

- Hydrocarbons
- Unsaturated Hydrocarbons
- Aromatic Hydrocarbons
- Quick Reference Table
- Common Mistakes and Misconceptions
- Glossary

Hydrocarbons

Classification of Hydrocarbons

Hydrocarbons are compounds composed exclusively of carbon and hydrogen atoms. They are primarily derived from coal and petroleum.

- **Saturated hydrocarbons:** Contain only single bonds between carbon atoms (C–C). Example: Ethane (CH₃–CH₃).
- **Unsaturated hydrocarbons:** Contain one or more double (C=C) or triple (C≡C) bonds. Examples: Ethene (CH₂=CH₂), Ethyne (CH≡CH).
- **Aromatic hydrocarbons:** Contain at least one aromatic ring, such as benzene (C₆H₆).

Alkanes (Saturated Hydrocarbons)

Alkanes are the simplest class of hydrocarbons with the general formula C_nH_{2n+2}, where n is the number of carbon atoms. They have strong C–C and C–H bonds and are called paraffins (from Latin: parum affinis, meaning little affinity).

Methane (CH₄) is the first member of the alkane family. It has a tetrahedral structure with bond angles of 109.5°, formed by the overlap of sp³ hybrid orbitals.

Compounds of Carbon and Hydrogen.

Hydrocarbon

Aromatic Hydrocarbons

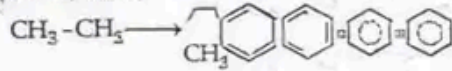
Generation of Electrophile
Electrophilic Substitution:

Aromatic alcohols

Aliphatic Hydrocarbons

- Types: Benzenoid — contain benzene ring; Non benzenoids — does not contain benzene ring (H₂C=CH-CH=CH₂)

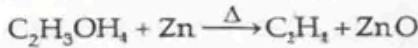
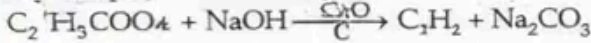
- Isomerism (Ortho, Meta)



- Aromaticity: Planarity, complete delocalization of the π -electrons in a ring structure of the $(4n+2)$ electrons in the ring where n is integer or $(2, 4, 6, \dots)$ (Hückel's rule)

Precautions:

- Pyrolysis polymerization of ethyne

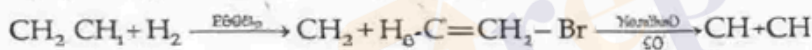
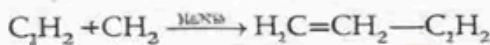


- Generation of Electrophile
- Formation of the carbocation intermediate
- Removal of proton

- IUPAC name: replacing 'ane' by the suffix 'ene'.

- Shows position, and chain isomerism

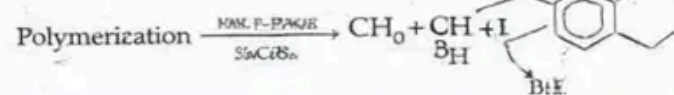
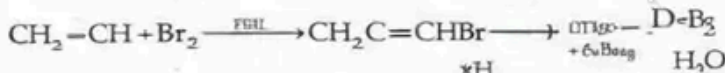
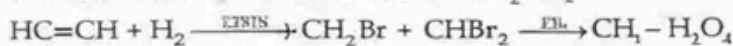
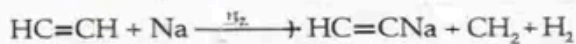
Preparation:



Physical Properties:

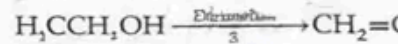
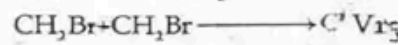
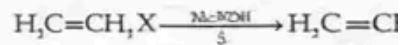
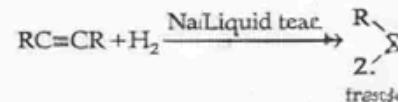
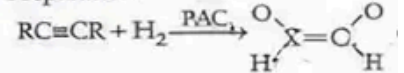
- First few members are gas, up to eight carbon higher ones solid.
- Colourless with lighter aromatic alkanes than water odorous.
- Lighter than water and insoluble in polar solvents but soluble in non-polar solvents.
- M.P., B.P., Density increases with increase in molar mass.

Chemical Properties:



- Shows structural and geometrical isomerism

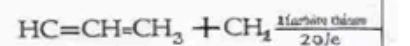
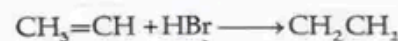
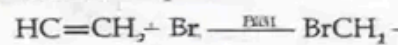
- Preparation:



- Physical Properties:

- First members are gas, up to eight carbon higher ones solid.
- Mass higher than corresponding alkanes.
- Increase in density in molecular weight.
- Increase in boiling point with increase in molecular weight.

- Chemical Properties:



Test in Mind

- First Level • Second Level

Isomerism in Alkanes

Alkanes exhibit various types of isomerism including chain isomerism, position isomerism, and conformational isomerism. Carbon atoms in tertiary (3°), or quaternary (4°).

Alkyl groups are substituents derived from alkanes by removing one hydrogen atom, with the general formula $\text{C}_n\text{H}_{2n+1}$.

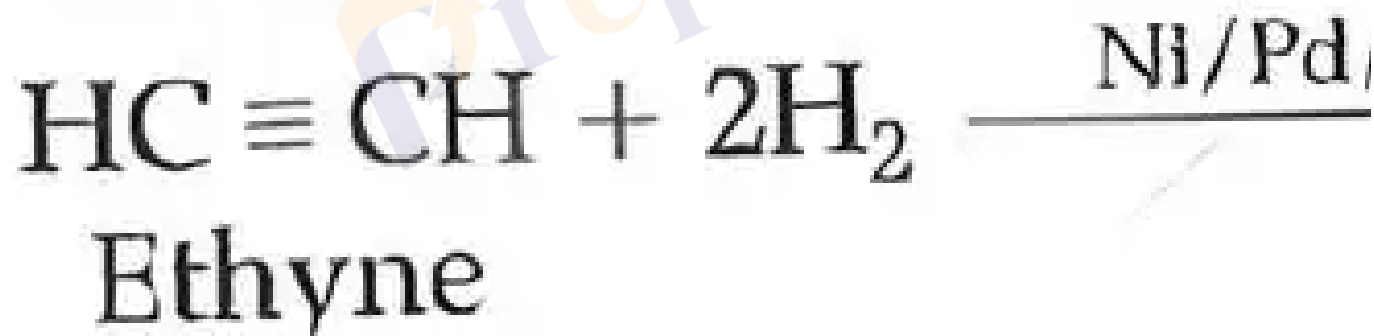
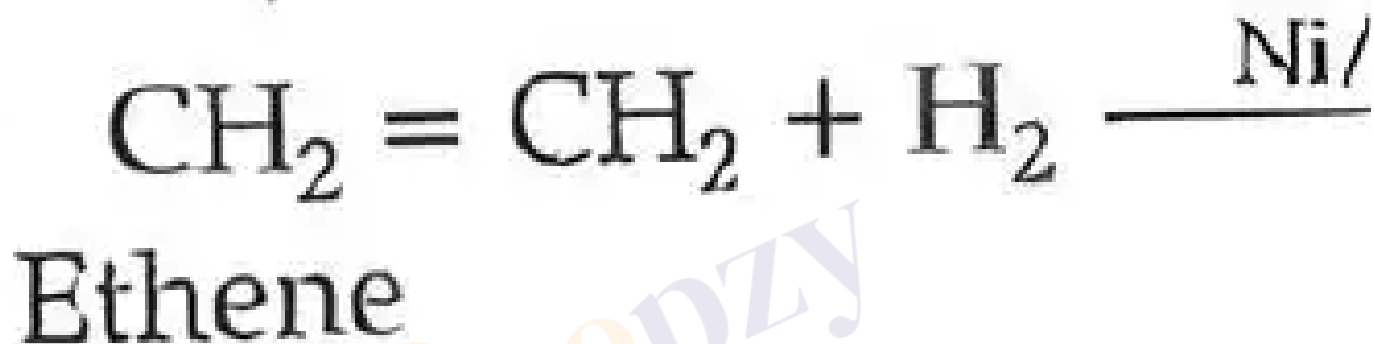
Nomenclature of Alkanes

Steps to write the correct structure from the IUPAC name:

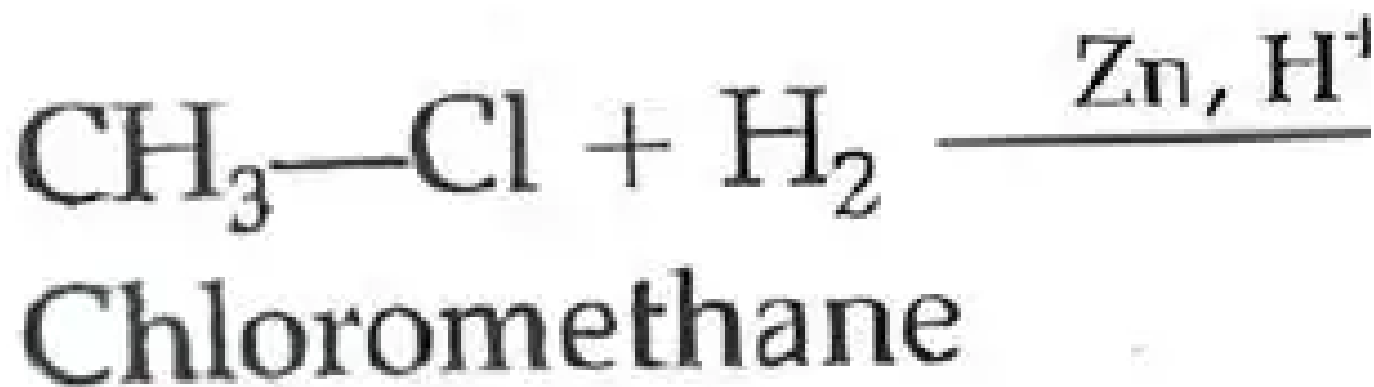
- Identify the longest carbon chain as the parent alkane.
- Number the carbon atoms in the chain starting from the end nearest to the substituent.
- Attach substituents to the correct carbon atoms according to their numbering.
- Complete the valency of each carbon atom by adding the appropriate number of hydrogen atoms.

Preparation of Alkanes

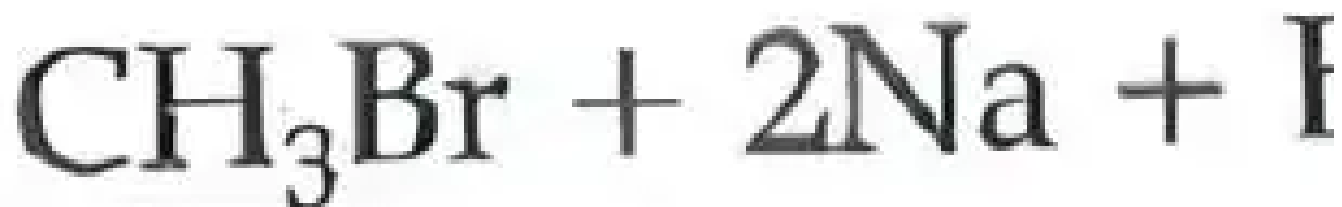
- **Hydrogenation of Unsaturated Hydrocarbons:** Unsaturated hydrocarbons can be converted to alkanes by adding hydrogen in the presence of a catalyst.



- **Reduction of Alkyl Halides:** Alkyl halides (except fluorides) can be reduced to alkanes using zinc and dilute hydrochloric acid.



- **Wurtz Reaction:** Two alkyl halides react with sodium metal in dry ether to form a higher alkane, increasing the carbon chain length.



- **Decarboxylation:** Sodium salts of carboxylic acids react with soda lime ($\text{NaOH} + \text{CaO}$) upon heating to produce alkanes with one less carbon atom.



- **Kolbe's Electrolytic Method:** Electrolysis of sodium salts of carboxylic acids produces alkanes, carbon dioxide, hydrogen gas, and sodium hydroxide.



Sodium acetate



Ethane

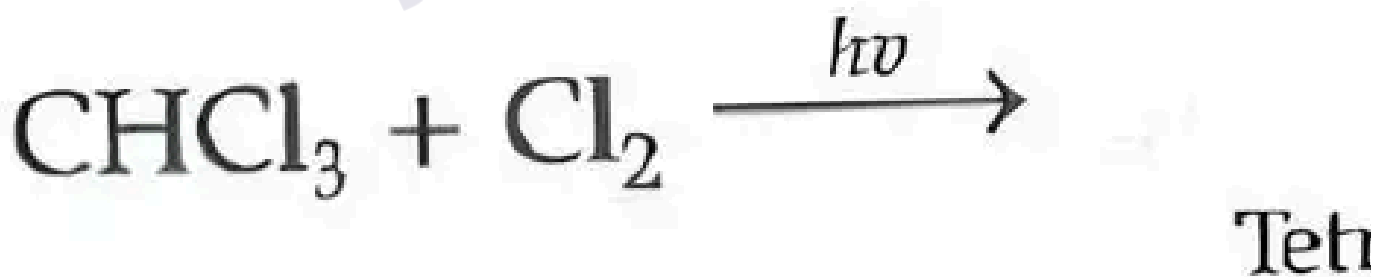
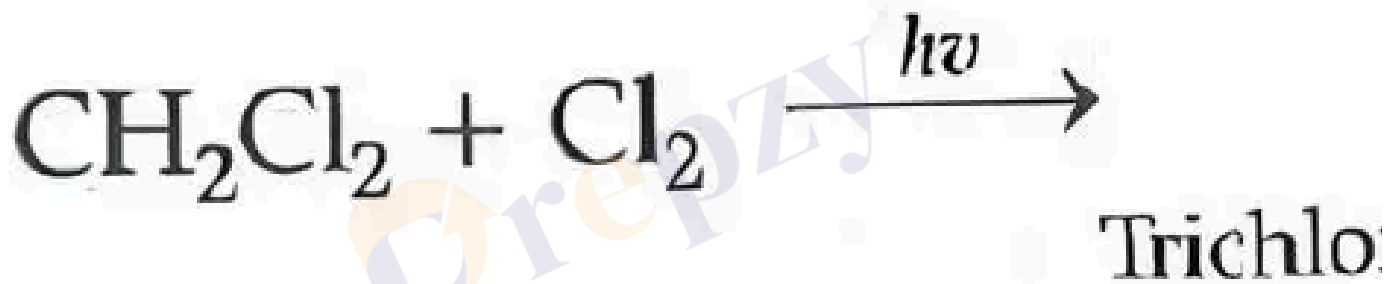
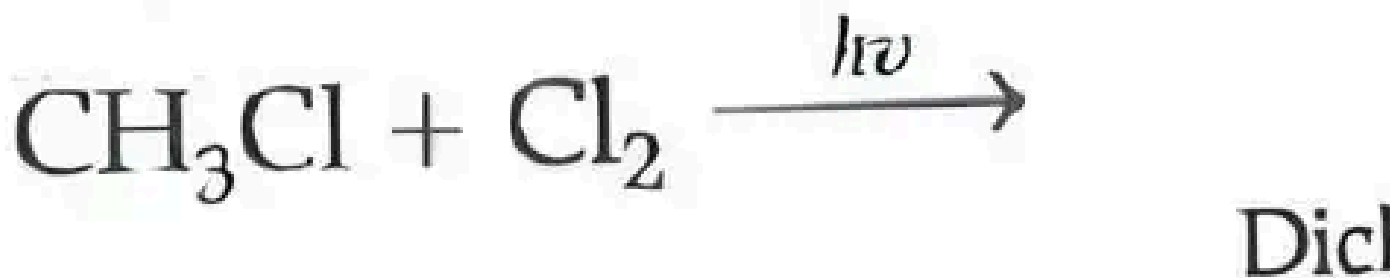
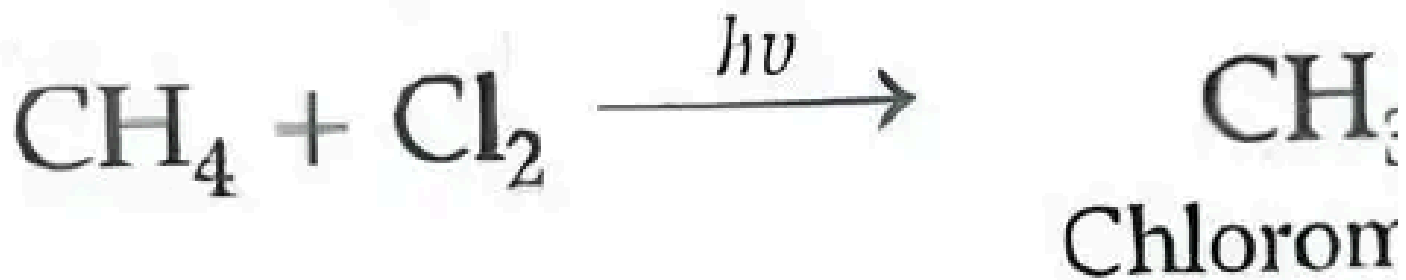
Physical Properties of Alkanes

Alkanes are non-polar molecules with weak van der Waals forces. The first four members (C₁ to C₄) are gases, C₅ to C₁₇ are liquids, and those with more than 17 carbons are solids. Increased branching lowers boiling points due to decreased surface area and weaker van der Waals forces. Alkanes with even numbers of carbons are more soluble in water than those with odd numbers.

Chemical Properties of Alkanes

Substitution Reactions

Alkanes undergo substitution reactions where one or more hydrogen atoms are replaced by halogens, nitro groups, or sulphonamic acid groups.



Mechanism of Halogenation

Initiation: Homolytic cleavage of chlorine molecule under light or heat produces chlorine radicals.



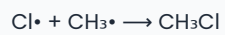
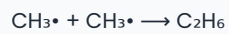
Propagation: Chlorine radical abstracts hydrogen from methane forming methyl radical and HCl.



Methyl radical reacts with chlorine molecule to form chloromethane and regenerate chlorine radical.



Termination: Combination of radicals to form stable molecules.



Combustion

Alkanes burn in oxygen to produce carbon dioxide and water, releasing large amounts of heat, making them useful fuels.

Prepzy



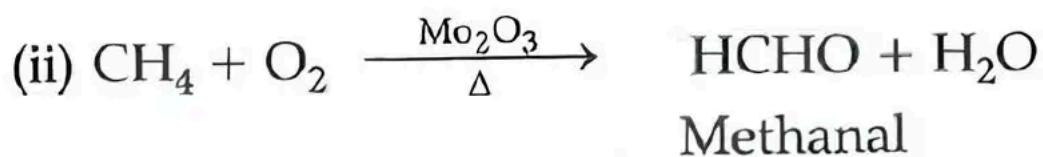
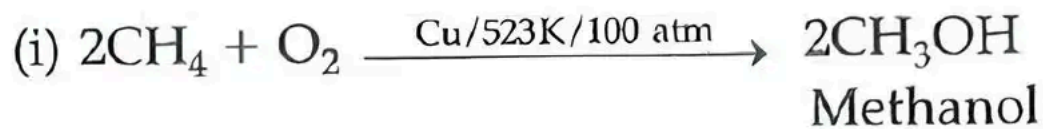
e.g.,



$$\Delta H^\circ = -2875.84 \text{ kJ mol}^{-1}$$

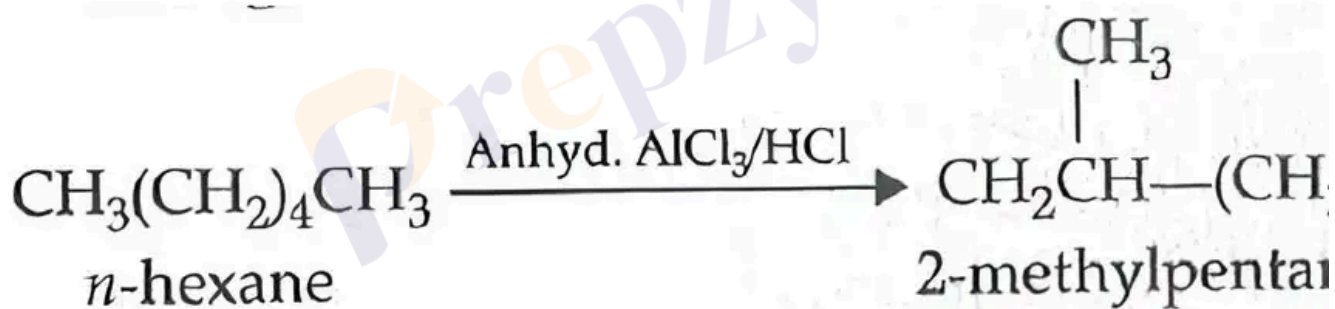
Controlled Oxidation

Alkanes can be oxidized under controlled conditions to form alcohols, aldehydes, acids, or other compounds using specific catalysts and co



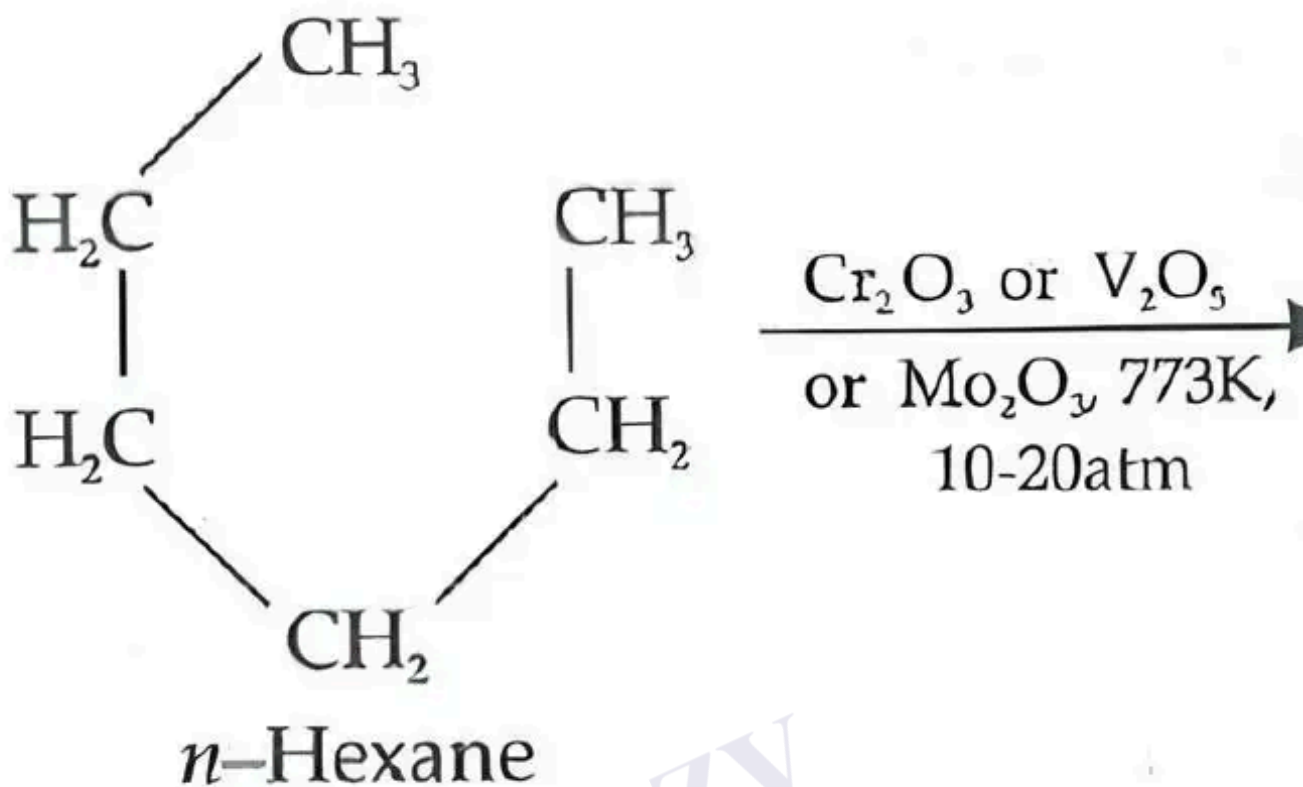
Isomerisation

n-Alkanes can be converted to branched chain alkanes by heating with anhydrous aluminium chloride and hydrogen chloride gas.



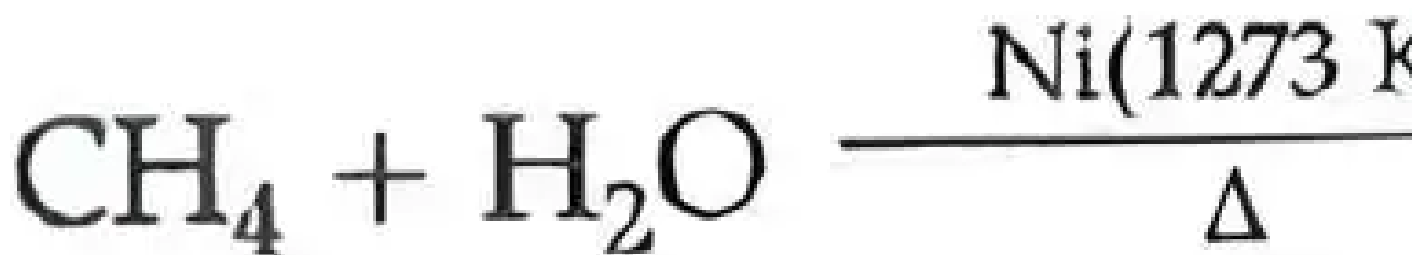
Aromatization (Reforming)

Dehydrogenation and cyclization of alkanes to benzene and its homologues occur under high temperature and pressure with catalysts.



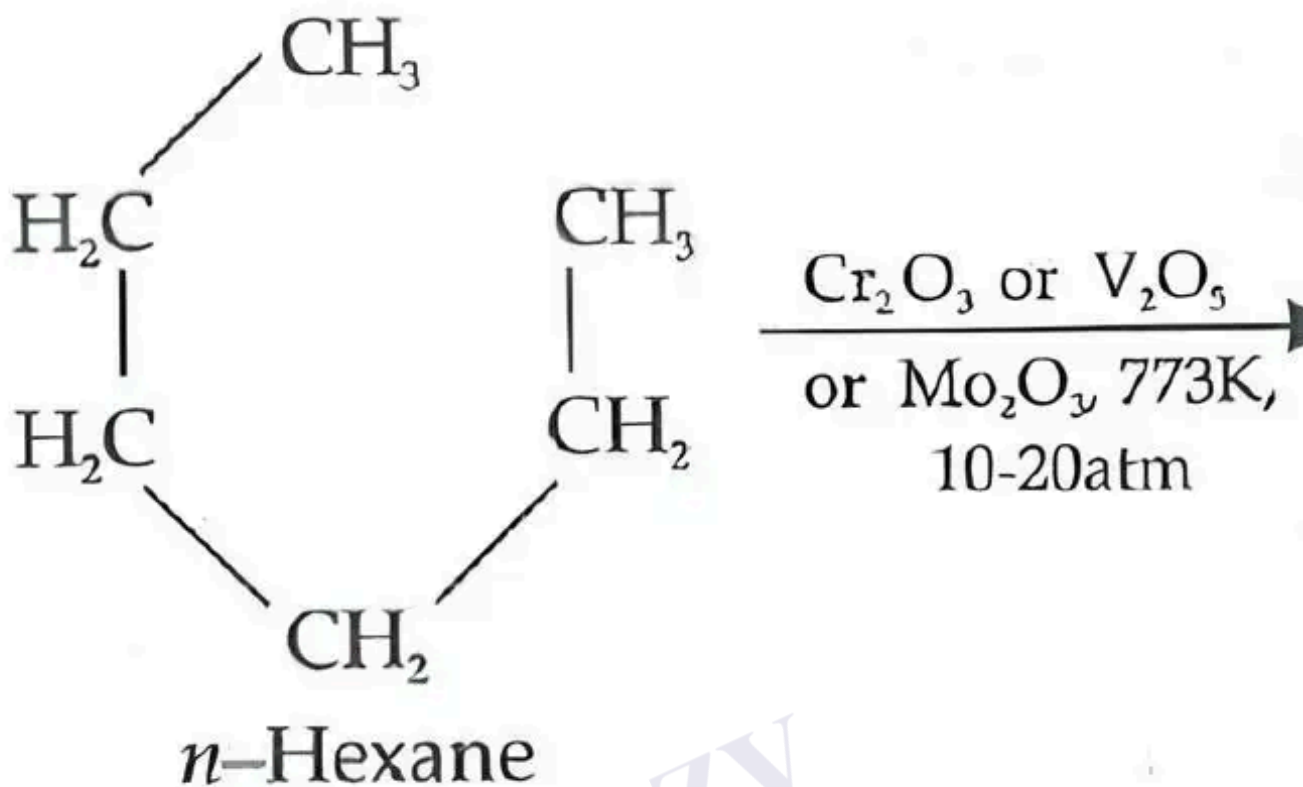
Reaction with Steam

Methane reacts with steam in the presence of nickel catalyst at high temperature to produce carbon monoxide and hydrogen gas, an industrial process known as steam reforming.



Pyrolysis (Cracking)

Higher alkanes decompose into lower alkanes and alkenes upon heating, a process called pyrolysis or cracking.

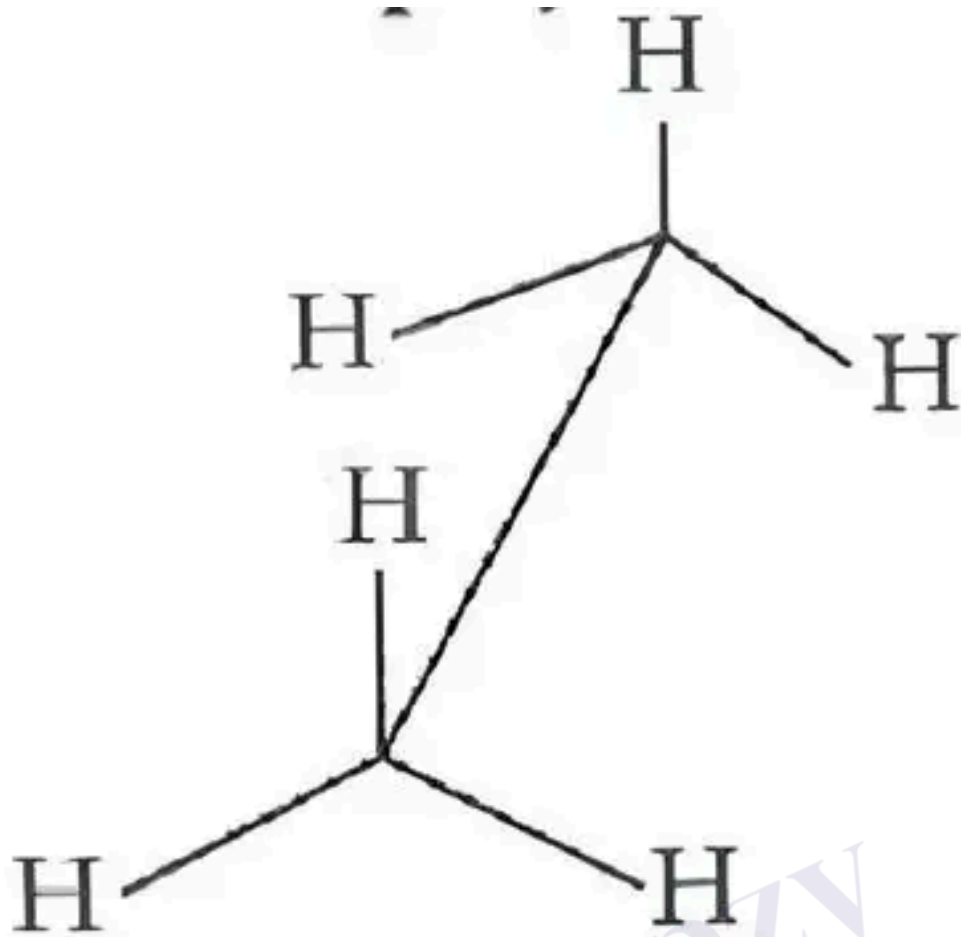


Conformations of Alkanes

Alkanes have sigma (σ) bonds between carbon atoms allowing free rotation, resulting in different spatial arrangements called conformations due to minimized torsional strain.

Sawhorse Projections

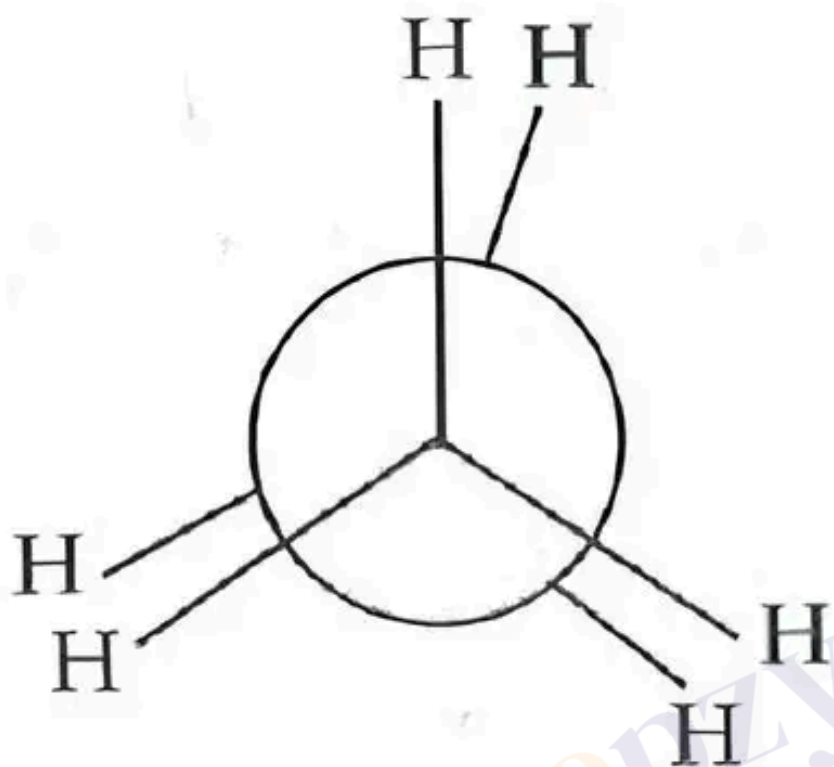
View of the molecule along the molecular axis showing relative positions of atoms.



(i) Eclipsed

Newman Projections

View of the molecule looking directly down the C-C bond axis, showing eclipsed and staggered conformations.



(i) Eclipsed



(ii) Staggered

Key Terms

- **Cycloalkanes:** Cyclic hydrocarbons with formula C_nH_{2n} , isomeric with alkenes.
- **Cracking:** Breaking down higher molecular weight hydrocarbons into lower molecular weight hydrocarbons by heating with catalysts.
- **Reforming:** Cyclization followed by aromatization of alkanes to form aromatic compounds.
- **Knocking:** Metallic rattling sound in internal combustion engines caused by premature combustion.
- **Octane Number:** Scale measuring knocking tendency of petrol; iso-octane is 100, n-heptane is 0.

Solved Examples

Practice Set

- **Level 1:** Define saturated hydrocarbons and give an example.
-
- **Level 2:** Explain the Wurtz reaction with an example.
-
- **Level 3:** Calculate the amount of oxygen required for complete combustion of 2 moles of propane (C_3H_8).

Answer Key

Level 1: Saturated hydrocarbons contain only single bonds between carbon atoms. Example: Methane (CH₄).

Level 2: Wurtz reaction involves the reaction of two alkyl halides with sodium metal in dry ether to form a higher alkane. For example, 2CH₃Br

Level 3: Combustion reaction: C₃H₈ + 5O₂ → 3CO₂ + 4H₂O. For 2 moles of propane, oxygen required = 2 × 5 = 10 moles.

Unsaturated Hydrocarbons

Alkenes

Alkenes are unsaturated hydrocarbons containing at least one carbon-carbon double bond (C=C) and have sp² hybridization with bond an

Examples include ethene (C₂H₄) and propene (C₃H₆).

Structure of Double Bond

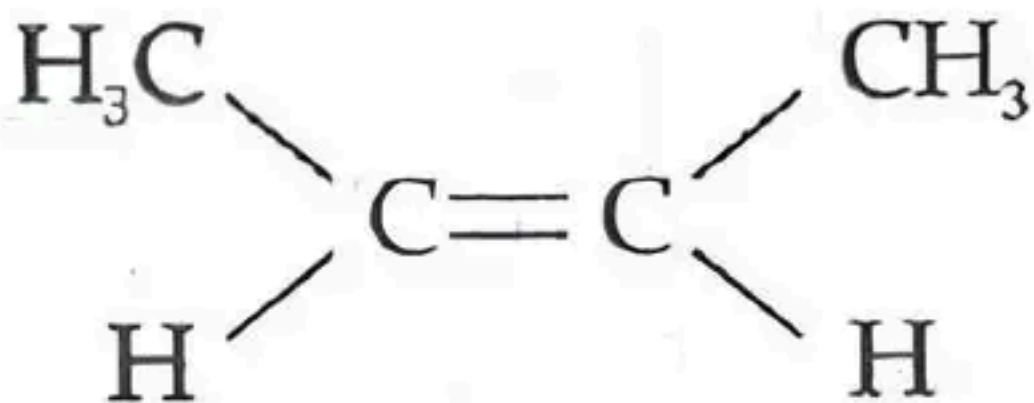
The double bond consists of one sigma (σ) bond formed by head-on overlap of sp² orbitals and one pi (π) bond formed by lateral overlap o

Nomenclature

- Longest chain containing the double bond is selected.
- Numbering starts from the end nearest the double bond.
- The suffix 'ene' replaces 'ane' of alkanes.

Isomerism in Alkenes

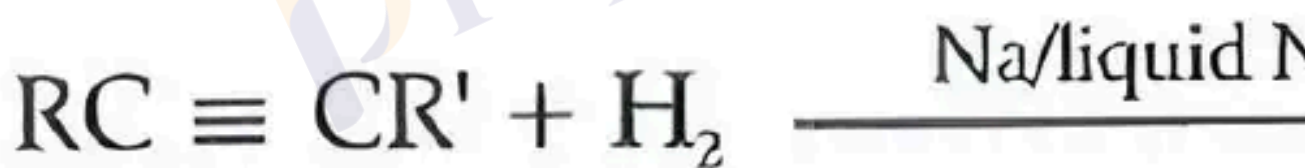
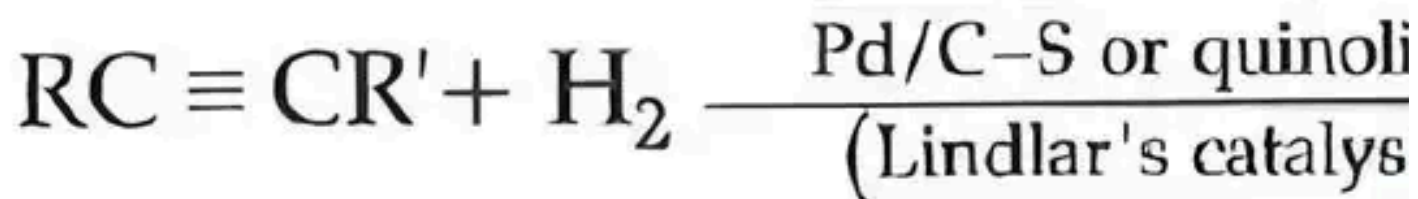
Alkenes exhibit chain, position, and geometrical (cis-trans) isomerism. Geometrical isomerism arises due to restricted rotation around the d



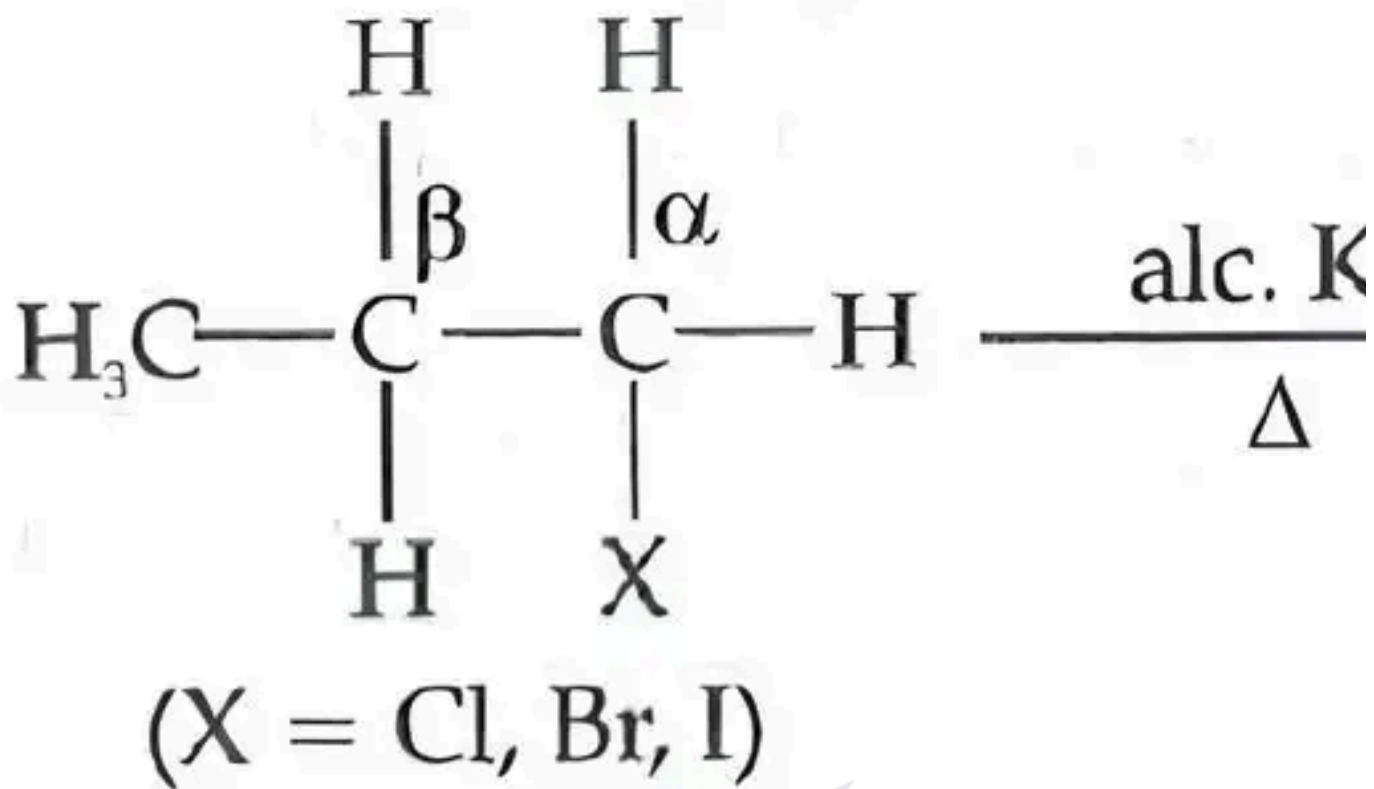
cis-But-2-ene

Preparation of Alkenes

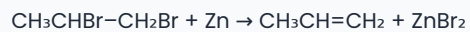
- **From Alkynes:** Partial hydrogenation of alkynes using Lindlar's catalyst produces cis-alkenes.



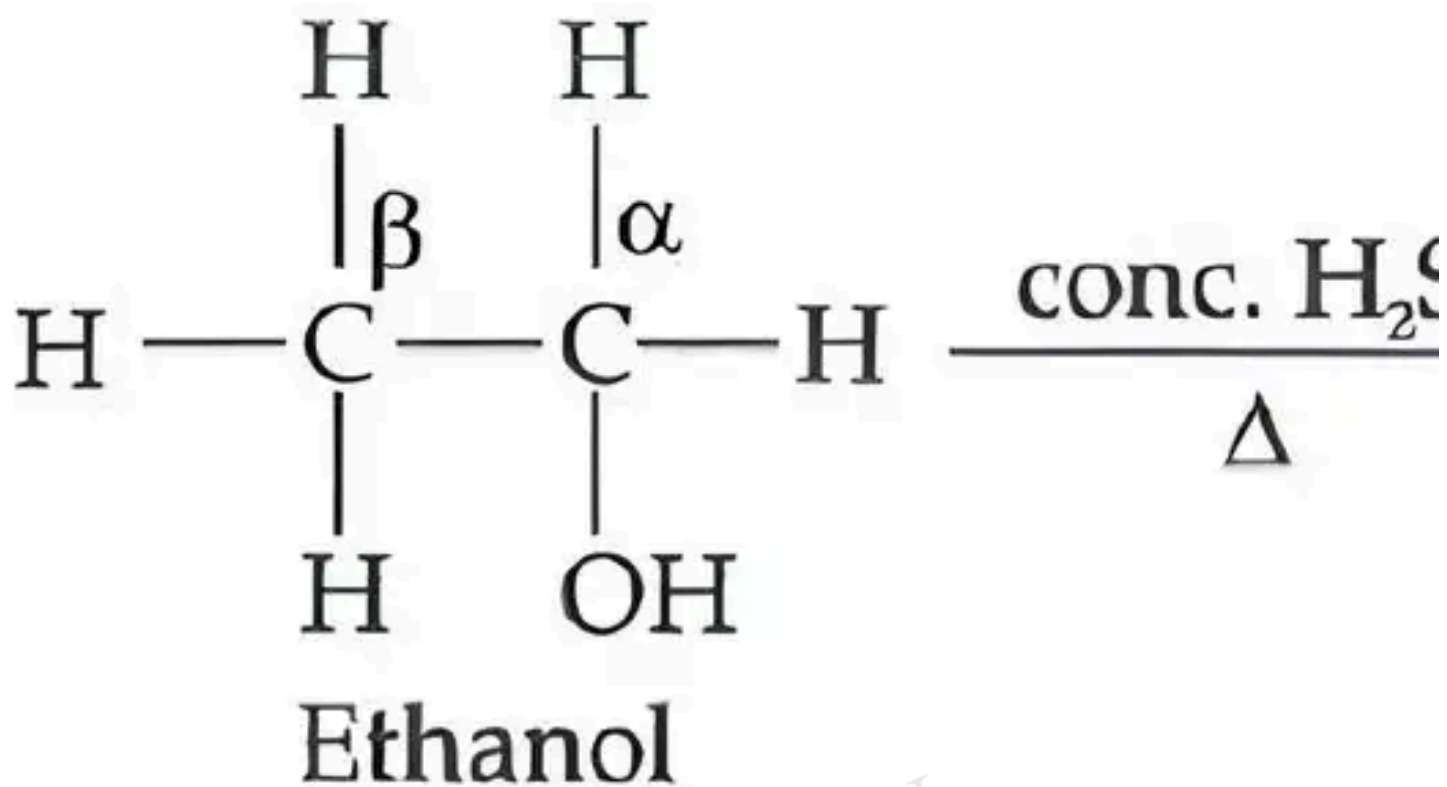
- **From Alkyl Halides:** Dehydrohalogenation of alkyl halides with alcoholic KOH forms alkenes.



- **From Vicinal Dihalides:** Treatment with zinc removes halogens to form alkenes.



- **From Alcohols:** Acidic dehydration of alcohols with concentrated sulfuric acid produces alkenes.



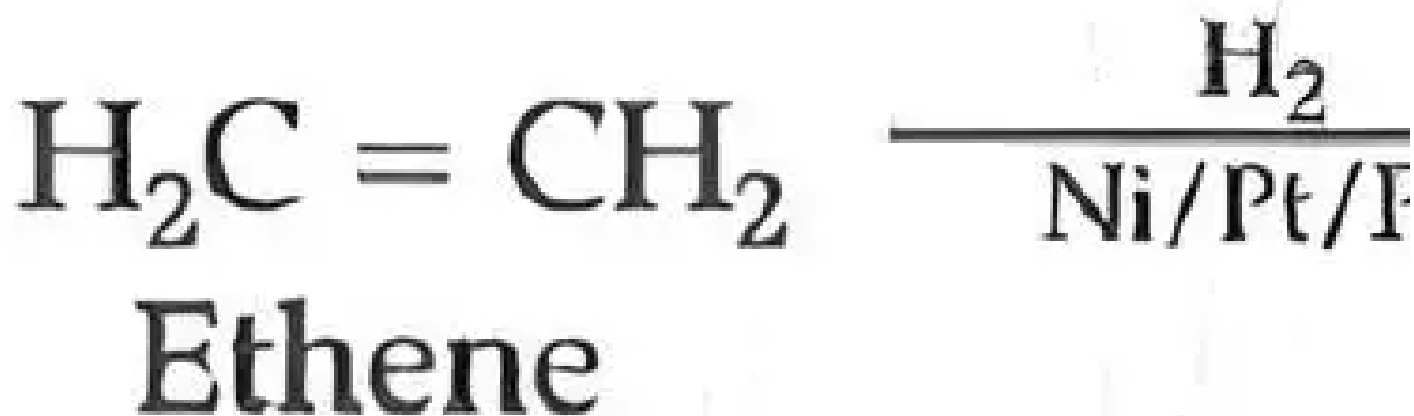
Physical Properties

Alkenes are generally colourless and odourless, insoluble in water but soluble in nonpolar solvents. Boiling points increase with molecular size.

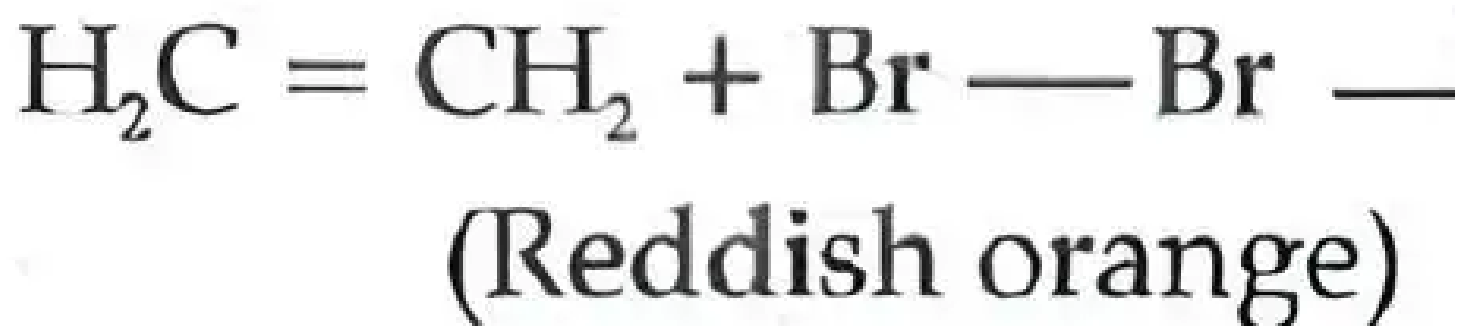
Chemical Properties

Electrophilic Addition Reactions

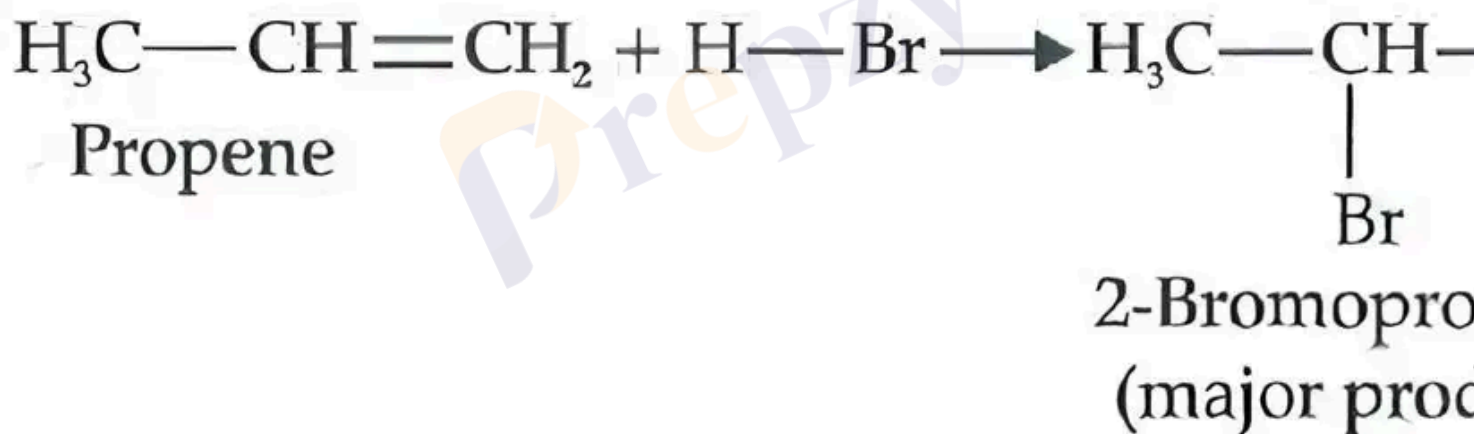
- **Addition of Hydrogen:** Alkenes react with hydrogen in the presence of metal catalysts to form alkanes.



- **Addition of Halogens:** Alkenes react with halogens to form dihalides, used as a test for unsaturation.



- **Addition of Hydrogen Halides:** Follows Markovnikov's rule where the halide attaches to the more substituted carbon.



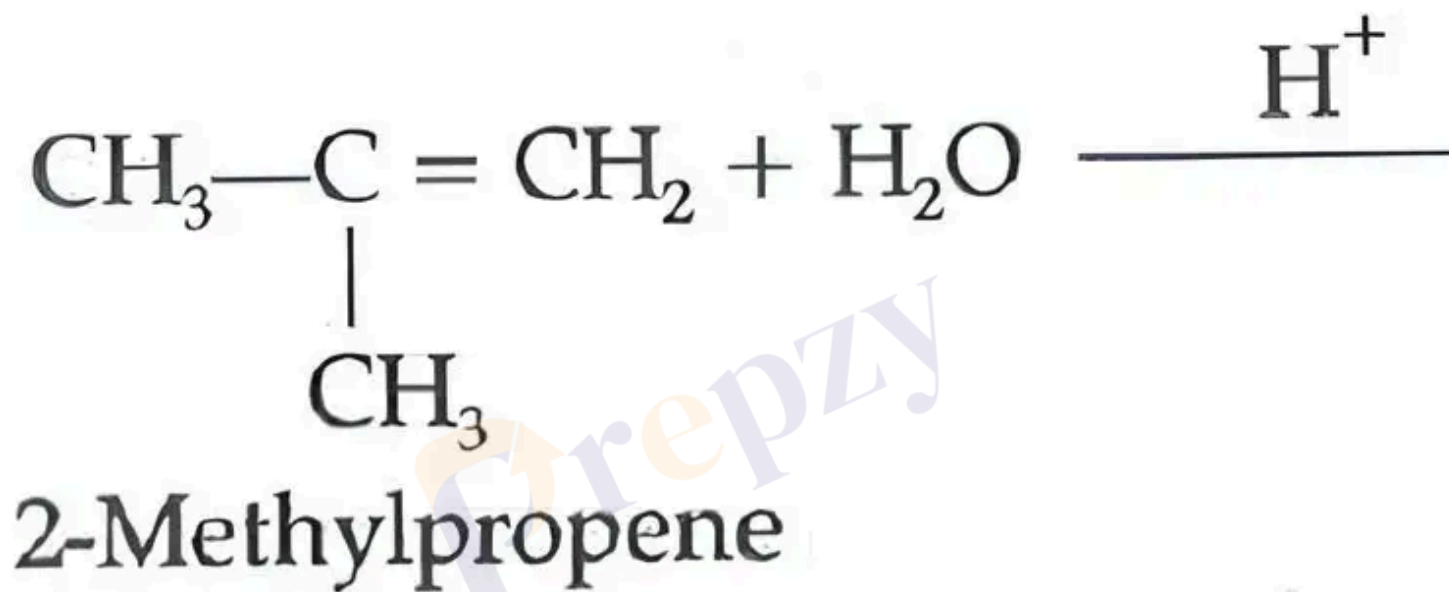
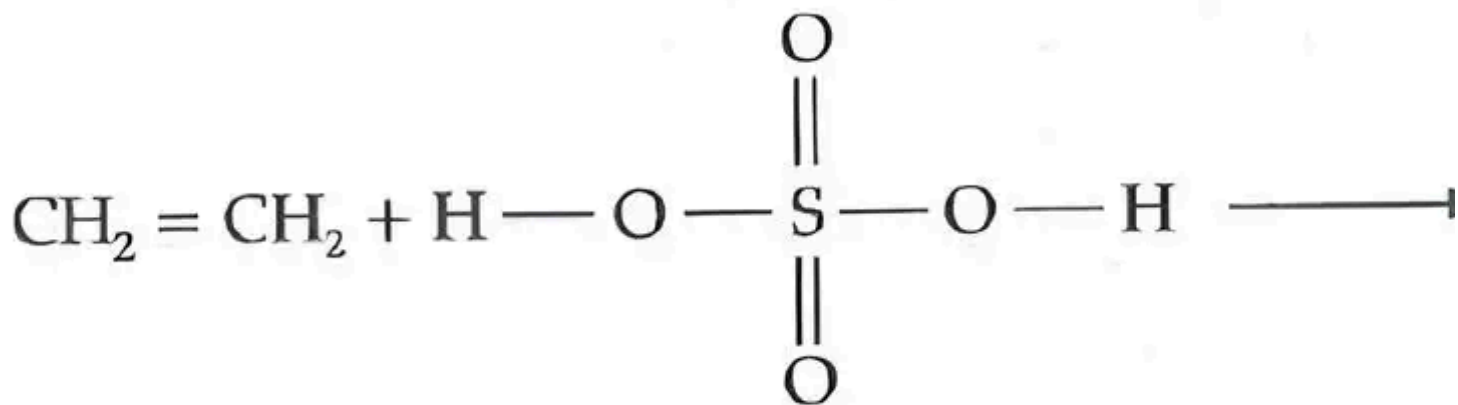
Peroxide Effect (Anti-Markovnikov Addition)

In the presence of peroxides, HBr adds to alkenes opposite to Markovnikov's rule via free radical mechanism.



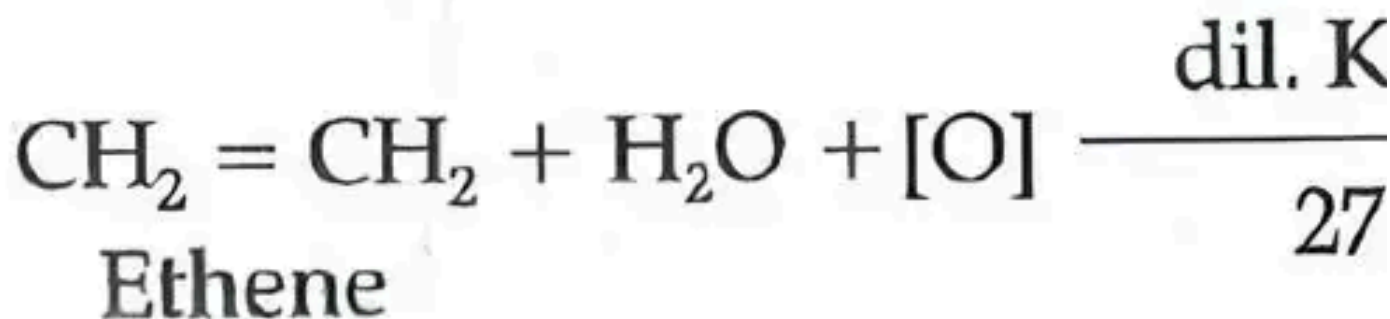
Addition of Sulfuric Acid and Water

Alkenes react with sulfuric acid to form alkyl hydrogen sulfates, which hydrolyze to alcohols.



Oxidation

- With Cold Dilute KMnO_4 (Baeyer's Test): Alkenes form glycols and decolourise the purple KMnO_4 solution.



- With Acidic KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$: Alkenes oxidize to ketones or acids.



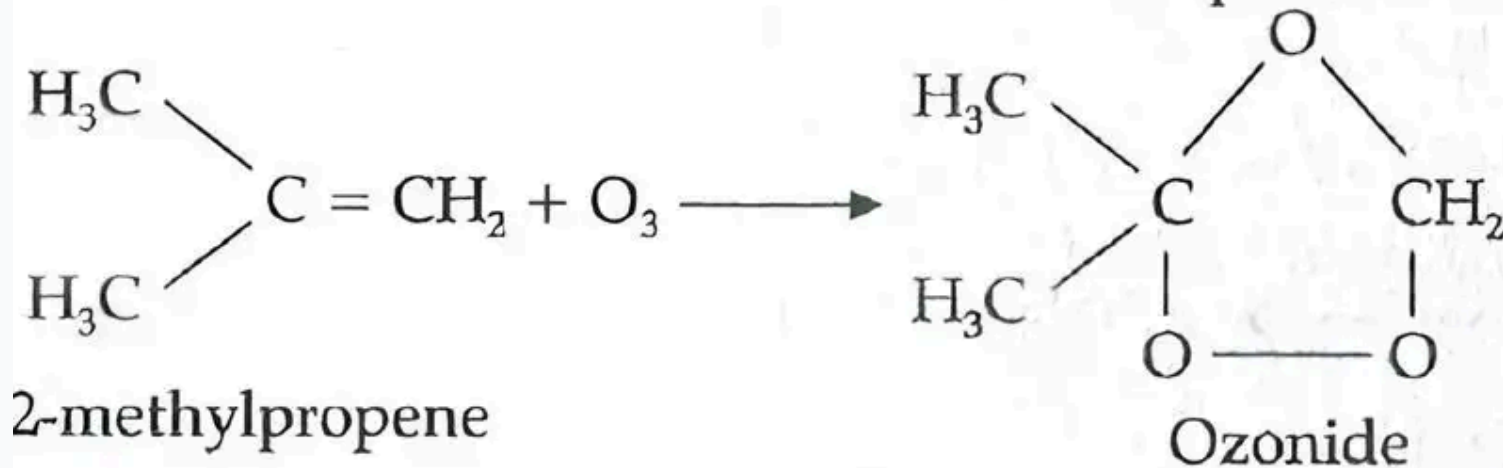
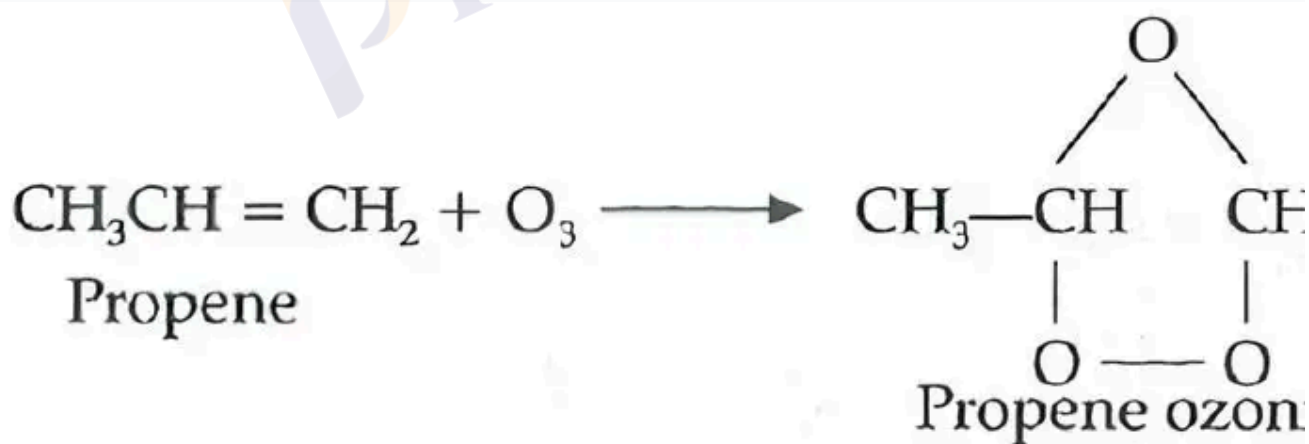
2-Methylpropene



But-2-ene

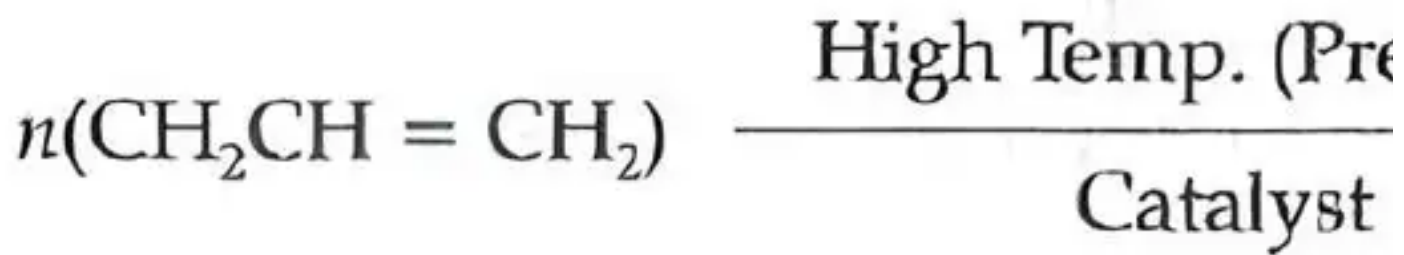
Ozonolysis

Alkenes react with ozone to form ozonides, which upon reduction yield aldehydes or ketones.



Polymerisation

Alkenes polymerize under high temperature, pressure, and catalysts to form polymers like polythene.



Alkynes

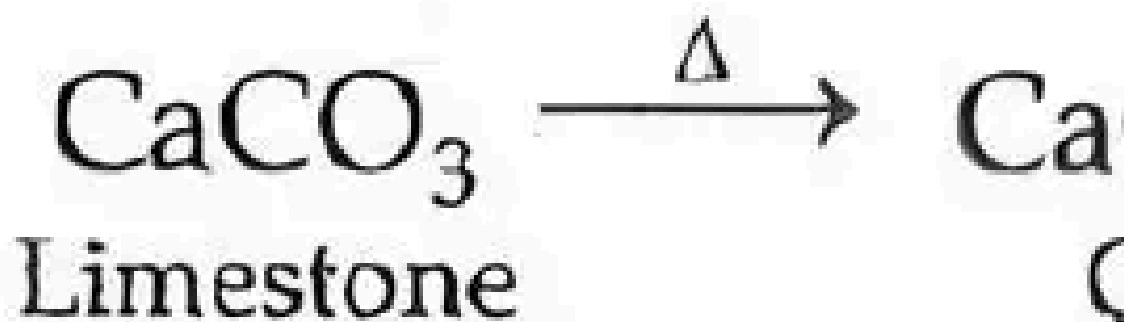
Alkynes are unsaturated hydrocarbons containing at least one carbon-carbon triple bond with the general formula $\text{C}_n\text{H}_{2n-2}$. Ethyne (acetylene)

Structure

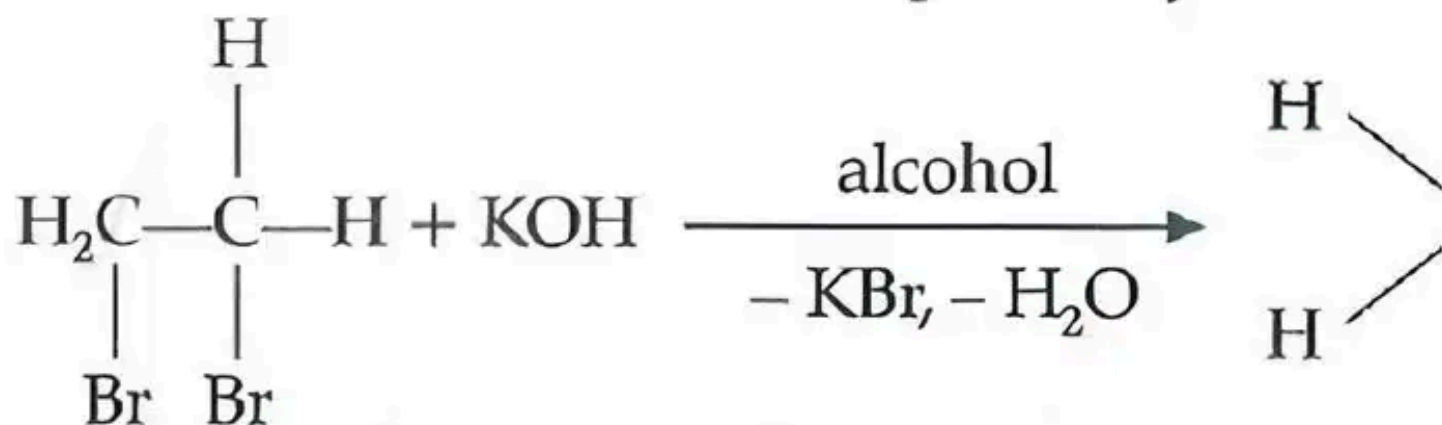
In ethyne, carbon atoms are sp hybridized with a linear structure and bond angle of 180° . The triple bond consists of one sigma and two pi bonds.

Preparation of Alkynes

- **From Calcium Carbide:** Calcium carbide reacts with water to produce ethyne.

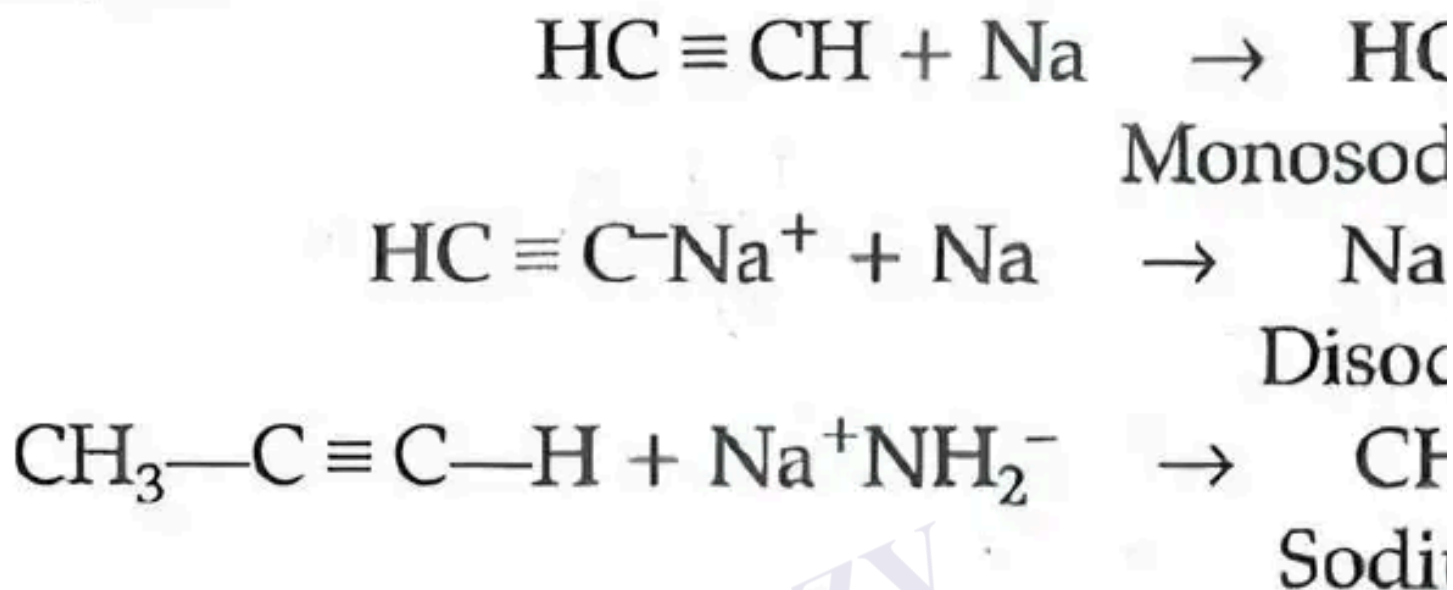


- From Vicinal Dihalides: Treatment with alcoholic KOH followed by sodium amide yields alkynes.



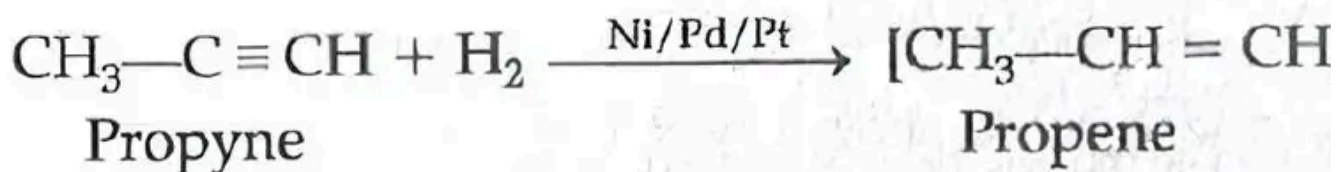
Chemical Properties

- **Formation of Acetylides:** Terminal alkynes react with sodium or sodium amide to form acetylide salts.

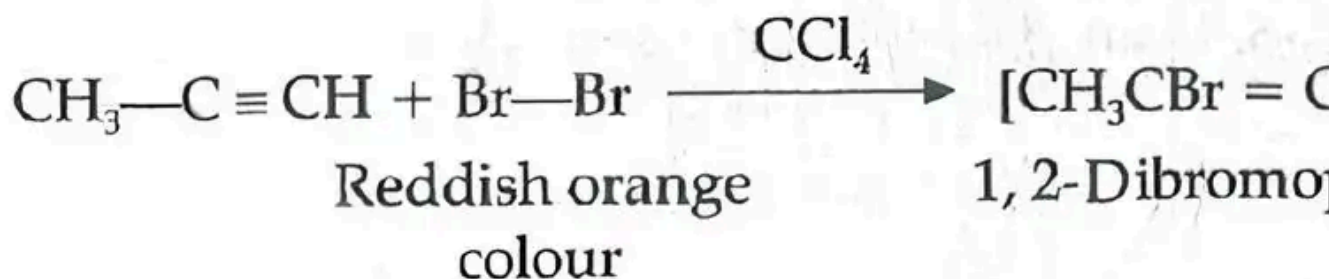


- **Addition Reactions:** Alkynes undergo electrophilic addition similar to alkenes, following Markovnikov's rule.

(a) Addition of dihydrogen:

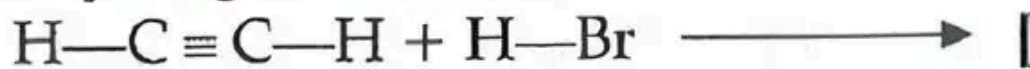


(b) Addition of halogens:

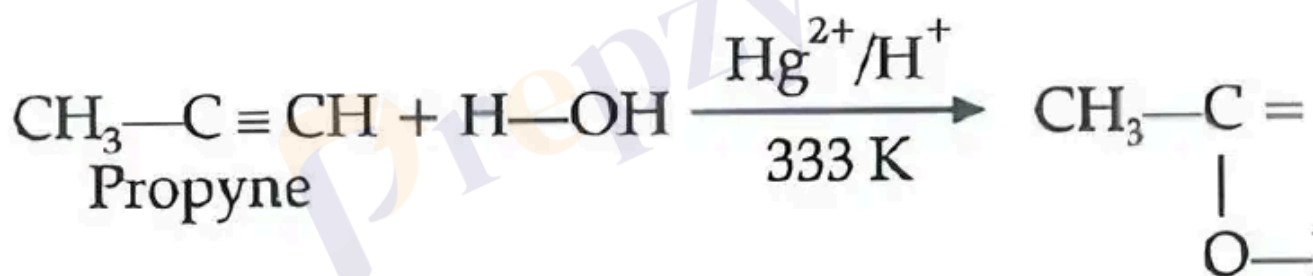
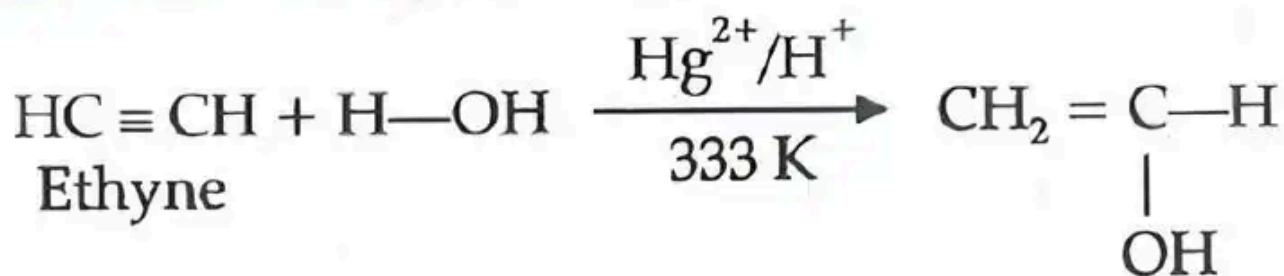


- **Test for Unsaturation:** Addition of bromine decolourises bromine solution.

(c) **Addition of hydrogen halides:**



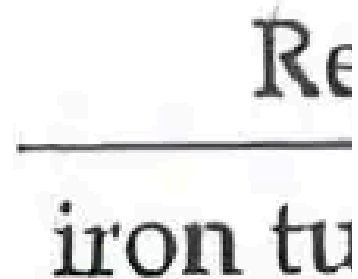
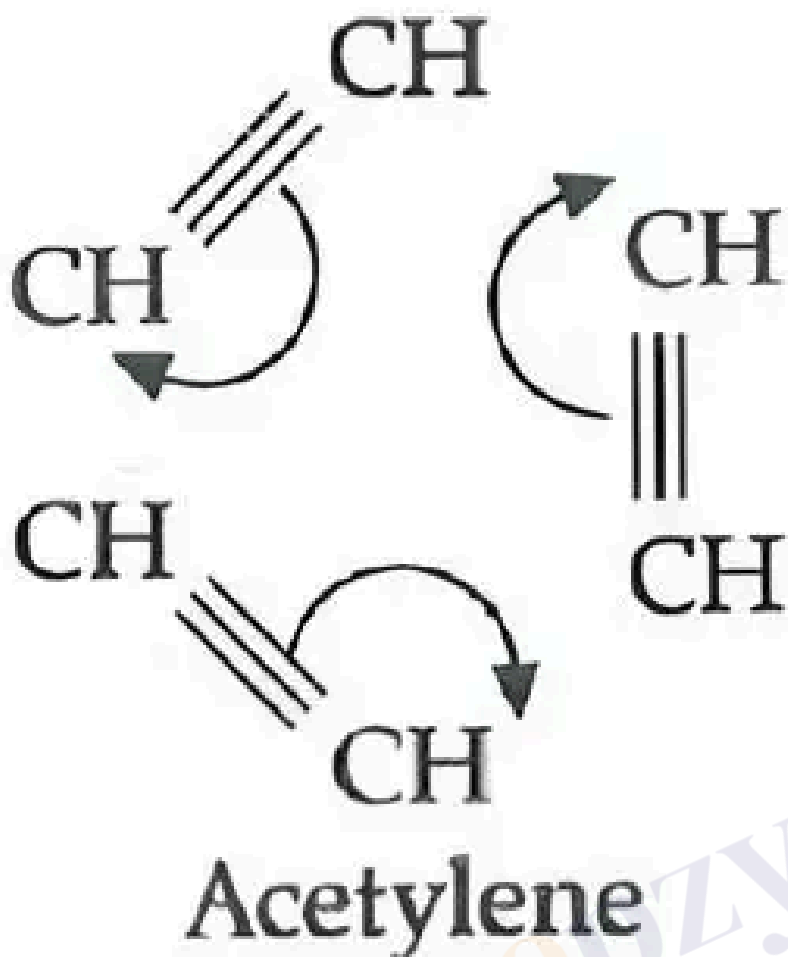
(d) **Addition of water:**



- **Addition of Hydrogen Halides and Water:** Alkynes add HBr and water to form haloalkenes and aldehydes/ketones respectively.

Polymerisation

Ethylene undergoes linear polymerisation to form polyacetylene and cyclic polymerisation to form benzene under high temperature.



Solved Examples

Practice Set

- **Level 1:** Define alkenes and give an example.
-
- **Level 2:** Explain the peroxide effect in the addition of HBr to alkenes.
-
- **Level 3:** Write the mechanism for the addition of HBr to propene according to Markovnikov's rule.

Answer Key

Level 1: Alkenes are unsaturated hydrocarbons containing at least one carbon-carbon double bond. Example: Ethene (C₂H₄).

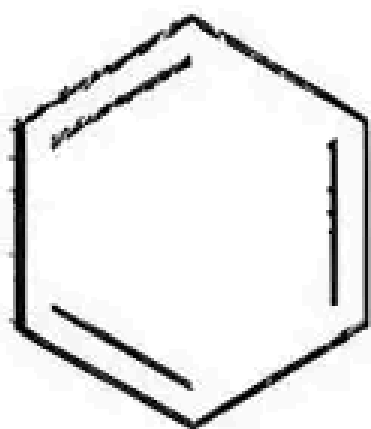
Level 2: In the presence of peroxides, HBr adds to alkenes via a free radical mechanism, resulting in anti-Markovnikov addition where bromin

Level 3: The addition of HBr to propene involves formation of a secondary carbocation intermediate followed by nucleophilic attack by Br⁻, le

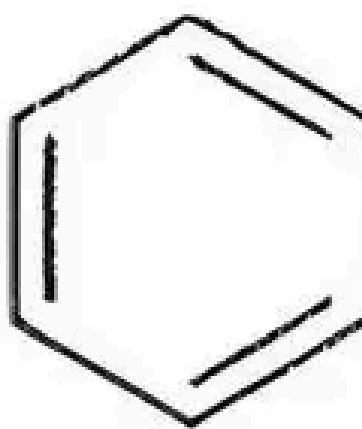
Aromatic Hydrocarbons

Benzene

Aromatic hydrocarbons, also called arenes, contain benzene rings. Benzene is a planar molecule with six sp^2 hybridized carbon atoms forming a ring of delocalized π electrons.



(A)



(B)

Isomerism in Benzene Derivatives

Disubstituted benzene compounds exhibit ortho (1,2-), meta (1,3-), and para (1,4-) isomerism depending on the positions of substituents.

Preparation of Benzene

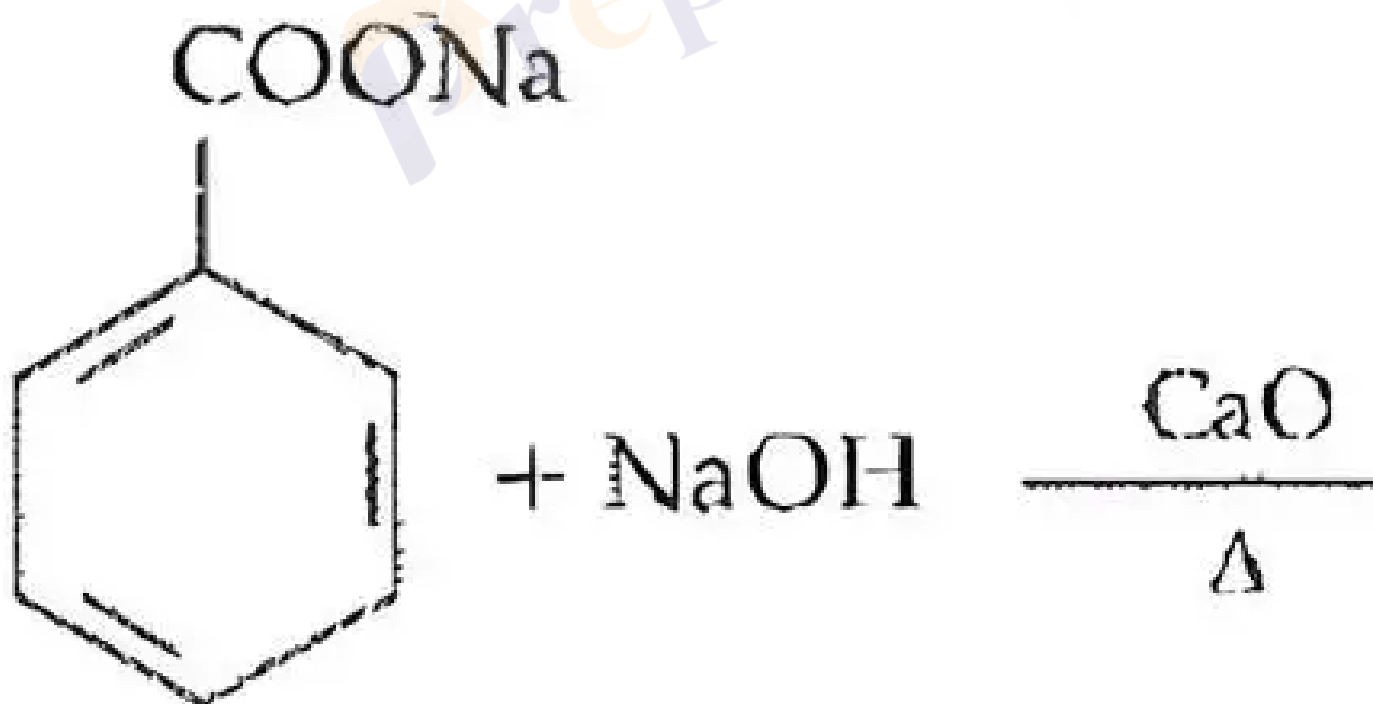
- **Cyclic Polymerisation of Ethyne:** Heating acetylene at 873 K in a red-hot iron tube forms benzene.



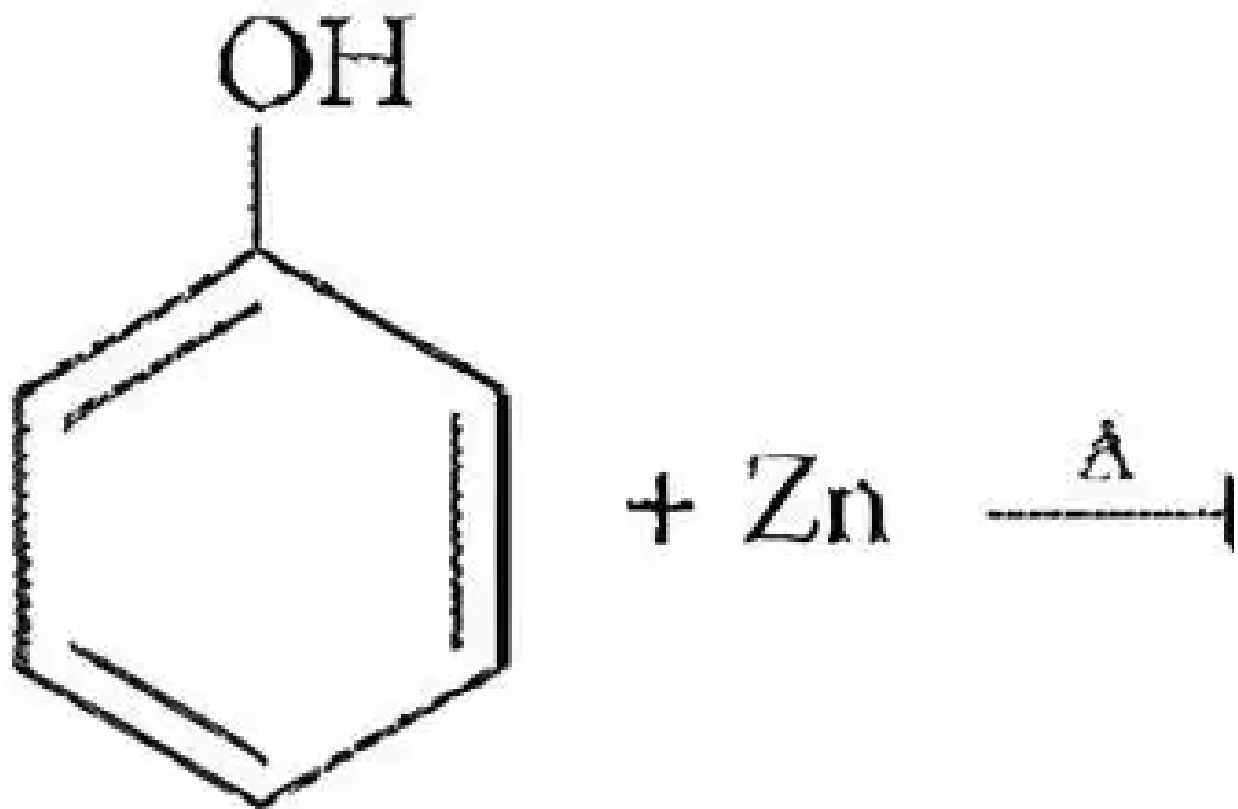
Red hot iron

873 K

- Decarboxylation of Aromatic Acids: Sodium salts of benzoic acid heated with soda lime yield benzene.



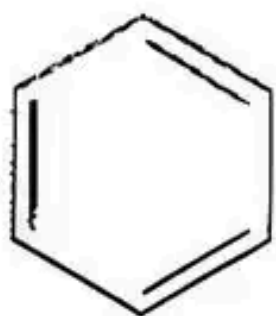
- Reduction of Phenol: Phenol vapours passed over heated zinc dust produce benzene.



Physical Properties

Aromatic hydrocarbons are non-polar, colourless liquids or solids with characteristic aromas. Benzene is a good solvent and burns with a so

(i) Nitration:

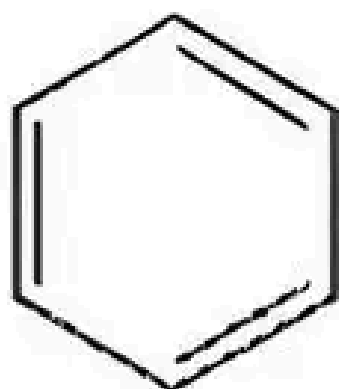


+ Conc. HNO_3 + conc. H_2SO_4
(nitrating mixture)

Chemical Properties

- **Nitration:** Benzene reacts with nitric acid and sulfuric acid mixture to form nitrobenzene.

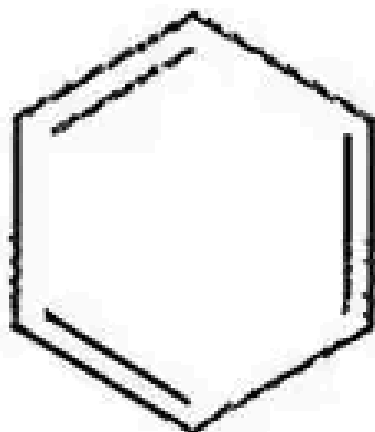
(ii) Halogenation:



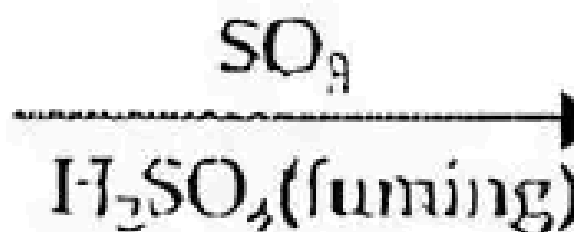
Anhydrous

- Halogenation: Benzene reacts with chlorine in presence of AlCl_3 to form chlorobenzene.

(iii) Sulphonation:



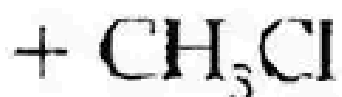
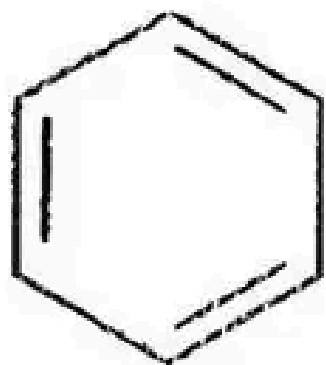
Benzene



A

- **Sulphonation:** Benzene reacts with SO_3 in fuming sulfuric acid to form benzene sulfonic acid.

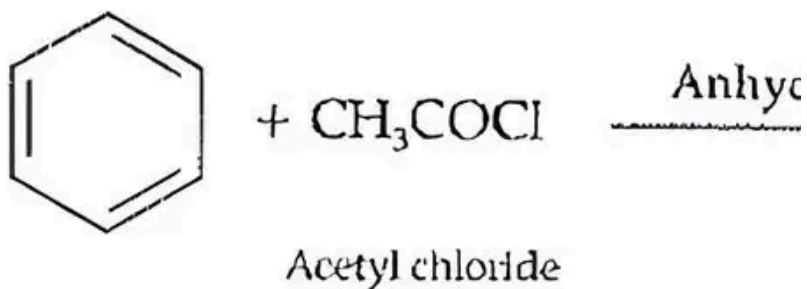
(iv) Friedel-Crafts alkylation reaction



Anhyd.

- **Friedel-Crafts Alkylation and Acylation:** Benzene reacts with alkyl or acyl chlorides in presence of AlCl_3 to form alkylated or acylated ben

(v) Friedel-Craft's acylation reaction:

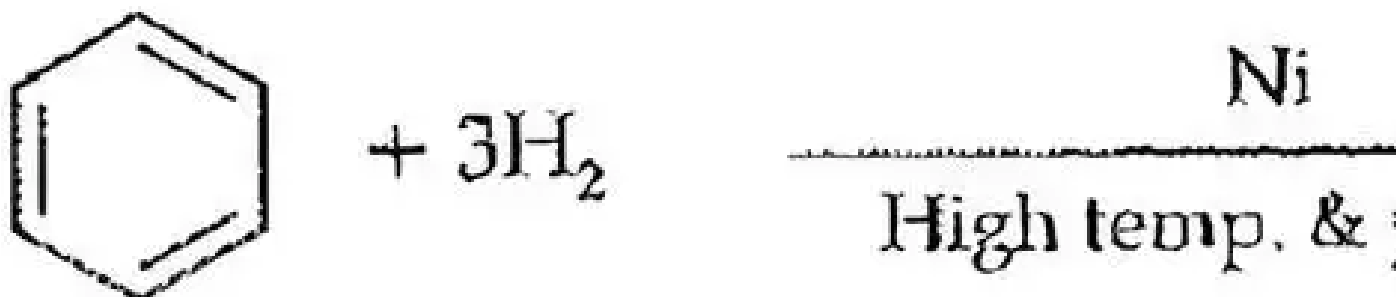


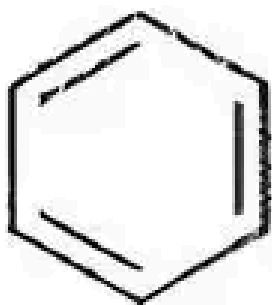
Benzene on treatment with excess of chlorine in the presence of anhydrous AlCl_3 yields hexachlorobenzene (C_6Cl_6)



Addition Reactions

- Hydrogenation of benzene under vigorous conditions produces cyclohexane.
- Under UV light, benzene reacts with chlorine to form benzene hexachloride.



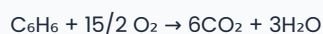


UV

500 K

Combustion

Benzene burns with a sooty flame producing carbon dioxide and water.



Substituent Effects

Electron donating groups activate the ring and direct substitution to ortho and para positions, while electron withdrawing groups deactivate

Mnemonics

PHMTOM: Para have High Melting Point Than Ortho and Meta.

m-directing groups: Quarternary amino, Ester, Sulphonic acid, Nitro, Carbonyl, Carboxyl, Cyano.

o, p-directing groups: Alkyl, Halogen, Alkoxy, Amino, Hydroxyl, Amide, Phenyl.

Key Terms

- **Aromaticity:** Stabilization of conjugated cyclic molecules due to delocalized π electrons in a planar ring.

Key Facts

- Originally, aromatic compounds were named for their fragrant properties.
- Benzene is mainly produced from petroleum.
- Heteroaromatics contain atoms other than carbon in the ring.
- Non-aromatic compounds do not follow Huckel's rule.

Solved Examples

Practice Set

- **Level 1:** Describe the structure of benzene.
-
- **Level 2:** Explain the nitration of benzene.
-
- **Level 3:** Discuss the effect of substituents on electrophilic substitution in benzene.

Answer Key

Level 1: Benzene is a planar hexagonal ring with six sp^2 hybridized carbon atoms and delocalized π electrons forming resonance structures.

Level 2: Benzene reacts with a mixture of concentrated nitric and sulfuric acids at 323–333 K to form nitrobenzene via electrophilic substitution.

Level 3: Electron donating groups activate the ring and direct substitution to ortho and para positions; electron withdrawing groups deactivate the ring and direct substitution to meta positions.

Quick Reference Table

Common Mistakes and Misconceptions

Glossary
