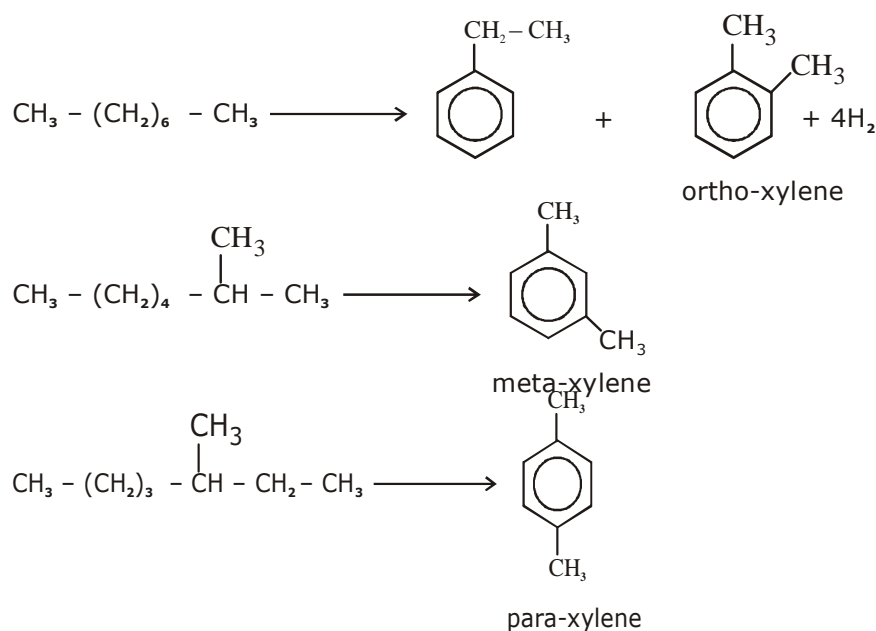
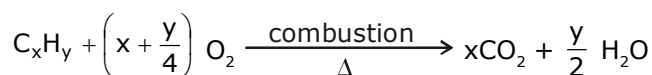
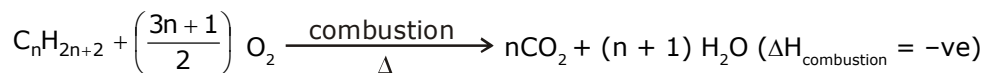
Relative amounts of the various isomers differ remarkably depending upon the halogen used from the above reaction, it is observed that chlorination gives mixture in which no isomer greatly dominates while, in bromination gives mixture in which one isomer dominates greatly (97% – 99%).

Factors determining the relative yields of the isomeric products.

- (i) Probability factor → This factor is based on the number of each kind of H atom in the molecule.
- (ii) Reactivity of hydrogen → The order of reactivity is $3^\circ > 2^\circ > 1^\circ$

Aromatisation:



**1.4.8 Combustion : (i.e. complete oxidation)**

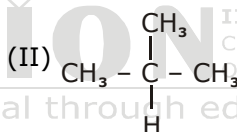
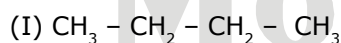
Heat of combustion : Amount of heat i.e. liberated when 1 mole of hydrocarbon is completely burnt into CO_2 & H_2O .

Heat of combustion as a measure of stability of alkane :

Combustion is used as a measurements of stability.

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

e.g.



stability : II > I

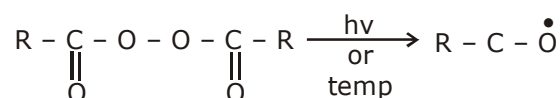
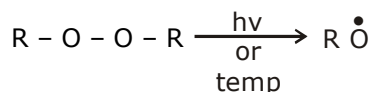
$\Delta H_{\text{comb.}}$: I > II

More branched alkane has more no. of primary C - H bonds. (therefore it has more bond energy).

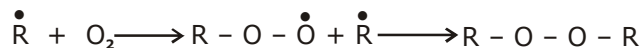
Homologues : Higher homologues have higher heat of combustion.

Isomers : Branched isomer has lower heat of combustion.

(i) Initiators → they initiate the chain reaction, initiators are R_2O_2 , Perester's etc.



(ii) **Inhibitors** → A substance that slow down or stop the reaction are known as inhibitors
For example O_2 is a good inhibitor

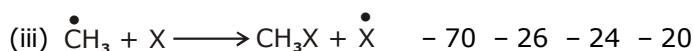
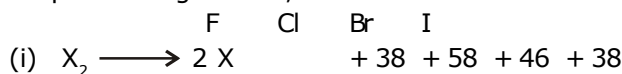


all reactive alkyl free radicals are consumed so reaction become stop for a period of time.

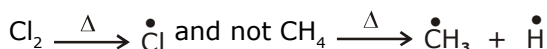
Relative reactivity of halogen toward methane →

Order of reactivity is $F_2 > Cl_2 > Br_2 > I_2$ which can be explained by the value of ΔH (energy change)

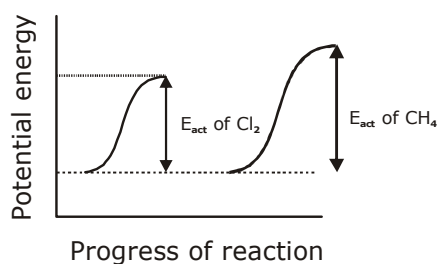
Steps of halogenation, value of ΔH for each step. (Kcal/mole)



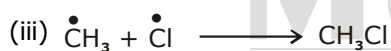
Ex.3 Explain why the chain initiating step in thermal chlorination of CH_4 is



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



Ex.4 Chlorination of CH_4 involves following steps :



Which of the following is rate determining ?

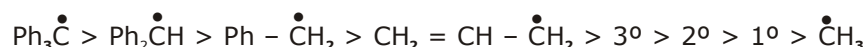
- (A) Step (i)
(B) Step (ii)
(C) Step (iii)
(D) Step (ii) and (iii) both

Ans. (B)

Reactivity of hydrogen → $3^\circ > 2^\circ > 1^\circ$

Because formation of alkyl free radical is Rds so, that H is more reactive which produce more stable free radical (less E_{act})

order of stability of F.R. →



ALKENE

1. INTRODUCTION

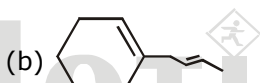
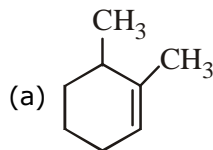
Alkenes are hydrocarbons with carbon-carbon double bonds, Alkenes are sometimes called olefins, a term derived from olefinic gas, meaning "oil forming gas". Alkenes are among the most important industrial compound and many alkenes are also found in plants and animals. Ethylene is the largest – volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals.

2. Structure and bonding in Alkenes

- (1) Alkenes are unsaturated hydrocarbons having at least one double bond.
- (2) They are represented by general Formula (G.F.) C_nH_{2n} (one double bond)
- (3) In Ethene $C = C$ bond length is 1.34 \AA
- (4) Its bond energy is $146 \text{ kcal.mol}^{-1}$
- (5) The hybridization of $(C = C)$ alkenic carbon is sp^2
- (6) The πe^- cloud is present above and below the plane of σ -bonded skeleton.
- (7) They are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.
- (8) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes

Note : That angle $a > b$ since repulsion due to π electrons (double bond - single bond repulsion $>$ single bond single bond repulsion according to VSEPR theory.

Ex.1 Write IUPAC names of

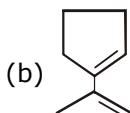
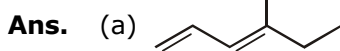


IIT-JEE|AIEEE
CBSE|SAT|NTSE
OLYMPIADS

- Ans.** (a) 2, 3-Dimethylcyclohexene
(b) 1-(2-butenyl) cyclohex -1-ene

Ex.2 Give the structure for each of the following

- (a) 4-Methyl-1, 3-hexadiene
- (b) 1-Isopropenylcyclopentene



5. Physical Properties of Alkenes / Hydrocarbons

Table : III

	Physical properties	Homologus series	Isomers
1.	Physical state	C ₁ – C ₃ gases C ₄ – C ₂₀ liquids >C ₂₀ : solids	
2.	Dipolemoment (μ)		cis > trans
3.	Polarity	–	cis > trans (for C _{ab} = C _{ab} type of alkenes)
4.	Melting point	increases with M.W.	trans > cis (due to more packing capacity)
5.	Boiling point	increases with M.W.	cis > trans # branching decreases B.P. $\begin{array}{c} \text{C} \\ \\ \text{C} - \text{C} = \text{C} < \text{C} - \text{C} = \text{C} - \text{C} \end{array}$ Polarity increases, boiling point increases
6.	Solubility	Practically insoluble in water but fairly soluble in nonpolar solvents like benzene petroleum ether, etc.	cis > trans Polarity increases, solubility in polar solvents increases.
7.	Stability		trans > cis (cis isomers has more Vander Waals repulsion)

6. Laboratory test of Alkene

Table - IV

Functional Group	Reagent	Observation	Reaction	Remarks
$\begin{array}{c} \diagup \quad \diagdown \\ \text{C} = \text{C} \\ \diagdown \quad \diagup \end{array}$	(1) Bayer's Reagent alk. dil. Cold KMnO ₄	Pink Colour disappears	$\text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{alk. KMnO}_4} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	Dihydroxylation
	(2) Br ₂ / H ₂ O	Bromine water Colour decolourises	$\text{Br}_2 + \text{CH}_2 = \text{CH}_2 \longrightarrow \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \\ \text{Br} \quad \text{Br} \\ \text{White ppt} \end{array}$	Dibromination
	(3) O ₃ (ozone)	$\begin{array}{c} \diagdown \quad \diagup \\ \text{C} = \text{O} \\ \diagup \quad \diagdown \end{array}$ Compounds	$\text{H}_2\text{C} = \text{CH}_2 + \text{O}_3 \xrightarrow{\text{Zn} / \text{H}_2\text{O}} 2\text{HCHO}$	Ozonolysis

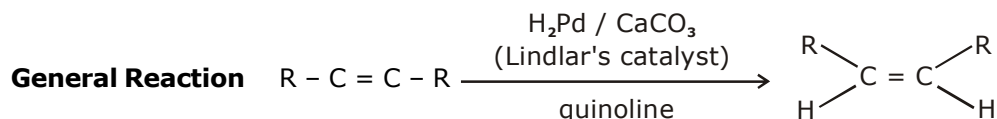
8. Methods of preparation of alkenes

(I) BY PARTIAL REDUCTION OF ALKYNES

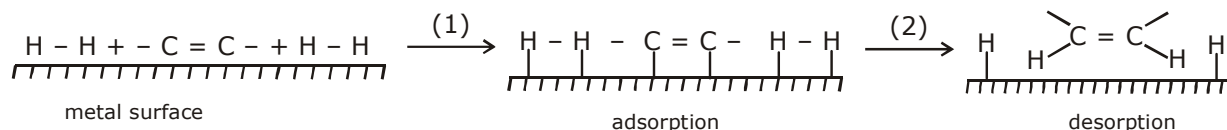
(a) **By Catalytic Hydrogenation of Alkynes in presence of poisoned catalyst** (A Syn Addition of Hydrogen : Synthesis of cis-Alkenes : This is performed by)

(i) **Lindlar's catalyst** : Metallic palladium deposited on calcium carbonate with lead acetate and quinoline.

(ii) **P-2 catalyst (Ni₂B nickel boride)**

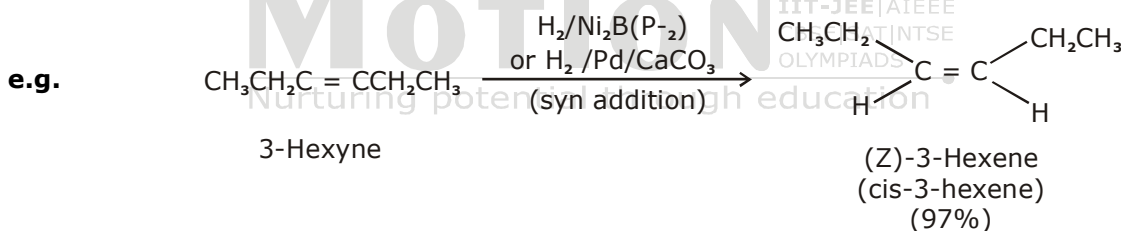


Mechanism of hydrogenation :

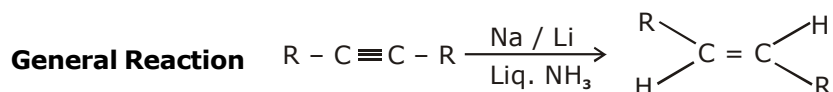


Steps : The reactant alkyne molecules and hydrogen molecules get adsorbed at the surface of metal catalyst. It is chemical adsorption (chemisorption).

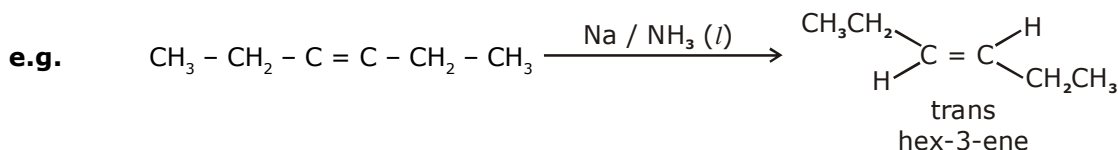
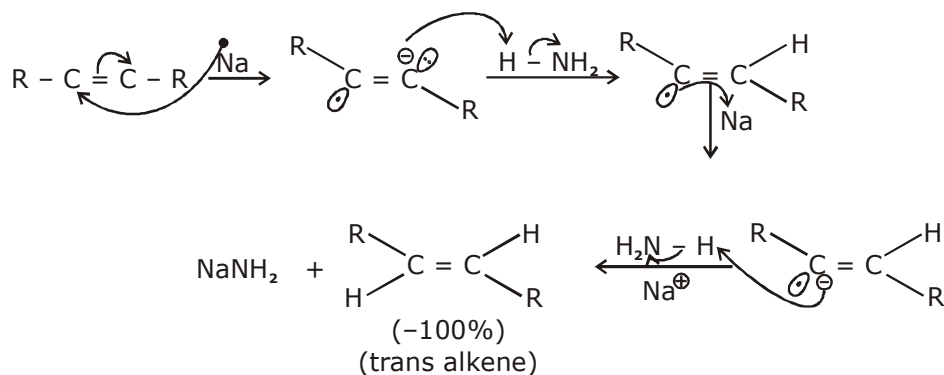
In this state, the reactants lie very close to each other and so the hydrogen atoms start forming bond with carbon. Two hydrogen atoms are added to two triply bonded carbon atom from the same side of π bond and a **cis or syn addition product** is formed. The product alkene now escapes away from the surface of the catalyst. Quinoline occupies the metal surface inhibiting further reduction to alkanes **Quinoline** therefore is called **catalyst poison** and palladium is called deactivated catalyst or poisoned catalyst.



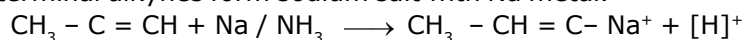
(b) **Birch Reduction** : (Anti Addition of Hydrogen : Synthesis of trans-Alkenes)



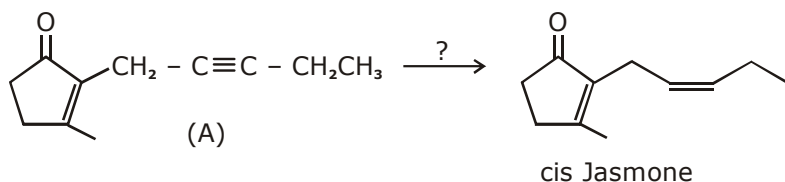
Mechanism : Reagents $\text{Na}(\text{or Li, K}) + \text{liq NH}_3 \longrightarrow \text{Na}^+ + \text{e}^-$ (solvated electron)



Note : This process of reduction is not eligible when terminal alkynes are taken. ($\text{R}-\text{C}\equiv\text{CH}$) because terminal alkynes form sodium salt with Na metal.



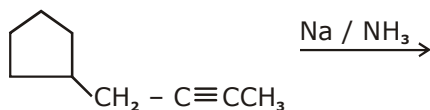
Ex.3 Identify the reagent for following synthesis.



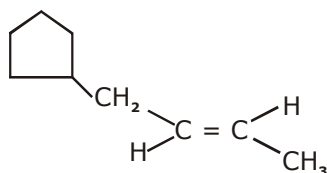
Ans. H_2 / Lindlar's catalyst.



Ex.4 Identify the products in the following reaction :



Ans.

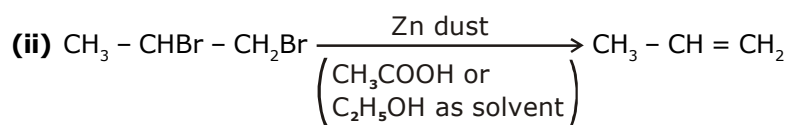
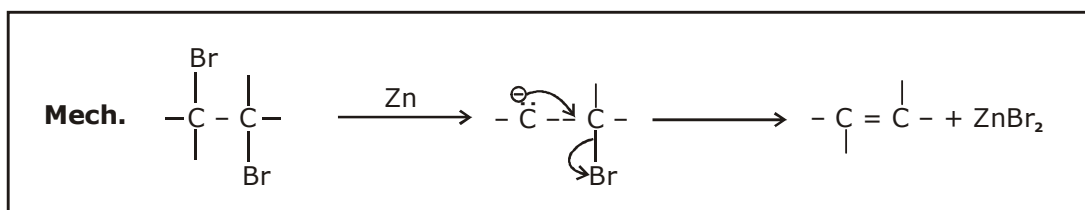
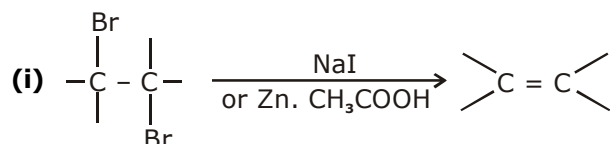


(II) BY DEHALOGENATION OF VICINAL DIHALIDES

There are two types of dihalides namely gem (or geminal) dihalides in which the two halogen atoms are attached to the same carbon atom and vicinal dihalides in which the two halogen atoms are attached to the adjacent carbon atoms.

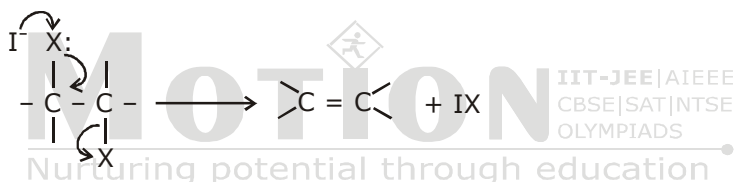
Dehalogenation of vicinal dihalides can be effect either by NaI in acetone or zinc in presence of acetic acid or ethanol.

General Reaction



Mech.

With NaI in acetone :



It involves an **antielimination** of halogen atoms

Remarks

- (1)** Both are E2 elimination.
(2) Both are stereospecific anti elimination.

(III) DEHYDRO HALOGENATION OF ALKYL HALIDES

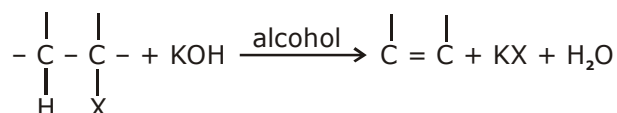
Dehydro halogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene.

Dehydro halogenation can take place by E1 and E2 mechanism.

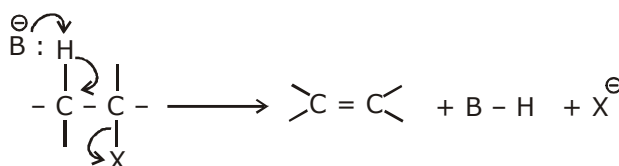
- (i) Hot alcoholic solution of KOH $\text{EtO}^- / \text{EtOH}$ (ii) NaNH_2
 (iii) t-BuO-K^+ in t-BuOH

(i) Dehydrohalogenation by the E2 mechanism : Second-order elimination is a reliable synthetic reaction, especially if the alkyl halide is a poor $\text{S}_{\text{N}}2$ substrate. E2 dehydrohalogenation takes place in one step, in which a strong base abstracts a proton from one carbon atoms as the leaving group leaves the adjacent carbon.

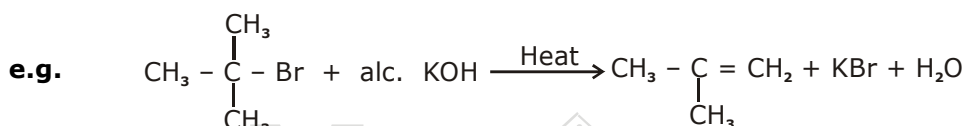
General reaction :



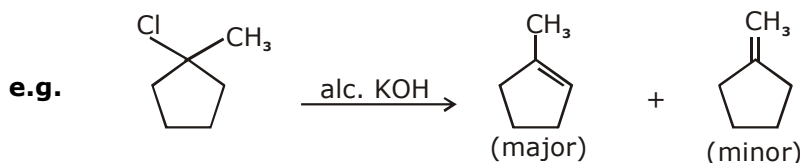
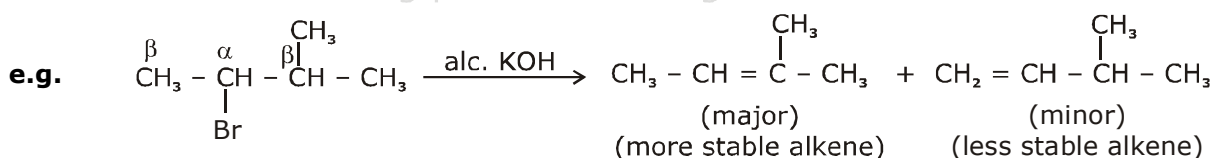
Mechanism

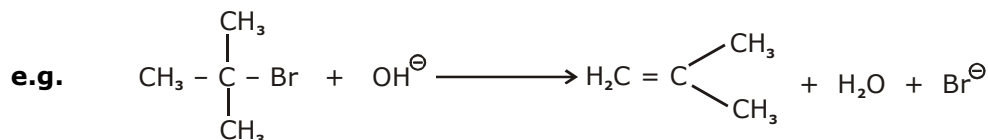
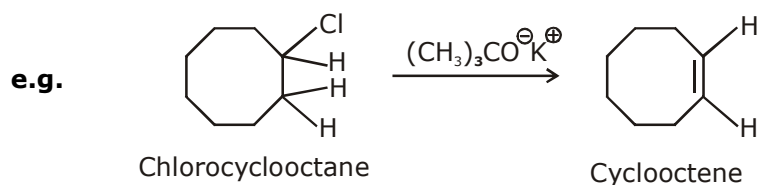


Undergo elimination of hydrogen halide (HX) leading to the formation of alkenes.



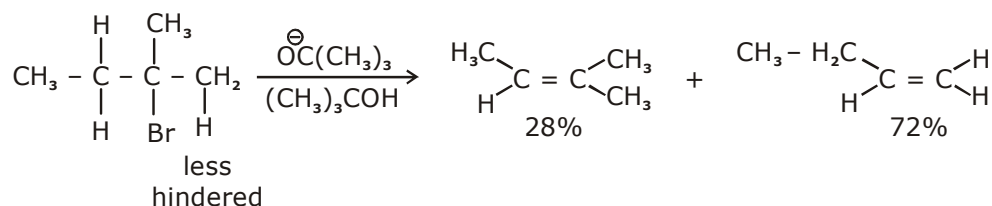
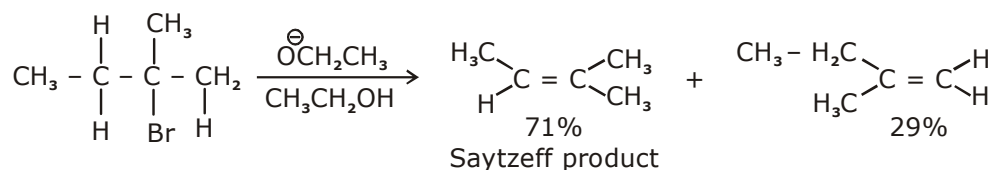
Here β - H is eliminated by base hence called β **elimination** following **Saytzeff rule**.
i.e, (Highly substituted alkene is major product). It also involves an anti elimination of HX.





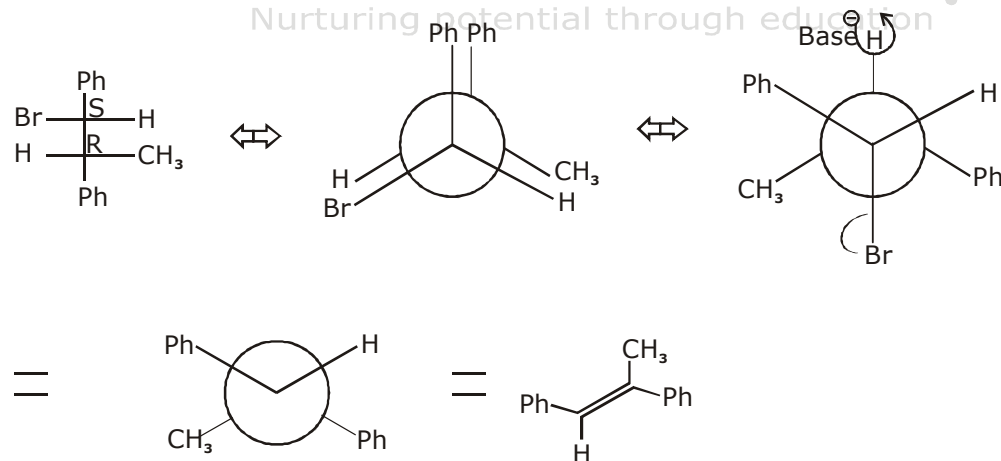
(ii) Formation of the Hoffmann product

Bulky bases can also accomplish dehydro halogenation that do not follow the saytzeff rule. Due to steric hindrance, a bulky base abstracts the proton that leads to the most highly substituted alkene. In these cases, it abstracts a less hindered proton, often the one that leads to formation of the least highly substituted product, called the Hoffmann product.

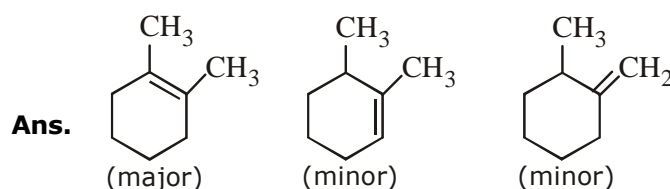
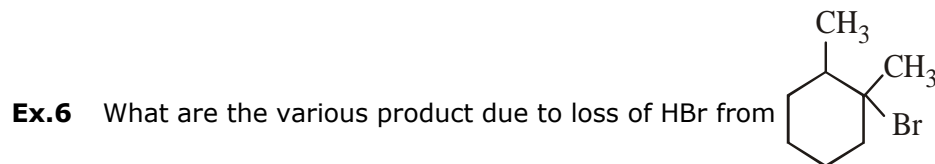
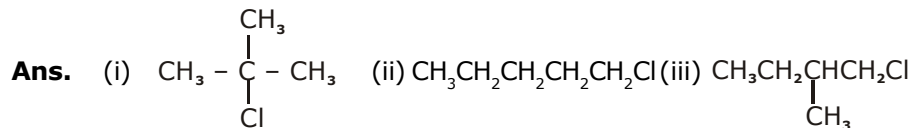
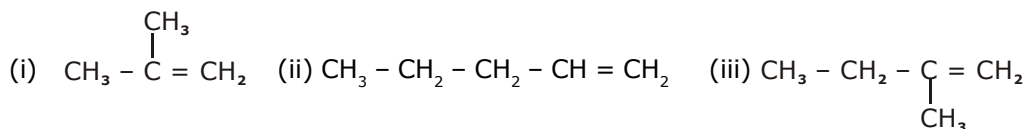


Stereospecific E2 reactions

The E2 is stereospecific because it normally goes through an anti and coplanar transition state. The products are alkene, and different diastereomers of starting materials commonly give different diastereomers of alkenes.

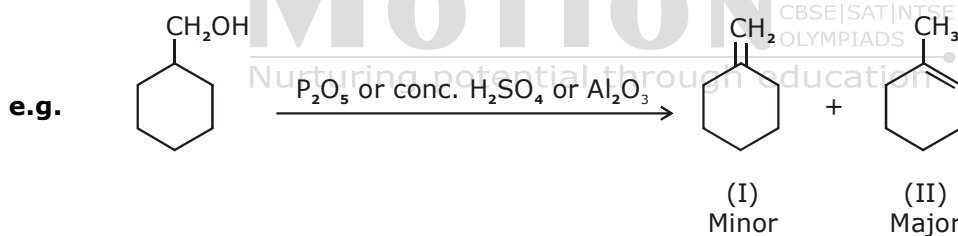
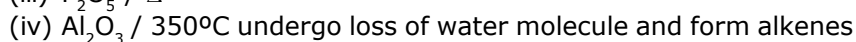
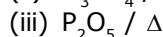
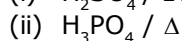
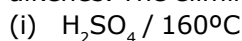


Ex.5 What alkyl halide would yield each of the following pure alkene on reaction with alcoholic KOH ?

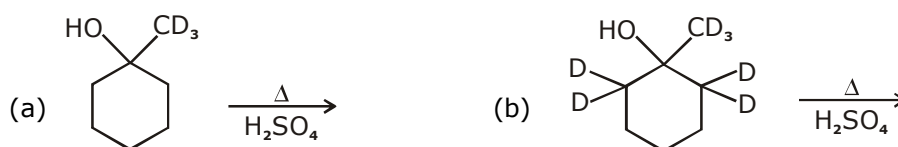


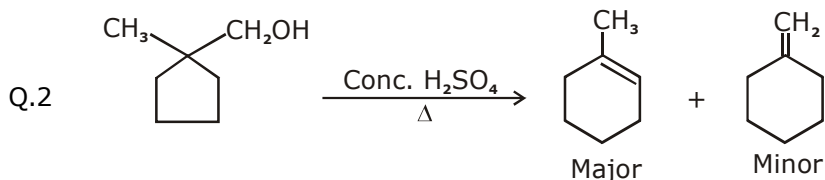
(IV) DEHYDRATION OF ALCOHOLS

Alcohols when heated in presence of following reagents undergo loss of water molecule and form alkenes. The elimination is β **elimination**.



Q.1 If the starting material is labelled with deuterium as indicated, predict how many deuterium will be present in the major elimination product ?

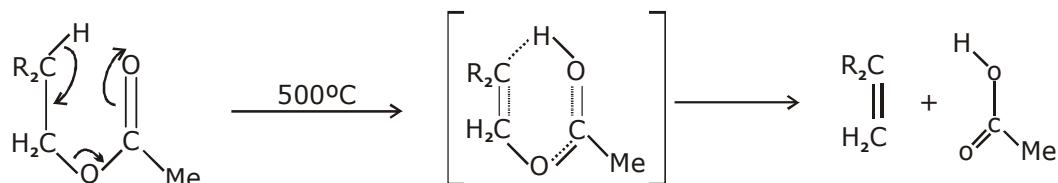




Explain the mechanism ?

(V) BY PYROLYSIS OF ESTERS

Thermal cleavage of an ester involves formations of a six membered ring in the transition state leading to the elimination of an acid leaving behind an alkene.

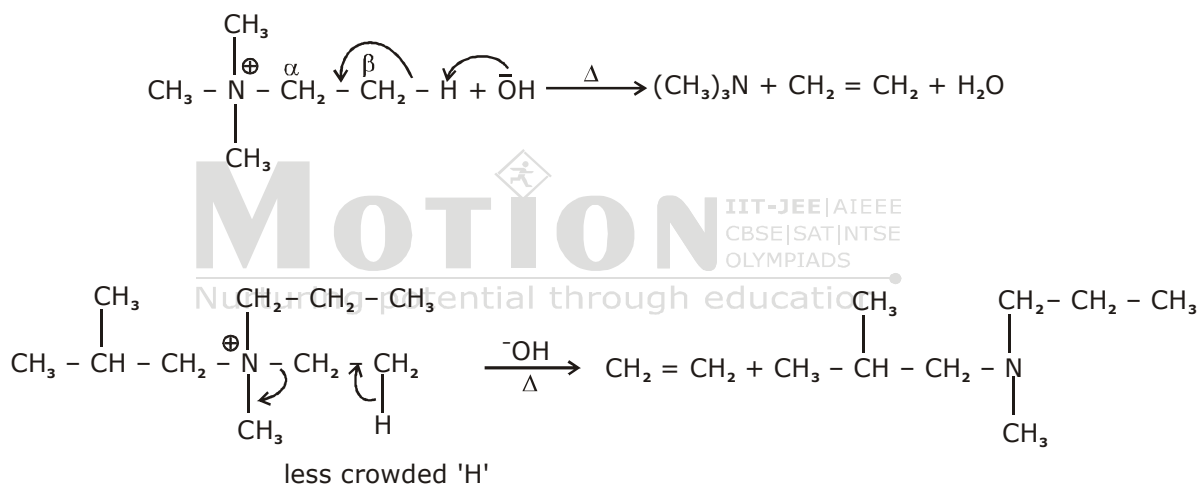


As a direct consequence of cyclic transition state, both the leaving groups namely proton and carboxylate ion are eliminated from the cis position. This is an example of **syn elimination**.

(VI) BY HOFMANN ELIMINATION METHOD

Alkenes can be prepared by heating quaternary ammonium hydroxide under reduced pressure at a temperature between 100°C and 200°C .

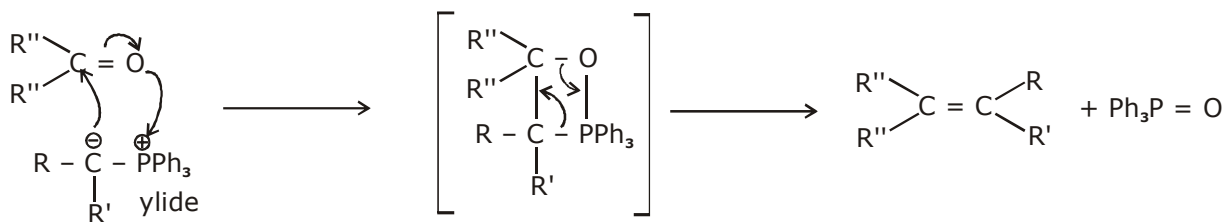
Less substituted alkenes are formed as major product in this case, which are defined as Hofmann alkenes.



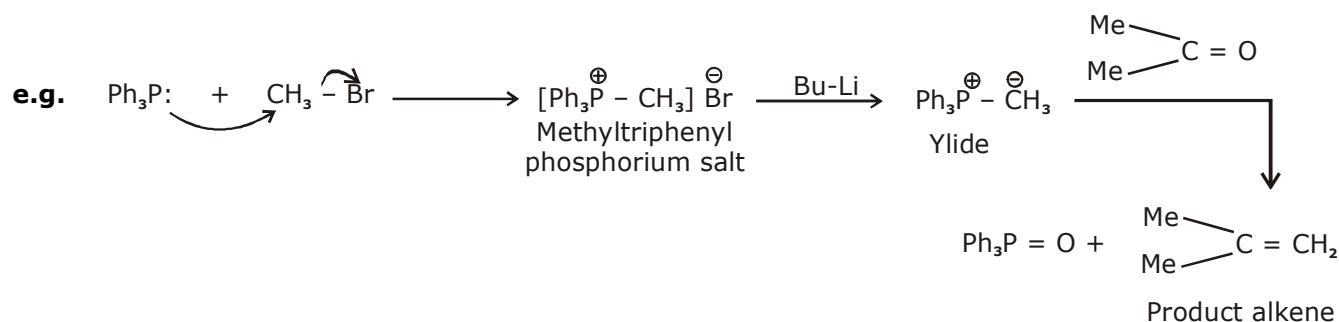
(VII) BY WITTIG REACTION

The aldehydes and ketones are converted into alkenes by using a special class of compounds called phosphorus ylides, also called Wittig reagents.

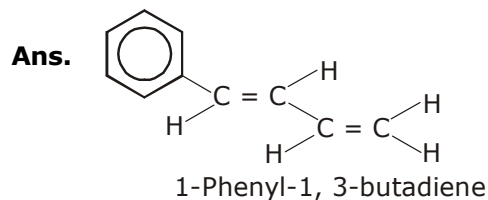
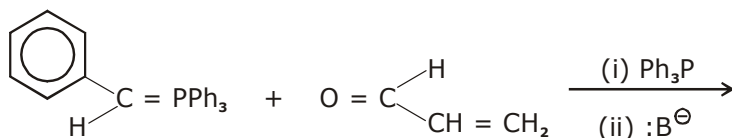
The Triphenyl group of phosphorane has a strong tendency to pull oxygen atom of the aldehyde or ketone via a cyclic transition state forming an alkene.



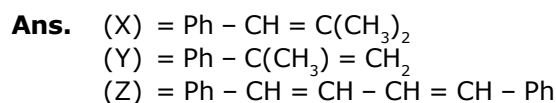
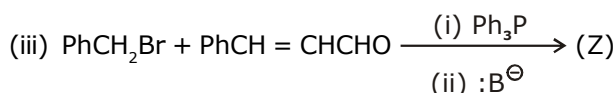
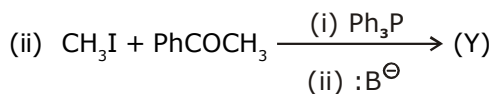
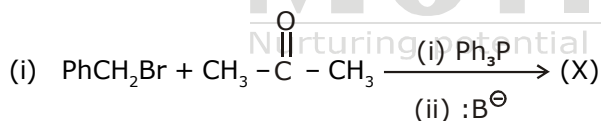
(R, R', R'' and R''' may be hydrogen or any alkyl group)



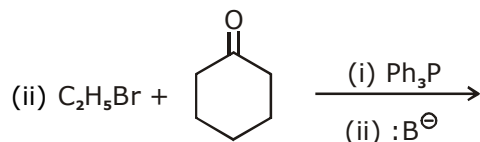
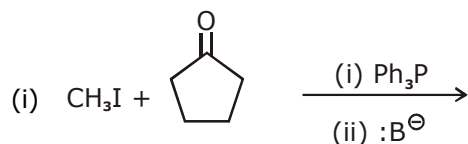
Ex.7 Complete the following reaction :



Ex.8 Identify the (X), (Y), and (Z) in the following reactions



Q.3 Complete the following reactions

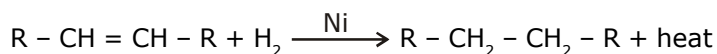


9. Chemical reactions of alkenes

(I) CATALYTIC HYDROGENATION OF ALKENES : (HETEROGENEOUS HYDROGENATION)

Hydrogenation : The function of catalyst

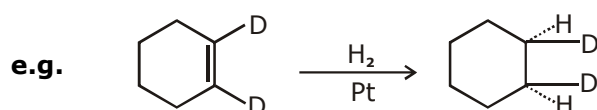
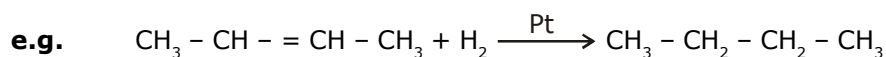
Hydrogenation of an alkene is exothermic reaction ($\Delta H^\circ = -120 \text{ kJ mol}^{-1}$)



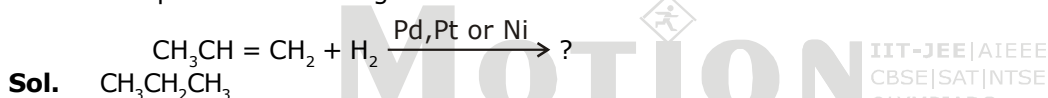
As a consequence, both hydrogen atoms usually add from the same side of the molecule. This mode of addition is called a **syn** addition.

Hydrogenation of an alkene is formally a reduction, with H_2 adding across the double bond to give an alkane.

The process usually requires a catalyst containing Pt, Pd or Ni.



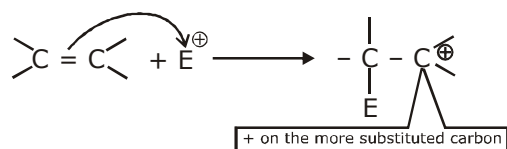
Ex.9 Complete the following reactions :



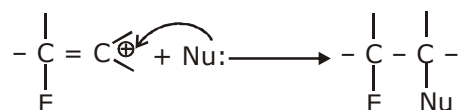
(II) ELECTROPHILIC ADDITION REACTIONS :

Mechanism

Step 1 : Attack of the electrophile on π bond forms a carbocation.

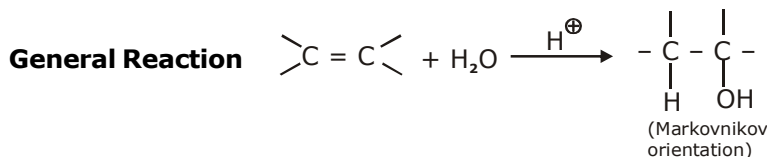


Step 2 : Attack by a nucleophile gives the product of addition

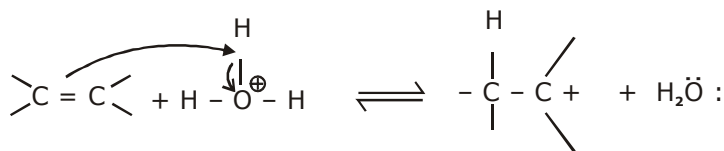


(i) Acid-Catalyzed Hydration of Alkenes

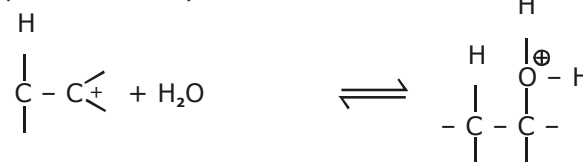
Alkenes add water in the presence of an acid catalyst to yield alcohols. The addition takes place with Markovnikov regioselectivity. The reaction is reversible, and the mechanism for the acid-catalyzed hydration of an alkene is simply the reverse of that for the dehydration of an alcohol. The carbocation intermediate may rearrange if a more stable carbocation is possible by hydride or alkyl migration. Thus, a mixture of isomeric alcohol products may result.

**Mech.****Step 1 :**

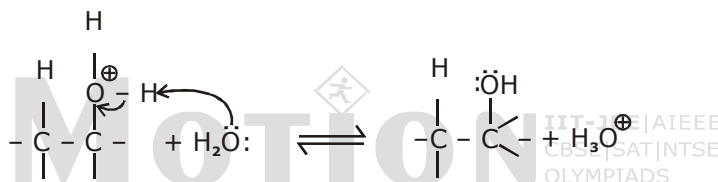
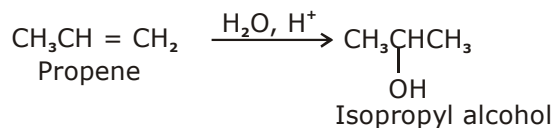
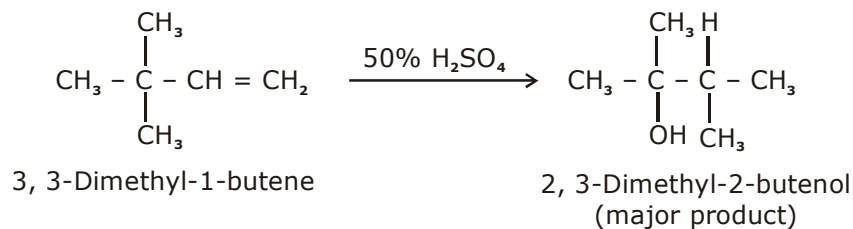
Protonation of the double bond forms a carbocation

**Step 2 :**

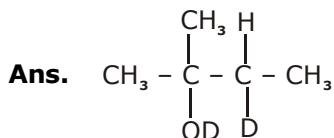
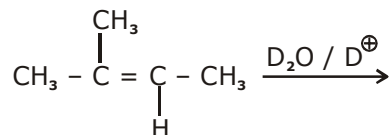
Nucleophilic attack by water

**Step 3 :**

Deprotonation to the alcohol

**e.g.****e.g.**

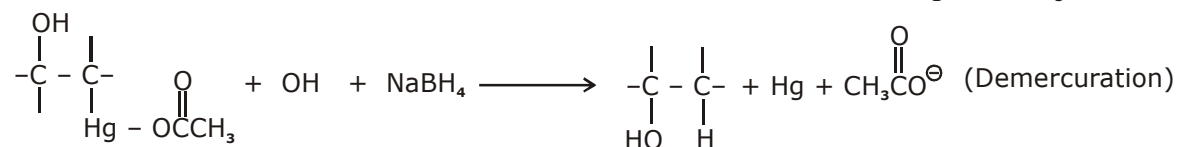
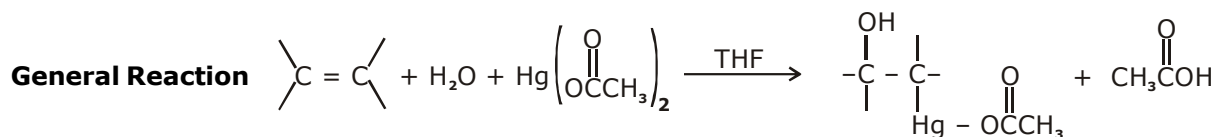
Ex.10 Identify the product in following reaction



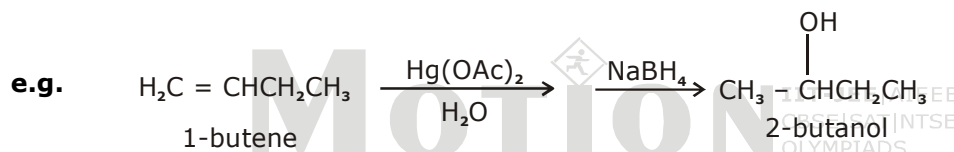
(ii) (a) Oxymercuration - Demercuration

Alkenes react with mercuric acetate in a mixture of water and tetrahydrofuran (THF) to produce (hydroxyalkyl) mercury compounds. These can be reduced to alcohols with sodium borohydride and water :

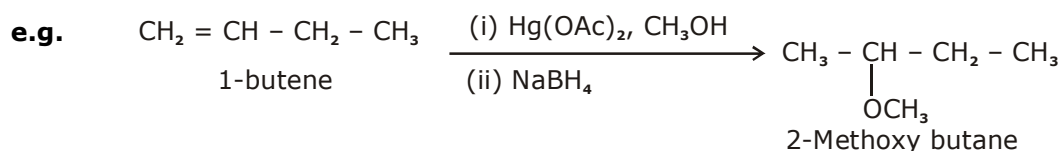
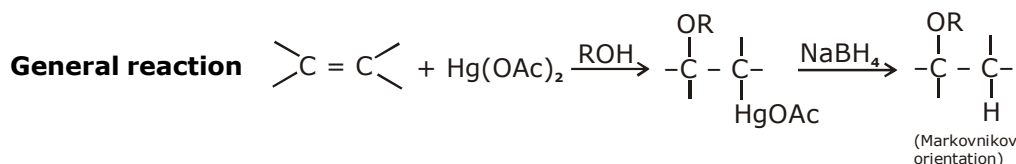
Oxymercuration



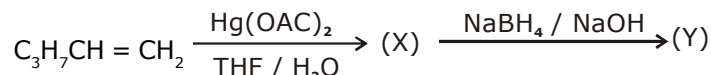
In the oxymercuration step, water and mercuric acetate add to the double bond; in the demercuration step, sodium borohydride reduces the acetoxymercury group and replaces it with hydrogen. Then net addition of H⁻ and -OH takes place with Markovnikov regioselectivity and generally takes place without the complication of rearrangements.



(b) Alkoxymercuration - demercuration

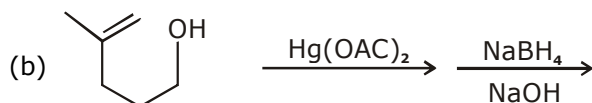
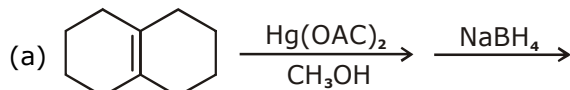


Ex.11 Supply the structures for (X) and (Y) in the following two – step reaction :

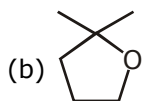
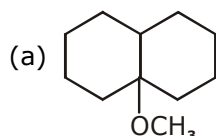


Sol. (X) = $\text{C}_3\text{H}_7\text{CH}(\text{OH})\text{CH}_2\text{-HgOAc}$ (Y) = $\text{C}_3\text{H}_7\text{CH}(\text{OH})\text{CH}_3$
(An organomercurial alcohol)

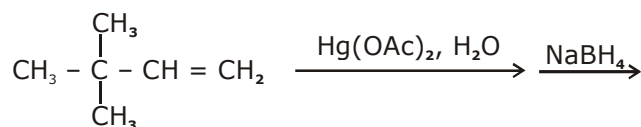
Ex.12 Identify final product in the following :



Ans.

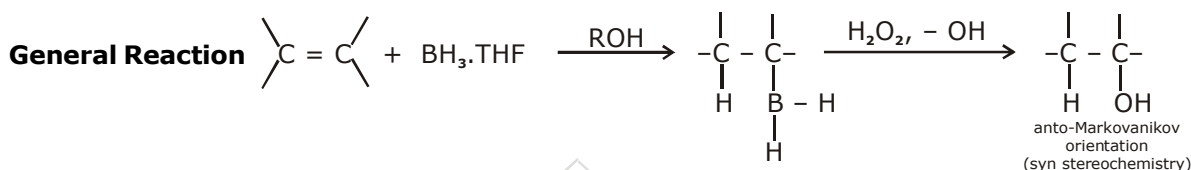


Q.4 Identify the product in the following reaction

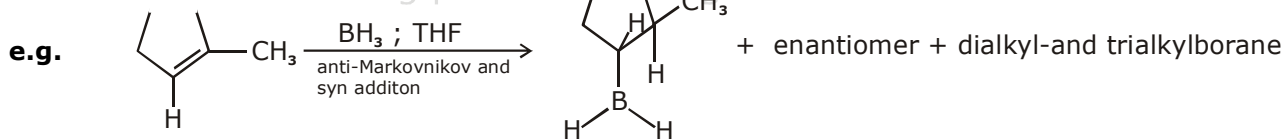


3, 3-Dimethyl - 1- butene

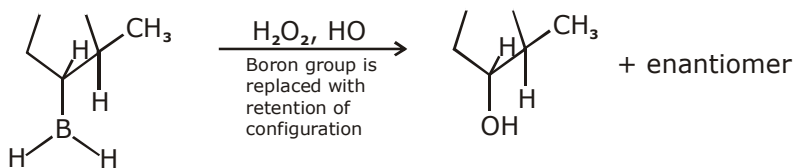
(iii) Hydroboration-oxidation (SYN ADDITION)



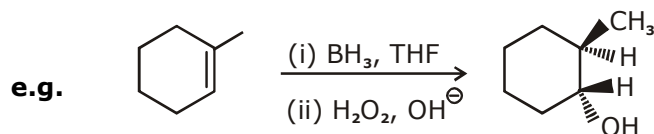
An alkene reacts with BH_3 : THF of diborane to produce an alkylborane. Oxidation and hydrolysis of the alkylborane with hydrogen peroxide and base yields an alcohol.



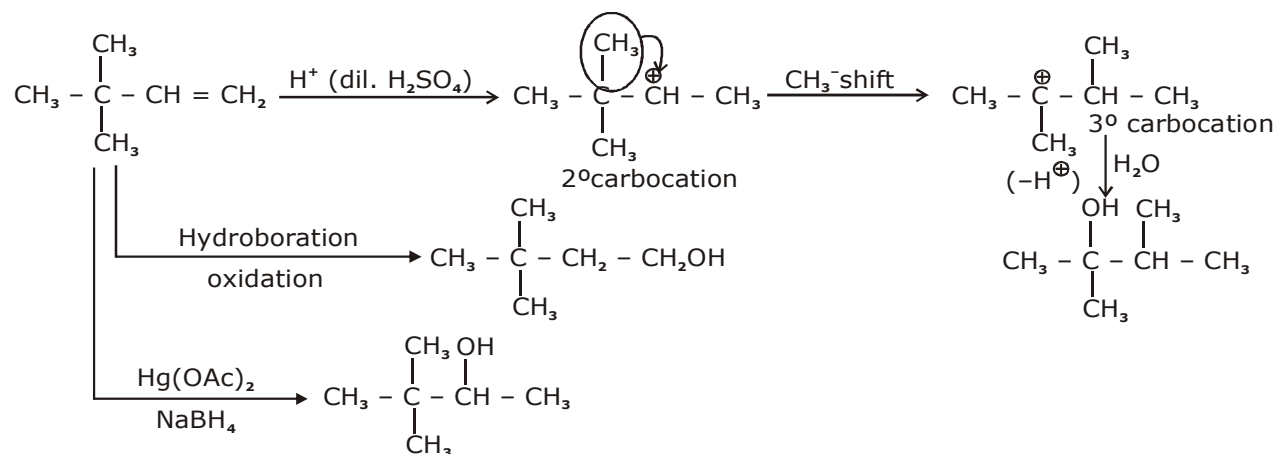
Oxidation



In the first step, boron and hydrogen undergo syn addition to the alkene in the second step, treatment with hydrogen peroxide and base replaces the boron with $-OH$ with retention of configuration. The net addition of $-H$ and $-OH$ occurs with anti Markovnikov regioselectivity and syn stereoselectivity. Hydroboration-oxidation therefore, serves as a useful regiochemical complement to oxymercuration-demercuration.

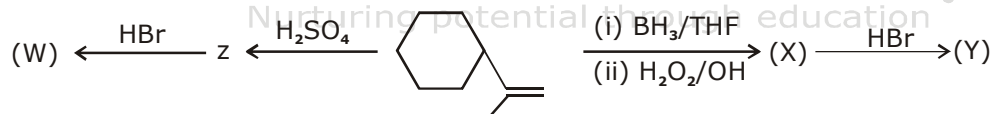


e.g.



- (i) Hydration with dil. H_2SO_4 proceeds via carbocation rearrangement
 (ii) Hydration with $Hg(OAc)_2$, H_2O , followed by $NaBH_4$ proceeds via Markovnikov's rule
 (ii) Hydration with $(BH_3)_2$ followed by H_2O_2 / OH^- proceeds via Anti Markovnikov's rule

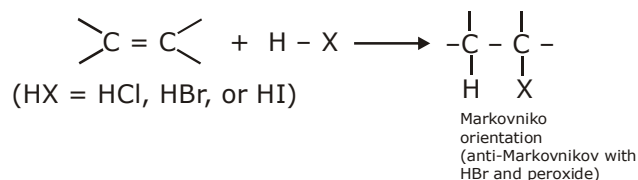
Q.5 Identify x, y, z and w in the following reaction :

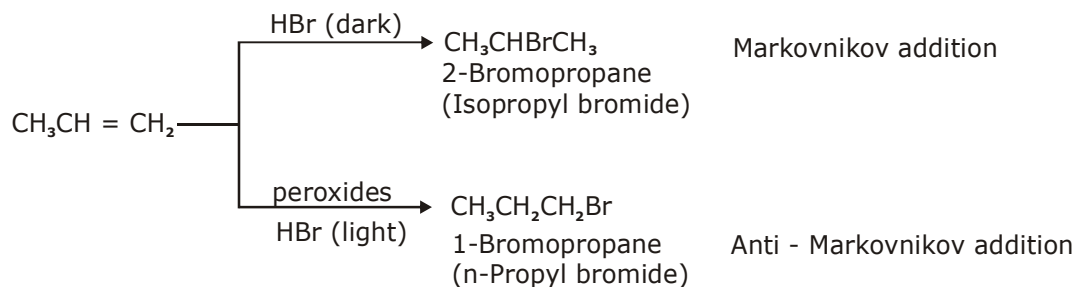


Also select pair of isomers if any

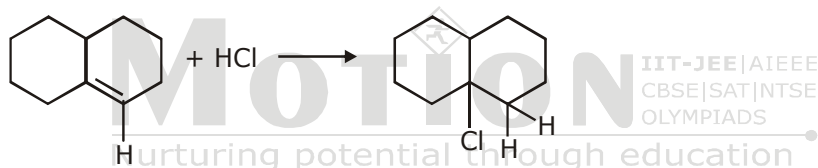
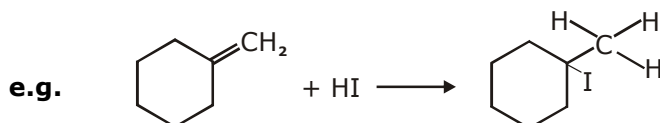
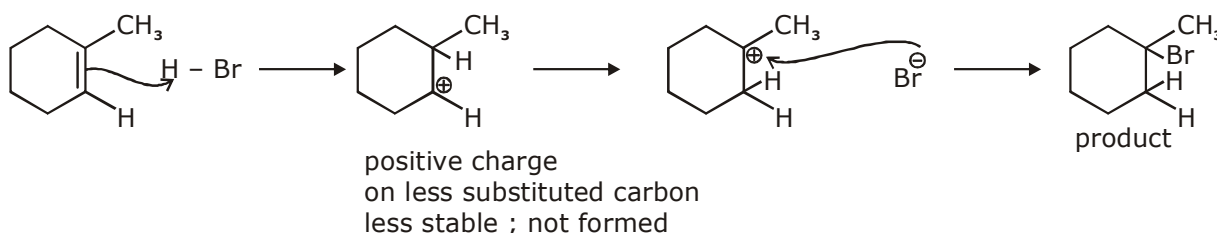
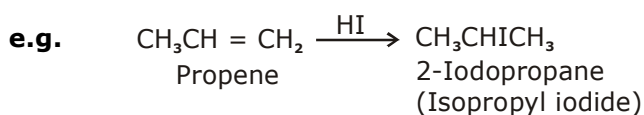
(iv) Addition of hydrogen halides

General Reaction

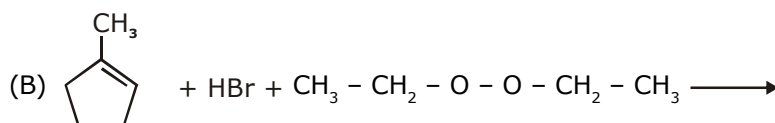
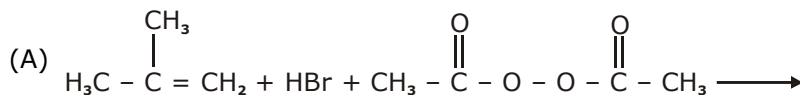


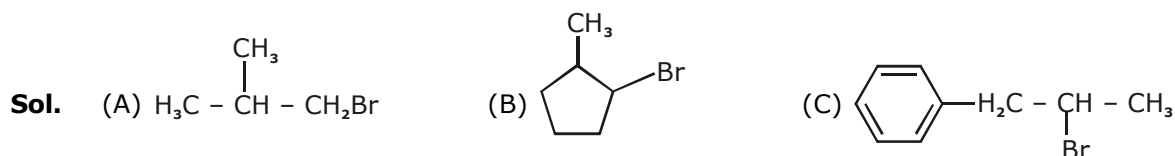
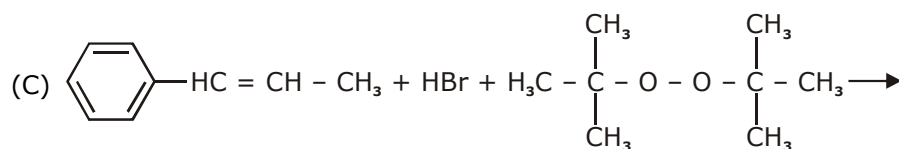


Note : (1) Anti Markovnikov addition is valid only for HBr in presence of peroxide and light only.
 (2) HF, HCl and HI give only polar addition and give Markovnikov product only.

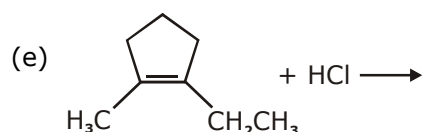
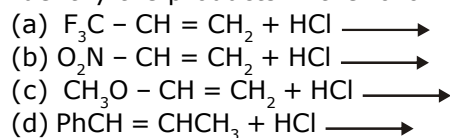


Ex.13 Predict the major products of the following reactions and propose mechanism to support your predictions.

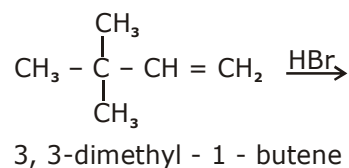




Ex.14 Identify the products in the following reactions :



Q.6 Give the products of the following reactions : -

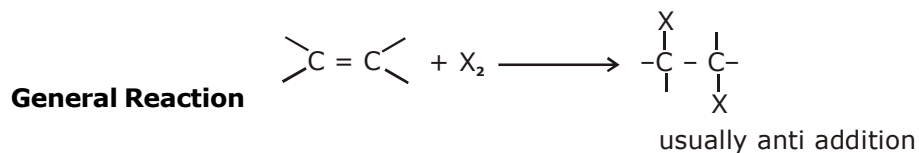


Q.7 Give the reactant (alkene) of the following products.



(v) Addition of halogen

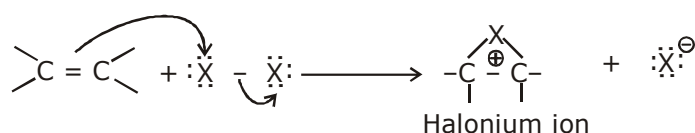
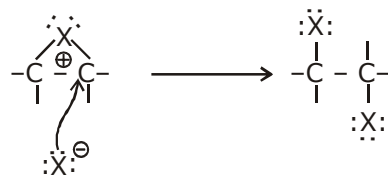
Halogen add to alkenes to form vicinal dihalides.



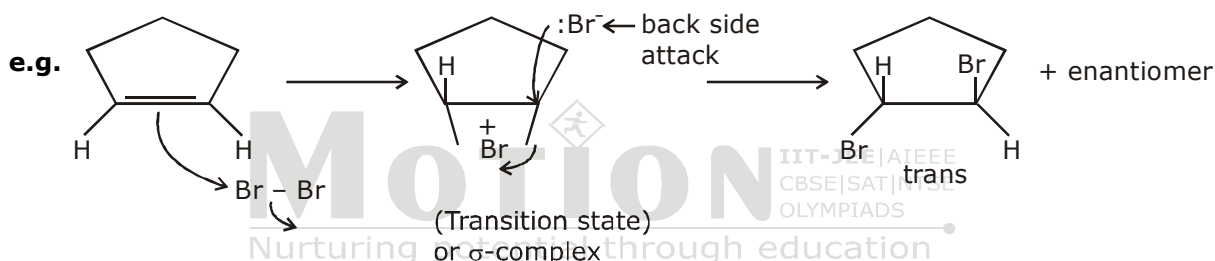
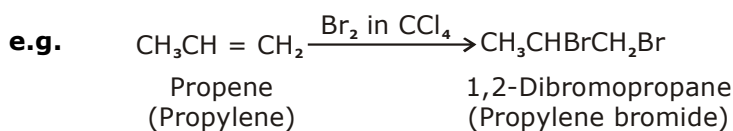
($\text{X}_2 = \text{Cl}_2, \text{Br}_2$)

The nucleophile attacks the electrophilic nucleus of one halogen atom, and the other halogen serves as the leaving group, departing as halide ion. Many reactions fit this general pattern.

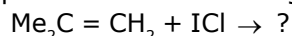
- Note :** (i) F_2 is not added because F^+ is never generated. Moreover reaction is explosive giving CO_2 & H_2O
 (ii) I_2 is not added because reaction is reversible with equilibrium in backward direction.
 (iii) Reaction with bromine is basis for test of alkenes.
 (iv) Halogen addition is stereospecific anti addition
 (v) Halogens can also be added in presence of sun light and give free radical addition.
 (Reactivity of halogen addition in sunlight is F_2 (explosive) $> Cl_2 > Br_2 > I_2$)

Mech.**Step-1** Formation of a halonium ion**Step-2** Opening of the halonium ion

X^- attacks from the back side of halonium ion.

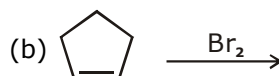
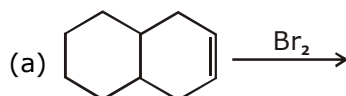


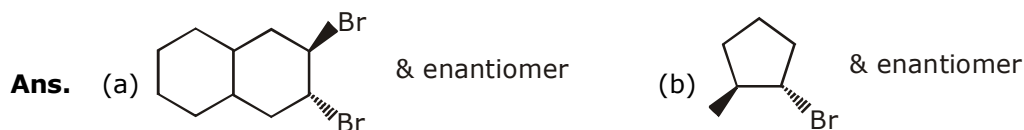
Ex.15 Give the product of the following reaction.



Sol. Cl is more electronegative than I making I the E^+ that, according to the Markovnikov rule, adds to the C with the greater number of H's. The product is 2-chloro-1-iodo-2-methylpropane, (Me_2CClCH_2I) .

Ex.16 What are the products and (type of isomers) when Br_2 adds to : -

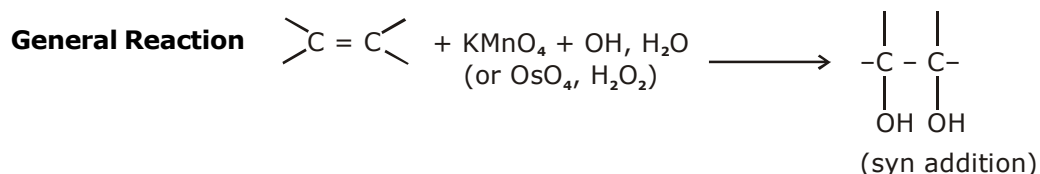




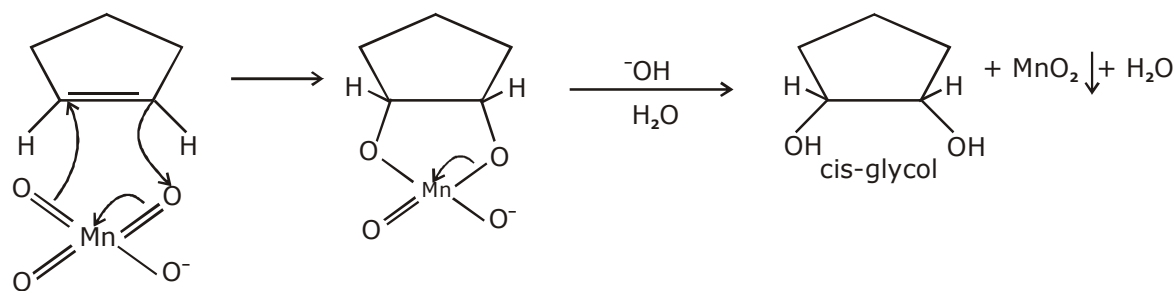
Q.8 Account for the acid-catalyzed isomerization of cis-2-butene to trans-2-butene

(vi) **Hydroxylation of Alkenes**

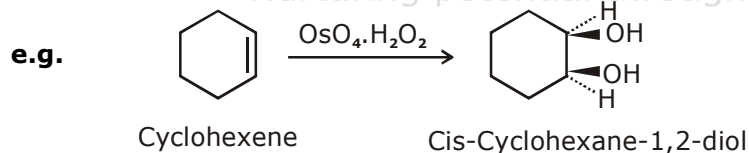
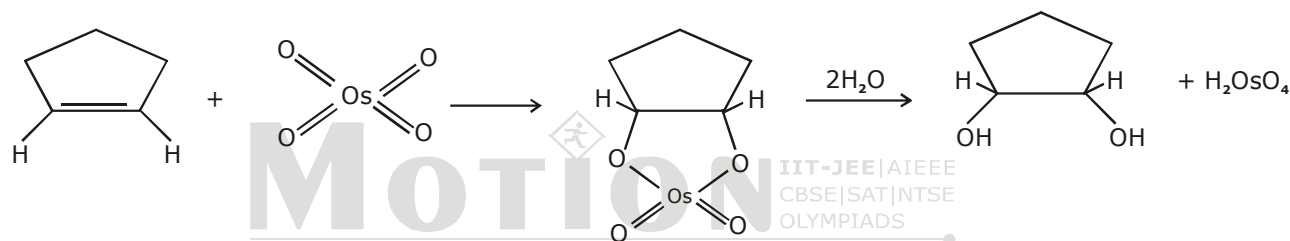
(a) Syn Hydroxylation : (Reaction with Bayer's reagent, (cold dilute alkaline KMnO_4 solution). Both OH groups are added from same stereochemical side. This addition is example of syn addition



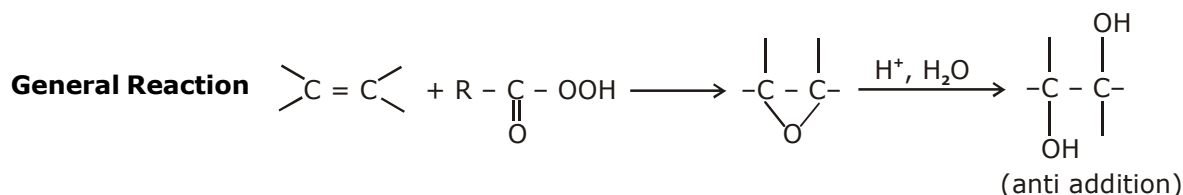
e.g.

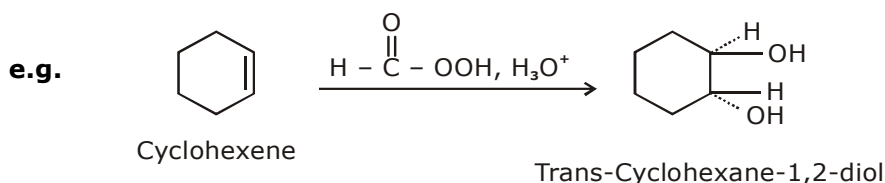


The same function of syn addition of 2 - OH groups is performed by $\text{OsO}_4 / \text{H}_2\text{O}_2$

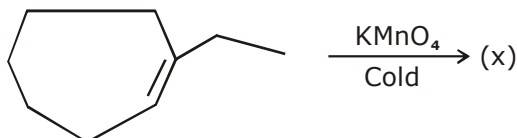


(b) **Anti hydroxylation**

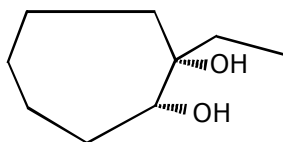




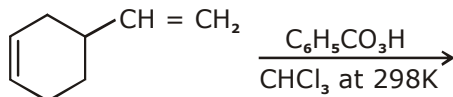
Ex.17 Identify the product in the following reaction :



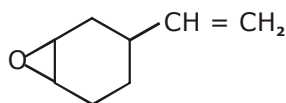
Ans.



Ex.18 Identify the product (X) in the following reaction :



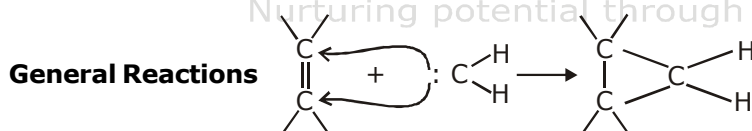
Ans. (x) :



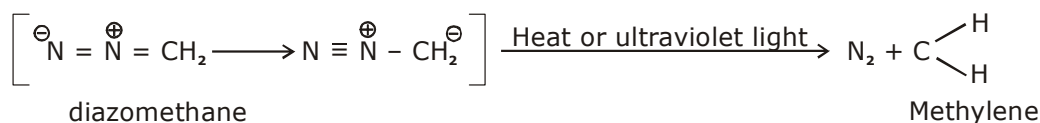
Since C = C bond in ring is more substituted than that in open chain.

(vii) Addition of carbenes to Alkenes :

Methylene is the simplest of the carbenes : uncharged, reactive intermediates that have a carbon atom with two bonds and two nonbonding electrons. Like borane (BH₃), methylene is a potent electrophile because it has an unfilled octet. It adds to the electrons rich pi-bond of an alkene to form a cyclopropane.

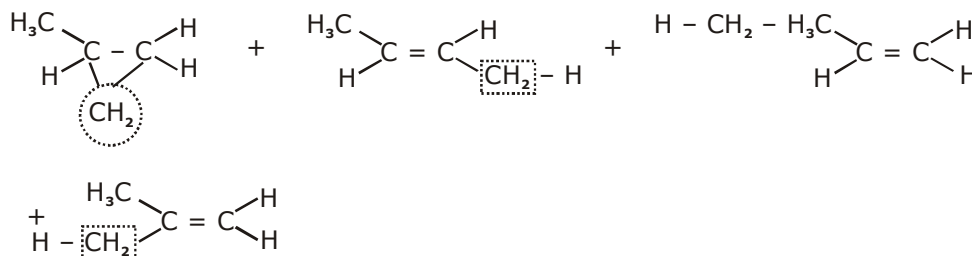
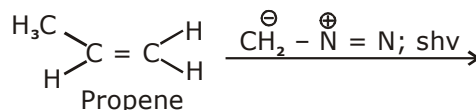
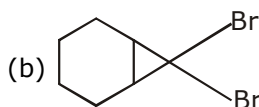
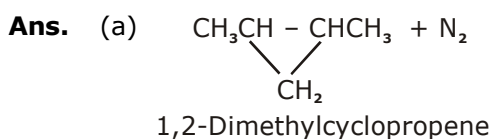
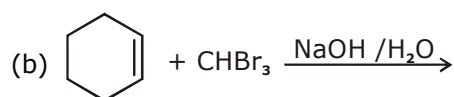
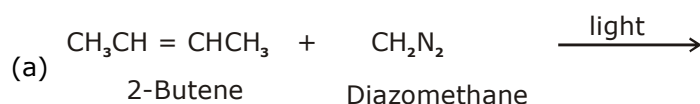


Heating or photolysis of diazomethane (CH₂N₂) gives nitrogen gas and methylene.

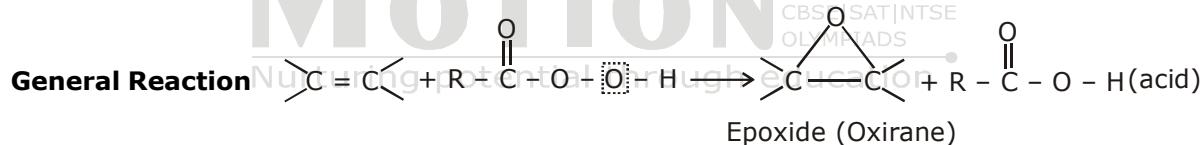


There are two difficulties with using CH₂N₂ to cyclopropene double bonds. First, it is extremely toxic and explosive. A safer reagent would be more convenient for routine use. Second, methylene generated from CH₂N₂ is so reactive that it inserts into C - H bonds as well as C = C bonds.

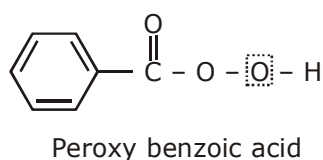
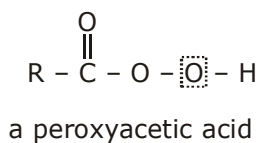
e.g.

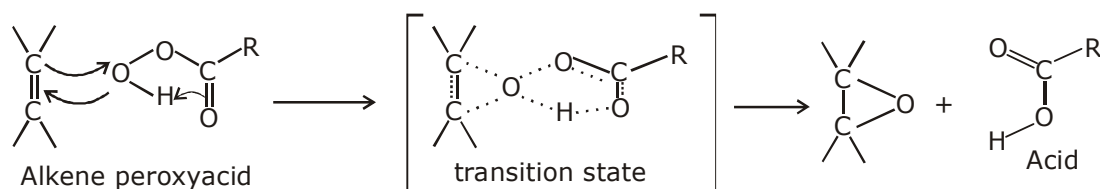
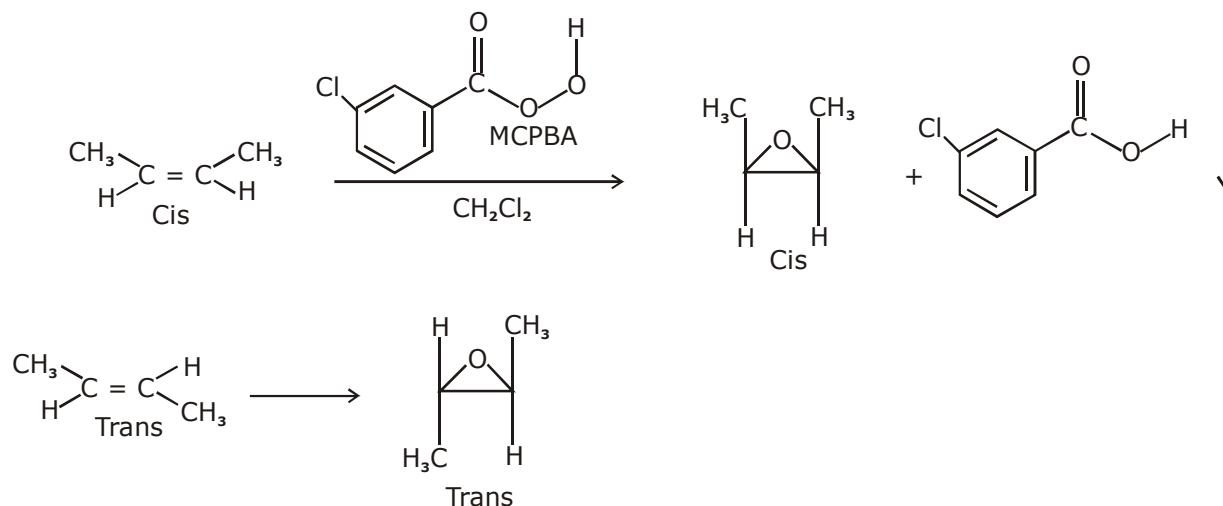
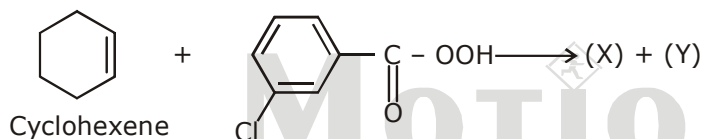
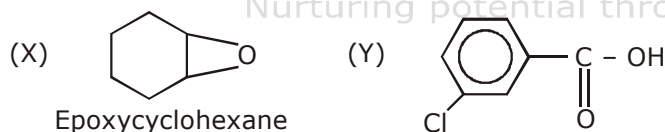
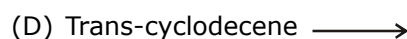
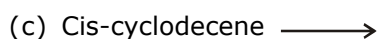
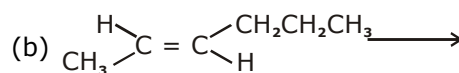
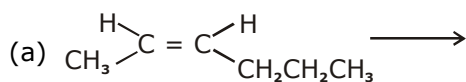
**Ex.19** Identify the product in the following reactions**(III) EPOXIDATION OF ALKENES :**

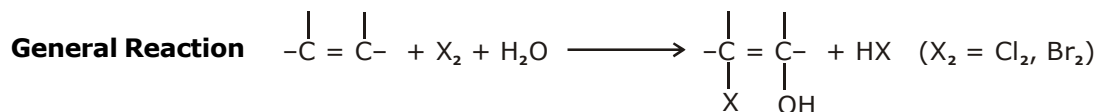
An alkene is converted to an epoxide by a peroxyacid, a carboxylic acid that has an extra oxygen atom in a $-\text{O}-\text{O}-$ (peroxy) linkage.



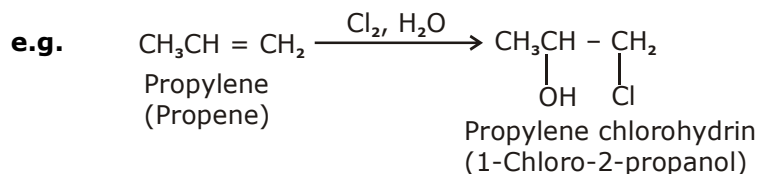
The epoxidation of an alkene is clearly an oxidation, since an oxygen atom is added. Peroxyacids are highly selective oxidizing agents. Some simple peroxyacids (sometimes called per acids) and their corresponding carboxylic acids are shown below :



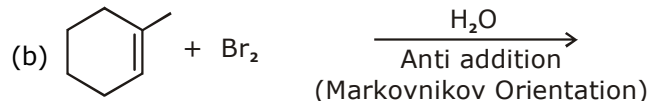
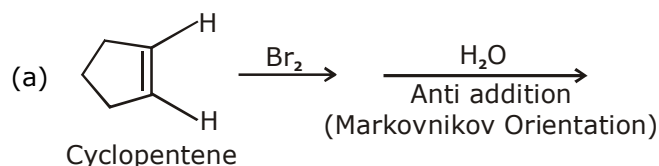
Mech.**e.g.****Ex.20** Complete the following reaction**Ans.****Ex.21** Predict the product, including stereochemistry where appropriate, for the m-chloroperoxy-benzoic acid epoxidations of the following alkenes.

(IV) HALOHYDRIN FORMATION

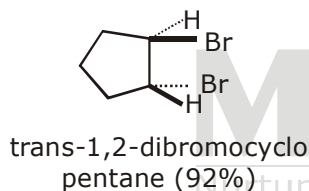
X' and H₂O are generated as attacking species from X₂ + H₂O



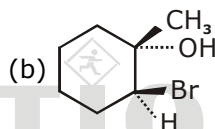
Ex.22 Predict the product in the following reactions



Ans. (a)



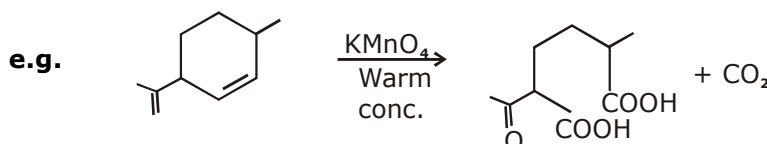
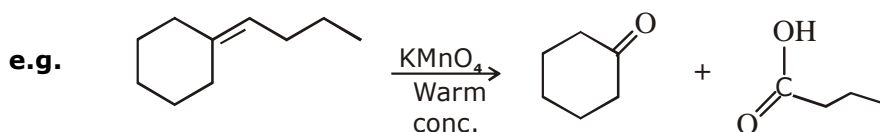
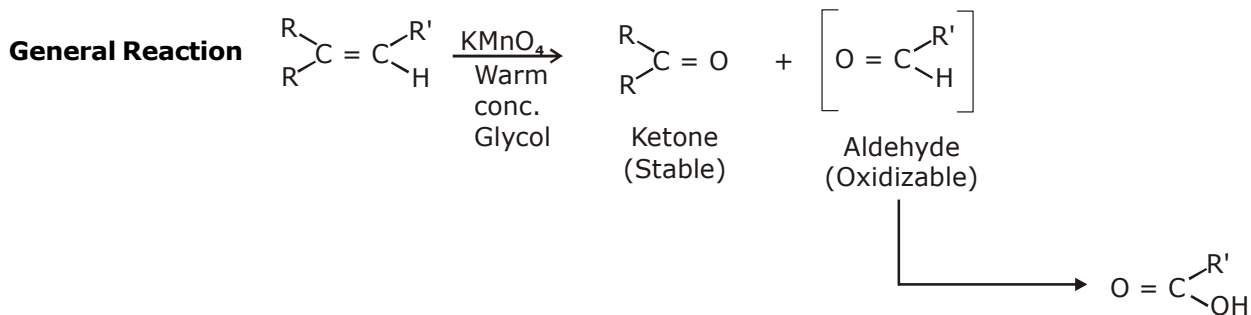
(b)



IIT-JEE|AIEEE
CBSE|SAT|NTSE
OLYMPIADS

(V) OXIDATIVE CLEAVAGE OF ALKENES**(i) Cleavage by permanganate**

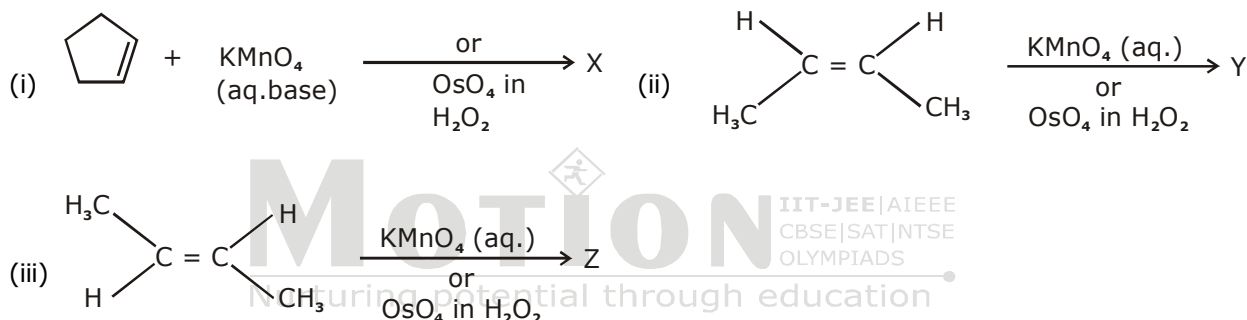
In a KMnO₄ hydroxylation, if the solution is warm or acidic or too concentrated, oxidative cleavage of the glycol may occur. Mixtures of Ketones and carboxylic acids are formed, depending on whether there are any oxidizable aldehydes in the initial fragments. A terminal = CH₂ group is oxidized to CO₂ and water.



Ex.23 What is the main utility of this reaction and why is it superior to KMnO_4 cleavage for this purpose

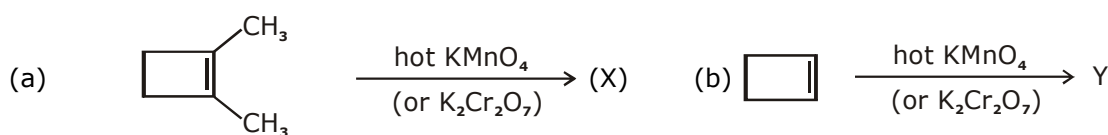
Sol. It locates the position of $\text{C} = \text{C}$'s in molecules. KMnO_4 cleavage is more vigorous and can oxidize other groups, i.e., OH .

Ex.24 Give the products of the following reactions :-



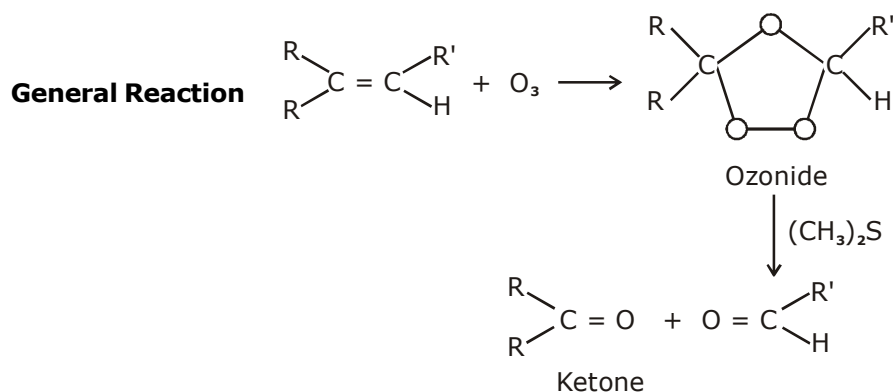
Sol. $\text{X} = \text{Cis-1, 2-Cyclopentanediol}$ $\text{Y} = \text{meso-CH}_3 - \text{CHOH} - \text{CHOH} - \text{CH}_3$
 $\text{Z} = \text{rac-CH}_3\text{CHOHCHOHCH}_3$

Q.9 Complete the following reactions

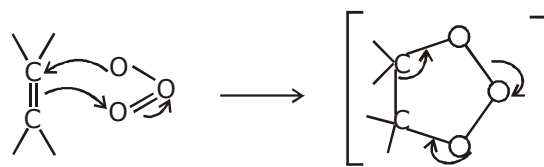


1,2-dimethylcyclobutene

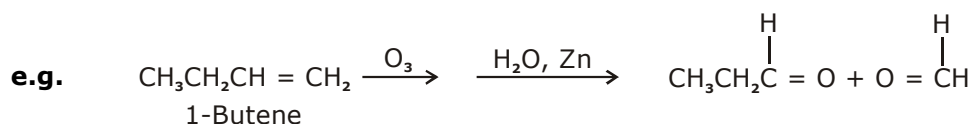
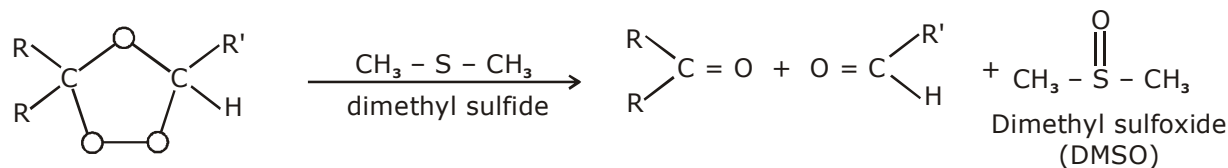
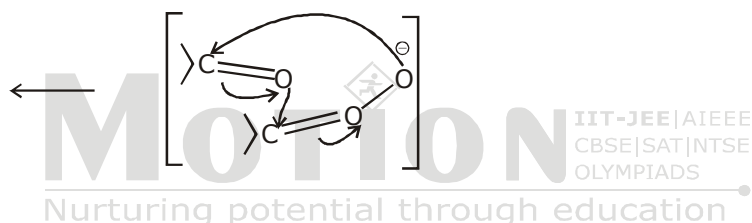
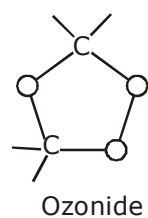
(ii) Ozonolysis : Like permanganate ozone cleaves double bonds to give ketones and aldehydes. However, ozonolysis is milder, and both ketones and aldehydes can be recovered without further oxidation.

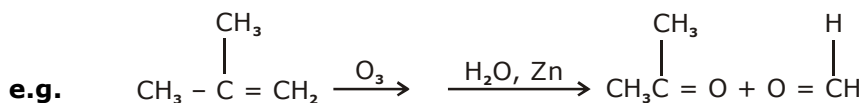
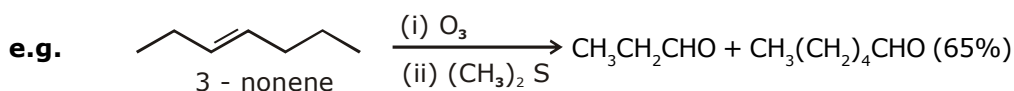
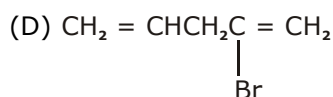
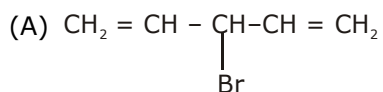
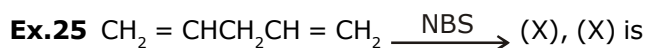
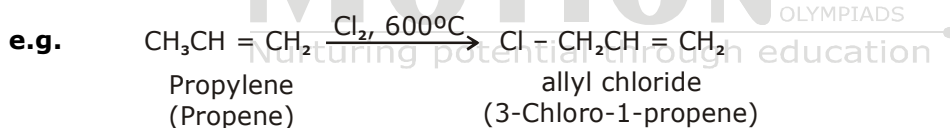
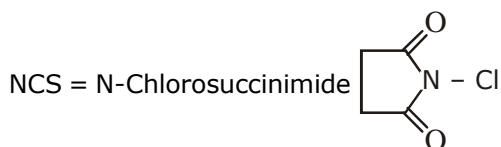
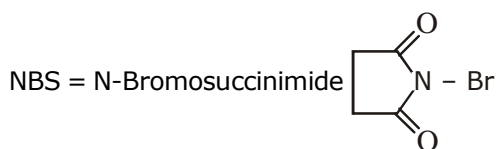
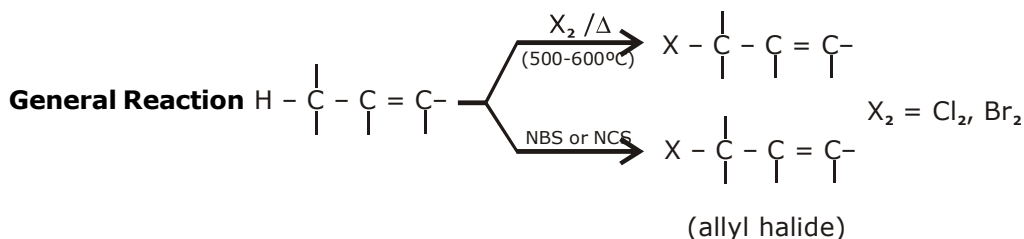


Mech.



Monozonide (Primary ozonide)



**(IX) HALOGENATION, ALLYLIC SUBSTITUTION**

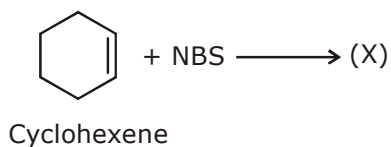
Ans. A

Ex.26 Assertion (A) : Propene ($\text{CH}_3\text{CH}=\text{CH}_2$) undergoes allylic substitution.

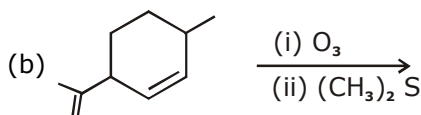
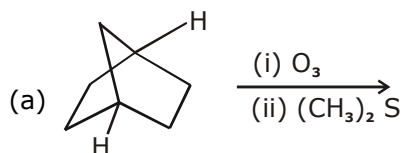
Reason (R) : $\text{CH}_2=\text{CHCH}_2$ (allylic) free radical is stabilised by resonance.

Ans. (A)

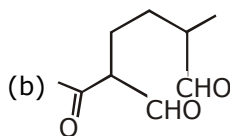
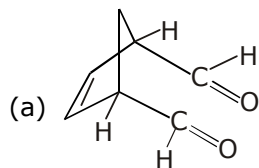
Q.10 Identify the product (X) in the following reaction



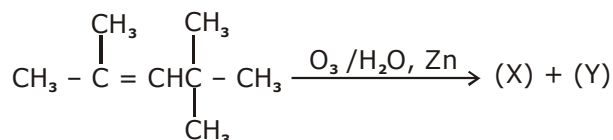
Ex.27 Identify the product in the following reactions



Ans.



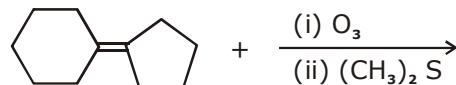
Ex.28 Identify the products (x, y) of following reaction : -



Ans.



Q.11 Predict the major product of the following reaction



10. **(a)** $\text{CH}_3 - (\text{CH}_2)_3 - \text{CH} = \text{CH}_2 < \text{CH}_3 - (\text{CH}_2)_2 - \text{CH} = \text{CH} - \text{CH}_3 < \text{H}_3\text{C} - (\text{CH}_2)_2 - \underset{\text{CH}_3}{\text{C}} = \text{CH}_2$

Ex.30 Isobutylene $\xrightarrow[\text{peroxides}]{+\text{HBr}}$ product is :

- (A) Tertiary butyl bromide (B) Isobutyl bromide
(C) Tertiary butyl alcohol (D) Isobutyl alcohol

Ans. (B)

ALKYNES

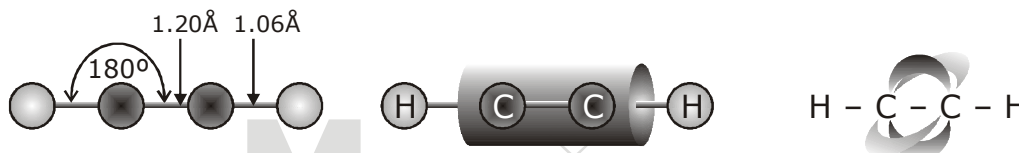
1. Introduction

A triple bond gives an alkyne four fewer hydrogen atoms than the corresponding alkane. Therefore the triple bond contributes two degree of unsaturation (DU).

Alkynes are not as common in nature as alkenes, but some plants do use alkynes to protect themselves against disease or predators. Acetylene is by far the most important commercial alkyne. Acetylene is an important industrial feedstock but its largest use is as the fuel for the oxyacetylene welding torch.

2. Structure and Bonding in Alkynes

- (1) Alkynes are hydrocarbons that contain carbon-carbon triple bond.
- (2) Alkynes are also called acetylenes because they are derivatives of acetylene.
- (3) The general formula is : C_nH_{2n-2} . (one triple bond)
- (4) In alkyne $C \equiv C$ bond length is 1.20 \AA .
- (5) Its bond energy is $192 \text{ kcal. mol}^{-1}$
- (6) The hybridization of carbon atoms having triple bond ($C \equiv C$) in alkynes is sp
- (7) Overlapping of these sp hybrid orbitals with each other and with the hydrogen orbitals gives the sigma bond framework which is linear (180°) structure.
- (8) Two π bonds result from overlap of the two remaining unhybridized p orbitals on each carbon atom. These orbitals overlap at **right angles** (90°) to each other, forming one π bond with electron density above and below the $C - C$ sigma bond, and the other with electron density in front and in back of the sigma bond. This results in a cylindrical π electron cloud around σ bonded structure

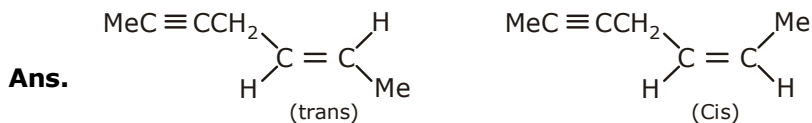


Note : Any type of stereoisomerism does not arise in acetylenic bond due to linearity of $C \equiv C$ bond.

Ex.1 Cis-trans isomerism is not possible in alkynes because of :

Ans. 180° bond-angle at the carbon-carbon triple bond.

Ex.2 Draw the geometrical isomers of hept-2-en-5-yne?



Q.1 C_6H_{10} (alkyne) is optically active. What is its structure?

Q.2 C_5H_8 (alkyne) has three-degree of unsaturation. What is the structure ? What is the isomerism show?

4. Physical Properties of Alkynes

394 - Rajeev Gandhi Nagar Kota, Ph. No. 0744-2209671, 93141-87482, 93527-21564

IVRS No. 0744-2439051, 0744-2439052, 0744-2439053, www.motioniitjee.com, email-info@motioniitjee.com

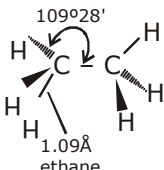
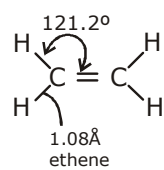
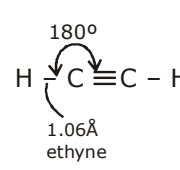
(1) Alkynes are relatively nonpolar (w.r.t. alkyl halides and alcohols) and are nearly insoluble in water (but they are more polar than alkenes and alkanes). They are quite soluble in most organic solvents, (acetone, ether, methylene chloride, chloroform and alcohols).

(2) Acetylene, propyne, and the butynes are gases at room temperature, just like the corresponding alkanes and alkenes. In fact, the boiling point of alkynes are nearly the same as those of alkanes and alkenes with same number of carbon atoms.

Table

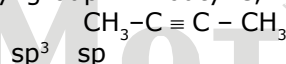
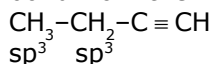
Name	Formula	M.p., °C	B.P., °C	Relative density (at 20°C)
Acetylene	$\text{HC} \equiv \text{CH}$	- 82	- 75	
Propyne	$\text{HC} \equiv \text{CCH}_3$	- 101.5	- 23	
1-Butyne	$\text{HC} \equiv \text{CCH}_2\text{CH}_3$	- 122	9	
1-Pentyne	$\text{HC} \equiv \text{C}(\text{CH}_2)_2\text{CH}_3$	- 98	40	0.695
2-Butyne	$\text{CH}_3\text{C} \equiv \text{CCH}_3$	- 24	27	0.694
2-Pentyne	$\text{CH}_3\text{C} \equiv \text{CCH}_2\text{CH}_3$	- 101	55	0.714
3-Methyl-1-butyne	$\text{HC} \equiv \text{CCH}(\text{CH}_3)_2$		29	665

TABLE - COMPARATIVE STUDY OF ALKANES, ALKENES, ALKYNES

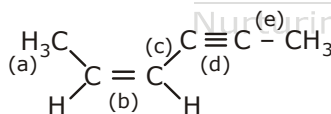
S.No.	Properties	Alkanes	Alkenes	Alkynes
1.	Bond length	1.54 (C - C)	1.32 (C = C)	1.20 (C \equiv C)
2.	Bond energy (KJmol ⁻¹)	415 (C - C)	615 (C = C)	835 (C \equiv C)
3.	Hybridization	sp ³	sp ²	sp
4.	% s character	25%	33%	50%
5.	pKa	50	44	25
6.	Electronegativity of 'C'		Increases	→
7.	Polarity		Increases	→
8.	Rate of hydrogenation		less	more
9.	Rate of electrophilic addition reaction		more	less
10.	Heat of combustion	C ₂ H ₆ (-373)	C ₂ H ₄ (-337k cal)	C ₂ H ₂ (-317kcal)
11.	Density (g/cm ³)	C ₃ H ₈ (-373)	C ₃ H ₆ (0.52k cal)	C ₃ H ₄ (0.67)
12.	Structure			
13.	Shape	Tetrahedral	Planar	Linear

Ex.3 Which has a longer carbon-methyl bond, 1-butyne or 2-butyne. Explain?

Ans. The bond from the methyl group in 1-butyne is to an sp³-hybridised carbon and so is longer than the bond from the methyl group in 2-butyne, which is to an sp-hybridised carbon.

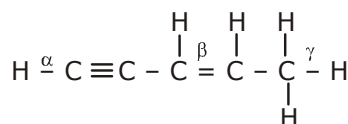


Ex.4 Arrange the following bond-lengths in increasing order.



Ans. (d) < (b) < (c) < (e) < (a)

Q.3 Arrange C - H bond -lengths (α, β, γ) in increasing order as shown : -



6. Laboratory test of Alkyne

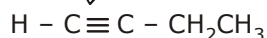
Table-V

Functional Group	Reagent	Observation	Reaction	Remarks
$-C \equiv C-$	(1) Bayer's Reagent alk. dil. cold $KMnO_4$	Pink Colour disappears	$HC \equiv CH + H_2O + O \xrightarrow{alk. KMnO_4} OHC - CHO$	Hydroxylation
	(2) Br_2/H_2O	Red Colour decolourises	$Br_2 + HC \equiv CH \rightarrow CHBr_2 - CHBr_2$ White ppt	Bromination
	(3) O_3 (ozone)	Acid Formed	$R - C \equiv C - R' \xrightarrow{O_3} RCOOH + R'COOH$	Ozonolysis

7. Laboratory test of terminal alkynes

When triple bond comes at the end of a carbon chain. The alkyne is called a terminal alkyne.

acetylenic hydrogen



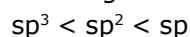
1-Butyne, terminal alkyne

Table-VI

Functional Group	Reagent	Observation	Reaction
$R-C \equiv C-H$	(1) Cuprous chloride + NH_4OH	Red ppt.	$R - C \equiv CH + CuCl \xrightarrow{NH_4OH} R - C \equiv C Cu \downarrow (red)$
	(2) $AgNO_3 + NH_4OH$	White ppt	$R - C \equiv CH + Ag^+ \longrightarrow R - C \equiv C Ag \downarrow (white)$
	(3) Na in ether	Colourless gas	$HC \equiv CH + 2Na \longrightarrow Na - C \equiv C - Na + H_2 \uparrow$

8. Acidity of Terminal Alkynes

Terminal alkynes are much acidic than other hydrocarbons due to more electronegative sp hybridised carbon. The polarity (acidity) of a $C - H$ bond varies with its hybridization, increasing with the increase in percentage's character of the orbitals.

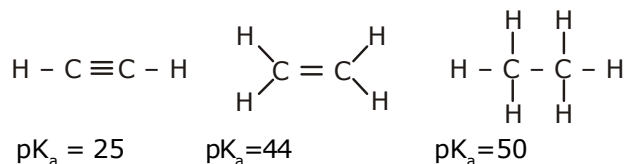


S.No.	Compound	Conjugate Base	Hybridization of C ⁻	%Character	pK _a
1.	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}-\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}-\text{C}: \\ & \\ \text{H} & \text{H} \end{array}$	sp ³	25%	50
2.	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} = \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	$\begin{array}{c} \text{H} & & \\ & \diagdown & \\ & \text{C} = \text{C} \\ & / & \\ \text{H} & & \end{array}$	sp ²	33%	44
3.	:NH ₃	:NH ₂ ⁻			
4.	H - C≡C - H	H - C≡C ⁻	sp	50%	25
5.	R - OH	R - O ⁻			16-18

Weakest acid

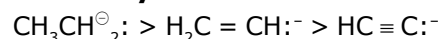
Stronger acid

The hydrogen bonded to the carbon of a terminal alkyne is considerably more acidic than those bonded to carbons of an alkene and alkane (see section). The pK_a values for ethyne, ethene & ethane illustrate this point

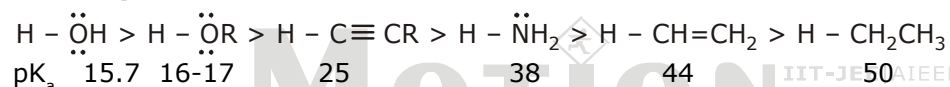


The order of basicity of their anions is opposite to that of their relative acidity:

Relative Basicity



Relative acidity

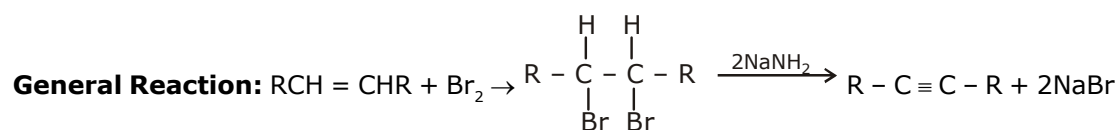


Relative Basicity



9. General methods of preparation :

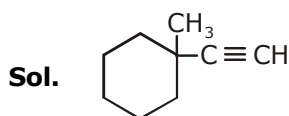
(I) By dehydro halogenation of gem and vic dihalide:



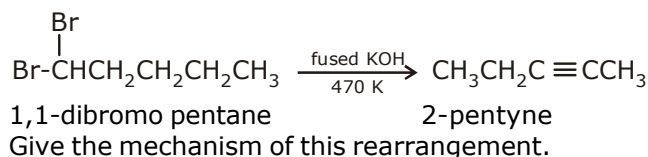
A vic - dibromide

The dehydrohalogenations occur in two steps, the first yielding a bromoalkene and the second alkyne.

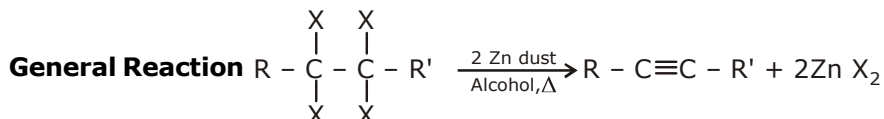
Mechanism :



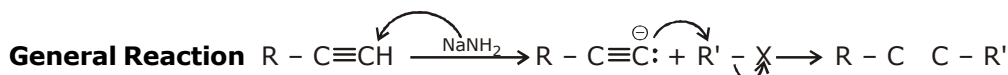
Q.4 1,1-dibromopentane on reaction with fused KOH at 470 K gives 2-pentyne



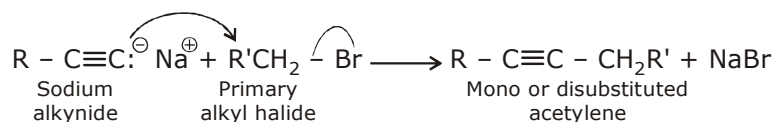
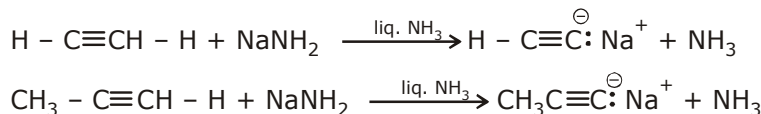
(II) By Dehalogenation of Tetrahaloalkane:



(III) Replacement of The Acetylenic Hydrogen atom of terminal Alkynes.

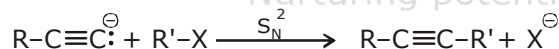
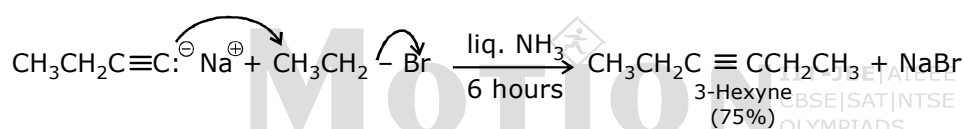


Sodium ethynide and other sodium alkynides can be prepared by treating terminal alkynes with sodium amide in liquid ammonia.



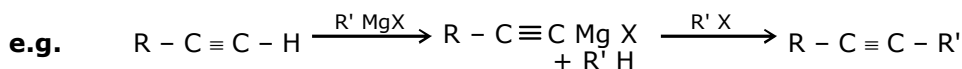
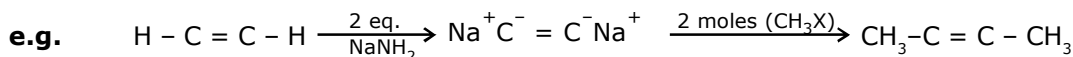
(R or R' or both may be hydrogen)

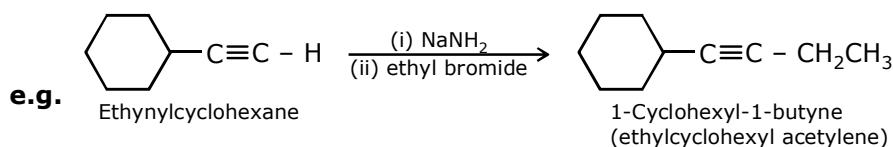
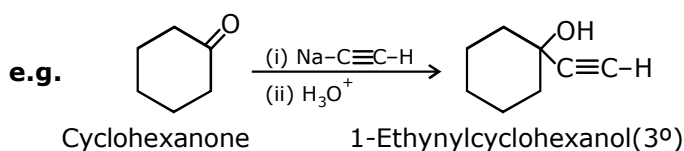
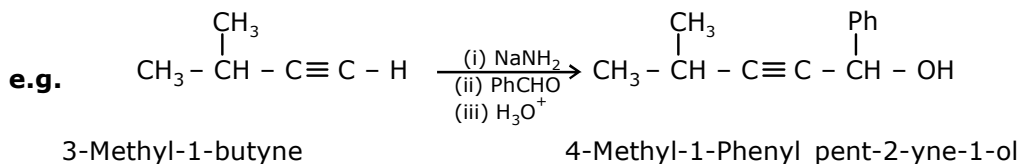
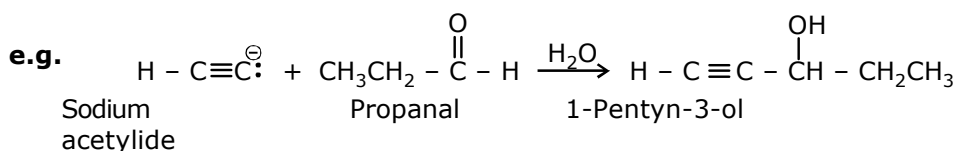
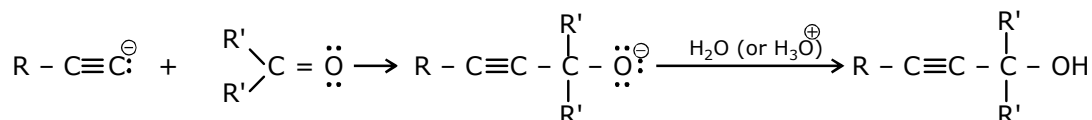
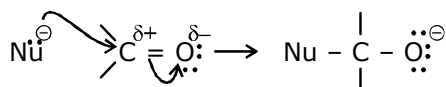
The following example illustrates this synthesis of higher alkyne homologues.



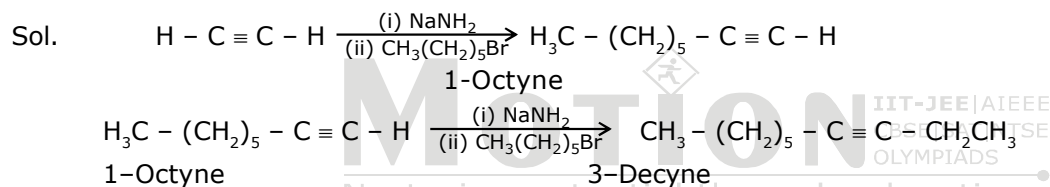
(R'-X must be an unhindered primary halide or tosylate)

The unshared electron pair of the alkynide ion attacks the back side of the carbon atom that bears the halogen atom and forms a bond to it. The halogen atom departs as a halide ion.

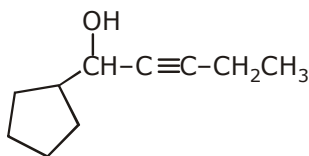
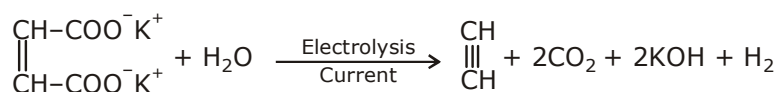


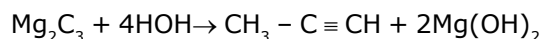
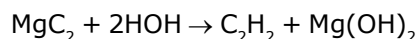
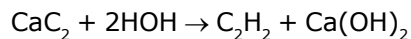
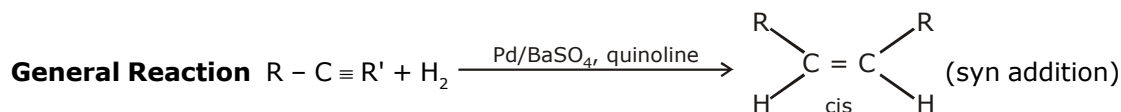
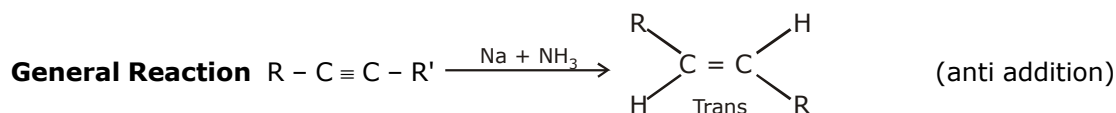
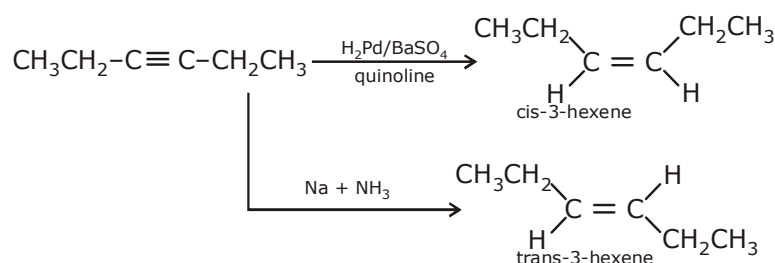
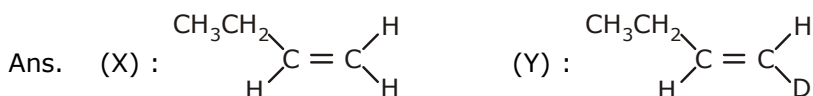
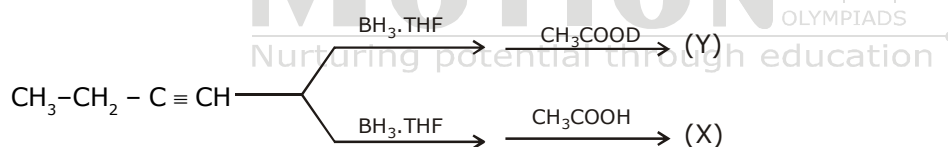
**Addition of acetylide ions to carbonyl groups**

Ex.7 Show how to synthesize 3-decyne from acetylene along with necessary alkyl halides.



Q.5 Show how you would synthesize the following compound, beginning with acetylene and any necessary additional reagents.

**(IV) By Kolbe's Electrolytic synthesis.**

(V) By Hydrolysis of carbides**10. Chemical reactions of Alkyne****(I) Reduction to alkenes****(a) By Lindlar's reagent****(b) By Birch reduction****e.g.****(c) By hydroboration reduction****Ex.8** Identify (X) and (Y) in the following reaction**Q.6** Use two methods to convert 2-butyne to (z) - 2,3-dideutero-2-butene

Q.7 From 1-butyne, synthesize
 (a) (E) -1-deutero-1-butene and
 (b) 2-deutero -1-butene

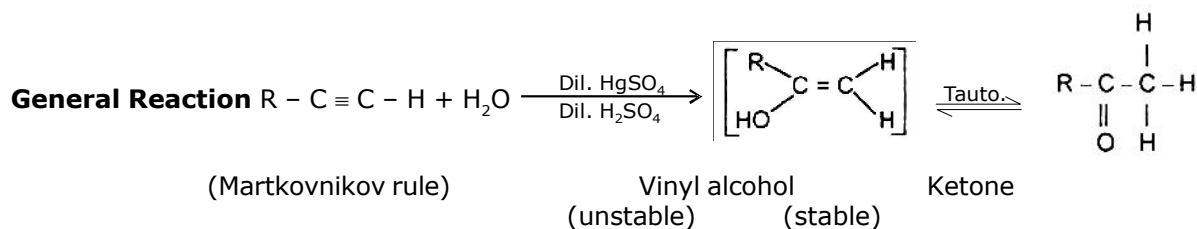
Q.8 Write the equation for the reduction of 2-butyne with Na with EtOH.

Ans. After first HBr molecule is added, product is $\text{CH}_3\text{C}(\text{Br})=\text{CH}_2$: Second addition $\text{CH}_3-\overset{\oplus}{\text{C}}(\text{Br})-\text{CH}_3$ and $\text{CH}_3-\overset{\oplus}{\text{C}}(\text{Br})-\text{CH}_2$.

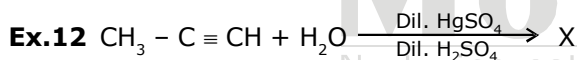
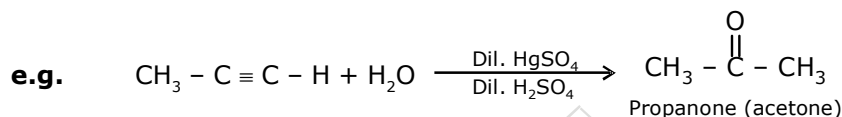
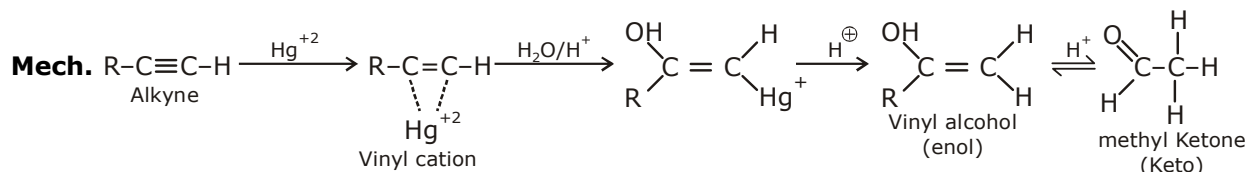
Since 2° carbocation ion is more stable than 1° , hence final product is $\text{CH}_3-\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}-\text{CH}_3$ Y is $\text{CH}_3\text{CH}_2\text{CHBr}_2$

(IV) Addition of water

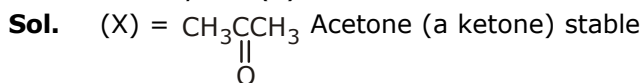
(a) Mercuric ion catalyzed hydration:



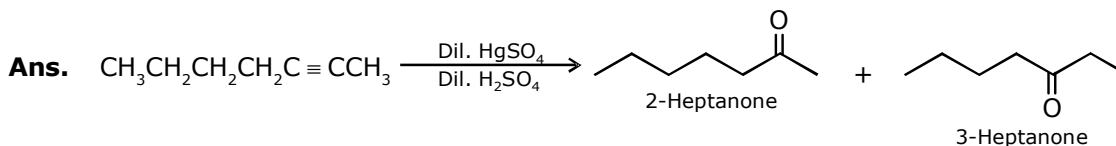
Electrophilic addition of mercuric ion gives a vinyl cation, which reacts with water and loses a proton to give an organomercurical alcohol. Under the acidic reaction condition, Hg is replaced by hydrogen to give a vinyl alcohol, called an enol.



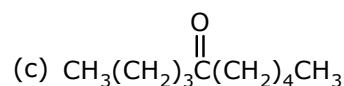
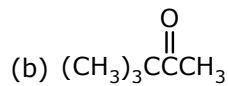
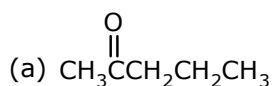
Identify the (X) in the above reaction



Ex.13 When 2-heptyne was treated with aq. H_2SO_4 containing some HgSO_4 , two products, each having the molecular formula $\text{C}_7\text{H}_{14}\text{O}$, were obtained approximately in equal amounts. What are these two compounds?



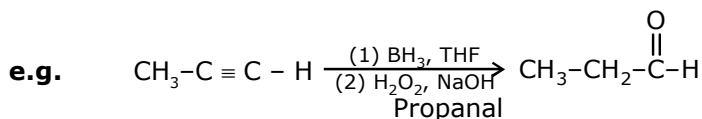
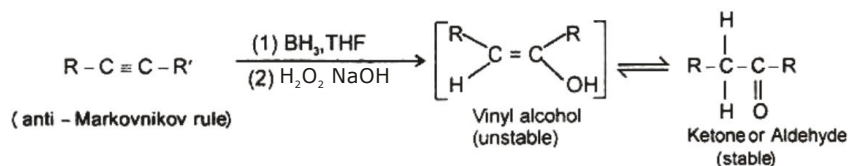
Q.9 From which alkyne could each of the following compound be prepared by acid-catalysed hydration?



(b) Hydroboration-oxidation




In alkyne, except that a hindered dialkylborane must be used to prevent addition of two molecules of borane across the triple bond.

General Reaction



Ex.14 Compare the results of hydroboration oxidation and mercuric ion-catalysed hydration for
(a) 2-butyne (b) Cyclohexyl-actylene

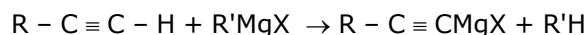
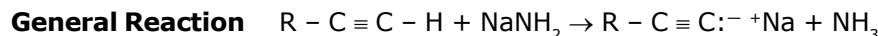
Ans.

Reactant	Product by	
	Hydroboration oxidation	Hg ²⁺ ion-catalysed hydration
(a) $\text{CH}_3\text{C}\equiv\text{CCH}_3$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_3$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_3$
(b)  -C≡CH	 -CH ₂ CHO	 -C(=O)CH ₃

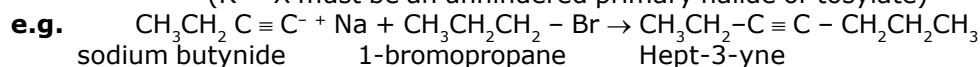
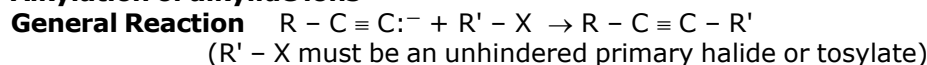
(V) Formation of Alkylide anions (Alkynides)

Sodium, lithium and magnesium alkynide

MOTION IIT-JEE | AIEEE
CBSE | SAT | NTSE
OLYMPIADS
Nurturing potential through education

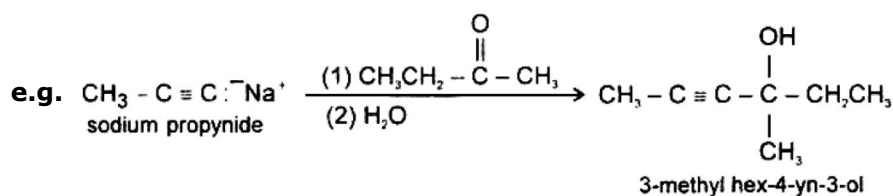
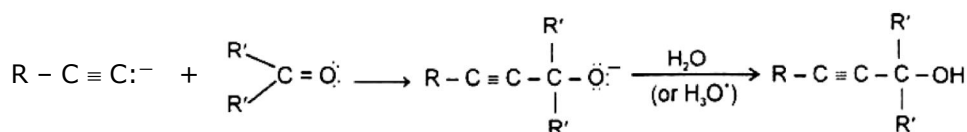


(VI) Alkylation of alkynide ions

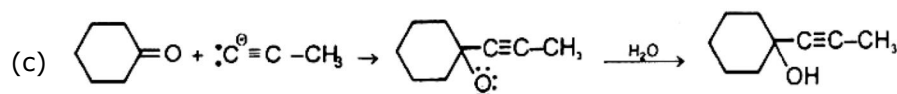
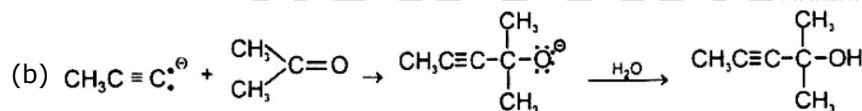
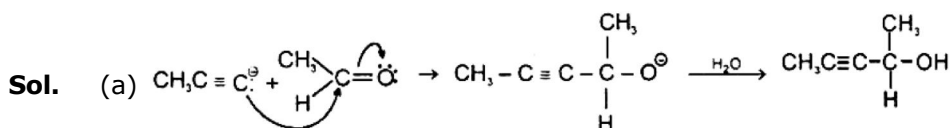
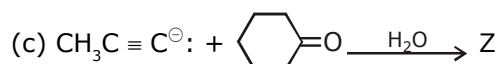
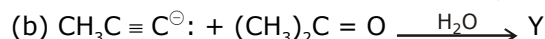
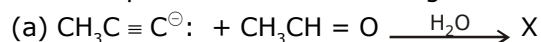


(VII) Reactions with Carbonyl Groups

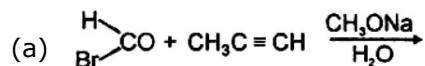
General Reaction

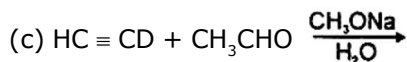
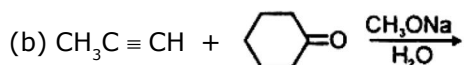


Ex.15 Give the products of the following reactions.

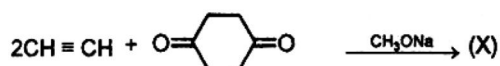


Q.10 What are the products of the following reactions:



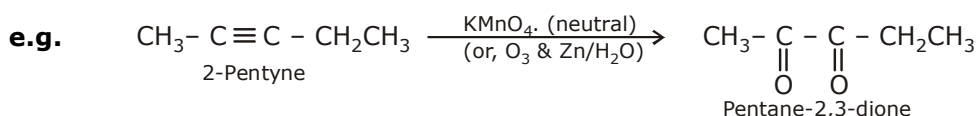
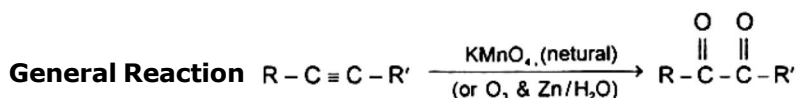


Q.11 Identify 'X' in the following reaction

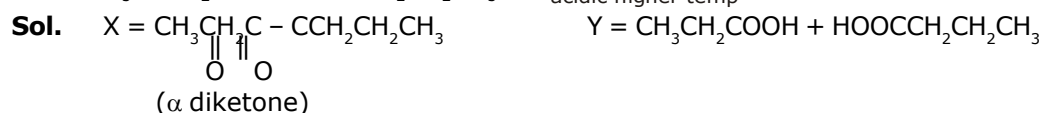
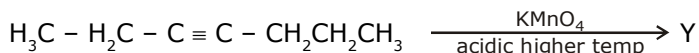
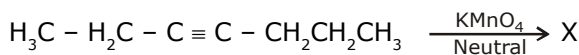


(VIII) Oxidation of α -Diketones

If an alkyne is treated with aqueous KMnO_4 under nearly neutral conditions, an α -diketone results.

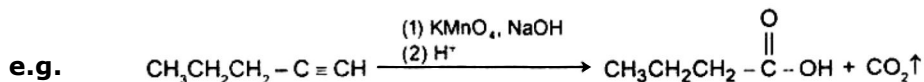
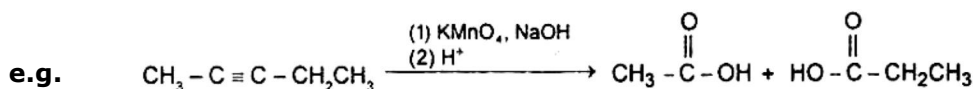
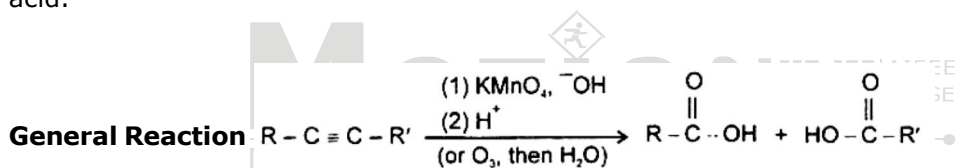


Ex.16 Give the product of the following reactions.

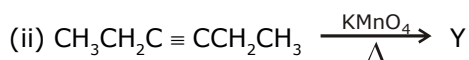
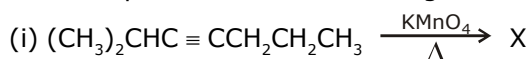


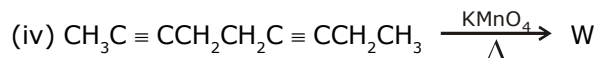
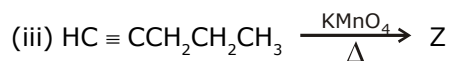
(IX) Oxidative Cleavage

If the reaction mixture becomes warm or too basic the diketone undergoes oxidative cleavage. The products are the salts of carboxylic acids, which can be converted to the free acids by adding dilute acid.



Ex.17 Give the products of the following reactions

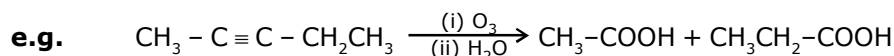
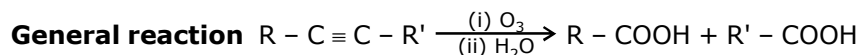




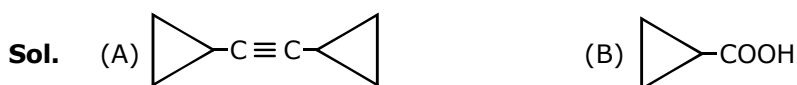
Sol. X: $(\text{CH}_3)_2\text{CHCOOH} + \text{HOOCCH}_2\text{CH}_2\text{CH}_3$
 Y: $2\text{CH}_3\text{CH}_2\text{COOH}$, symmetrical internal alkynes give one acid
 Z: $\text{CH}_3\text{COOH} + \text{HOOCCH}_2\text{CH}_2\text{COOH} + \text{HOOCCH}_2\text{CH}_3$

Q.12 C_5H_8 on KMnO_4 oxidation gives CO_2 and isobutyric acid. Identify C_5H_8 .

(X) Ozonolysis



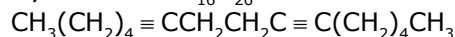
Ex.18 C_8H_{10} (A) $\xrightarrow{\text{O}_3, \text{H}_2\text{O}}$ Acid (B) Identify (A) and (B) in the above reaction



Ex.19 A certain hydrocarbon has the formula $\text{C}_{16}\text{H}_{26}$. Ozonation followed by hydrolysis gave $\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$ and succinic acid as the only product. What is hydrocarbon

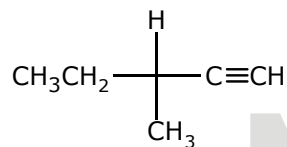
Sol. DU = 4

Hydrocarbon $\text{C}_{16}\text{H}_{26}$ is

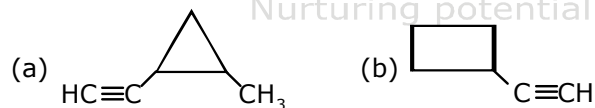


Solution Unsolved problems

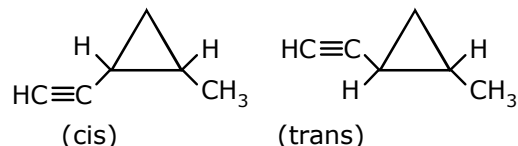
1. It means there is chiral carbon, hence structure is

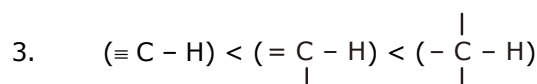


2. Alkyne ($-\text{C} \equiv \text{C}-$) has unsaturation hence C_5H_8 has also one ring of three or four carbon atoms.



(a) Exists as cis-and trans-isomer

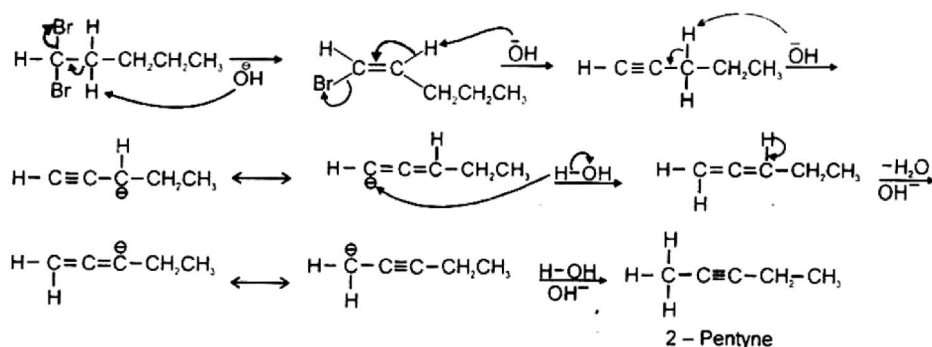




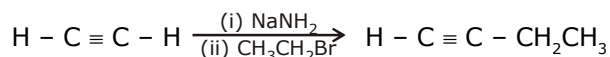
Hence $\alpha < \beta < \gamma$

4. As the S-character of the orbital that binds carbon to another atom increases, the pair of electrons in that orbital is more strongly held and it requires more energy for homolytic cleavage of both the C - H and C - C bonds.

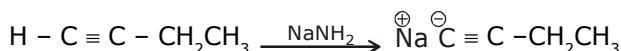
5. **Mech.**



6. We need to add two groups to acetylene and ethyl group and a six-carbon aldehyde (to form the secondary alcohol). If we formed the alcohol group first, the weakly acidic - OH group would interfere with the alkylation by the ethyl group. Therefore, we should add the less reactive ethyl group first, and add the alcohol group later in the synthesis.



The ethyl group is not acidic and it does not interfere with the addition of the second group



Reason : Electron donating groups such as R's make the π -bond more electron - rich and more reactive. Conversely, electron - withdrawing groups such as halogens make the π -bond more electron-poor and less reactive.

