

Chapter 12

Hydrocarbons and Environmental Chemistry

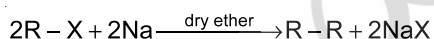
HYDROCARBONS

ALKANES

Methods of Preparation :

I. Reactions where number of carbon atoms are increased

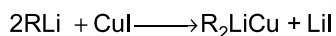
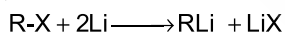
1. Wurtz Reaction



Here other metals in the finely divided state may also be used such as Cu, Ag etc.

- (i) Methane cannot be prepared by this method.
- (ii) Only symmetrical alkane with even number C-atoms can be prepared by this method in good yield.
- (iii) The reaction fails with 3°-alkyl halides.
- (iv) Alkenes are produced as by products.

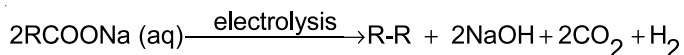
2. Corey-House Synthesis:

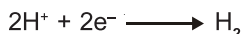


- (i) R_2LiCu also known as Gilman reagent.
- (ii) This reaction proceeds via S_N2 mechanism.
- (a) $R_2LiCu + 2R-X \longrightarrow 2R-R + LiX + CuX$ ($R-X$ may be 1° or 2° only)
- (b) $R_2LiCu + 2R'-X \longrightarrow 2R-R' + LiX + CuX$ ($R'-X$ may be 1° or 2° only)

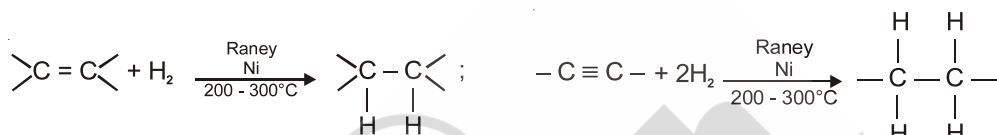
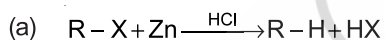
It can be used for preparing both symmetrical and unsymmetrical alkanes.

3. Kolbe's Electrolytic Decarboxylation

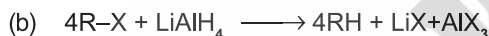


Mechanism:**Anodic Reaction****Cathodic Reaction**

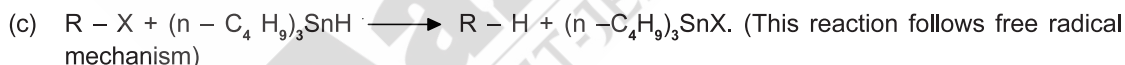
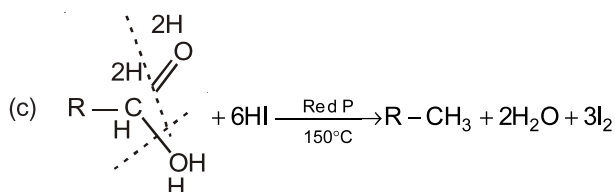
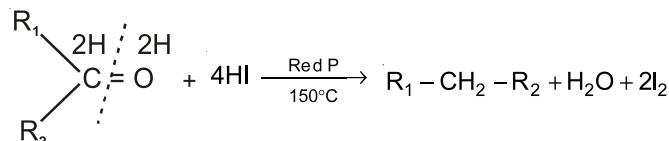
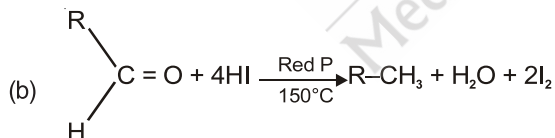
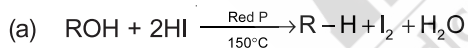
- (i) Methane cannot be prepared by this method
- (ii) Unsymmetrical hydrocarbon (alkane) cannot be prepared

II. Reactions where number of carbon atoms are retained**1. Sabatier-Senderen's Reduction****2. Reduction of Alkyl Halides**

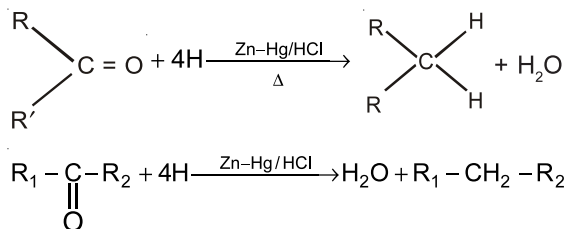
Zn - Cu and $\text{C}_2\text{H}_5\text{OH}$ or Na and alcohol can also be used



This is a nucleophilic substitution reaction with the nucleophile H^- coming from LiAlH_4 .

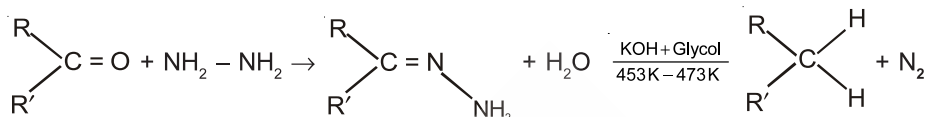
**3. Reduction of Alcohols, Aldehydes, Ketones and Carboxylic Acids with HI/Red P.**

(d) Clemmensen's Reduction



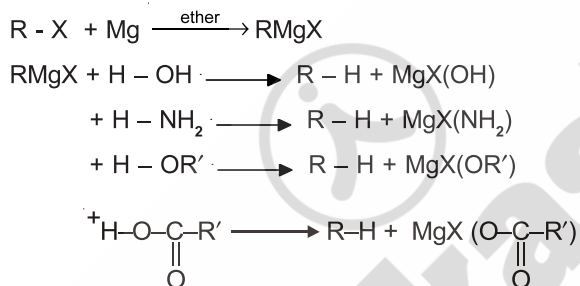
When acid sensitive group is present in a compound, Clemmensen's reduction is not used.

(e) Wolff-Kishner's Reduction:



When base sensitive groups are present in the compound, Wolff-Kishner's reduction is not used.

4. (a) Using Grignard's Reagent

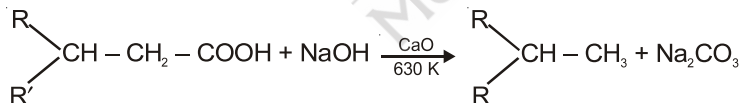
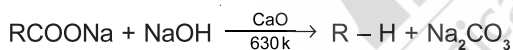


(b) Using Alkyl lithium compound



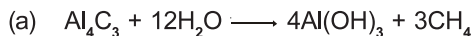
III. Reaction where number of carbon atoms are decreased

Decarboxylation by sodalime

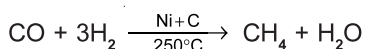


IV. Some other methods of preparation

(1) Methane from carbides



(2) Methane from carbon monoxide



This is also called **Sabatier Senderen's** reduction

Physical Properties

Boiling Point (B.P.)

B.P. increases with the increase of molecular mass. Among the isomers, straight chain alkanes have higher b.p. than branched chain alkanes.

Melting Point (M.P.)

The melting points do not show regular variation with increase in molecular size. The even number members have higher m.p. as compared to next alkanes with odd number of carbon atoms (ALTERATION EFFECT).

Solubility

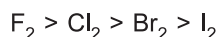
They are soluble in non-polar solvents. Hence, insoluble in polar solvents such as water.

Chemical Properties

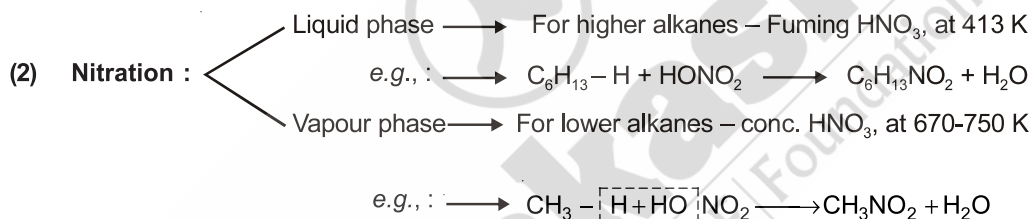
Alkanes are generally inert towards acids, bases, oxidising and reducing agents but they give following reactions:

- (1) **Halogenation.** Alkanes undergoes substitution reaction with halogen. Cl_2 and Br_2 only in presence of ultra violet light or high temperature (573 – 773K).

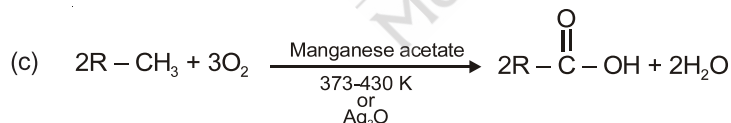
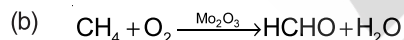
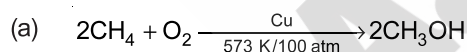
Decreasing order of reactivity of halogens towards alkanes.



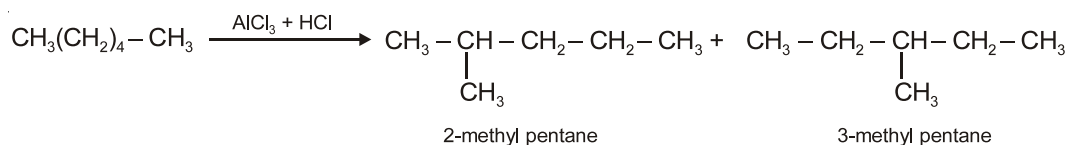
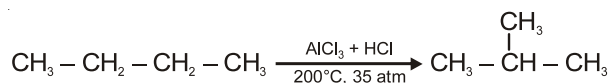
Fluorination and chlorination are less selective as these reagents are more reactive, while bromination of alkane is more selective (less reactive).

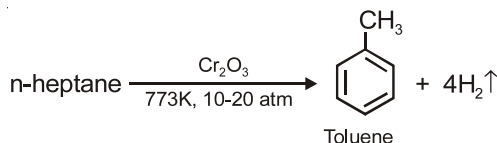
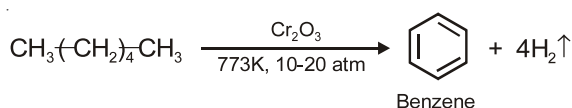
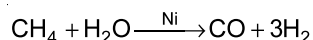


- (3) **Oxidation :**

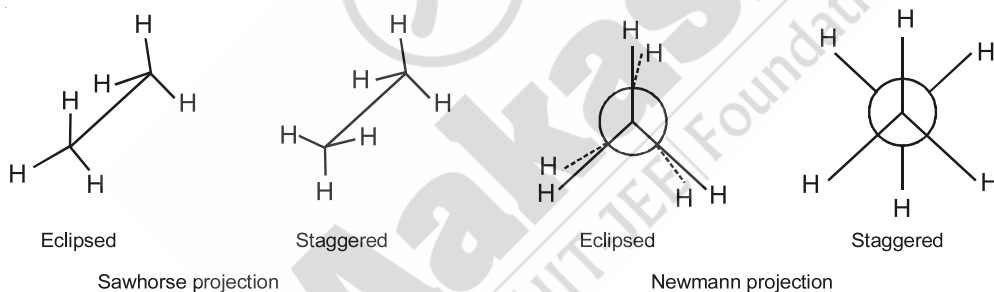


- (4) **Isomerization :**

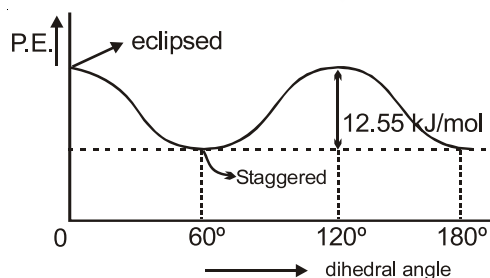


(5) Aromatization :**(6) Reaction with steam :****Conformations of Alkanes**

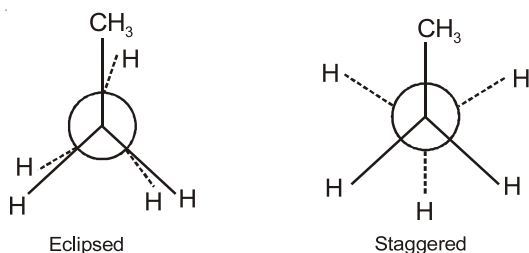
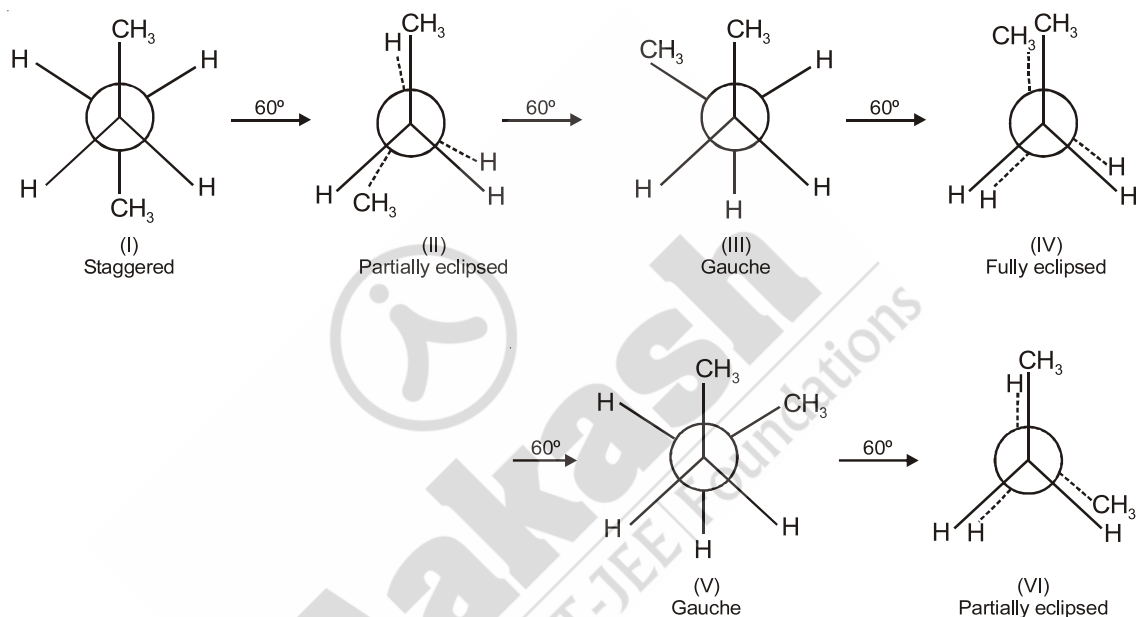
When different three dimensional arrangements are possible for a compound due to rotation along a single bond, then these different arrangements are known as conformers and the phenomenon is known as conformation. In fact C–C rotation is hindered by an energy barrier of **1 to 20 kJ mol⁻¹**. There are infinite number of conformers possible. Out of infinite number of conformers, extremes can be discussed as

Conformers of ethane :

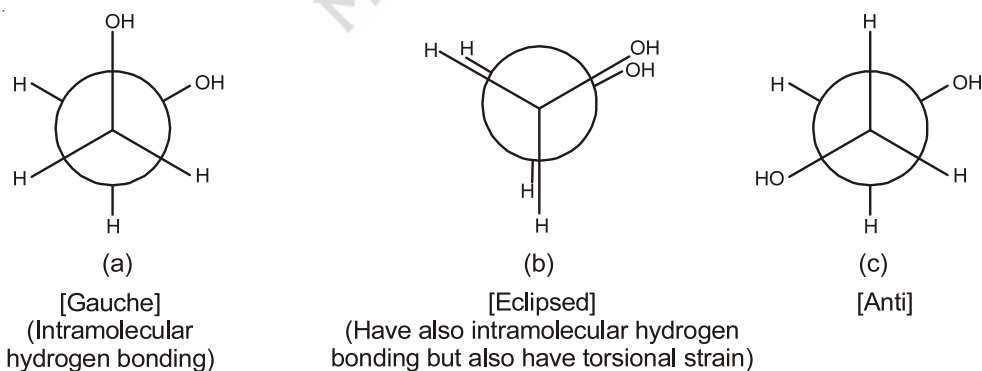
- (i) It may be noted that one extreme conformation of ethane can be converted into other extreme conformer by rotation of 60° about C–C bond.
- (ii) Skew conformers have energy in between staggered and eclipsed.



Staggered > Skew or Gauche > Eclipsed
 ↓
 Decreasing order of stability

Conformers of propane :**Conformers of Butane :**

Stability order : I > III $\approx$ V > II $\approx$ VI > IV

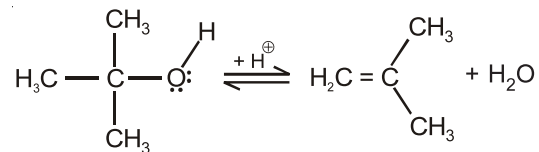
Conformers of Ethylene glycol ($\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH}$):

Stability order : Gauche > Anti > Eclipsed

ALKENES

Preparations of Alkenes

From Alcohols: When alcohol is treated with conc. acids (H_2SO_4 , H_3PO_4) at higher temperature alkene is obtained.



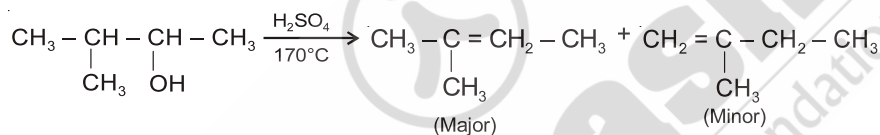
Acid catalyzed dehydration of alcohol is a reversible reaction. Alcohols can be converted to alkene in the presence of conc. H^+ , while alkenes can be converted to alcohol in the presence of dilute H^+ .

The ease of dehydration of alcohols depends on the stability of carbocations formed. Hence, the order of reactivity of alcohols is *ter*-> *sec*-> *pri*- because the incipient carbocation stability is *ter*-> *sec*-> *pri*-

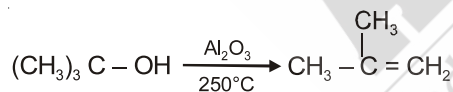
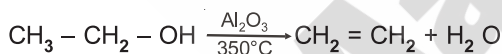
Note : Since the carbocation stability is the primary criteria, so, the initially formed carbocation undergoes molecular rearrangement to give more stable carbocation.

Hydride shift

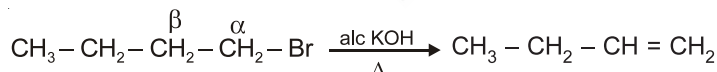
Example (Hydride shift)



- (i) Dehydration of alcohols follow Saytzeff's rule.
Product (A) is the major product because it is more substituted alkene.
- (ii) Dehydration by passing over alumina (Lewis Acid)



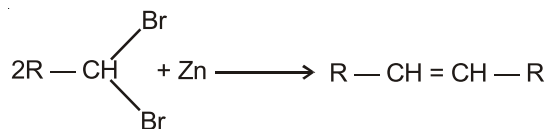
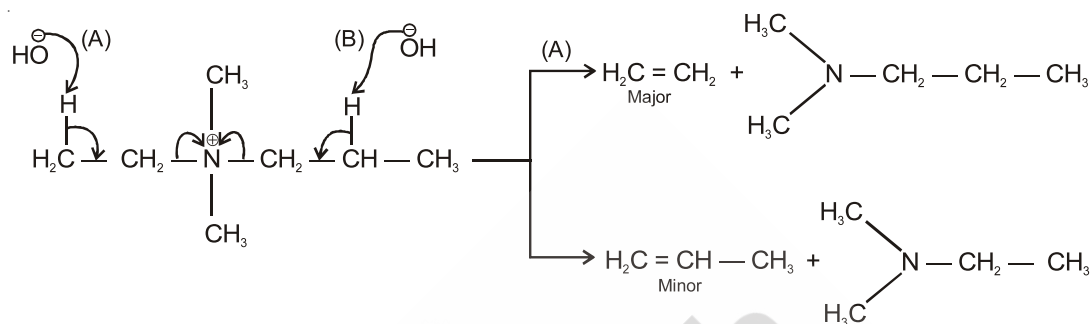
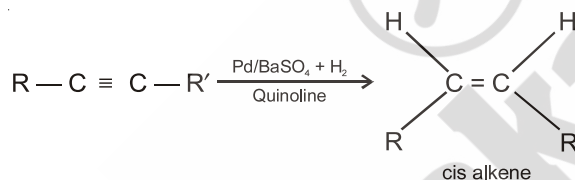
I. Dehydrohalogenation of alkyl halides



- (i) The base used may be strongly basic anions like OH^- , RO^- , $\text{C}_2\text{H}_5\text{O}^-$ (CH_3)₃ CO^- etc.)
- (ii) Alkyl substrates with good leaving group (X^- , etc) give good yield of elimination product.
- (iii) One may also use sulphonates.

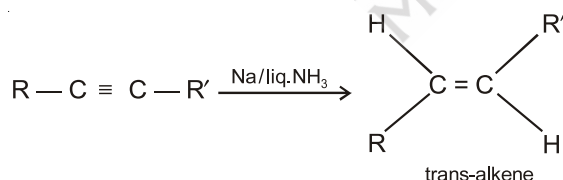
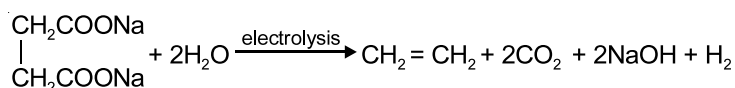
II. Dehalogenation reactions of vicinal dihalide :



III. Dehalogenation of Geminal dihalide :**IV. By heating Quaternary ammonium hydroxide again Hofmann elimination occurs and less substituted alkene is formed as the major product :****V. By catalytic hydrogenation of alkyne :**

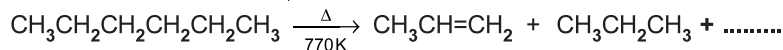
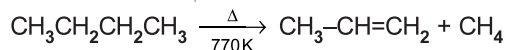
Lindlar's catalyst = Pd supported on BaSO_4 or CaCO_3 and poisoned with quinoline.

P-2-Catalyst = Nickel boride (Ni_2B) is known as P-2 catalyst.

VI. Under the presence of alkali metals in liquid ammonia, substituted alkynes are converted into trans-alkene. It is important to remember that terminal alkynes do not give this reaction.**VII. Kolbe's Electrolysis**

Sodium succinate

Mechanism follows free radical pathway.

VIII. Pyrolysis**Physical Properties****Solubility**

They are insoluble in water but soluble in organic solvents.

Boiling point

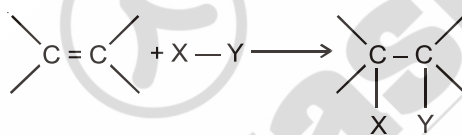
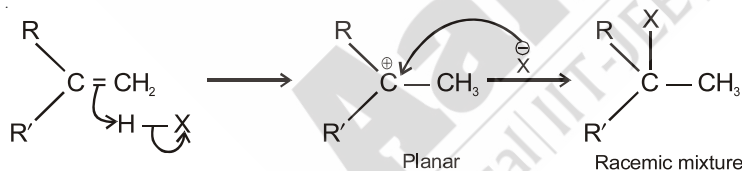
The boiling point of cis-alkenes is usually higher than corresponding trans-alkenes (More polarity).

Melting point

The melting point of trans-alkenes is usually greater than cis-alkene. (trans form is more symmetrical).

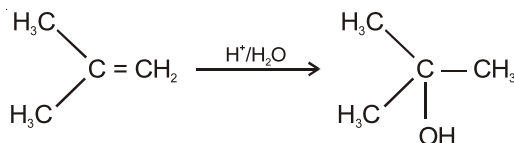
Chemical Properties

Electrophilic addition reaction is the most important reaction of alkenes and alkynes. Beside electrophilic addition reaction, it also gives Free radical addition, hydrogenation and oxidation reactions.

**1. Addition of Hydrogen halide (HX)**

As the reaction proceeds through carbocationic intermediate it results into racemization.

HI (strong acid) is most reactive while HF is least reactive.

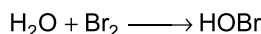
2. Acid catalysed hydration of alkenes :

This reaction also involves carbocation reactive intermediate.

3. Halogenation of alkenes :

This reaction proceeds through cyclic halonium ion complex and hence it is a stereoselective reaction.

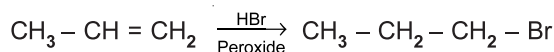
Note : *Trans-symmetrical alkenes give meso-dibromo product*

4. Addition of Hypohalous Acid (HOX) :

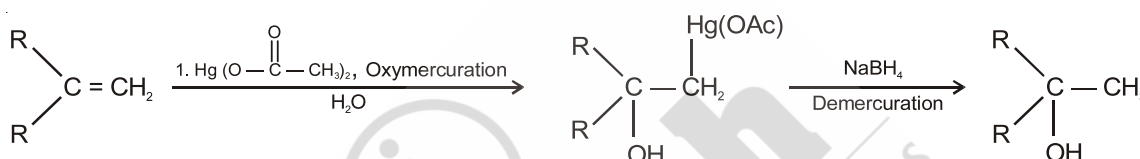
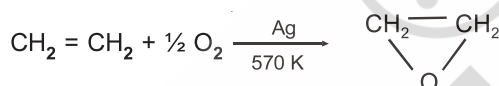
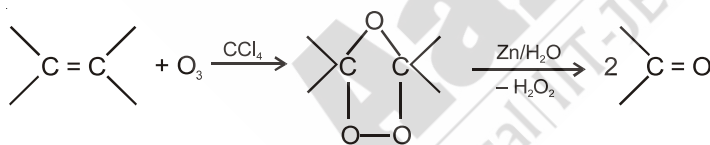
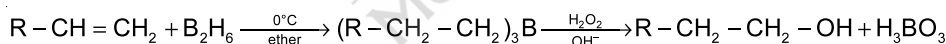
In this reaction, X_2 or $\text{X}^\oplus$ acts as an electrophile and H_2O acts as nucleophile

Kharasch - Mayo Effect (Anti-Markownikoff's rule)

If the above reaction is carried out in the presence of some peroxide then addition takes place contrary to Markownikoff's Rule.



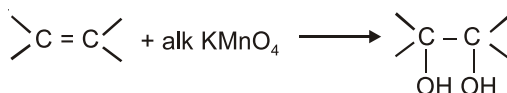
Note : Only HBr adds to unsymmetrical double bond according to anti-Markownikoff's rule. Other HX (HF, HCl and HI) do not give peroxide effect.

5. Oxy-Mercuration-Demercuration**6. Addition of Oxygen:****7. Ozonolysis:****8. Hydroboration Oxidation**

Hydroboration oxidation reaction gives overall anti-Markownikoff's product. There is no rearrangement in this reaction.

9. Oxidation Reactions

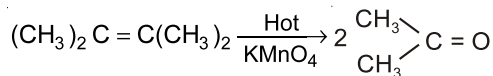
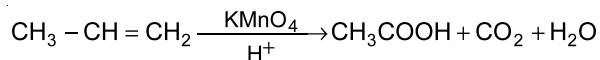
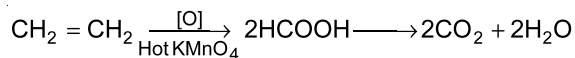
(a) Reaction with Baeyer's Reagent (Cold dilute Alkaline KMnO_4 , syn-dihydroxylation.)



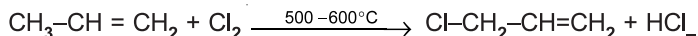
The addition is a syn addition to form vicinal dihydroxy compounds.

Note : Decolorization of Baeyer's reagent is also used as a test for unsaturation.

(b) With hot KMnO_4 or acidic KMnO_4

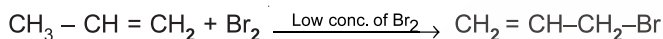


10. Substitution Reaction



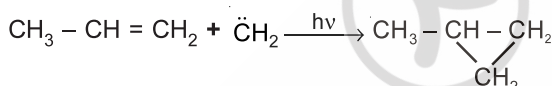
This type of reaction takes place at a carbon atom attached to double bond carbon. This is called allylic substitution.

11. Wohl Ziegler Reaction

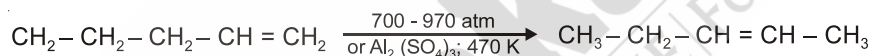


The low concentration of Br_2 is obtained from NBS

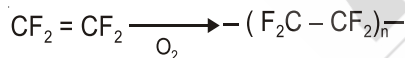
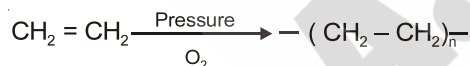
12. Addition of Carbenes



13. Isomerization :



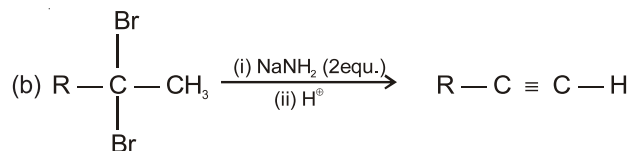
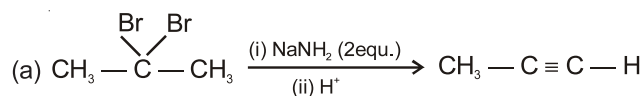
14. Polymerization :

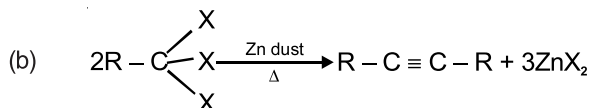
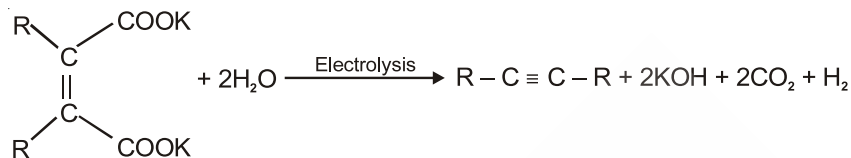


ALKYNES

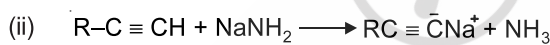
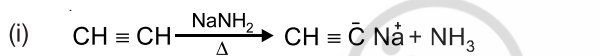
Preparation of Alkynes

1. From Dehydrohalogenation of vicinal or geminal dihalides



2. Dehalogenation Reaction**3. Kolbe's Electrolytic Decarboxylation**

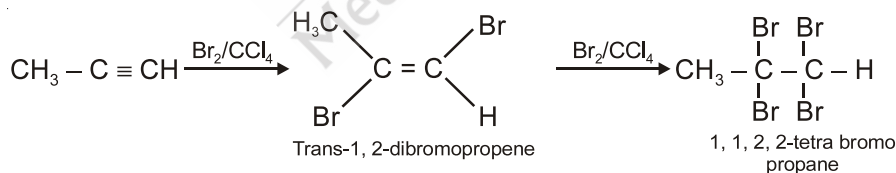
cis or trans

4. Formation of Higher alkyne**Chemical Properties**

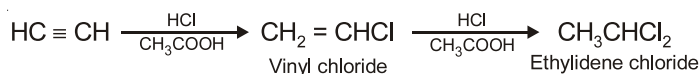
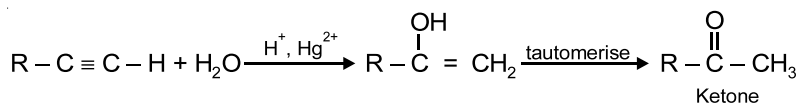
Alkynes undergo electrophilic addition generally but in the presence of salt of heavy metals which forms complexes with multiple bonds they undergo nucleophilic addition reaction.

1. Addition Reaction**Electrophilic addition reaction :**

(i) Addition of halogen

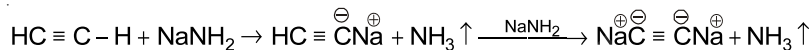
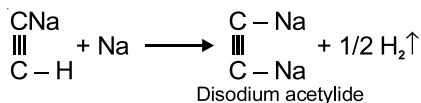
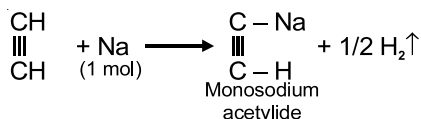


(ii) Addition of halogen acids

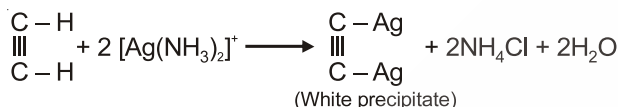
(iii) Addition of H_2O or hydration of alkyne or Kucherov reaction

2. Reaction of Acidic H Atom

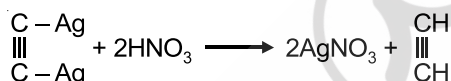
- (i) Alkynes having acidic H atom react with metals like Na, K to evolve H_2 gas.



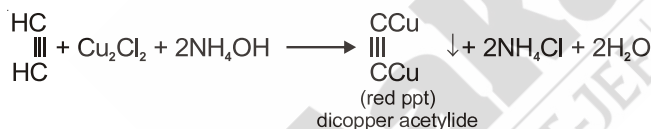
- (ii) **Reaction with Tollens reagent :** When terminal alkyne reacts with Tollen's reagent (Ammoniacal $AgNO_3$ solution) white precipitate of silver acetylide is obtained,



These acetylides are not decomposed by H_2O like acetylide of Na but by mineral acids like dil HNO_3 .



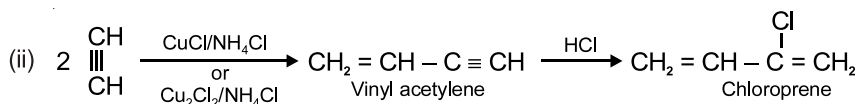
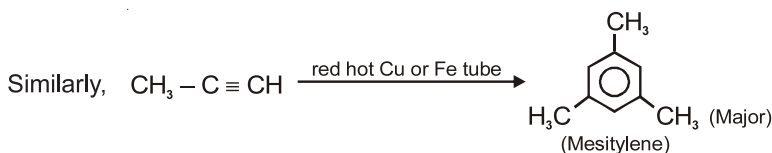
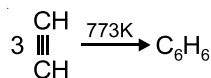
- (iii) **Reaction with Ammonical Cuprous Chloride :**



These reactions are used to distinguish terminal alkynes from other alkynes.

3. Polymerization Reaction

- (i) When acetylene is passed through red hot Cu tube, benzene is obtained.



Chloroprene on polymerization gives polymer called neoprene; used as artificial rubber.

AROMATIC HYDROCARBONS

Huckel's rule of Aromaticity : Cyclic, conjugated, planar and having $(4n + 2) \pi$ electrons.

where, $n = 0, 1, 2, 3 \dots$ (Any positive integer including zero)

Few Examples of Aromatic Species :



Aromatic ions are more stable than corresponding acyclic non-aromatic ions.

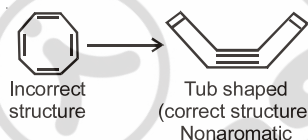
Antiaromatic Compounds :

Antiaromatic compounds are cyclic, conjugated, planar and contain $4n\pi$ electrons (where n is a positive integer) Anti-aromatic compounds are less stable than acyclic counter part.

Examples :

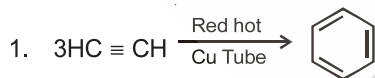


It is important to note that cyclooctatetraene is a nonaromatic compound because it is non-planar.

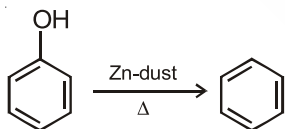


Stability order : Aromatic > Non-aromatic > Anti-aromatic

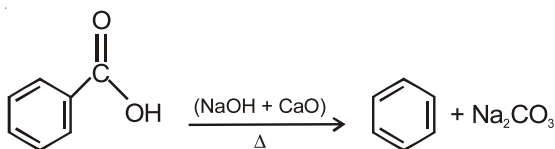
Preparation of Benzene :



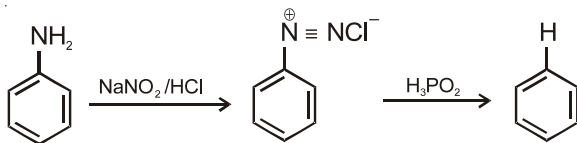
2. When phenol is treated with Zn dust, benzene is obtained :



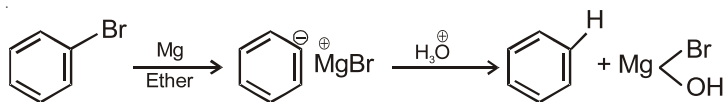
3. From the decarboxylation of benzoic acid :



4. Deamination of aniline through benzene diazonium chloride will give benzene.



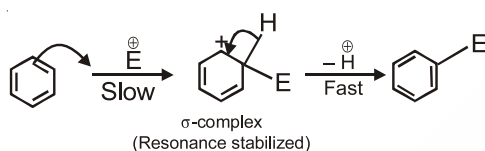
5. Through Grignard reagent.



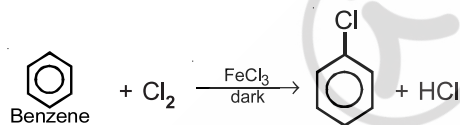
1. Electrophilic Aromatic substitution reactions in Benzene : (EAS)

Benzene and its homologues readily undergo EAS. As a consequence of complete delocalization of π electrons in benzene, it has π electron cloud above and below σ -plane allowing it to interact with electrophiles and give electrophilic substitution reaction. It resists addition because it wants to maintain its aromatic character.

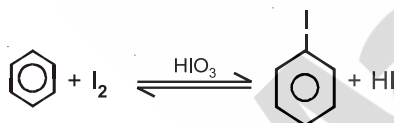
General Mechanism :



(i) Halogenation

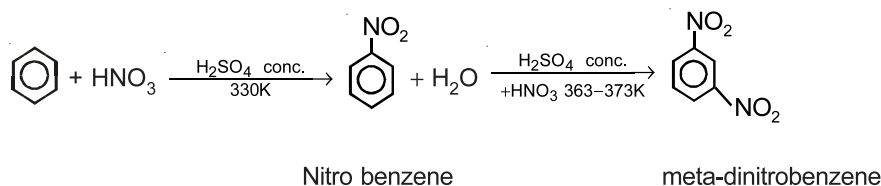


Reaction with I_2 is reversible.

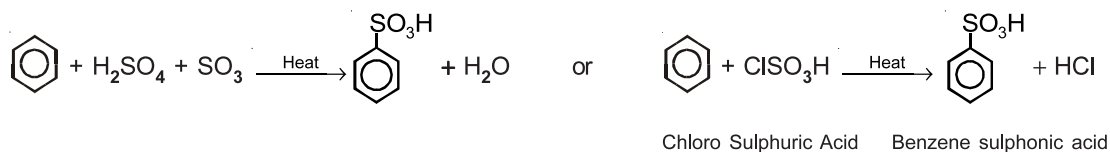


Hence, it is carried out in the presence of conc. nitric acid or HIO_3 to oxidise the Hydrogen Iodide formed.

(ii) Nitration

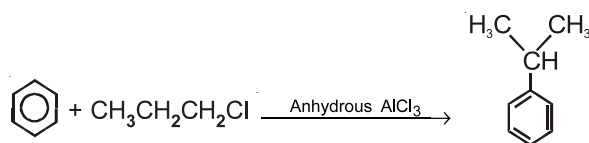
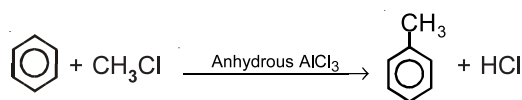


(iii) Sulphonation : Sulphonation of benzene is a reversible reaction

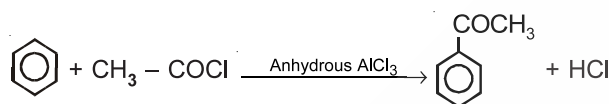


(iv) Friedel Crafts Reaction

Alkylation : Reactive intermediate is carbocation which can undergo rearrangement.



Acylation : Reactive intermediate is acylium ion $\left(\text{R}-\overset{\text{:O:}}{\underset{\text{||}}{\text{C}}}^+ \right)$ which cannot undergo rearrangement.

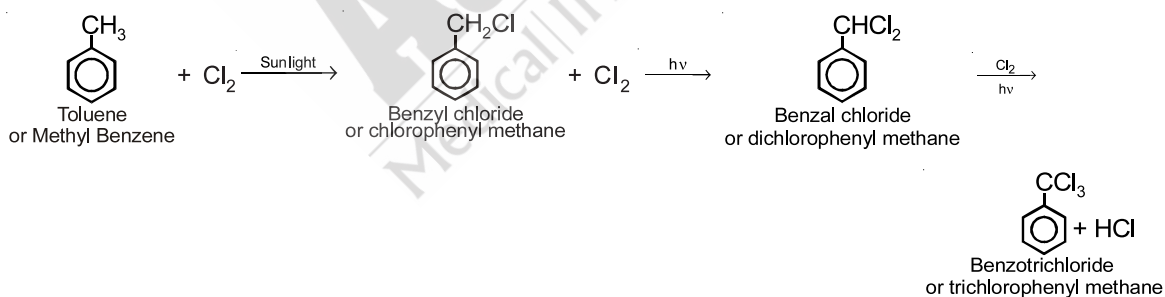
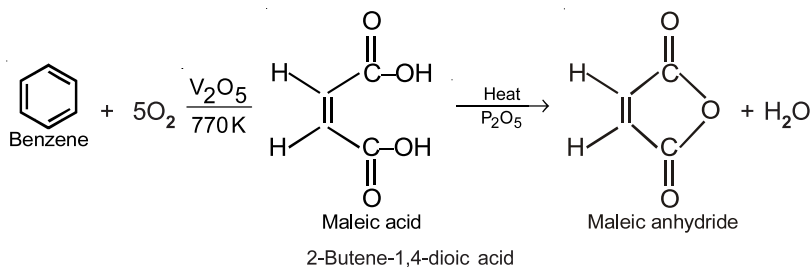


Acetyl chloride

Acetophenone

Ortho and para substitution : Electron releasing groups like - R (alkyl), - $\ddot{\text{O}}\text{H}$, - $\ddot{\text{O}}\text{R}$, - $\ddot{\text{N}}\text{HR}$, - $\ddot{\text{N}}\text{HCOR}$ are activating groups *i.e.*, they increase electron density at ortho and para position, therefore, are ortho and para directing towards electrophilic substitution reactions.

Meta substitution : Electron withdrawing groups such as - NO_2 , - CHO , - COOH , - COCH_3 , - CN , - SO_3H , - COOR are called deactivating groups. They decrease electron density at ortho and para-position, therefore, electrophilic substitution takes place at meta-position.

2. Halogenation of side chain :**3. Oxidation :**

ENVIRONMENTAL CHEMISTRY

ENVIRONMENTAL POLLUTANTS

Any substance which causes pollution in the environment is known as **environmental pollutant**. It can be atmospheric, water and soil pollution.

WATER POLLUTION

The quality of drinking water is very important for human welfare. The pollution of water by sewage has been linked with the spreading of diseases such as cholera and typhoid fever.

In addition, water is also contaminated by industrial wastes, like :

- (i) **Heavy Metals** : Such as Cd, Pb and Hg may be present.
- (ii) **Detergent and Fertilizers** : They may contain PO_4^{3-} as additives which encourages the growth of algae that reduces the dissolved oxygen concentration of water. This process is known as Eutrophication.
- (iii) **Acid Polluted Water (pH < 3)** : This is deadly to most forms of aquatic life.
- (iv) **Polychlorinated Biphenyls (PCBs)** : PCBs are resistant to oxidation and their release into the environment causes skin disorders in humans. They are reported to be carcinogenic.

Determination of quality of waste water : It is done through BOD and COD.

Biological Oxygen demand (BOD) - It is the amount of oxygen required for biological oxidation by microbes in any unit volume of water. This test is done for at least 5 days. BOD values generally approximates the amount of oxidisable organic matter.

Chemical oxygen demand (COD) : BOD measurement takes few days, so another parameter called COD measurement is required. In COD measurement sample of fixed volume is treated with oxidising agent (usually $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium). The reagent oxidises most of the polluting substances including those which are resistant to microbial oxidation.

AIR POLLUTION

Air is very essential for life, particularly oxygen which is needed for breathing. But at the same time air is polluted due to various human activities. Man made, pollutants such as gases like CO , NO , NO_2 , SO_2 , H_2SO_4 , hydrocarbons and aerosols etc are being constantly released in the atmosphere leading to air pollution.

Atmospheric Pollution

Tropospheric pollution : Troposphere extends upto height of 10 km from sea level. It contains 80% of total mass of air and water vapour. Pollution is also caused by SO_2 , SO_3 , NO_2 etc.

Stratospheric pollution : Extends (10–50) km above sea level. It contains N_2 , O_2 and ozone.

Table : Sources of Air Pollution

Sl. No.	Class	Aerosols	Gases and Vapours
1.	Combustion processes	Dust, fumes, smoke	SO_2 , NO_2 , CO , Organic vapours
2.	Chemical processes (cement and fertilizers)	Dust, fume, mist	Process dependent (CO_2 , SO_2 , CO , NH_3 , NO_2 organic vapours)

3.	Petroleum operations	Dust, mist	SO ₂ , H ₂ S, NH ₃ , CO, hydrocarbons mercaptans
4.	Metallurgical processes (Al-refineries, steel plant)	Dust, fumes	SO ₂ , CO, fluorides, organic vapours
5.	Mineral processing	Dust, fumes	Process dependent
6.	Food and feed operation	Dust, mist	Odorous materials
7.	Agricultural activities crop spraying, field burning	Dust, mist, smoke, fly ash	Organic phosphates, chlorinated hydro sulphur oxide, organic vapours
8.	Nuclear energy programme (i) Fuel fabrication (ii) Ore preparation (iii) Bomb explosion	Dust	Fluorides, I-131, Ar-41 radioactive gases (Sr-90, Cs-137, C-14 etc.)

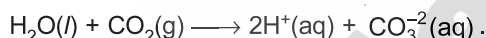
Smog

It is a combination of smoke and fog. This is the best known example of air pollution. Smog is of two types:

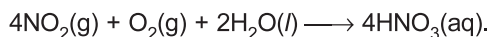
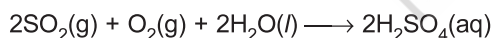
- (1) **Classical smog** : Occurs in cool humid climate and is chemically reducing smog and has high concentration of SO₂.
- (2) **Photochemical smog** : Occurs in warm, dry and sunny climate. It is an oxidising smog. Major component of photochemical smog is NO.

Acid Rain

Rain water normally has pH of 5.6 due to the formation of H⁺ ions from the reaction of rain water with CO₂ present in atmosphere.



When pH of rain water drops below 5.6 it becomes acidic. Acid rain caused by the presence of oxides of sulphur and nitrogen in the atmosphere. Oxides of sulphur are released into the environment largely because of fossil fuel combustion, ore smelting etc. Nitrogen oxides emitted into the atmosphere mainly from automobile exhausts and fossil fuel combustion. SO₂ and NO₂ after oxidation and reaction with water are major contributors to acid rain.



Acid rain is toxic to vegetation and aquatic life. It damages building and statues and dissolves heavy metals from soils, rocks etc. The heavy metals such as Cu, Pb, Hg, Al etc leached from soil enters well water and produce a variety of toxic effects.

SOIL POLLUTION

It is caused by pesticides and other chemicals which are added to the soil to grow better crops. Solid wastes are another cause of land pollution.

Pesticides are used to kill unwanted organisms. Synthetic pesticides are of great concern for us. Pesticides affect human being through eating, drinking and so on.

Insecticides : Control of insects by insecticides help to curb disease for example (malaria and yellow fever) and protects crops. e.g., organochlorine like DDT.

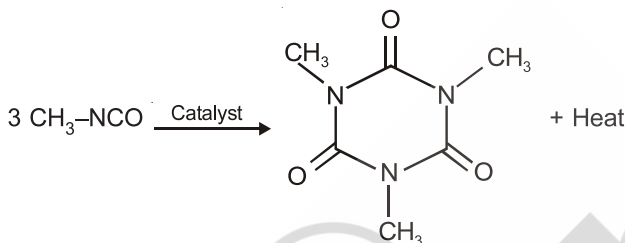
Bhopal gas tragedy occurred on 2nd Dec. 1984 in Bhopal (Union Carbide Ltd.).

Methyl iso-cyanate (MIC) was used to manufacture the insecticide called Carbyl or Sevin (commercial name). There were three tanks in the plant that stored MIC. Due to increase of pressure in one of the tanks valve was released, hence MIC escaped into atmosphere. This MIC was

(a) Hydrolysed due to presence of water in surrounding ponds.



(b) Impurities of metals present in water caused polymerisation reaction



Both reactions are exothermic in nature. So escaping tendency of MIC increased and caused immense loss of life and injury to people and livestock.

