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CHEMISTRY

Target : JEE (Main)

HYDROCARBONS
(ALKANES, ALKENES AND ALKYNES)

HYDROCARBONS

(ALKANES, ALKENES AND ALKYNES)

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JEE (Main) Syllabus

Hydrocarbons (Alkanes, Alkenes and Alkynes) : Alkanes - Conformations: Sawhorse and Newman projections (of ethane); Mechanism of halogenation of alkanes.
Alkenes - Geometrical isomerism; Mechanism of electrophilic addition: addition of hydrogen, halogens, water, hydrogen halides (Markownikoff's addition and peroxide effect); Ozonolysis and polymerization.
Alkynes - Acidic character; Addition of hydrogen, halogens, water and Hydrogen halides; Polymerization.

JEE (Advanced) Syllabus

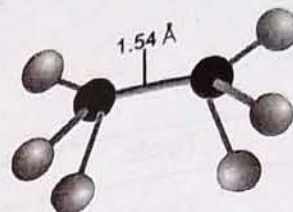
Alkanes – Preparation, properties and reactions of alkanes: Homologous series, physical properties of alkanes (melting points, boiling points and density); Combustion and halogenation of alkanes; Preparation of alkanes by Wurtz reaction and decarboxylation reactions.
Alkenes & Alkynes – Preparation, properties and reactions of alkenes and alkynes: Physical properties of alkenes and alkynes (boiling points, density and dipole moments); Acidity of alkynes; Acid catalysed hydration of alkenes and alkynes (excluding the stereochemistry of addition and elimination); Reactions of alkenes with KMnO_4 and ozone; Reduction of alkenes and alkynes; Preparation of alkenes and alkynes by elimination reactions; Electrophilic addition reactions of alkenes with X_2 , HX , HOX and H_2O ($\text{X}=\text{halogen}$); Addition reactions of alkynes; Metal acetylides.

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HYDROCARBON

ALKANE



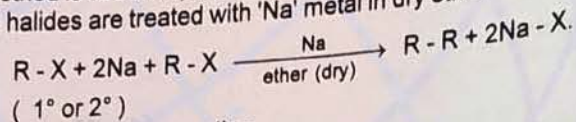
1. Structure and Bonding

- (a) Alkanes are saturated hydrocarbons.
- (b) These are represented by general Formula (G.F.) C_nH_{2n+2}
- (c) In Ethane C — C bond length is 1.54 Å
- (d) The hybridization of (C — C) carbon is sp^3
- (e) These are also known as paraffin's.

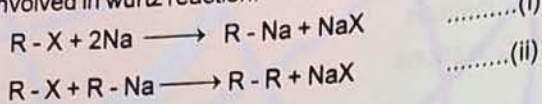
2. Preparation of alkane

2.1. Wurtz Reaction :

This method is used for preparation of higher alkanes from 1° or 2° alkyl halides. In this method two moles of alkyl halides are treated with 'Na' metal in dry ether.

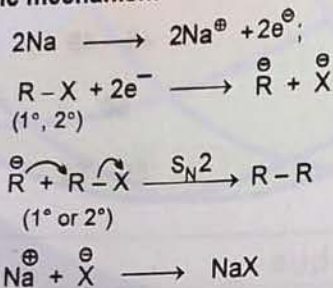


Steps involved in wurtz reaction.

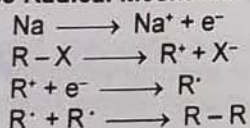


Mechanism

(a) Ionic mechanism

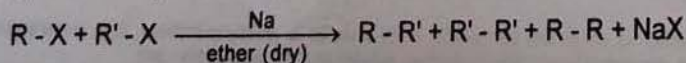


(b) Free Radical Mechanism



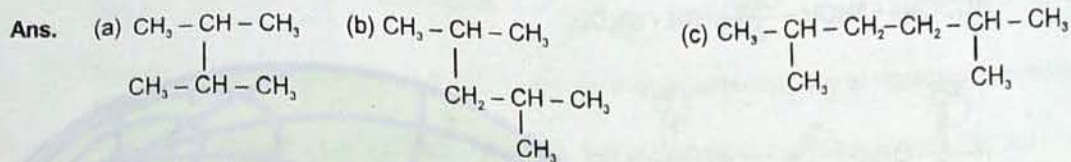
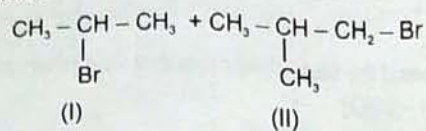
Remark :

- (a) With 3° R-X S_N2 and free radical coupling is not possible due to steric hinderence so in that case elimination or disproportionation takes place.
- (b) In the ionic mechanism alkyl sodium ($\overset{\ominus}{R}Na^{\oplus}$) is strong base as well as nucleophile which gives S_N2 with R-X
- (c) Ether should be dry if moisture is present then ROH is produced instead of R — R with water .
- (d) This method is not used for preparation of CH_4 .
- (e) To get pure alkanes having even number of carbon atoms both alkyl halides must be of same type.
- (f) On using two type of alkyl halide we get a mixture of three alkanes because two type of alkyl halides will give us two types of alkyl free radical. Which may combine to each other as well as itself.



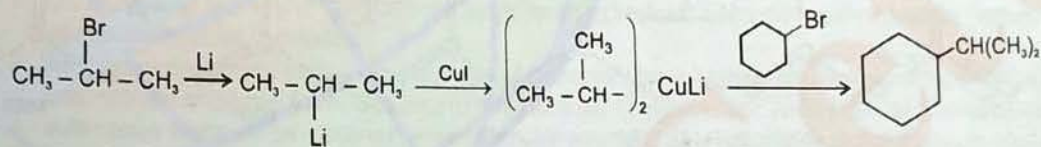
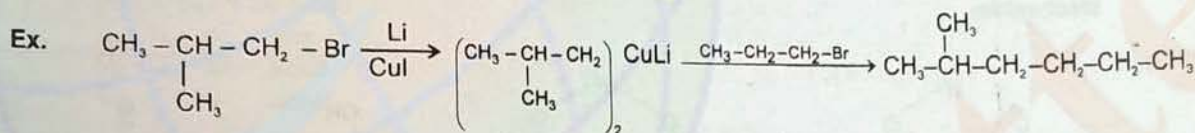
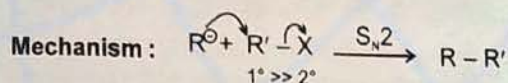
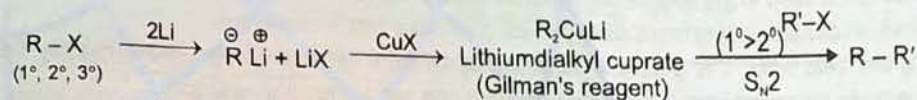
Hydrocarbons (alkanes, Alkenes and Alkynes)

Que. Write the structure of products when structure Ist and IInd undergo Wurtz reaction



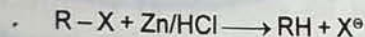
2.2. By Corey House alkane synthesis :

It is used for the preparation of pure alkane having odd number of carbon atom.

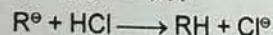
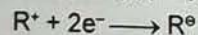
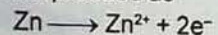


2.3. Reduction of alkyl halides :

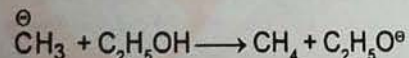
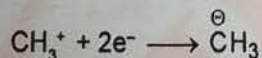
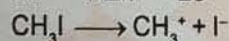
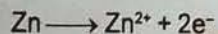
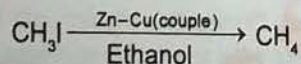
(i) By Zn/HCl



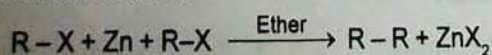
Reaction is proceed as



Purest form of methane can be obtained as :



(ii) Frankland reaction



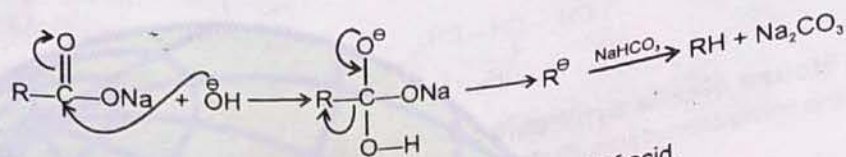
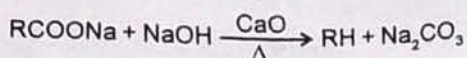
Hydrocarbons (alkanes, Alkenes and Alkynes)

2.4. Preparation of Alkane from acid :

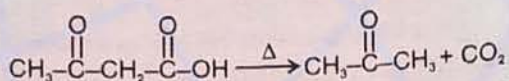
(i) Decarboxylation of sodium salt of acid :

It is removal of CO₂. This reaction is used to desend the series and proceeds via carbanion intermediate.

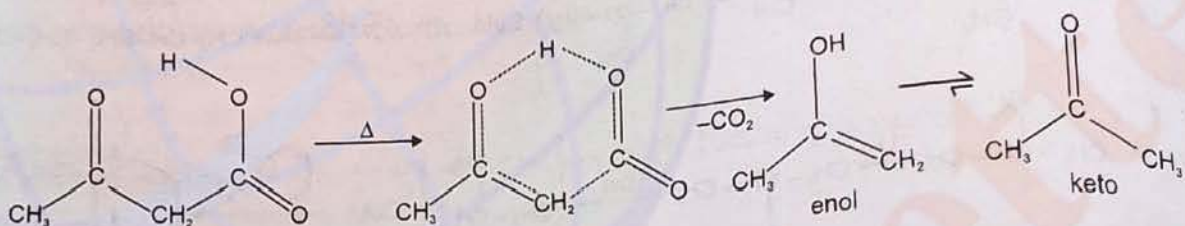
Reagent → Sodalime [mixture of NaOH + CaO]



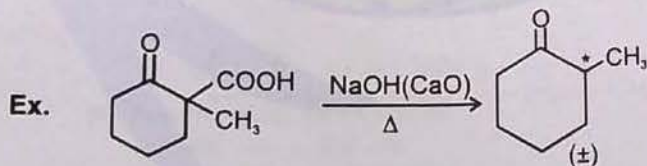
- Note :**
1. This method is used to get alkane corresponds to alkyl part of acid.
 2. That acid will decarboxylate more readily which give more stable carbanion **more readily** because it proceeds via six membered cyclic transition state and syn elimination reaction.
 3. Among the keto acid, it is **β-keto acid** which undergoes decarboxylation **more readily** because it proceeds via six membered cyclic transition state and syn elimination reaction.



Mechanism

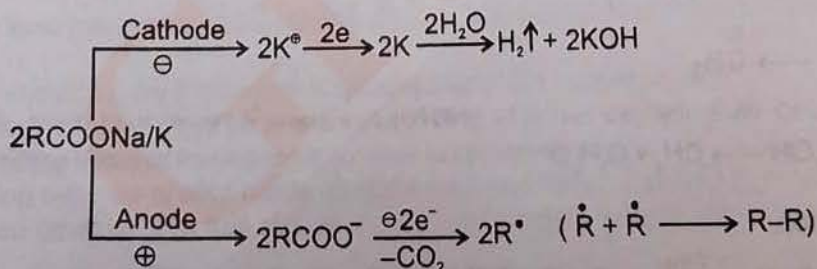


4. During decarboxylation if COOH is present at chiral carbon, then decarboxylation product will be (d + l) mixture.



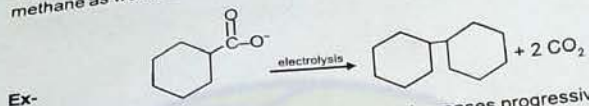
(ii) Kolbe's electrolytic method :

In this method two moles of Na/K - salt of fatty acids is used. During the electrolysis hydrogen gas is liberated at cathode because discharge potential of hydrogen is less than of that metal, while alkane is liberated at anode and this alkane will be dimer of alkyl part of acid.



Hydrocarbons (alkanes, Alkenes and Alkynes)

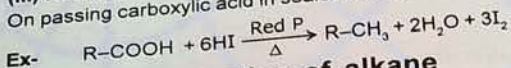
Note : 1. This method is used for the preparation of alkane having even number of carbon atoms. It is not used for methane as well as alkanes having odd number of carbon atom.



2. During Kolbe's electrolysis pH of electrolyte increases progressively due to increases in concentration of alkali.
3. On using two types of Na/K-salt of fatty acids. We get the mixture of three alkanes. Because two types of salt of fatty acids gives us two types of free radicals which may combine to each other as well as itself.

(iii) Reduction of carboxylic acid :

On passing carboxylic acid in sealed tube containing HI/P at 200°C. We get alkane corresponding to acid.



3. Physical properties of alkane

Alkane molecules are held together by weak Vander waal force which depends upon surface area. On increasing molecular mass surface area increases hence Vander waal forces also increased and thus physical properties are increased

- $C_1 - C_4 \Rightarrow$ gas
- $C_5 - C_{17} \Rightarrow$ liquid
- $C_{18} \dots \dots \Rightarrow$ solid

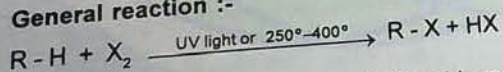
- Note :**
1. On increasing branching surface area tends to be spherical i.e. Vander waal interaction reduced and hence boiling point decreased.
 2. Melting point of alkane having even number of carbon atoms is higher than neighbouring alkanes having odd number of carbon atom. Because in even number of alkanes two ends are facing towards opposite side hence there will be minimum intermolecular repulsion as a result they fit better into crystal lattice.
 3. Density of alkane increases with molecular mass and then acquires a constant value 0.8 gm/cc³. Thus also it is clear that alkane is lighter than water.

4. Chemical reactions of alkane

4.1. Halogenation :

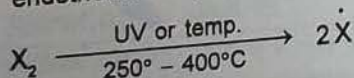
Reagents :- UV light / hv / high temp (250°-400°C) / Peroxide + X₂ (Cl₂ + Br₂)

General reaction :-

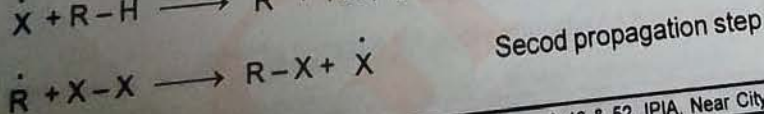
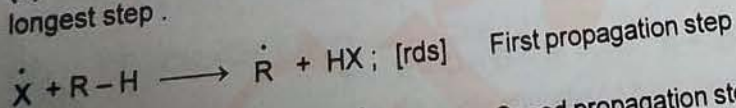


Mechanism :- Free radical substitution this reaction is chain reaction which is completed in following three steps.

(I) Chain initiation step : It is homolytic cleavage of chlorine molecule to give chlorine free radical . It is an endothermic step .



(II) Chain propagation step - The step in which reactant and product, both are having free radical . It is longest step .



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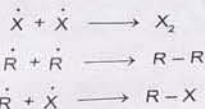
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MAINHYDROCARBON - 4



Hydrocarbons (alkanes, Alkenes and Alkynes)

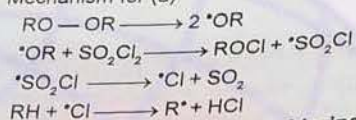
(iii) **Chain Termination step** - It is the step in which any two free radicals combine to give a product without free radical. It is always exothermic step.



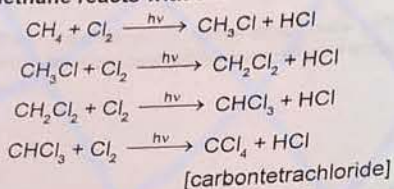
Remark:

- (i) **Other halogenating reagent is**
 (a) Chlorination SO_2Cl_2 / Peroxide
 (b) Bromination SO_2Br_2 / Peroxide

Mechanism for (a)



(ii) Methane reacts with excess of chlorine in diffused sunlight to give the final product as



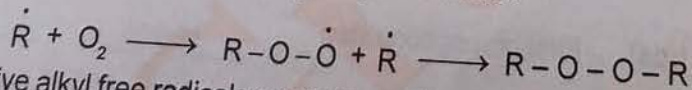
- (iii) Reactivity of H = $3^\circ H > 2^\circ H > 1^\circ H$
 (iv) Reactivity of X_2

| Reactivity of $X_2 = F_2 > Cl_2 > Br_2 > I_2$ | |
|--|---|
| 1. Direct fluorination of alkane is not possible because it is very explosive. So F_2 is react with alkane in dark and at room temperature | Bromination is similar to chlorination but slower in rate. |
| 2. Halogen exchange Reagents (i) $AgF + H_2O$ (Major) + C_2H_5OH (Minor) (Swart's Reaction) Only AgF is soluble among all silver halides in water. $R-X \xrightarrow[S_N1]{AgF} R^+ \xrightarrow{F^-} R-F + AgX \downarrow$ ppt. (ii) $2C_2H_5Br + HgF_2 \rightarrow 2C_2H_5F + HgBr_2$ | 1. Iodination is reversible reaction since $H-I$ is formed as a by product, that is strong reducing agent so reduces alkyl iodide back to alkane. Hence iodination can be done only in presence of strong oxidizing agent like HIO_3 , HNO_3 and HgO etc. which destroy HI into I_2 . $CH_4 + I_2 \longrightarrow CH_3I + H-I$ $HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$ 2. Halogen exchange Reactions : (Finkelstein Reaction) $R-X + NaI \xrightarrow[S_N2]{Acetone} R-I + NaX \downarrow$ (Cl, Br) (ppt. in acetone) In acetone, NaI is soluble/Ionised but $NaCl/NaBr$ are insoluble. So $NaCl/NaBr$ get precipitate out. |

(v) In a chain reaction following reagents are involved :

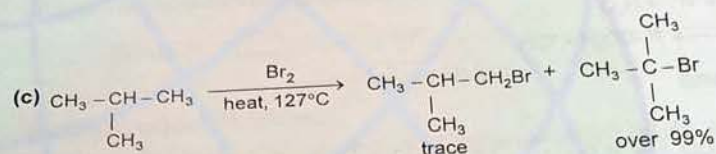
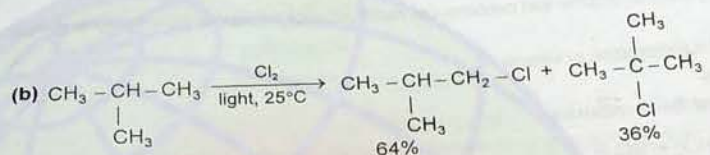
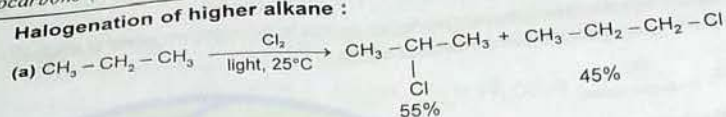
(a) **Initiators** : They initiate the chain reaction, Initiators are peroxide (R_2O_2), Perester's etc.

(b) **Inhibitors** : A substance that slows down or stops the reaction is known as inhibitors
 For example O_2 is a good inhibitor.



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

Hydrocarbons (alkanes, Alkenes and Alkynes)

Halogenation of higher alkane :**Factors affecting the relative yields :**

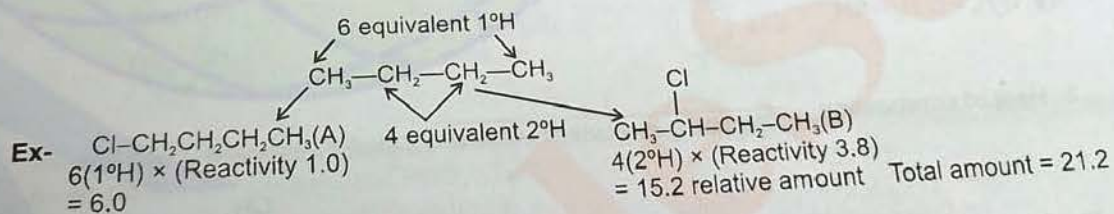
(i) **Probability factor :** This factor is based on the number of each kind of H atom in the molecule.

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

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

(iii) Reactivity v/s selectivity principle :

The more reactive substance is less selective.

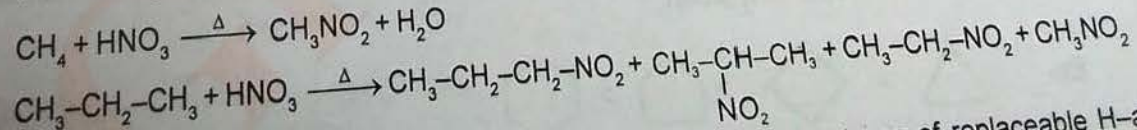
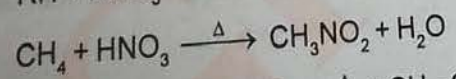
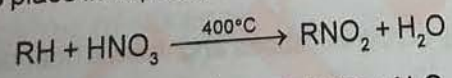


$$\% \text{ yield A} = \frac{6}{21.2} \times 100 = 28.3 \%$$

$$\% \text{ yield B} = \frac{15.2}{21.2} \times 100 = 71.2 \%$$

4.2. Nitration of alkane :

It takes place in vapour phase and gives a mixture of nitroderivatives due to cracking.

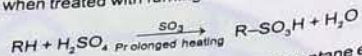


Note : Nitration of propane gives a mixture of four nitroderivatives as it as two types of replaceable H-atom (1° and 2°) and also it undergoes cracking at high temperature.

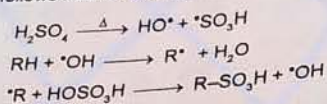
Hydrocarbons (alkanes, Alkenes and Alkynes)

4.3. Sulphonation of alkane :

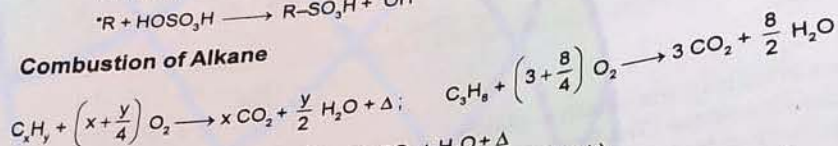
Lower alkanes do not undergo sulphonation easily but higher members (from hexane onward) are sulphonated slowly when treated with fuming acid (oleum) at around 400°C



- Note :
1. Lower members like propane, butane and pentane etc. react with SO_3 in vapour phase to give corresponding sulphonic acid.
 2. Decreasing order of sulphonation of alkane $3^\circ > 2^\circ > 1^\circ$ H-atom
 3. It follows free radical mechanism as

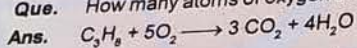


4.4. Combustion of Alkane



Hydrocarbon + sufficient supply of $O_2 \Rightarrow CO_2 + H_2O + \Delta$
 Hydrocarbon + insufficient supply of $O_2 \Rightarrow CO + H_2O$ or C (black)

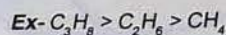
Que. How many atoms of oxygen are needed for complete combustion of 2.2 g of propane ?



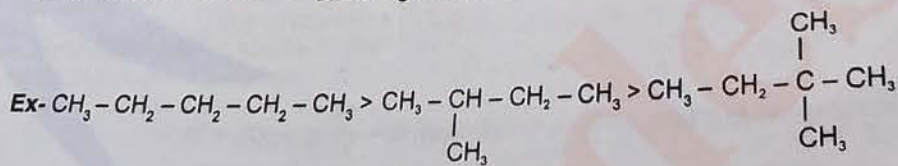
44 gm of C_3H_8 needs = 5 moles of Oxygen = $5 \times N_A$ molecule of Oxygen = $5 \times 2 \times N_A$ atom

$$2.2 \text{ gm of } C_3H_8 \text{ needs} = \frac{5 \times 2 \times 2.2 \times N_A}{44} = 0.5 \times N_A \text{ atoms of Oxygen}$$

Note : 1. Heat of combustion \propto higher homologues



2. Heat of combustion $\propto \frac{1}{\text{Branching of alkane (in isomers)}}$



3. Heat of combustion $\propto \frac{1}{\text{size of ring (cycloalkane)}}$

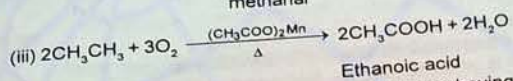
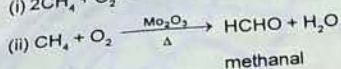
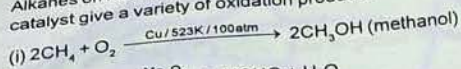
On increasing the size of ring from three to six stability of ring increases and hence heat of combustion (its value) decreases per CH_2 group.



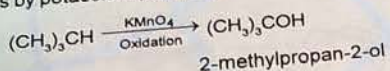
Hydrocarbons (alkanes, Alkenes and Alkynes)

4.5. Controlled oxidation :

Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalyst give a variety of oxidation products.

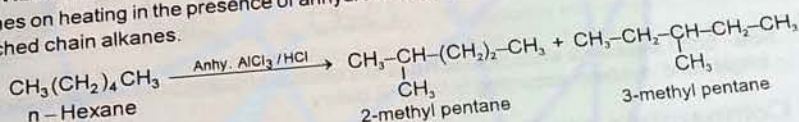


(iv) Ordinarily alkanes resist oxidation but alkanes having tertiary H atom can be oxidized to corresponding alcohols by potassium permanganate.



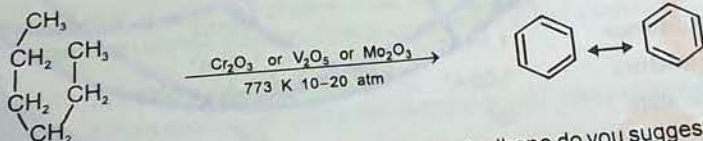
4.6. Isomerization of alkane :

n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.



4.7. Aromatization of alkane :

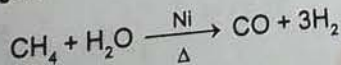
n-alkanes having six or more carbon atoms on heating to 773 K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming.



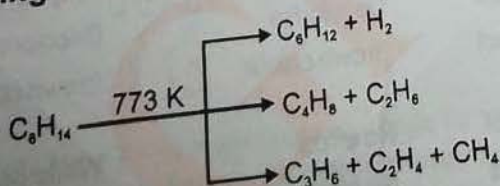
Que. Toluene (C₇H₈) is methyl derivative of benzene. Which alkane do you suggest for preparation of toluene ?
Ans. n-Heptane

4.8. Reaction with steam

Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen.



4.9. Cracking of alkane



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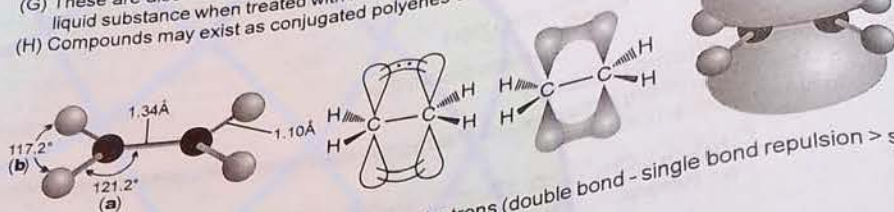
MAINHYDROCARBON - 8

Hydrocarbons (alkanes, Alkenes and Alkynes)

ALKENE

1. Structure and Bonding :

- (A) Alkenes are unsaturated hydrocarbons having at least one double bond. Alkenes are also known as olefins.
 (B) These are represented by general Formula C_nH_{2n} (one double bond).
 (C) In Ethene C = C bond length is 1.34 Å
 (D) Its bond energy is 146 kcal.mol⁻¹
 (E) The hybridization of (C = C) carbon is sp²
 (F) The π e⁻ cloud is present above and below the plane of σ-bonded skeleton.
 (G) These are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.
 (H) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes



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

2. Comparative study of alkane, alkene & alkyne :

| Hydrocarbon | Alkane | Alkene | Alkyne |
|---------------------------|-------------------------------|---|--|
| (i) C—C Bond distance | 1.54 Å | 1.34 Å | 1.20 Å |
| (ii) C—H Bond distance | 1.09 Å | 1.08 Å | 1.05 Å |
| (iii) Hybridisation state | sp ³ | sp ² | sp |
| (iv) Structure | Tetrahedral | Planner | Linear |
| (v) Electronegativity | less than sp ² /sp | less than sp more than sp ³ | more than sp ² /sp ³ |
| (vi) C—C bond energy | 415 kJ | 615 kJ | 835 kJ |
| (vii) density | 0.5 g/cm ³ | 0.52 g/cm ³ | 0.67 g/cm ³ |
| (viii) % s-character | 25% | 33.33 % | 50 % |

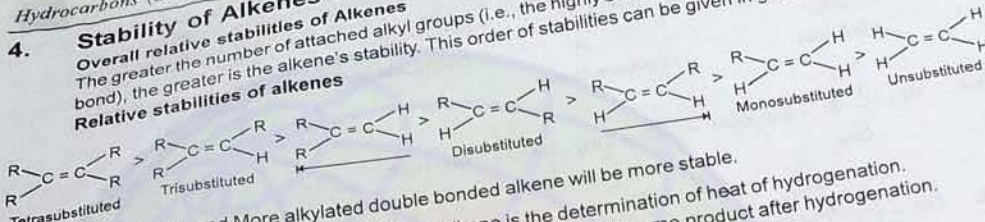
3. Lab Test :

| Hydrocarbon | Alkane | Alkene | Alkyne (Terminal) |
|--|-----------|--------------|----------------------------------|
| (i) Br ₂ /H ₂ O solution | No effect | Decolorise | Decolorise |
| (ii) Cold dil. alkaline + KMnO ₄ Solution | No effect | Brown colour | Brown colour |
| (iii) Tollen's Reagent | No effect | No effect | White ppt. of silver acetenilied |
| (iv) Ammonical cuprous chloride solution | No effect | No effect | Red ppt. of cuprous acetenilied |

Hydrocarbons (alkanes, Alkenes and Alkynes)

4. **Stability of Alkenes :**

Overall relative stabilities of Alkenes
 The greater the number of attached alkyl groups (i.e., the highly substituted the carbon atoms of the double bond), the greater is the alkene's stability. This order of stabilities can be given in general terms as follows.



- Note-**
1. More and More alkylated double bonded alkene will be more stable.
 2. The way of measuring stability of alkene is the determination of heat of hydrogenation. It is applicable only those isomeric alkene which gives same product after hydrogenation.

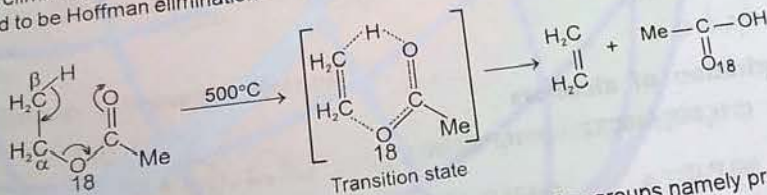
$$\text{Stability} \propto \frac{1}{\text{Heat of Hydrogenation}}$$

i.e. more stable the alkene \rightarrow less will be heat of hydrogenation.

5. **Preparation of Alkene :**

5.1. **Pyrolysis of Ester :**

It is the preparation of alkene along with carboxylic acid via formation of six membered cyclic transition state. It is syn elimination and alkene is formed corresponding to alkyl part of alcohol from ester. This addition is also said to be Hoffman elimination.

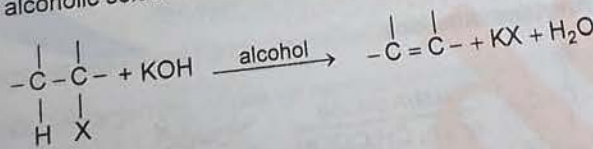


Note : As a direct consequence of cyclic transition state, both the leaving groups namely proton and carboxylate ion are eliminated from the syn position. This is an example of **syn elimination**.

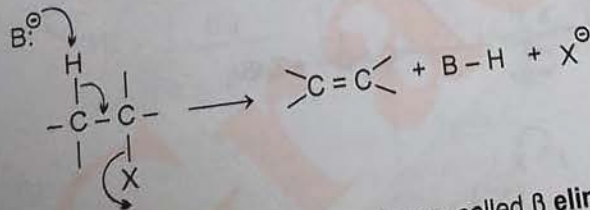
5.2. **Dehydro-halogenation of alkyl halide :**

It is removal of H-X from alkyl halide where this reaction is said to be β -elimination reaction.

Reagent (i) Hot alcoholic solution of KOH (EtO⁻ / EtOH) (ii) NaNH₂ (iii) t-BuO⁻K⁺ in t-BuOH

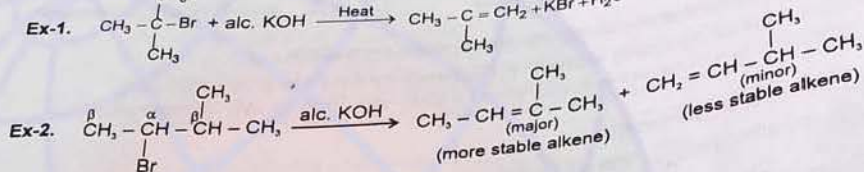
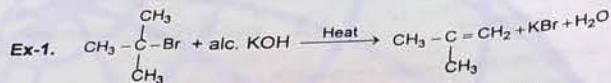
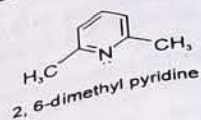
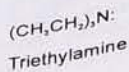
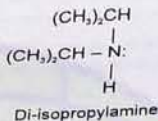
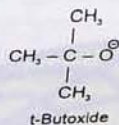


Mechanism

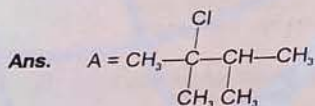
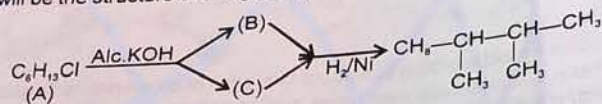


Remark : (i) Here β -H is eliminated by base hence called β elimination (follows Saytzeff rule). i.e. (Highly substituted alkene is major product). It also involves an anti elimination of HX.
 (ii) Bulky bases give hofmann alkenes

Hydrocarbons (alkanes, Alkenes and Alkynes)



Que. What will be the structure of A in given question ?

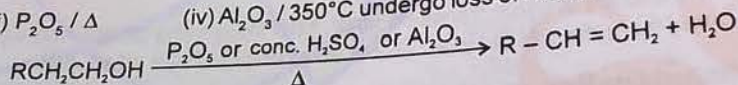


5.3. By Dehydration of alcohols

Reagents : (i) $\text{H}_2\text{SO}_4 / 160^\circ\text{C}$ (ii) $\text{H}_3\text{PO}_4 / \Delta$

(iii) $\text{P}_2\text{O}_5 / \Delta$

(iv) $\text{Al}_2\text{O}_3 / 350^\circ\text{C}$ undergo loss of water molecule and form alkenes



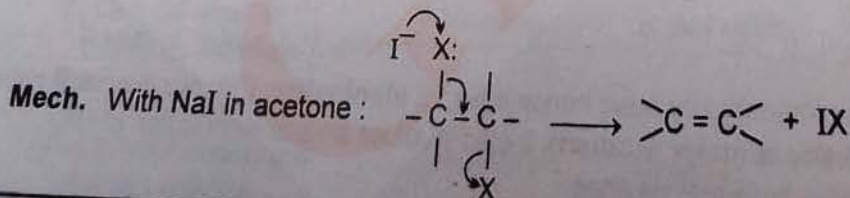
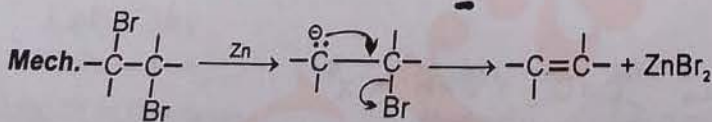
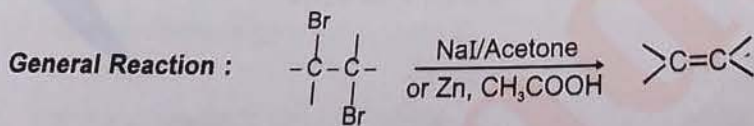
5.4. Dehalogenation of dihalo-alkane :

It is removal of X_2 from dihalo alkane.

Reagent: NaI in acetone or zinc in presence of acetic acid or ethanol or Zn/Δ

Dihalides are of two types :

(A) Vicinal dihalide or Alkylene dihalides

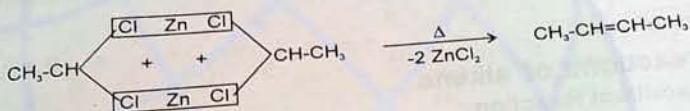
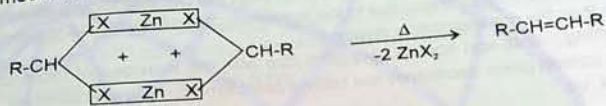


Hydrocarbons (alkanes, Alkenes and Alkynes)

Remark : Both are E2 elimination and stereospecific antielimination.

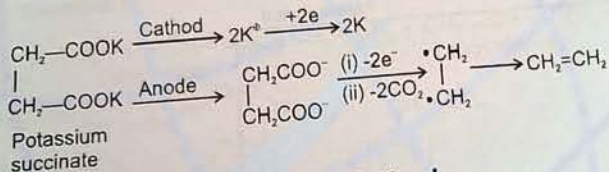
(B) Gem-dihalide or Alkylidene halides
 Ex : $\text{CH}_3-\text{CHCl}_2$ (ethylidene chloride)

When gem dihalide is heated with Zinc dust at 300°C then higher alkenes are formed, which is based on free radical mechanism.

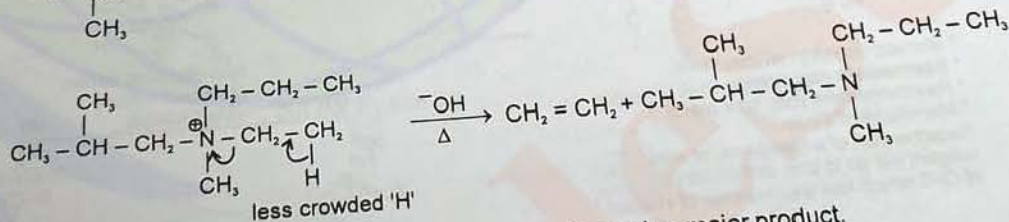
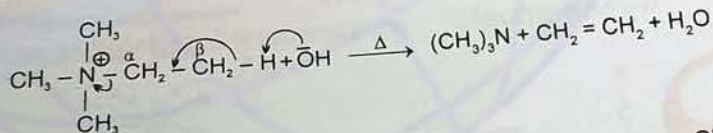


5.5. Electrolysis of Potassium succinate :

This reaction gives ethylene as follows

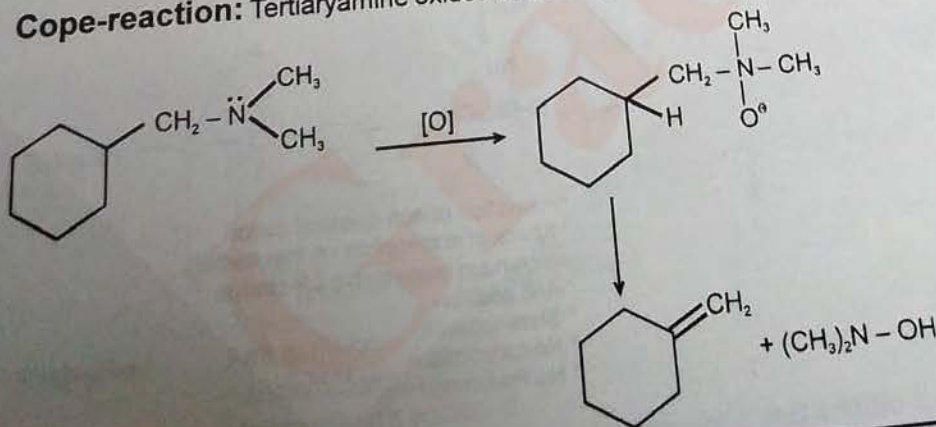


5.6. By Hofmann Elimination Method



Remark : Less substituted alkenes (Hofmann alkenes) are formed as major product.

5.7. Cope-reaction: Tertiaryamine oxides on heating form alkene, if there is β -hydrogen atom in it.



Hydrocarbons (alkanes, Alkenes and Alkynes)

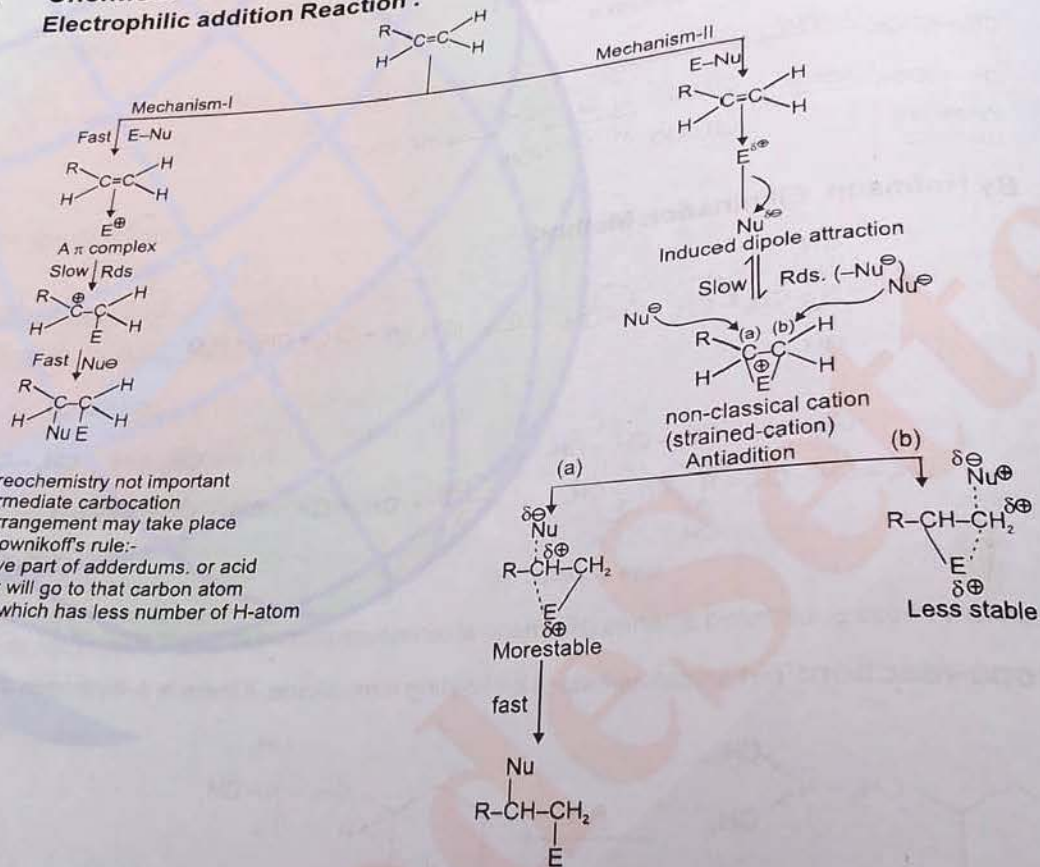
6. Physical Properties of Alkene

- (i) From $C_2 - C_4$ they are colourless, odourless gases, from $C_5 - C_{17}$ they are colourless liquids, C_{18} onwards alkenes are solids.
 - (ii) Alkenes are practically insoluble in water because they can not form hydrogen bonds with H_2O molecules, etc. They dissolve freely in organic solvents like benzene, chloroform, CCl_4 , petroleum ether, etc.
 - (iii) The boiling and melting points of alkenes are slightly higher than the corresponding alkanes because the intermolecular forces of attraction are stronger due to the presence of easily polarizable π bond. Alkenes are therefore, lesser volatile than the corresponding alkanes. Their boiling points, melting points and specific gravities rise with the increase of molecular weight. Increase in branching in carbon chain decreases the boiling point among isomeric alkenes.
- MP, and BP \propto mol. wt.

$B.P \propto \frac{1}{\text{branching in alkenes}}$

7. Chemical reactions of alkene

Electrophilic addition Reaction :



- * Stereochemistry not important
 - * Intermediate carbocation
 - * Rearrangement may take place
 - * Markownikoff's rule:-
- Negative part of addendums, or acid reagent will go to that carbon atom of $C=C$ which has less number of H-atom

- * Formation of non classical cation
- * Attack of nucleophile on that carbon which have more stable δ^\oplus charge
- * Anti addition
- * Stereospecific
- * No carbocation
- * No Rearrangement

Hydrocarbons (alkanes, Alkenes and Alkynes)

Example of mechanism-I

- (1) Addition of hydrogen halide
- (2) Acid-catalysed hydration.
- (3) Addition of H₂SO₄.

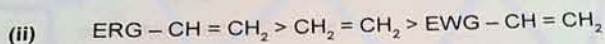
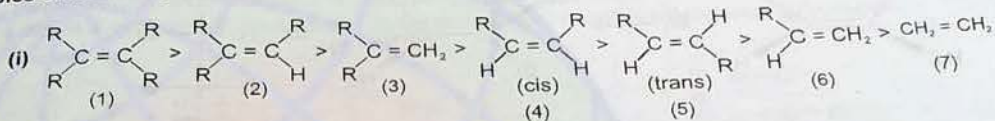
Example of mechanism-II

- (1) Addition of halogen.
- (2) Addition of hypohalous acid.
- (3) Oxymercuration-demercuration
- (4) Addition of NOCl

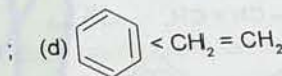
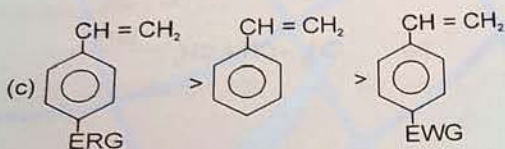
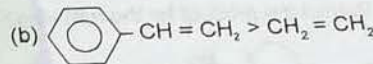
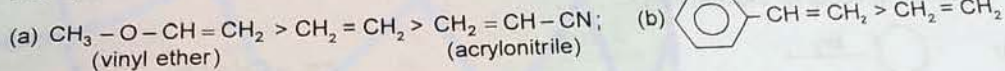
Reactivity of an Alkene:

- (1) Presence of electron releasing groups (+m, +I) at C = C increases electrophilicity and reactivity.
- (2) Presence of ERG stabilises the intermediate carbocation.
- (3) More stable C[⊕], more is reactivity.

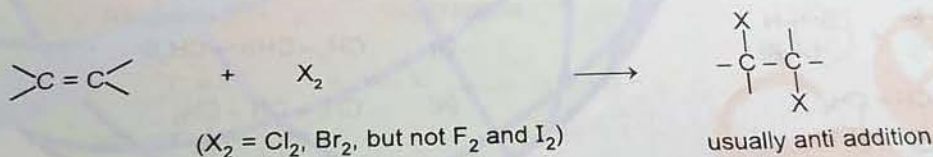
Examples of Reactivity Orders :



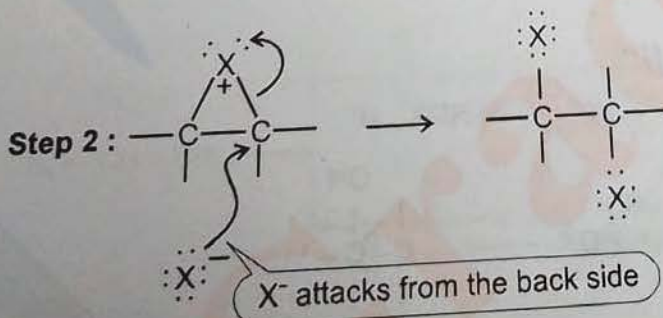
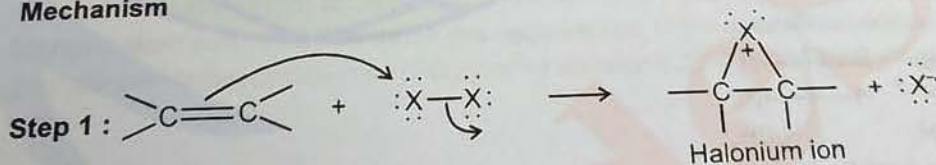
Example :



7.1. Addition of halogen (Halogenation) : "Mechanism-II"



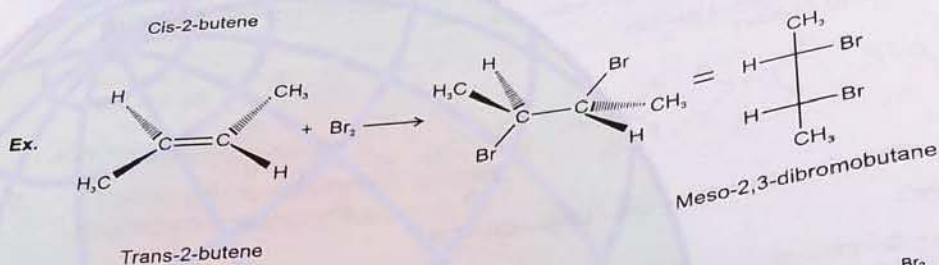
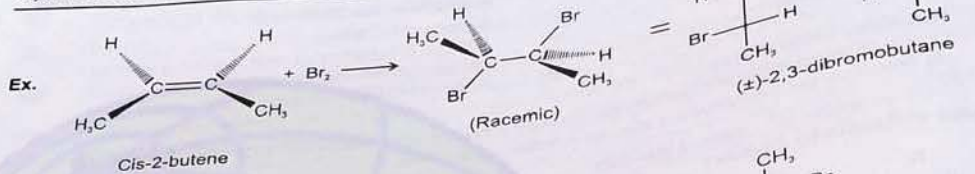
Mechanism



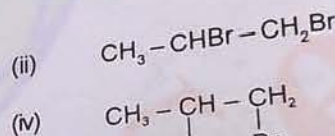
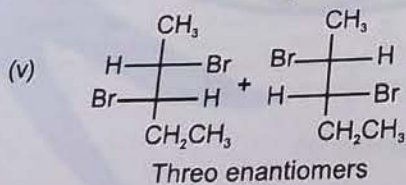
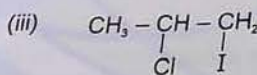
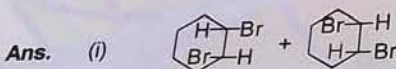
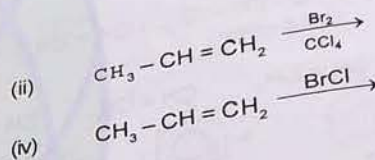
- Remarks :**
- Anti addition
 - No rearrangement
 - Markovnikoff's additions

The addition of bromine to cyclopentene is a stereospecific anti addition.

Hydrocarbons (alkanes, Alkenes and Alkynes)

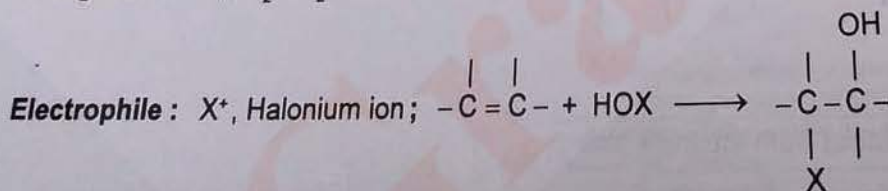


Que. Predict the product for the following :-



7.2. Addition of HOX : "Mechanism-II"

Reagents : (i) X₂ + H₂O → HOX + HX or (ii) HOX, H⁺

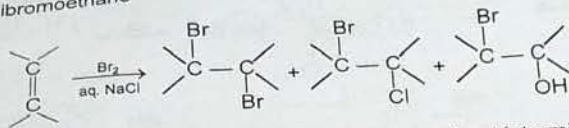


Remarks : Anti addition ; No rearrangement ; Markovnikoff's additions

Hydrocarbons (alkanes, Alkenes and Alkynes)

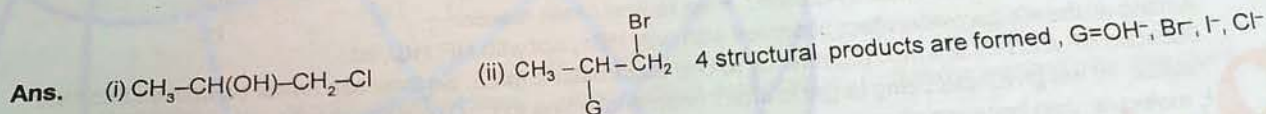
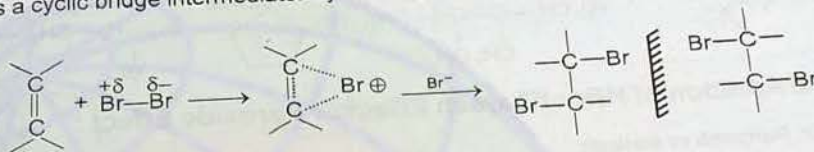
Evidence to support of formation non classical cation :
When addition of Br₂ was carried out in the presence of aq. NaCl we get 3-products.

- (i) 1,2-dibromoethane
- (ii) 1-Bromo-2-chloroethane
- (iii) 2-Bromoethanol



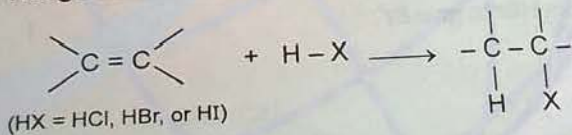
Formation of these three products clearly indicates about intermediate (A) thus addition of bromine water over alkene is electrophilic addition reaction.

Note : This addition always takes place in trans manner because of bulky nature of bromine atom in bromonium, which is a cyclic bridge intermediate. Cyclic bridge intermediate is not classical carbonium ion.

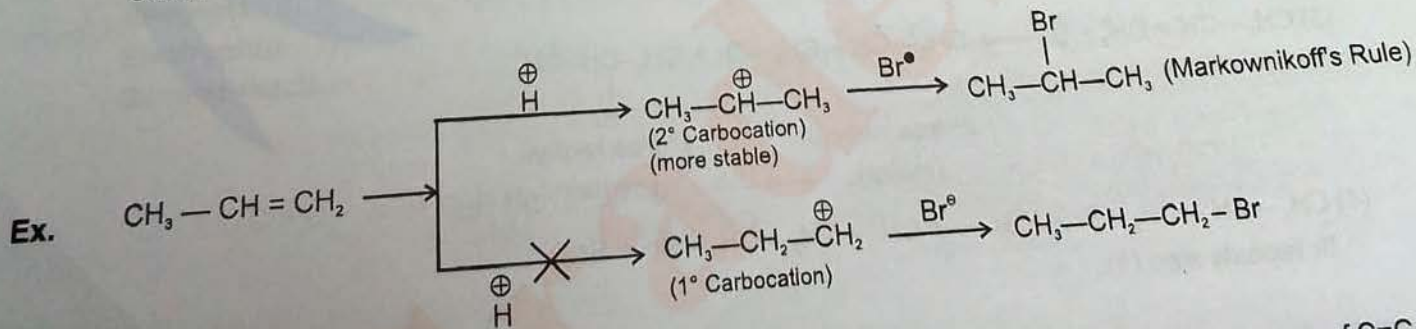


7.3. Addition of Hydrogen Halides (+ HX) : "Mechanism-I"

Reagents : HX ; Electrophile : H⁺



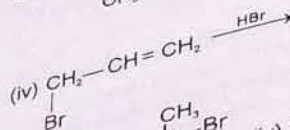
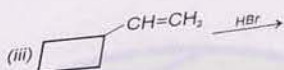
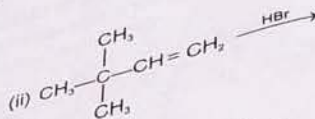
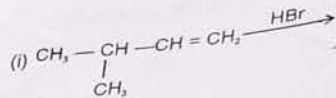
Remarks : Markovnikoff addition ; Intermediate carbocation ; Rearrangement may take place
Markovnikoff rule : The rule states that negative part of the addendum (adding molecule) or acid reagent gets attached to that carbon atom of unsymmetrical alkene (C=C) which possesses lesser number of hydrogen atom.



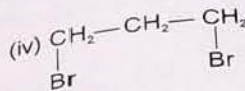
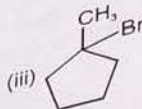
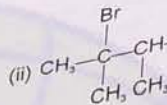
Above reaction is electrophilic addition reaction hence electrophile will go to that carbon atom of C=C which has more no. of H-atoms.
Since 2° carbocation is more stable hence major product is 2-bromopropene.

Hydrocarbons (alkanes, Alkenes and Alkynes)

Que. Predict the product for the followings :

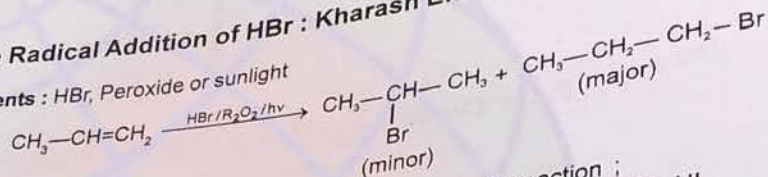


Ans. (i) $(\text{CH}_3)_2\text{C}(\text{Br})\text{CH}_2\text{CH}_3$



7.4. Free Radical Addition of HBr : Kharash Effect or Peroxide Effect :

Reagents : HBr, Peroxide or sunlight

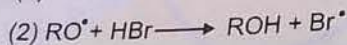
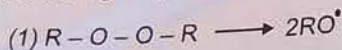


Remarks:- Anti Markovnikov's Addition ; Free radical chain reaction ; Among all the HX peroxide effect observed with only HBr , not with HF, HCl, HI.

Because HF and HCl are held together by strong electrostatic force. So they can never be broken into free radical. HI will give I[•] but being larger in size I[•] (inspite of going to C=C) will combined with another I[•] to give I₂ molecule. Just because of comparable size.

Mechanism : Mechanism of this reaction is completed in following three steps.

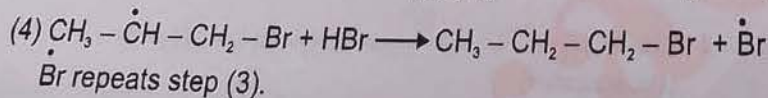
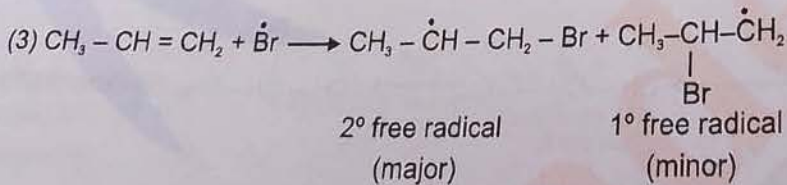
(i) Chain initiation step : This reaction is free radical addition reaction in this reaction peroxide undergoes homolytic cleavage to give a free radical from HBr to give Br[•].



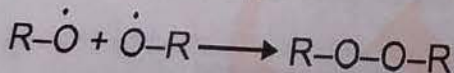
(ii) Chain propagating step : This Br[•] will go to either carbon of carbon-carbon double bond of propene to give two type of free radicals.

(i) 1^o free radical (ii) 2^o free radical

Since 2^o free radical is more stable than 1^o free radical, hence major product is 1-bromopropane.

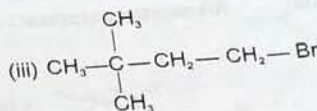
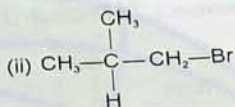
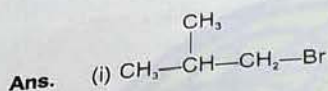
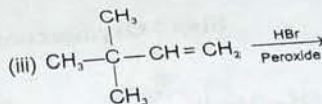
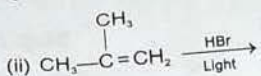
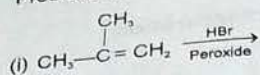


(iii) Chain termination step :



Hydrocarbons (alkanes, Alkenes and Alkynes)

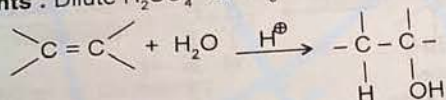
Que. Predict the product for the followings.



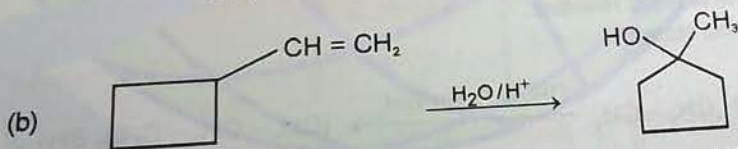
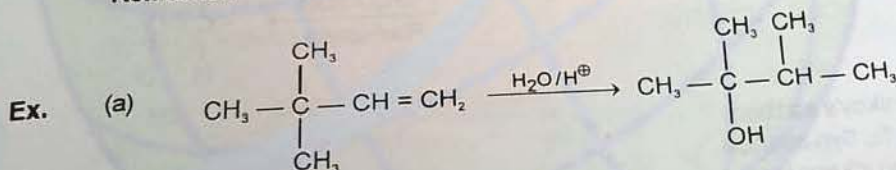
7.5. Addition of H₂O (Hydration Reaction)

(i) Acid-Catalyzed Hydration of Alkenes : "Mechanism-I"

Reagents : Dilute H₂SO₄ or H₃O⁺



Remarks : Markovnikoff addition ; Intermediate carbocation ; Rearrangement may take place

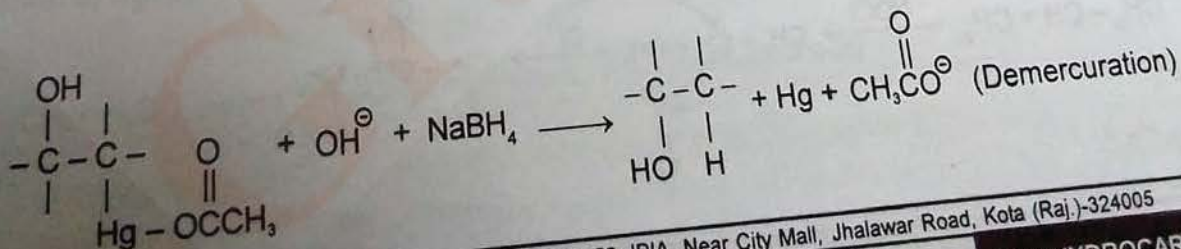
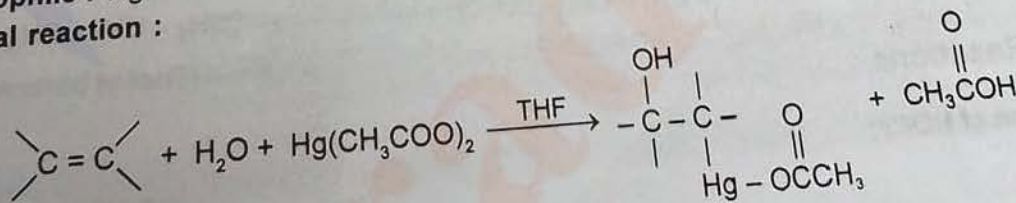


(ii) Oxymercuration-Demercuration : "Mechanism-II"

Reagents : (i) Hg(OAc)₂, H₂O (ii) NaBH₄

Electrophile : Hg^+OAc

General reaction :



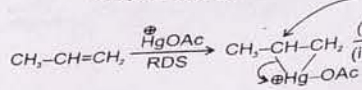
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MAINHYDROCARBON - 18

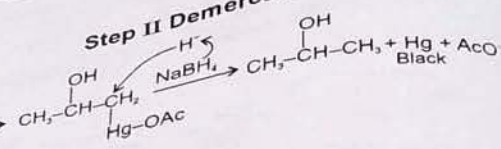
Hydrocarbons (alkanes, Alkenes and Alkynes)

Mechanism :

Step I Oxymercuration

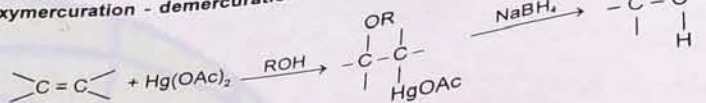


Step II Demercuration



Remarks : No rearrangement ; Markovnikoff's additions

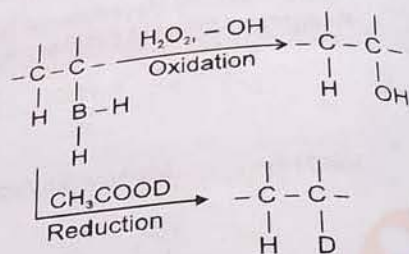
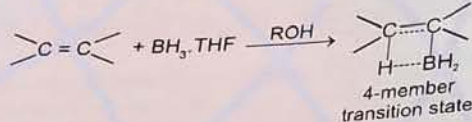
(iii) Alkoxymercuration - demercuration : "Mechanism-II"



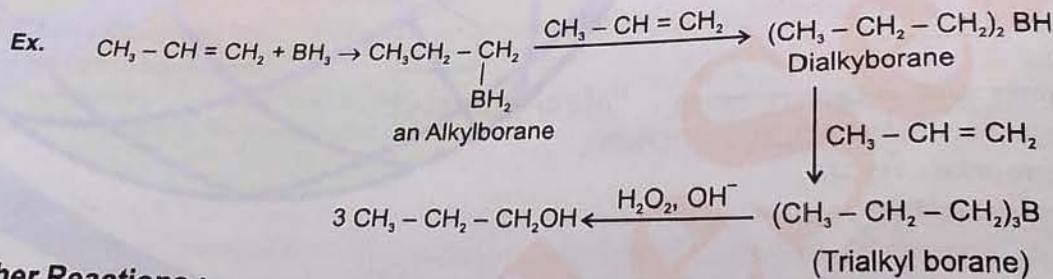
(iv) Hydroboration-oxidation : (Syn addition)

Reagents : $\text{BH}_3, \text{THF}/\text{H}_2\text{O}_2, \text{OH}^-$

Mechanism :

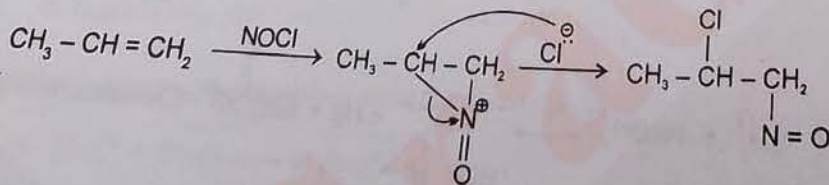


Remarks :
Anti Markovnikov's addition.
Stereo specific Syn addition.
Less hindered alkene is more reactive.
4-membered transition state.



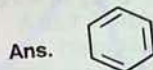
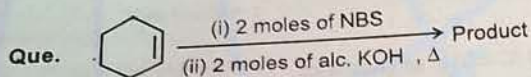
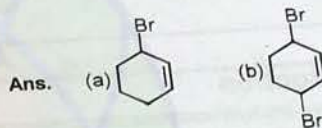
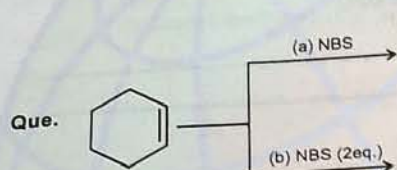
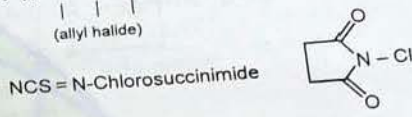
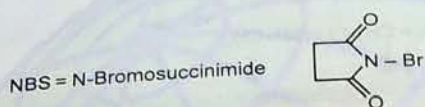
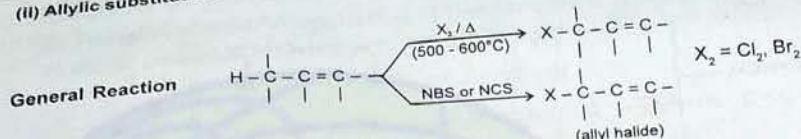
7.6 Other Reactions :

(i) Addition of NOCl :



Hydrocarbons (alkanes, Alkenes and Alkynes)

(ii) Allylic substitution Halogenation :



(iii) Addition of Carbene :

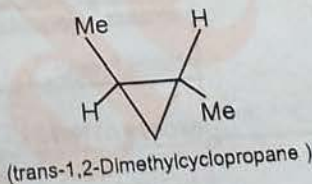
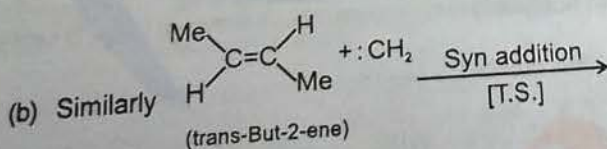
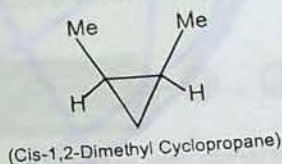
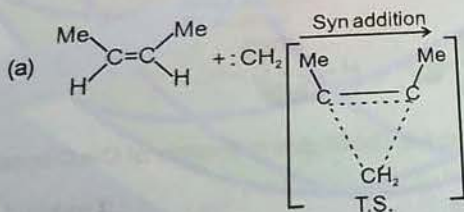
Reagents :

(i) CH_2N_2 , Δ or $h\nu$

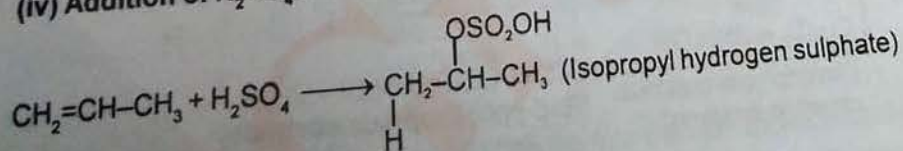
(iii) $\text{CH}_2\text{I}_2 + \text{Zn/Cu}$ Couple

(ii) $\text{CH}_2 = \text{C} = \text{O}$, Δ or $h\nu$

(iv) $\text{CHCl}_3 + \text{NaOH}$

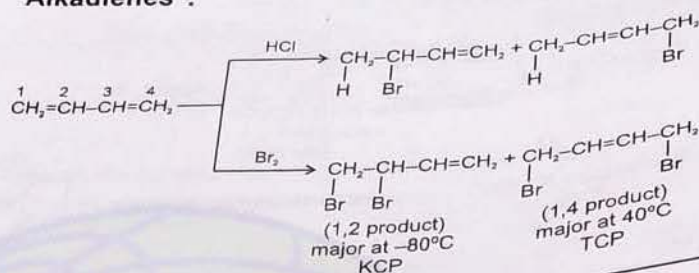


(iv) Addition of H_2SO_4 :



Hydrocarbons (alkanes, Alkenes and Alkynes)

8. Alkadienes :



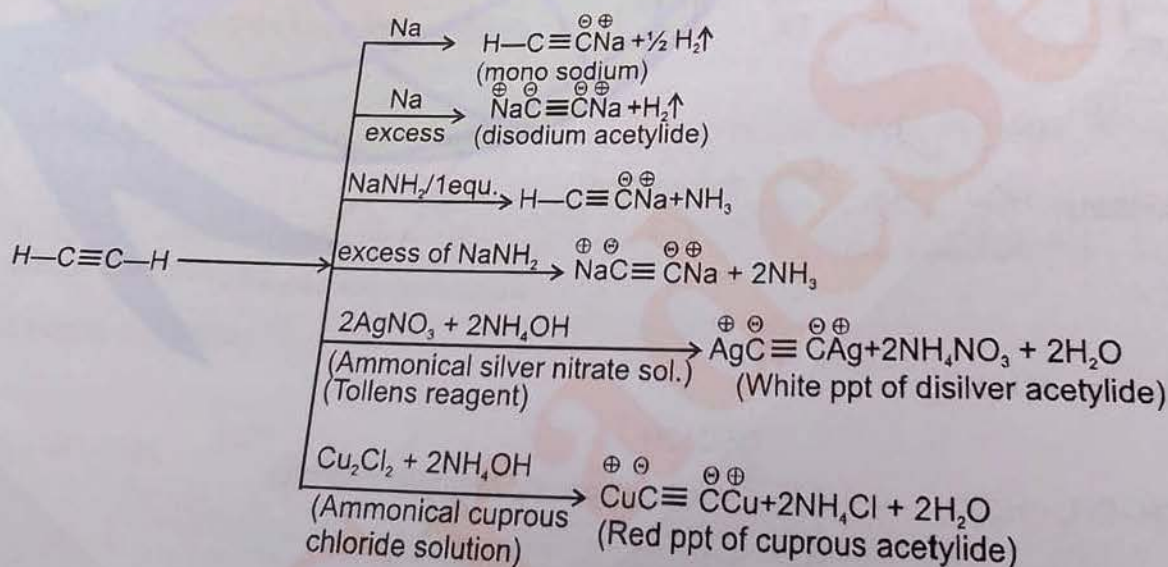
ALKYNE

1. Introduction

- (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 Å
- (5) Its bond energy is 192 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 1-s of 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 result 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.



All these reactions are possible with 1-alkyne or acetylene.

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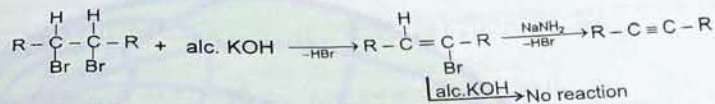
MAINHYDROCARBON - 21

Hydrocarbons (alkanes, Alkenes and Alkynes)

2. Methods of preparation :

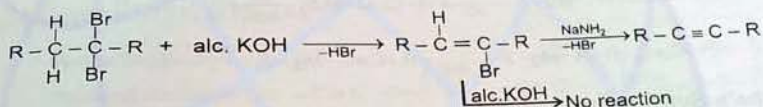
2.1. By Double Dehydrohalogenation of Gem and Vicinal Dihalide :

(A) Vicinal Dihalide :

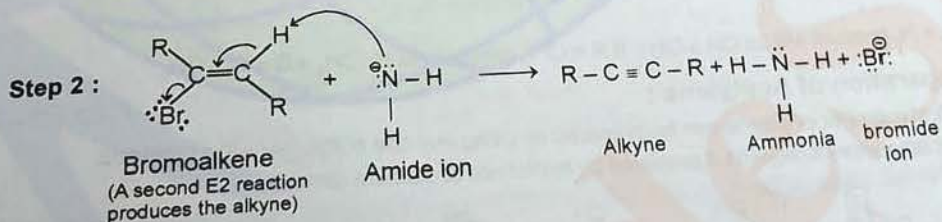
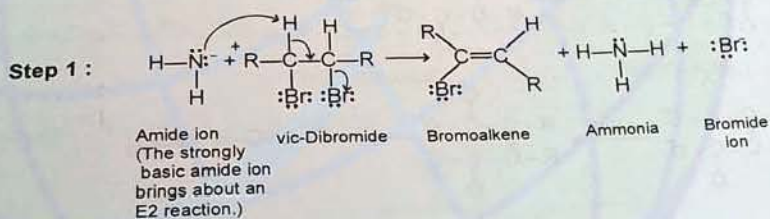


NaNH₂ is more basic than alc. KOH.

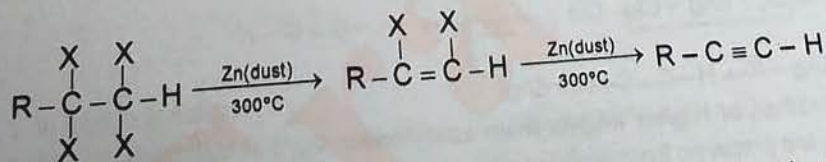
(B) Gem Dihalides :



Mechanism :



2.2. From Tetrahaloalkanes (Dehalogenation) :

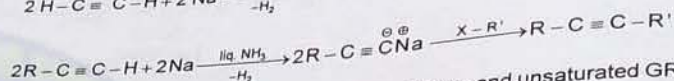
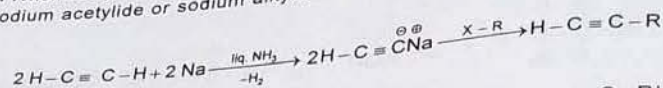


Note : In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product cyclo alkene is obtained.

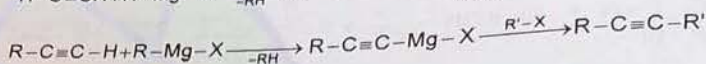
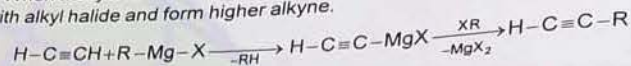
Hydrocarbons (alkanes, Alkenes and Alkynes)

2.3. Synthesis of Higher Alkynes :

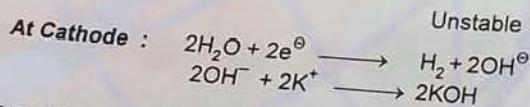
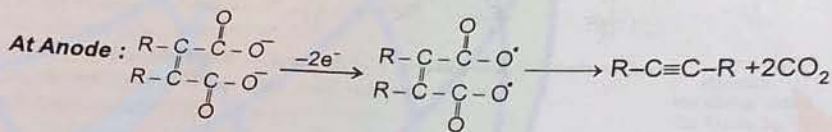
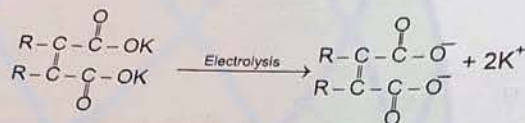
(A) With Na : When acetylene or 1-alkyne react with Na in presence of liq. NH₃ then an intermediate compound sodium acetylides or sodium alkynides is formed which gives higher alkyne with alkyl halide.



(B) With GR : When acetylene or 1-alkyne react with GR then alkane and unsaturated GR is formed which further react with alkyl halide and form higher alkyne.



2.4. From Kolbe's Synthesis :

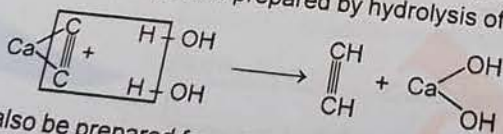


If R = H, product will be CH₂=CH₂; If R = CH₃, product will be CH₃-C≡C-CH₃.

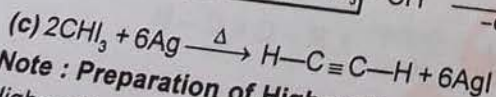
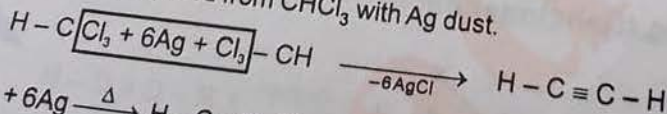
2.5. Preparation of Acetylene :

It is first member of alkyne can be prepared by using any one of the following methods.

(a) In laboratory acetylene is prepared by hydrolysis of calcium carbide.

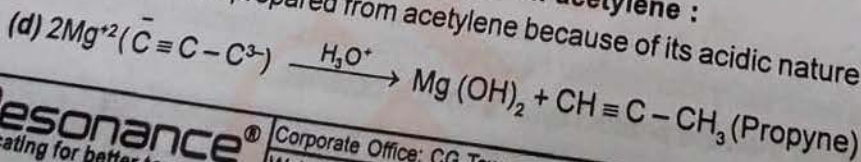


(b) It can also be prepared from CHCl₃ with Ag dust.



Note : Preparation of Higher alkyne from acetylene :

Higher alkyne are prepared from acetylene because of its acidic nature.



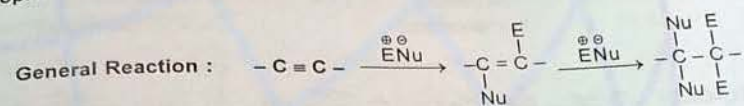
Hydrocarbons (alkanes, Alkenes and Alkynes)

3. Physical Properties of Alkyne :

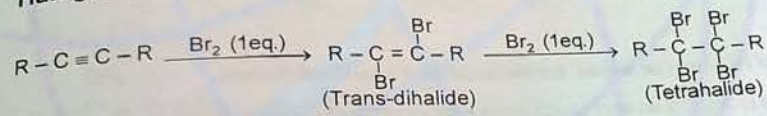
- Alkynes are colourless, odourless and tasteless.
- (i) Lower alkynes are partially soluble in H₂O. (It is due to its polarizability)
- (ii) Higher alkynes are insoluble in water due to more % of covalent character.
- (iii) Completely soluble in organic solvents.
- (iv) Melting point and boiling point are directly proportional to molecular mass and inversely proportional to number of branches.
- (v) Upto C₄ alkynes are gaseous, C₅-C₁₁ liquid, C₁₂ & above are solids.
- (vi) Acetylene & 1-alkyne are acidic in nature. It is due to presence of active H.
- (vii) Order of Solubility, density, B.P., M.P. and Acidic nature : Alkyne > Alkene > Alkane
- (viii) All terminal alkynes are acidic in nature.

4. Chemical Properties of Alkyne :

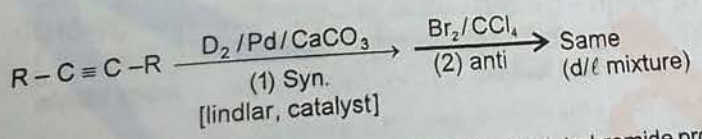
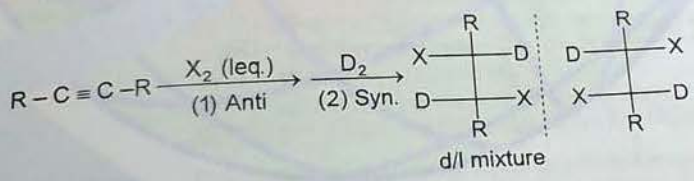
Electrophilic Addition to Alkynes :



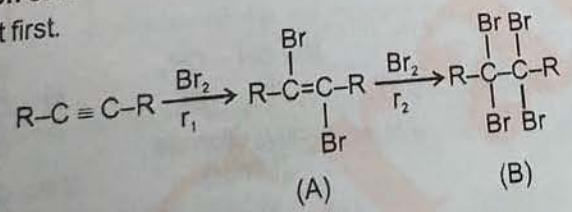
4.1. Halogenation :



Remark : - Reaction is Anti in both step



Addition of bromine : Over triple bond finally give tetrabromide product ; which involves formation of dibromo product first.

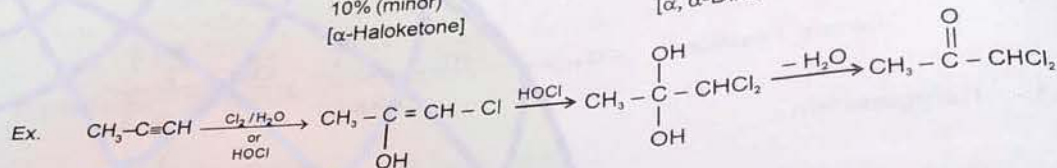
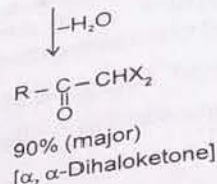
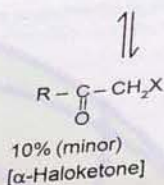
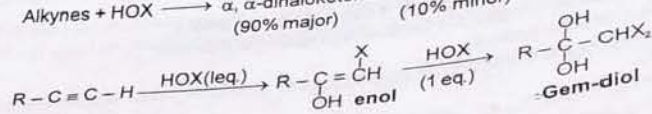


- Remarks
1. In above reaction $r_2 > r_1$
 2. Alkyl carbocation is more stable than vinyl carbocation

Hydrocarbons (alkanes, Alkenes and Alkynes)

4.2. Addition of HOX :

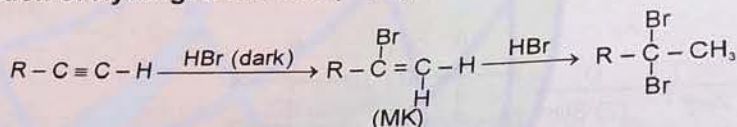
Alkynes + HOX \longrightarrow α , α -dihaloketone + α -haloketone
(90% major) (10% minor)



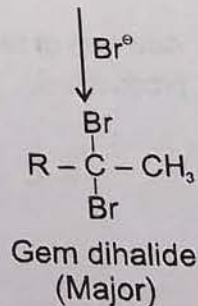
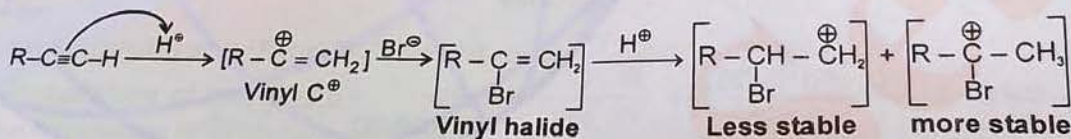
Remarks :

- (i) Two molecules of HOX can be added, the end product is α , α -Dihaloketone.
- (ii) The intermediate product is an enol which gives a minor product α -haloketone.

4.3. Addition of Hydrogen Halides (+ HX) :



Mechanism :

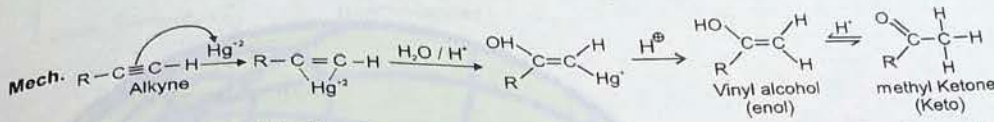
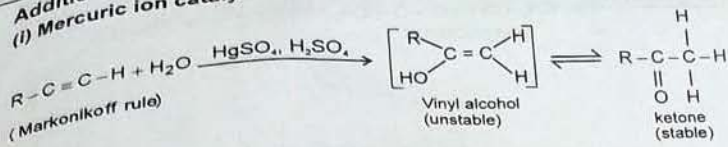


Remarks :

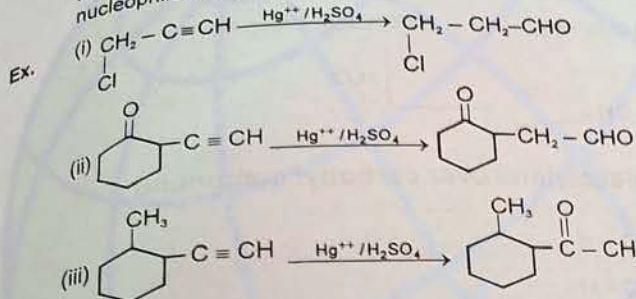
- (i) Markovnikov's Addition in both steps.
- (ii) If two moles of HX are added the final product is Gemdihalide.
- (iii) Electrophilic addition to terminal alkyne is regioselective.

Hydrocarbons (alkanes, Alkenes and Alkynes)

4.4. Addition of H₂O (Hydration Reaction) :
(i) Mercuric ion catalyzed hydration :



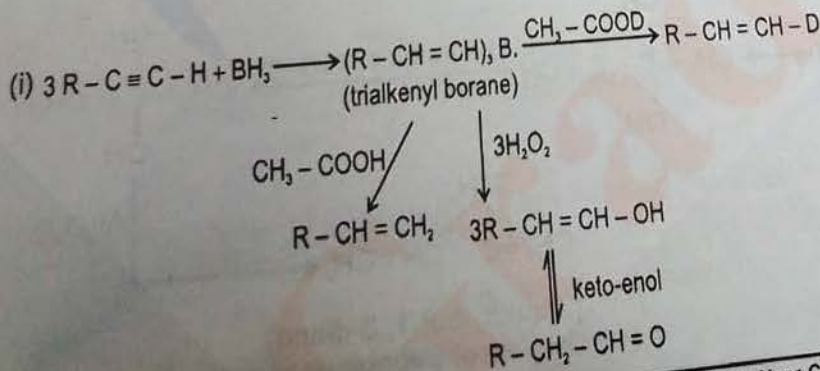
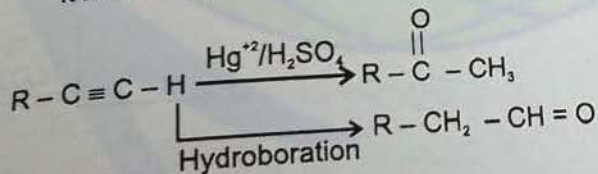
Note: By above reaction it is clear that carbonyl carbon is formed from that carbon of 'C≡C' over which nucleophile water attacks.



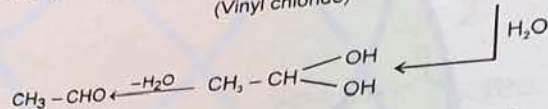
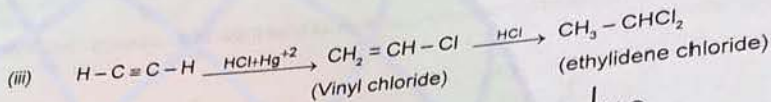
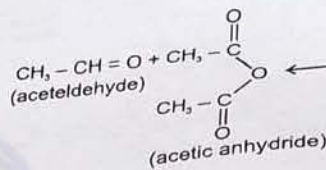
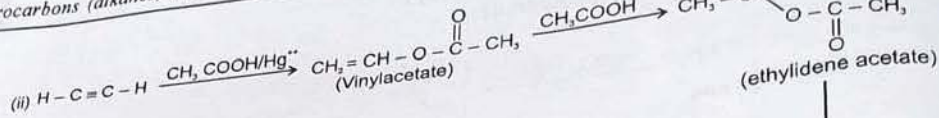
- Remarks :
- (1) Alkynes add one molecule of water.
 - (2) The product enol tautomerises to a carbonyl compound (aldehyde or ketone) and further addition does not take place.
 - (3) The reaction is catalysed by Hg²⁺ ions.
 - (4) The product is Markonnikoff Addition of water.
 - (5) If hydroboration method is used, then Anti Markonnikoff addition of water takes place.

Important:- The product does not appears to be addition product.

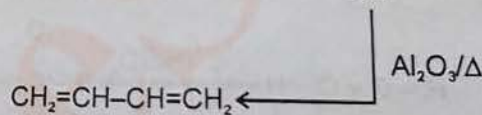
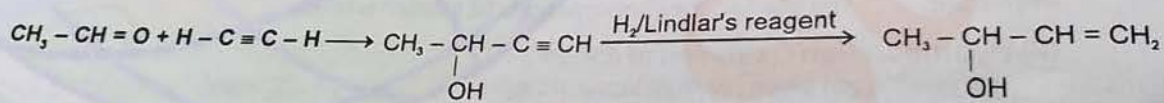
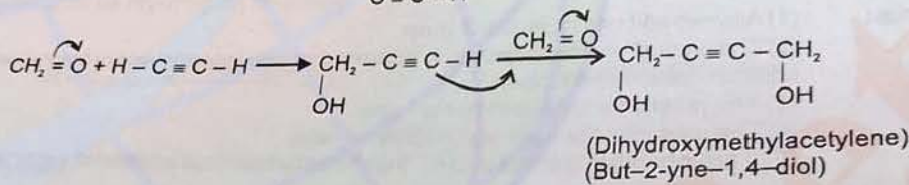
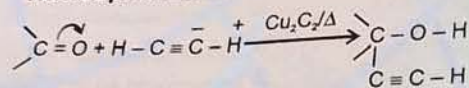
(ii) Hydroboration Oxidation of Alkynes :
It is used to get aldehyde from terminal alkyne.



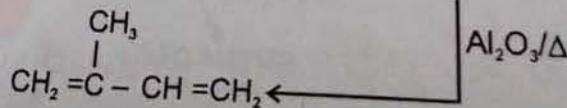
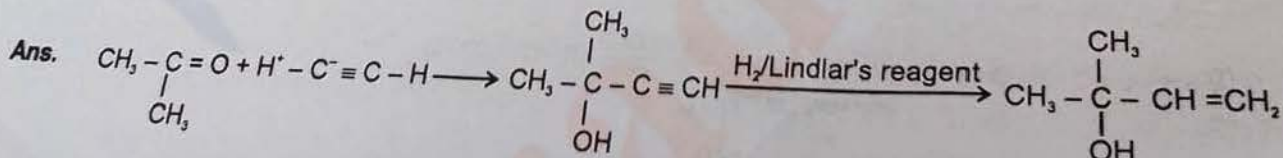
Hydrocarbons (alkanes, Alkenes and Alkynes)



4.5. Nucleophilic addition of 1-alkyne/acetylene over carbonyl compound



Que. How will you get isoprene from acetone.



(2-methylbut-1, 3-diene)
 (Isoprene) (monomer of natural rubber)

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