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Hydrocarbons

HYDROCARBONS

Organic compounds composed of only carbon and hydrogen

Saturated Hydrocarbon (Alkanes)

Represented by C_nH_{2n+2} ($n =$ no of C-atoms)

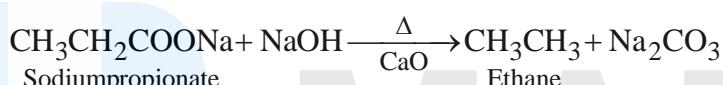
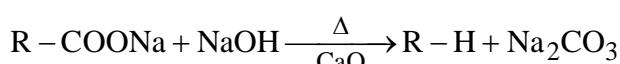
Called paraffins (parum ≡ little; affinis ≡ affinity)

Bond angle is 109.5° or $109^\circ 28'$

General methods of Preparation of Alkanes

1 Decarboxylation of carboxylic acids (Laboratory preparation)

An alkane is prepared by heating strongly the anhydrous sodium or potassium salt of a carboxylic acid with sodalime ($\text{NaOH} + \text{CaO}$)

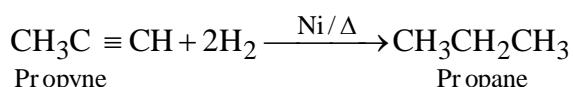
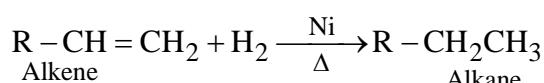


Note :

- (i) The alkane prepared contains one carbon atom less than that of the original acid.
 - (ii) CaO increases the porosity of the mixture and acts as a dehydrating agent and catalyst.

2. Sabatier-Senderen's Reaction

Alkane may be obtained by the catalytic hydrogenation of alkenes or alkynes in presence Ni catalyst at 200°C – 300°C



Note :

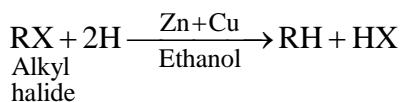
- (i) Platinum or Palladium or Raney nickel may also be used as catalyst at ordinary temperature.
 - (ii) Methane cannot be prepared by this method.

3. By the Reduction of Alkyl Halides :

Alkyl halides are directly reduced by either of the following reducing agent to form alkanes.

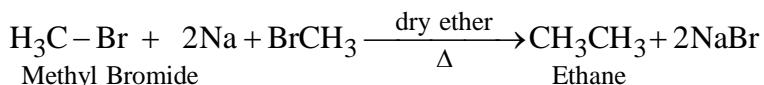
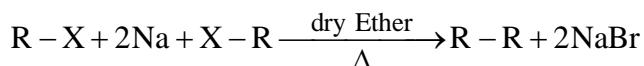
- (a) Zn/Cu + (C₂H₅OH)
 - (b) Zn + HCl
 - (c) Zn + Acetic acid (CH₃COOH)
 - (d) LiAlH₄

- (e) Red phosphorous and hydrogen iodide
 - (f) H₂ + nickel or palladium or platinum



4. Wurtz Reaction :

An etherial solution of alkyl halide when treated with sodium metal forms alkane.

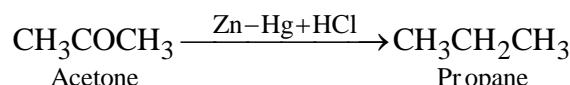
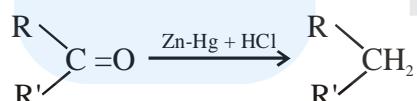


Note :

- (i) Wurtz Reaction is useful only for the preparation of symmetrical alkanes containing even number of carbon atoms.
 - (ii) When a mixture of two different alkyl halides are used a mixture of three alkanes are obtained.
 - (iii) Methane cannot be prepared.
 - (iv) This reaction fails with tertiary alkyl halides.

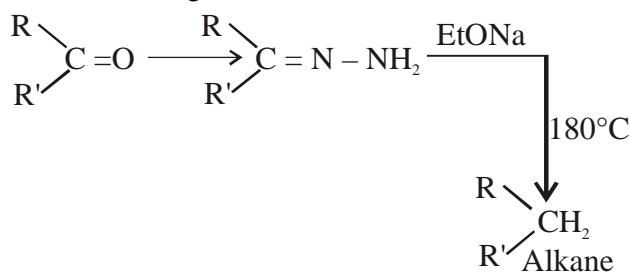
5. Clemmensen's Reduction :

Carbonyl compounds like aldehydes and ketones are reduced by amalgamated zinc and conc. HCl to produce the corresponding alkanes having the same number of carbon atoms.



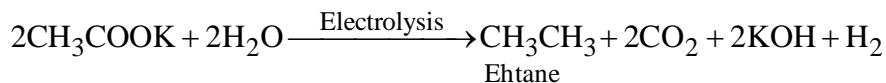
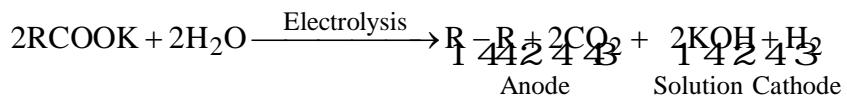
6. Wolf-Kishner Reduction :

Carbonyl compounds can be reduced to hydrocarbons in presence of excess of hydrazine or semicarbazide and sodium alkoxide on heating.



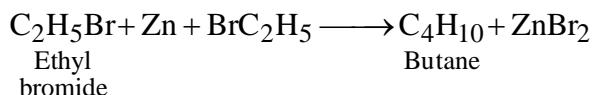
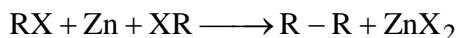
7. Kolbe Reaction (Electrolytic Method) :

An alkane is prepared by the electrolysis of a concentrated aqueous solution of sodium or potassium salt of a saturated monocarboxylic acid using platinum electrodes.

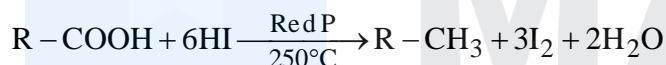
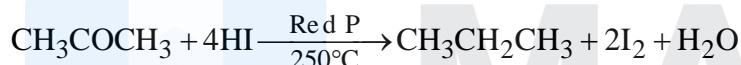
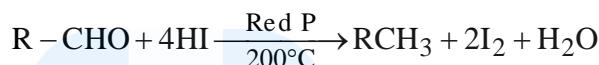
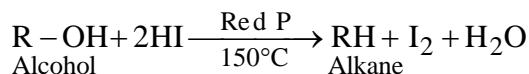


8. Frank Land Method :

The alkyl halide is heated with zinc in inert solvent.

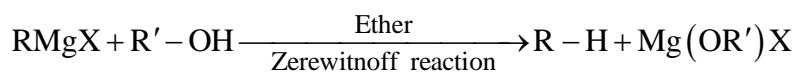
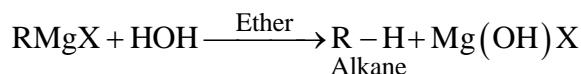


9. By the reduction of alcohols, aldehydes, Ketones and Carboxylic acids, by red phosphorus and HI



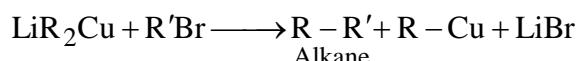
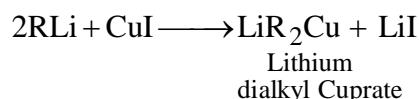
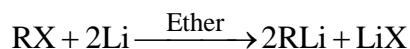
10. By the Decomposition of Grignard Reagents :

A Grignard reagent can be decomposed by active hydrogencontaining compound to produce alkane.



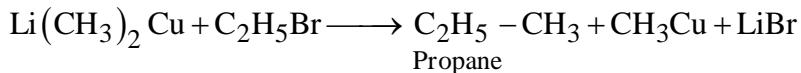
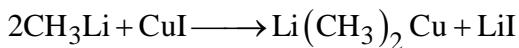
11. Corey-House Alkane Synthesis :

Symmetrical as well as unsymmetricalalkanes can be prepared by the action of alkyl halides with an etherial solution oflithium dialkyl cuprate (LiR_2Cu)



Note : R' should be mainly 1°.

Examples :



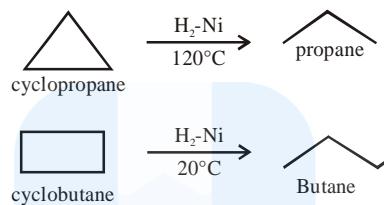
12. Hydroboration of Alkenes :

Diborane (B_2H_6) reacts with alkenes to form trialkyl-boranes which on treatment with acetic acid or propionic acid yields corresponding alkane.

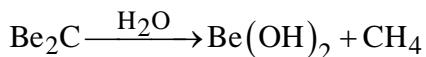


13. By Cycloalkane :

Cycloalkanes can be reduced to alkanes by cleavage of C — C bond which minimises the strain.



14. Hydrolysis of Metal Carbides :



N.B. :

This method is applied only for methane.

PROPERTIES

A. Physical Properties

First four members are gases, next 13 members are colourless liquids and rest are solids.

The alkanes are insoluble in water but soluble in organic solvents like ether, carbon tetrachloride, benzene etc.

The density and boiling points increase with the increase of molecular weights. The boiling points of isomeric branched chain alkanes, are generally lower than those of straight chain alkanes.

B. Chemical Properties

Alkanes are generally stable and chemically inert.

The C — H and C — C bonds in alkanes are almost non-polar, attacking reagents find no reaction sites to

which they could be attacked.

Under suitable conditions the alkanes undergo two types of reactions

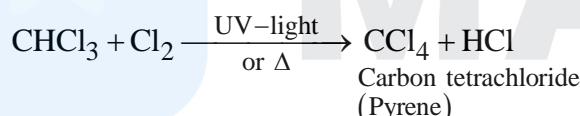
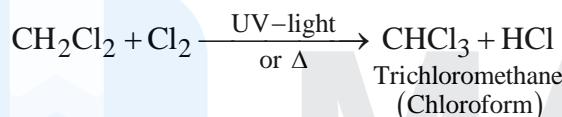
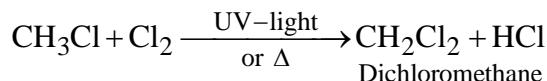
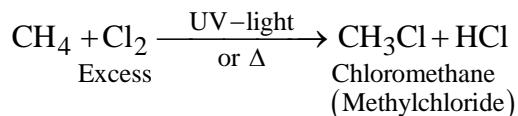
- (a) Free radical substitution Reaction
- (b) Thermal; and Catalytic Reaction

(a) Substitution reaction

1. Halogenation :

In presence of diffused sunlight or in ultra violet light or at relatively high temperature ($300^{\circ}\text{C} - 500^{\circ}\text{C}$) the H-atoms ($1^{\circ}, 2^{\circ}, 3^{\circ}$ H) of alkanes are replaced by equal number of halogen atoms yielding a mixture of halogenated alkanes.

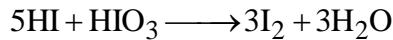
(i) Chlorination : (Free Radical Substitution)



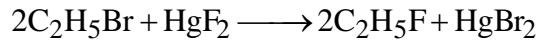
Note : Methyl Chloride is the major product if an excess of methane is used.

(ii) Bromination : Bromine reacts with alkanes in a similar manner but less vigorously.

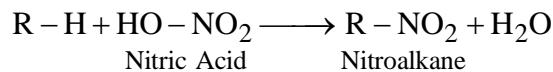
(iii) Iodination : The reaction between iodine and alkane is reversible. Iodination can be done in the presence of an oxidising agent such as HIO_3 (or HNO_3) which removes the hydroiodic acid (HI).

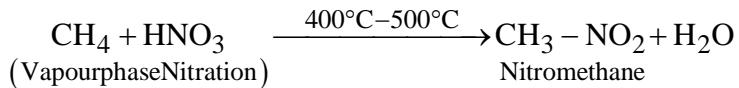


(iv) Fluorination : Fluorine reacts with alkanes at ordinary temperature explosively. So fluorination can be done by diluting fluorine with an inert gas or indirectly.

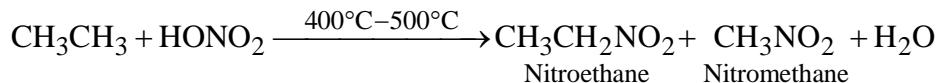


2. Nitration : A mixture of an alkane and nitric acid vapours is heated at $400^{\circ}\text{C} - 500^{\circ}\text{C}$, one hydrogen atom of the alkane is replaced by a nitro group. This reaction is also free radical substitution.

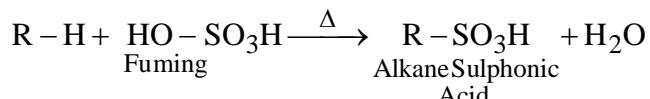




N.B. : This temperature ($400^{\circ}\text{C} - 500^{\circ}\text{C}$) is sufficient to break C–H as well as C–C bond homolytically and thus mixture of products are obtained.



3. Sulphonation : Sulphonation is carried out with fuming H_2SO_4 :

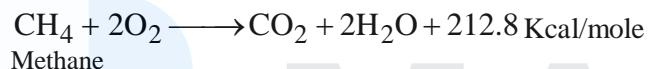


Note : R = C₆H₁₃ or larger alkyl group

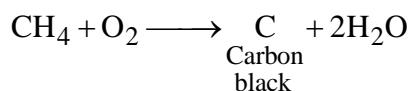
4. Oxidation :

(i) Complete Combustion:

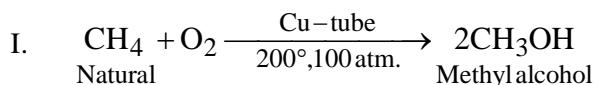
In the presence of excess oxygen alkane burn to form carbon dioxide water.



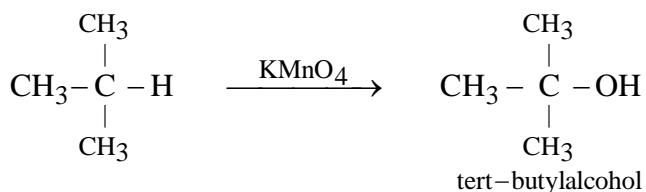
(ii) Incomplete Combustion :



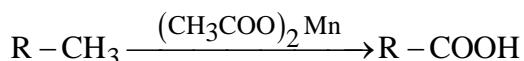
(iii) Catalytic Oxidation :

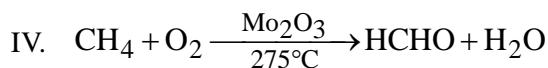


II. ~~A~~^{g_{as}}Alkane having 3° H on oxidation with KMnO₄ gives 3°-alcohol.

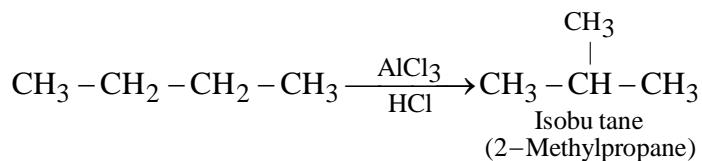


III. Higher alkane on oxidation with manganese acetate gives carboxylic acids.

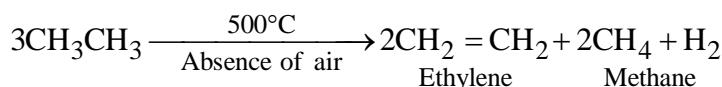




5. Isomerisation : Normal alkanes are converted to their branched chain isomers in the presence of aluminium chloride and HCl at 25°C.

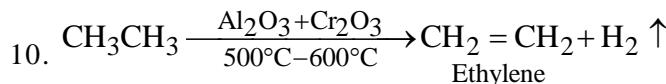
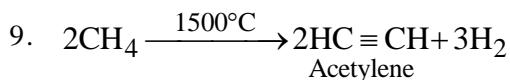
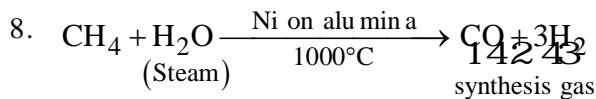
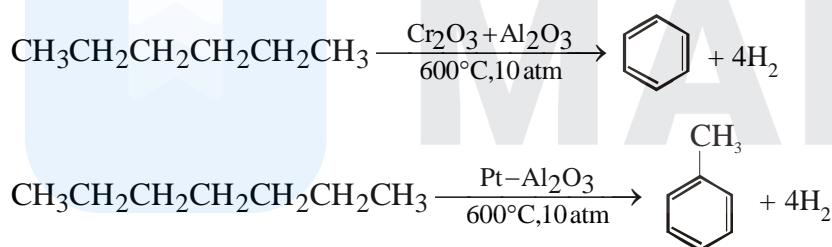


6. Prolysis (Cracking) : Decomposition of higher alkane into a mixture of lower alkanes, alkenes and hydrogen on heating at high temperature in the absence of air.

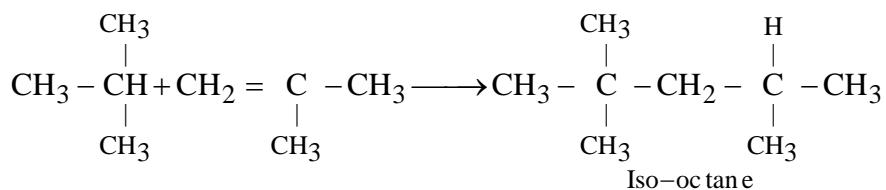


N.B. : In the presence of finely divided silica-alumina as catalyst, this reaction can be carried at less high temperature. This is called catalytic cracking.

7. Aromatisation :



11. Reaction with Alkenes



Uses :

C₁ to C₄ alkanes are used as domestic fuels.

In the manufacture of fuels.

Gasoline (petrol) is a mixture of alkanes alkenes and aromatic hydrocarbons. The quality of gasoline is determined by the amount of iso-octane (2, 2, 4-trimethyl pentane) present in it.

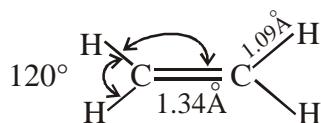
Methane is used in the manufacture of carbon black used in printer's ink, black paints etc.

ALKENE

H – C – C or H – C – H bond angle in ethylene is 120°.

C = C bond distance in ethylene is 1.34 Å

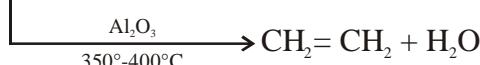
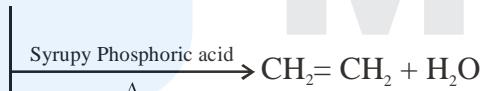
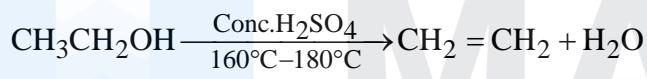
Alkenes are generally very active and due to the presence of pie-bond they exhibit addition reactions.



Generally represented by the general formula C_nH_{2n}.

Preparation

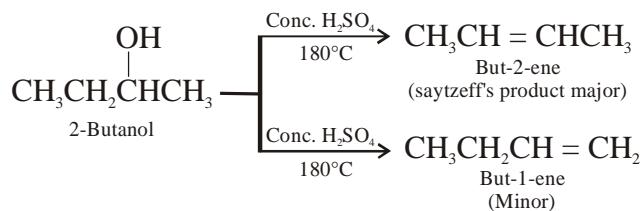
1. By the dehydration of alcohols :



Note :

- (i) Here conc. H₂SO₄ acts as a dehydrating agent as well as catalyst.
- (ii) The ease of dehydration of alcohols is

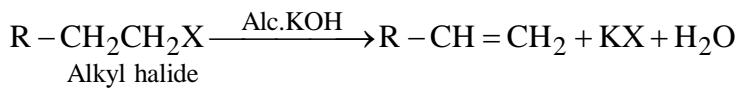
Tertiary alcohol > Secondary alcohol > Primary alcohol



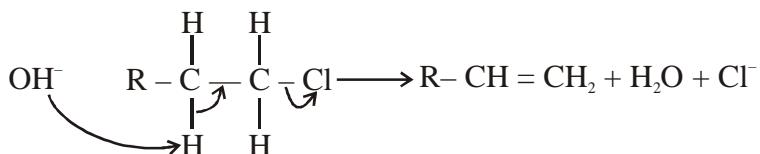
Note : Saytzeff's Rule :

During the dehydration of unsymmetrical alcohols the hydrogen atom is preferentially eliminated from that carbon atom which contains lesser number of hydrogen atoms (Dehydrohalogenation)

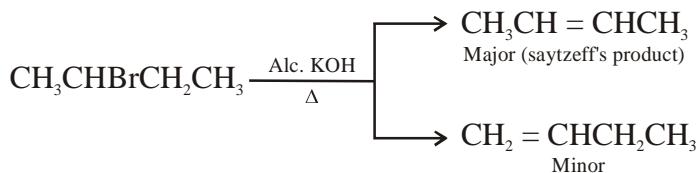
2. By the Removal of Hydrogen Halides from Alkyl Halides :



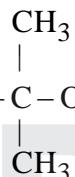
MECHANISM



For unsymmetrical alkyl halide.



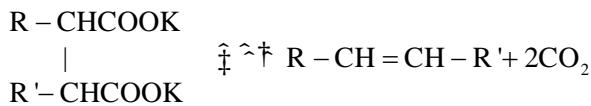
Note : If base taken in above reaction is highly hindered like $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{O}^-$ major product is



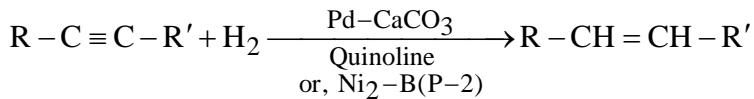
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$ and it is Hoffmann's product.

Ease of reactivity is $\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl}$

3. By Kolbe's Electrolytic Method : When concentrated aqueous solution sodium or potassium salt of vicinal saturated dicarboxylic acid is electrolysed, the alkene and CO_2 liberate at anode whereas alkali and H_2 at cathode.

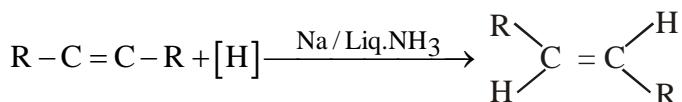


4. By the Partial Hydrogenation of Alkynes :



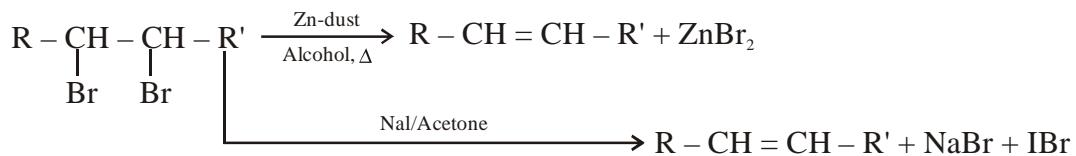
Note :

- (i) Lindlar's Catalyst : Finely divided palladium or platinum deactivated by poisons like BaSO_4 , CaCO_3 or quinoline. Partial reduction with Lindlar's catalyst gives cis-alkene
- (ii) P-2 Catalyst = Nickel boride also gives cis-alkene.
- (iii) Birch Reduction : Partial hydrogenation with Na and liquid NH_3 produces trans-alkene.

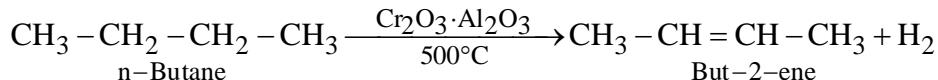


- (iv) B_2H_6 followed by treatment with CH_3COOH will give cis-alkene

4. By the dehalogenation of vicinal di-halides with Zn-dust in alcohol or NaI in acetone



7. By Dehydrogenation of Alkanes :



Properties

At room temperature, C₂ – C₄ → Gases

C₅ – C₁₃ → Liquids

C₁₃ Onwards → Solids

Gaseous alkenes are colourless and odourless. Only ethylene has a sweet smell.

All the alkenes are soluble in organic solvents like ether, benzene, etc.

The densities and boiling points increase with the increase of molecular weights. Their b.p. and m.p. are higher than corresponding alkanes. Cis-isomer has a higher boiling point than trans-isomer due to higher polarity whereas trans alkene has higher melting point than cis alkene.

Chemical :

Following types of reactions are given by alkenes

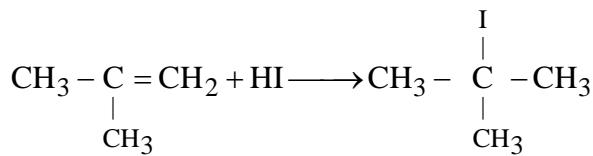
1. Addition Reaction (Electrophilic & radical addition)
2. Oxidation
3. Ozonolysis
4. Isomerisation
5. Substitution at α – carbon
6. Polymerisation

1. Addition Reaction

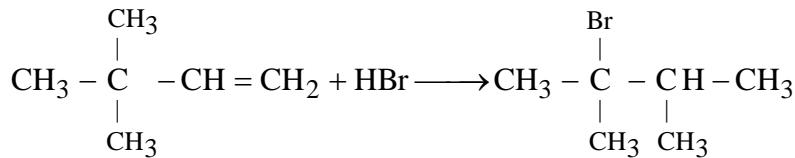
(a) Addition of HX(HCl, HBr and HI)

Electrophilic addition reaction.

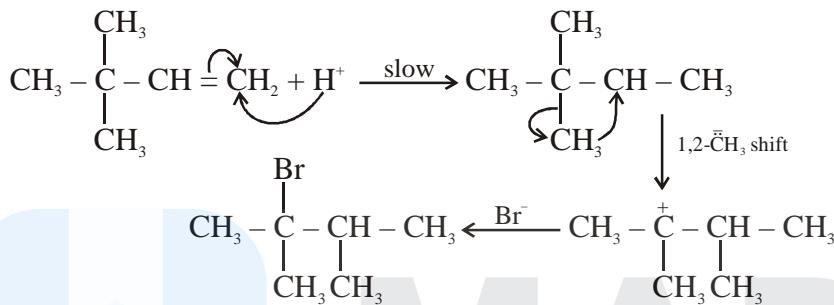
Product of formation takes place according to Markovnikov's rule.



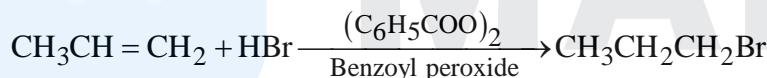
Note : Monosubstituted and disubstituted alkenes whose α -carbon is 4° give addition reaction through rearrangement.



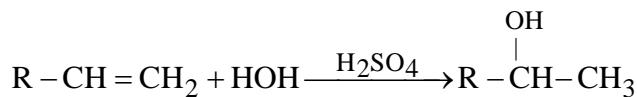
Mechanism :



Product according to Anit Markownikoff's rule. (Free radical addition)

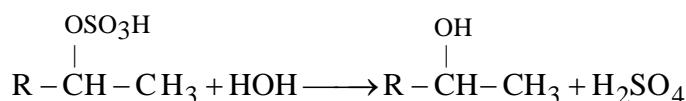
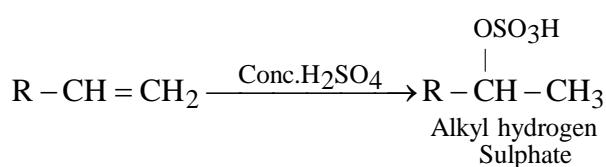
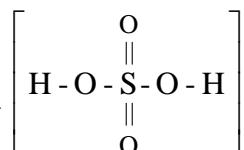


(b) Addition Reaction of Water : (Catalysed by acid) (Electrophilic addition)

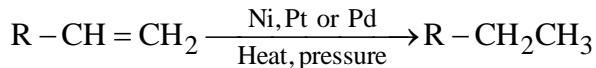


Mechanism is exactly same as that of previous reaction.

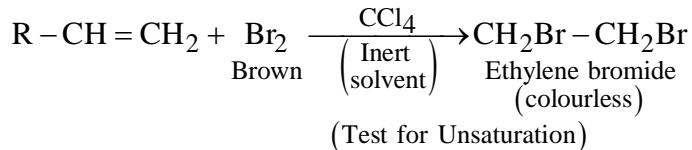
(c) Addition Reaction of Conc. H_2SO_4



(d) Addition of Hydrogen (Hydrogenation) :

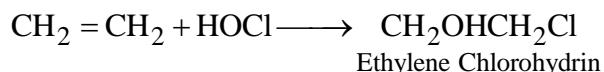


(e) Addition of Halogens : (Electrophilic addition)



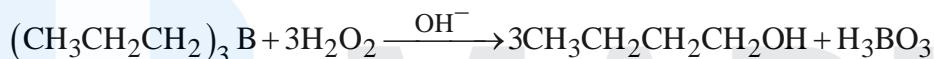
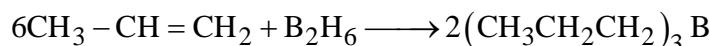
This reaction proceeds via cyclic intermediate that's why there's no chance of rearrangement and it is anti addition.

(f) Addition of hypohalous acids :



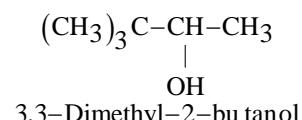
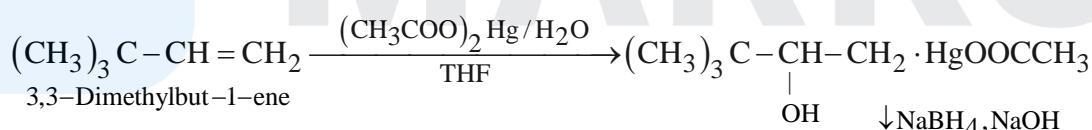
Follow electrophilic addition via cyclic intermediates as in previous reaction.

(g) Hydroboronation oxidation :



Overall result of above reaction is anti Markonikoff addition of H_2O with Syn Stereochemistry.

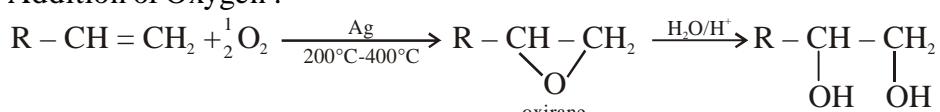
(h) Oxy-Mercuration demercuration :



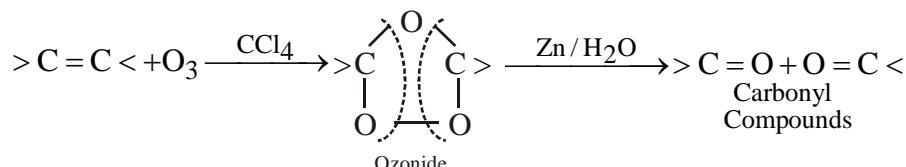
Overall result of above reaction is Markonikoff's addition of H_2O without rearrangement chance and with anti stereochemistry.

2. OXIDATION

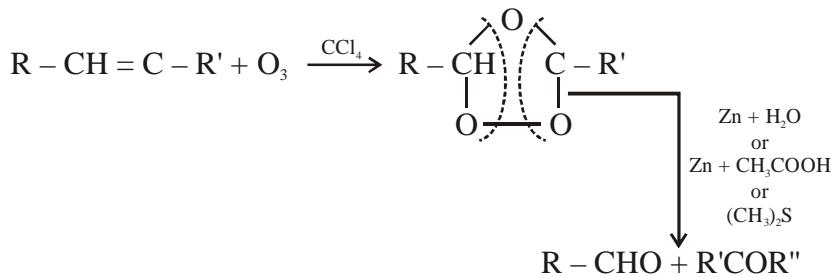
(a) Addition of Oxygen :



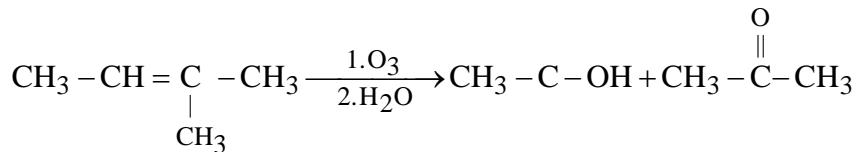
(b) Reductive ozonolysis :



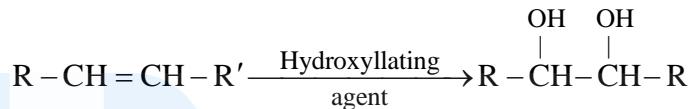
Note Zn-dust is added to prevent the oxidation of aldehyde into carboxylic group by H_2O_2



(c) Oxidative Ozonolysis :

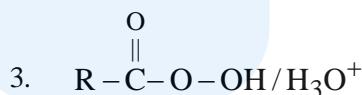


(d) Hydroxylation :

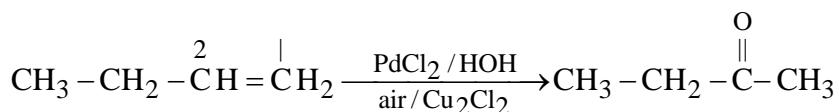


Hydroxylating agent

1. Cold dilute alkaline KMnO_4
2. $\text{OsO}_4/\text{H}_2\text{O}_2$

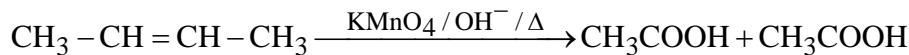
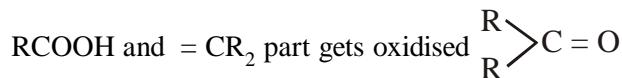


(e) Wacker Process :

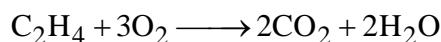
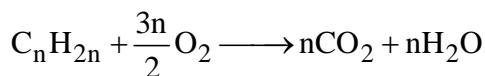


(f) Oxidation with hot basic KMnO_4 .

In this reaction $=\text{CH}_2$ part gets oxidised to CO_2 and H_2O , $=\text{CHR}$ part gets oxidised to

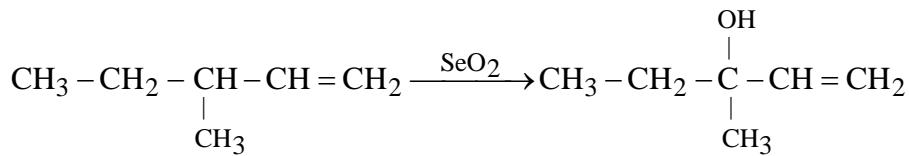
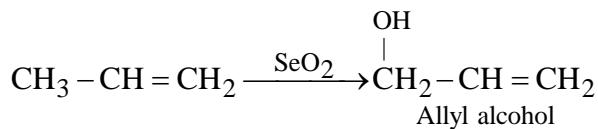


(g) Combustion :

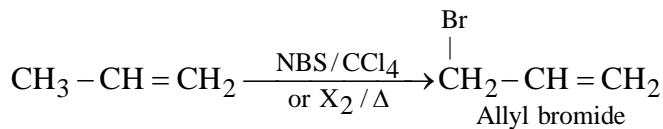


3. SUBSTITUTION AT -CARBON

(a) Allylic oxidation :



(b) Allylic halogenation :



Uses

Ethylene is used in the preparation of polythene and also used in the manufacture of synthetic rubber, ethylene dichloride and mustard gas.

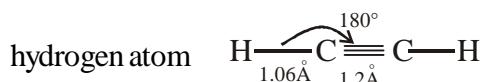
Ethene is used for artificial ripening of fruits.

Ethene is used as a general anaesthetic.

ALKYNES

General formula – $\text{C}_n\text{H}_{2n-2}$

The C – H bonds are formed by the overlapping of sp hybrid orbital of one carbon atom and s-orbital of

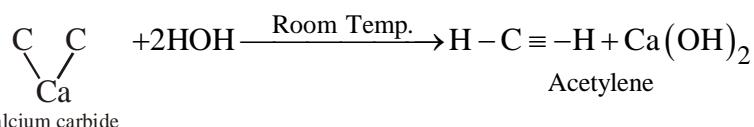


$\text{C} \equiv \text{C}$ distance is 1.20\AA and C – H bond length is 1.08\AA

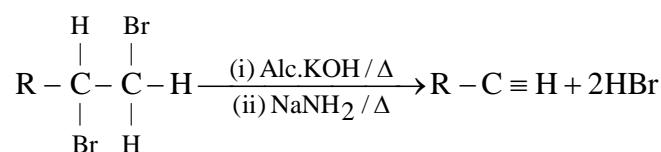
H – C – C bond angle is 180°

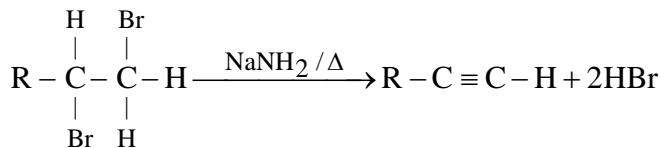
General Methods of Preparation of Alkynes

1. By the reaction of calcikum carbide with water :

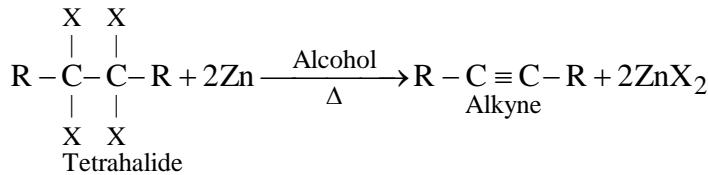


2. Dehydrohalogenation of Vicinal Dihalides

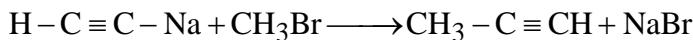




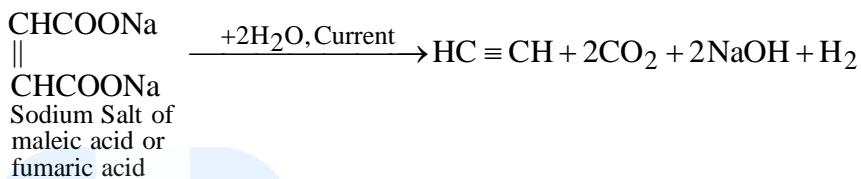
3. Dehalogenation of Tetrahalides :



4. Reaction of sodium acetylide with primary alkyl halides :



5. Kolbe's Method :



6. By heating Iodoform with Silver



Properties

A. PHYSICAL

The first three members are gases. The next 8 members are liquids and the rest are solids.
Alkynes are slightly soluble in water but dissolves in organic solvents like acetone, ethanol.

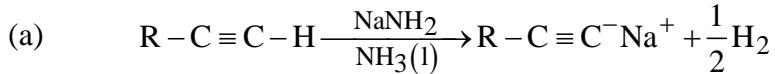
benzen,

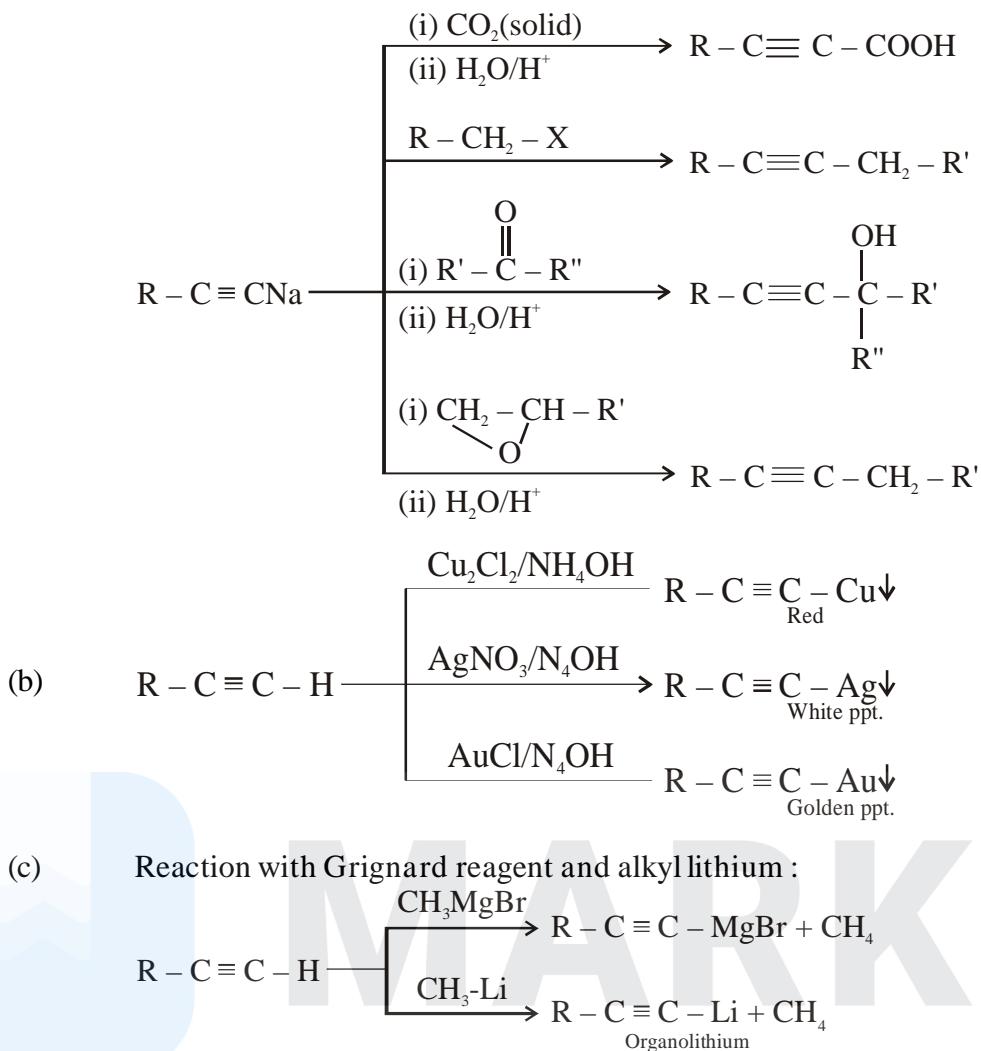
B. CHEMICAL

Alkynes give two types of chemical reaction

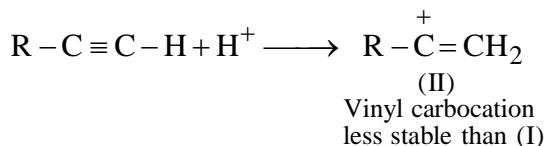
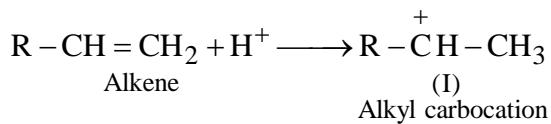
1. Reaction due to acidic hydrogen and
2. Reaction due to π -bonds.

1. Reaction due to Acidic Hydrogen



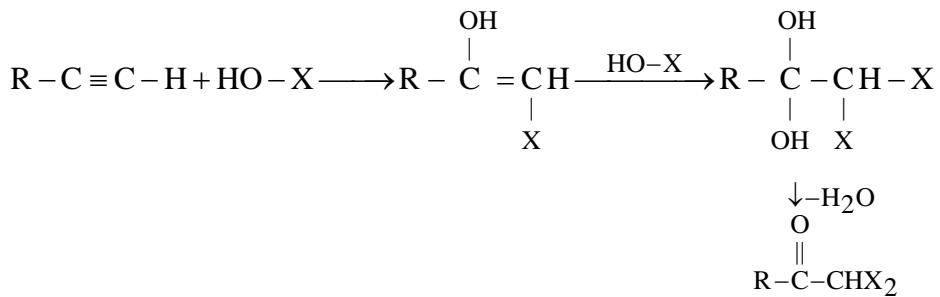


2. Reaction due to π -bonds (Addition Reaction of Alkynes)
- Alkynes generally gives electrophilic addition reaction and are less reactive than alkene for electrophilic addition reaction due to following reason

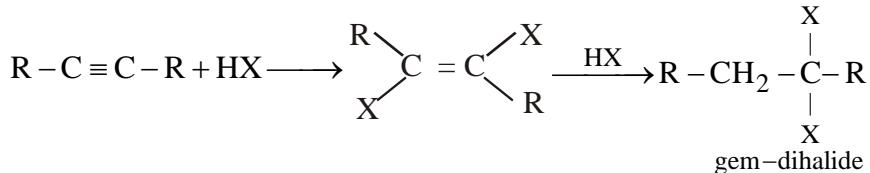


They also give nucleophilic addition reactions with HOH, HCN, ROH, RCOOH etc.

- I. Electrophilic Addition Reaction
- (a) Addition of HOX :

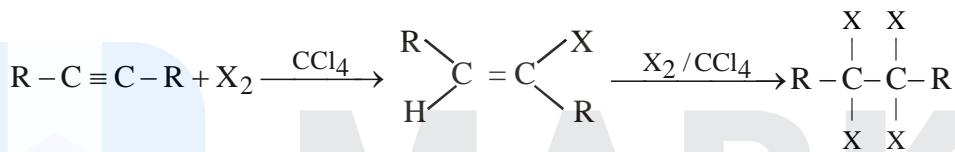


(b) Addition of HX :



Note : order of reactivity of HX is HI > HBr > HCl

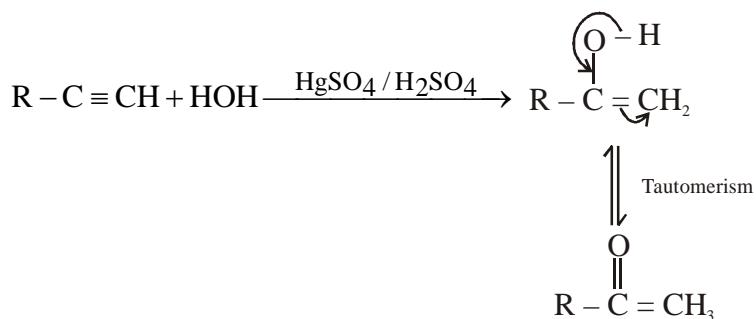
(c) Addition of X₂ (Cl₂, Br₂ and I₂) :



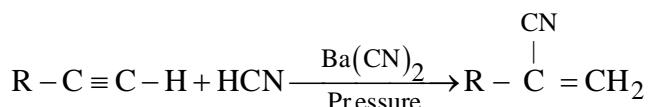
Note : The reactivity order of Halogen is Cl₂ > Br₂ > I₂

II. Nucleophilic Addition Reaction

(a) Addition of water



(b) Addition of HCN :

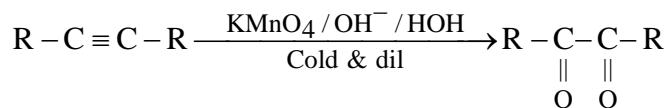


(c) Addition of CH₃—C—OH :

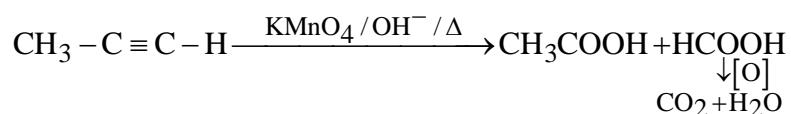
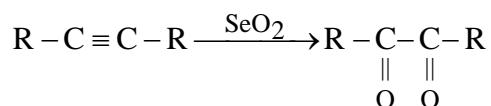
3. Other Reactions :

I. Oxidation of Alkynes

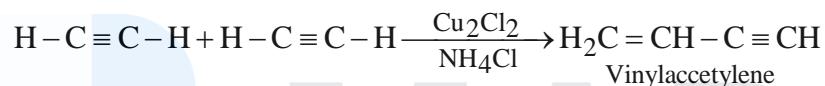
(a) Baeyer's Test :



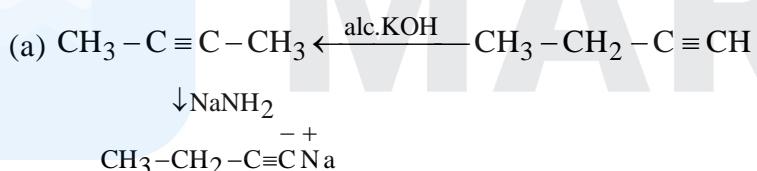
(b) Oxiation by SeO_2 :



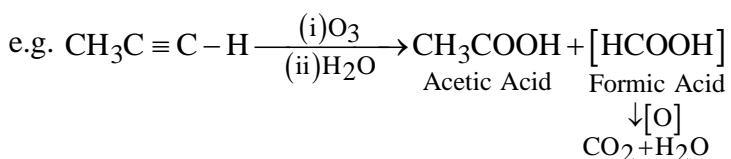
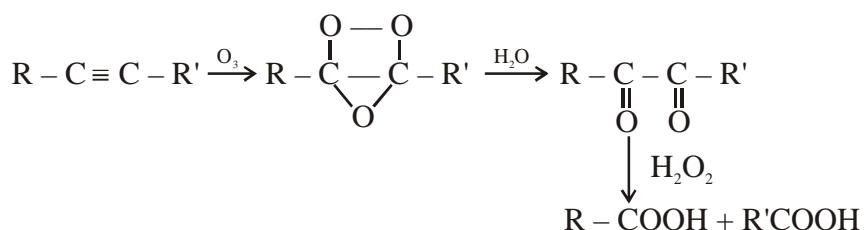
II. Coupling Reaction (linear polymerisation)



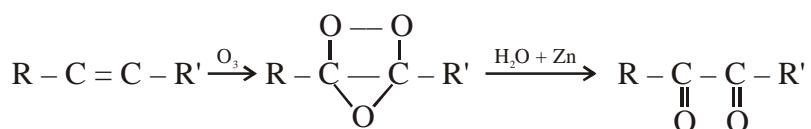
III. Isomerisation

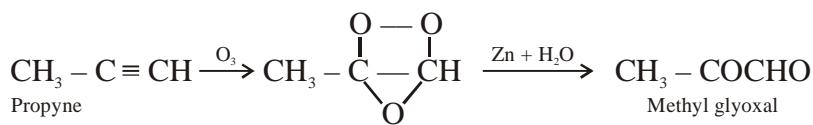


IV. Oxidative ozonolysis



V. Reductive ozonolysis





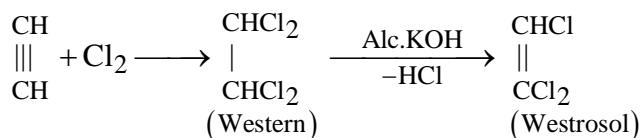
Uses :

(a) It is used for the production of oxy-acetylene flame, which is employed for cutting welding of metals. it provides the temperature above 300°C.

(b) Acetylene on electrical decomposition produces finely divided carbon and hydrogen.

Hydrogen is used in air ships. $\text{C}_2\text{H}_2 \rightarrow 2\text{C} + \text{H}_2$

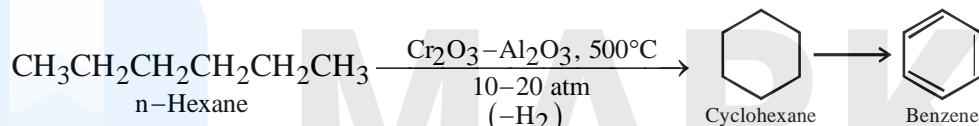
(c) It is used for the preparation of Weston and Westrosol (solvents).



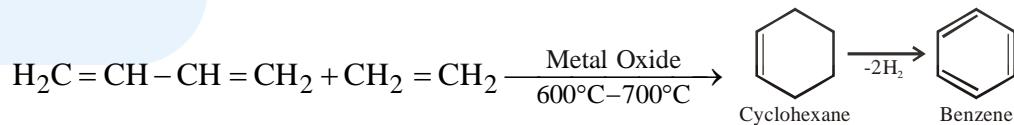
AROMATIC HYDROCARBON

Methods of Preparation :

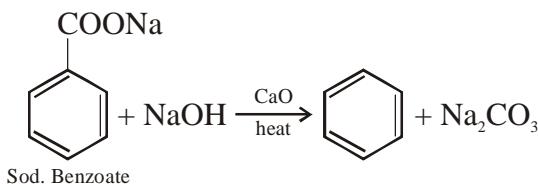
1. Hydroforming or Catalytic reforming :



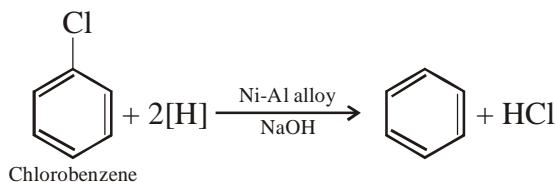
2. High Temperature Cracking :



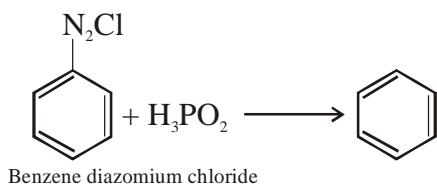
3. Laboratory Method :



4. From Chlorobenzene :

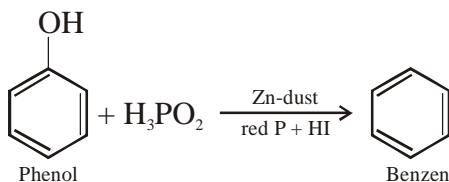


5. From Benzenediazonium Chloride :



Benzene diazomium chloride

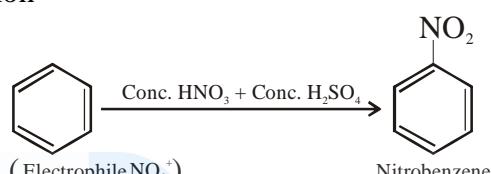
6. From Phenol :



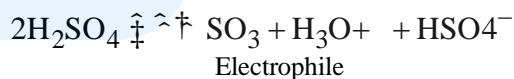
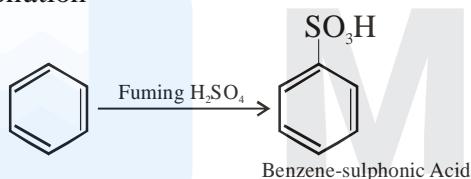
CHEMICAL PROPERTIES

A. Electrophilic Aromatic Substitution -

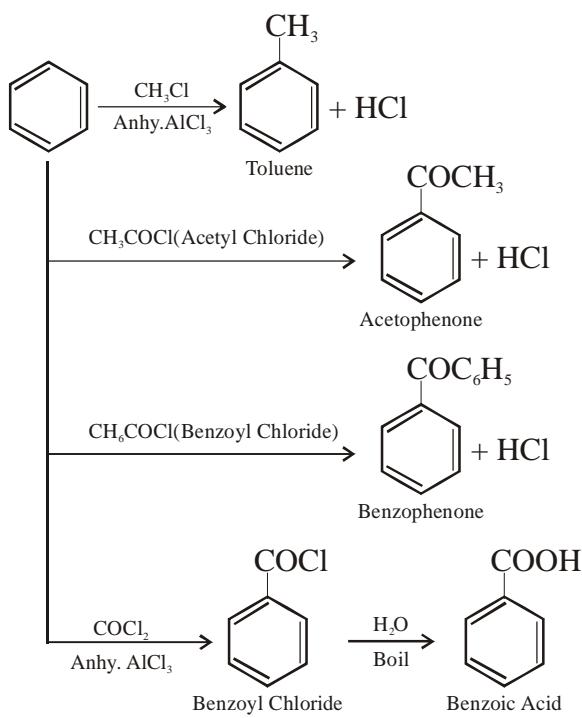
1. Nitration



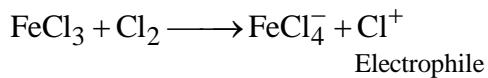
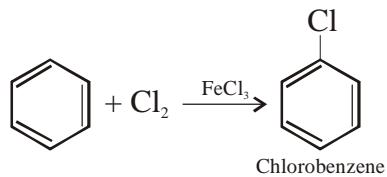
2. Sulphonation



3. Friedal Craft's Reaction

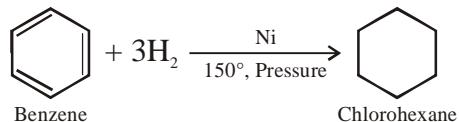


4. Halogenation :

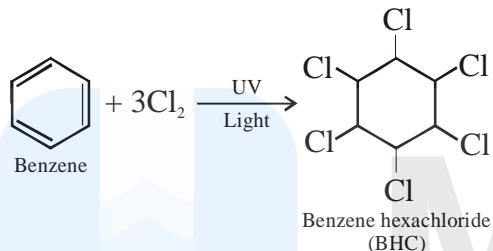


B. Addition Reaction

1. Addition of Hydrogen :

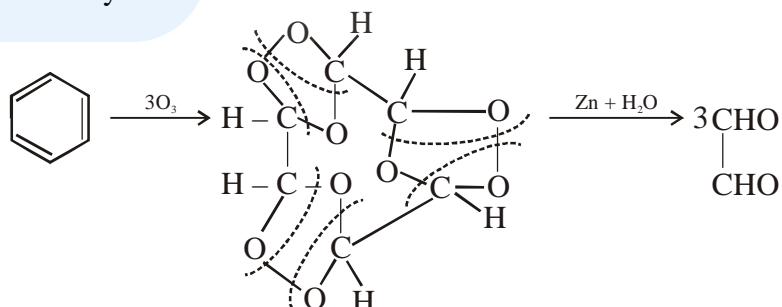


2. Addition of Halogens :

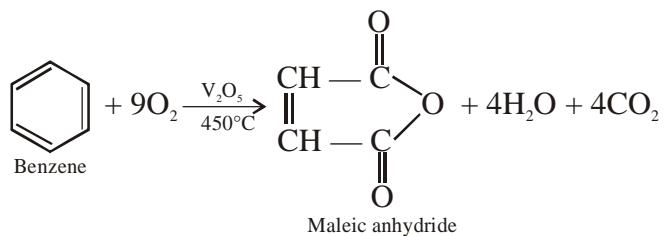


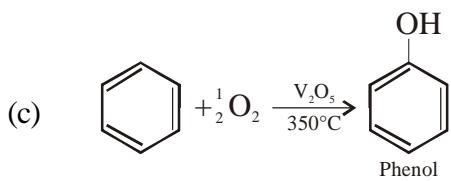
3. Oxidation Reaction :

(a) Ozonolysis :



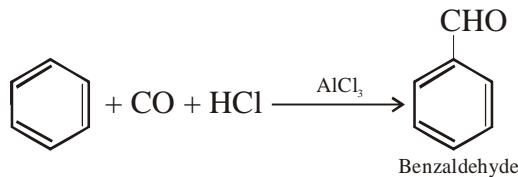
(b) Vapour Phase Oxiation :



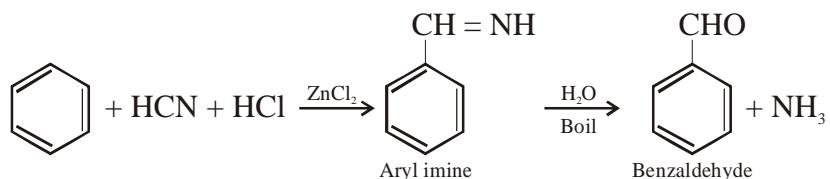


Other Reaction

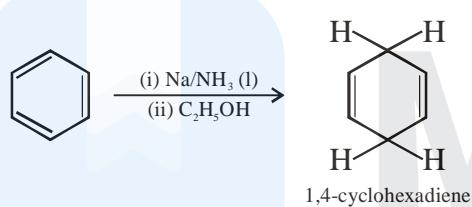
1. Gattermann Koch Aldehyde Synthesis :



2. Gattermann Aldehyde Synthesis :



3.



Uses of Benzene :

It is used as a solvent for oils and fats.

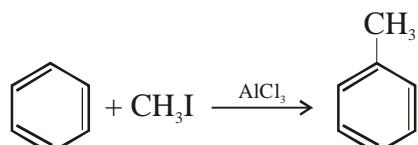
As synthetic liquid by mixing with petrol.

For the manufacture of toluene, nitrobenzene, acetophenone, etc.

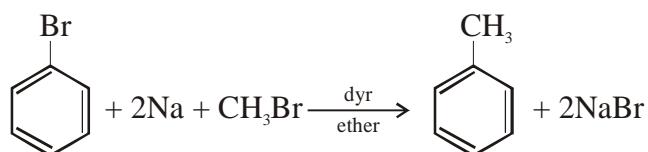
TOLUENE OR METHYL BENZENE

PREPARATION :

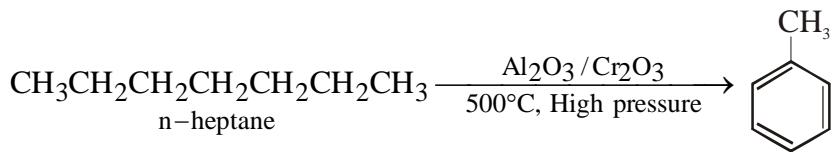
1. From Benzene



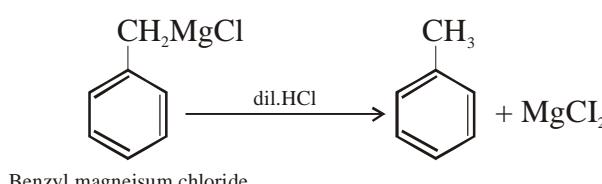
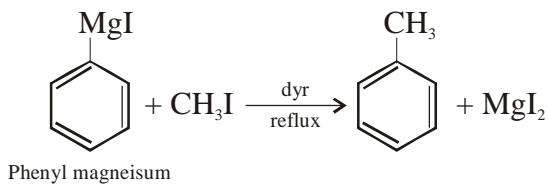
2. Wurtz Fittig Reaction



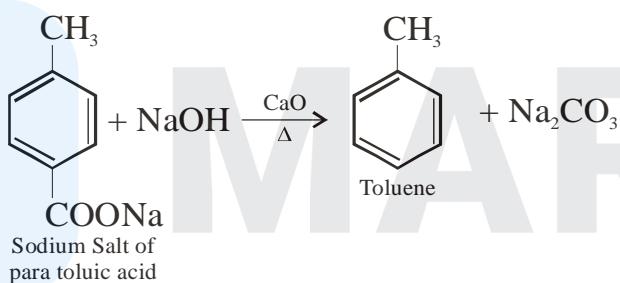
3. Aromatisation Reaction



4. From Grignard Reagent



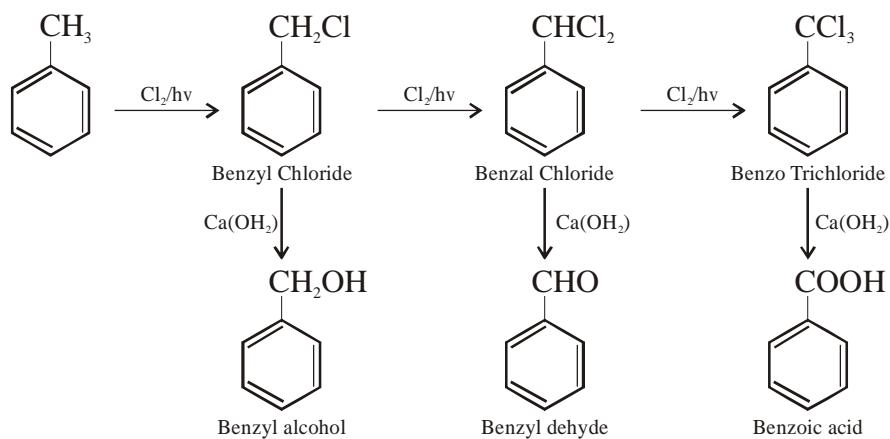
5. From Toluic Acid



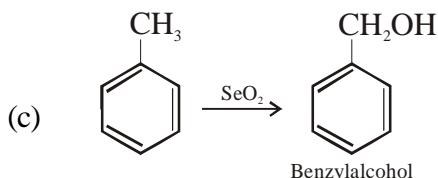
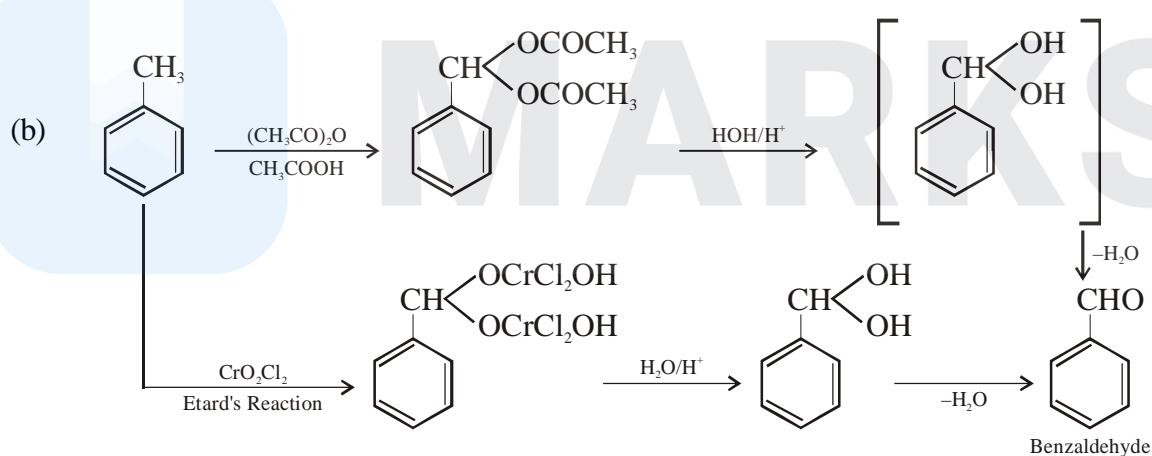
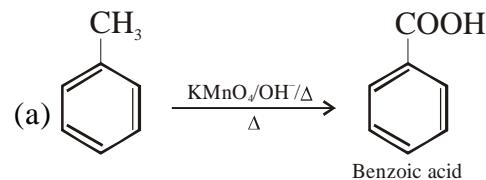
Properties

Toluene gives three types of Reaction

- (a) Side Chain Reaction
 - (b) Nuclear Chain Reaction
 - (c) Reduction Reaction
- A. Side Chain Reaction
1. Chlorination

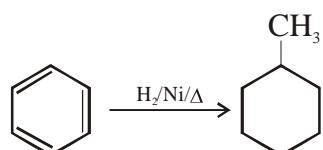


2. Side Chain Oxidation

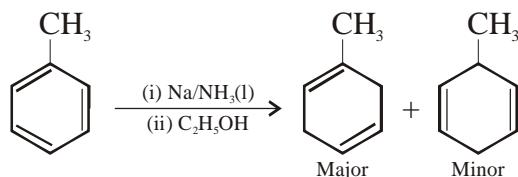


B. Reduction :

1. Total Reduction

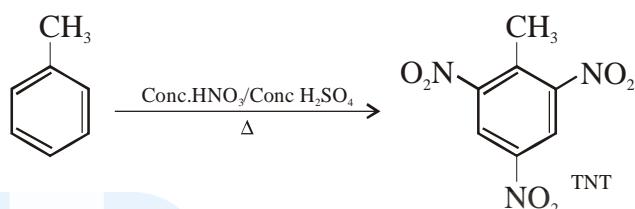
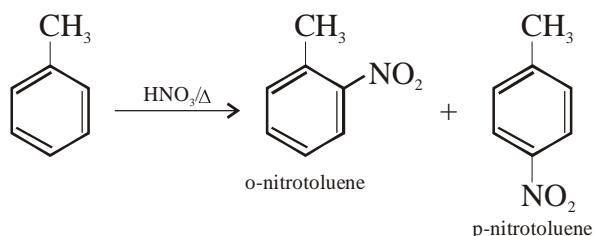


2. Birch Reduction :

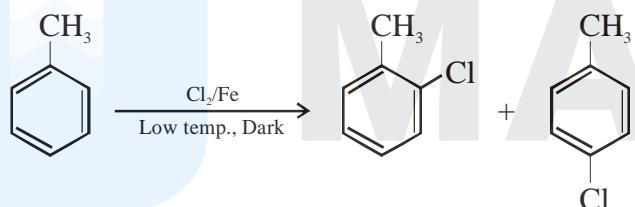


C. Nuclear Chain Reaction :

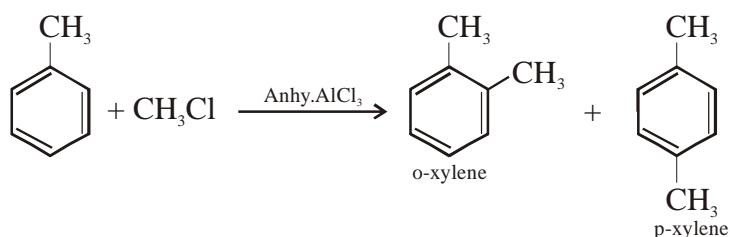
1. Nitration :



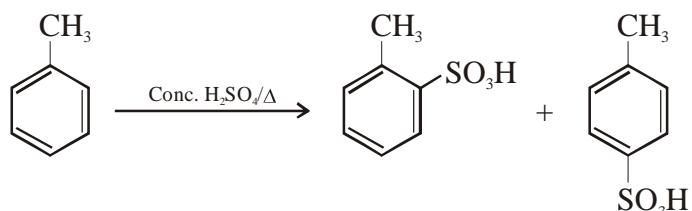
2. Reaction with Halogen :



3. Friedal Craft's Reaction :

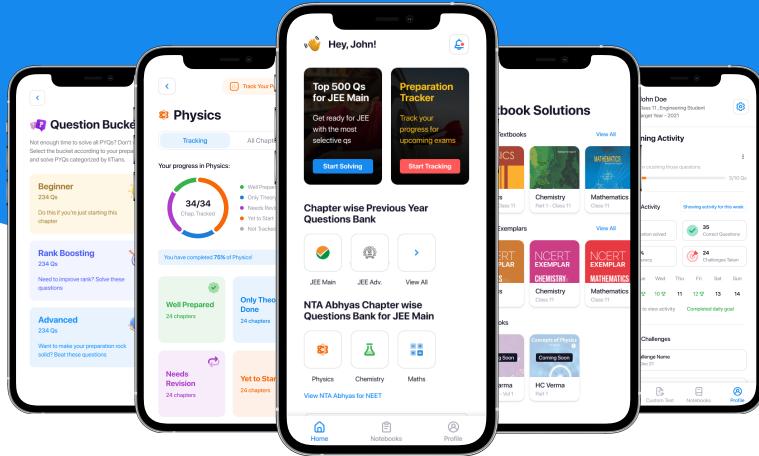


4. Sulphonation :





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