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HYDROCARBON

METHODS OF PREPARATION OF ALKANES

(I) Reduction of alkyl halides:

(RX where X = F, Cl, Br or I)

(Substitution of halogen by hydrogen)

This may be done in three different ways

(i) Reduction by for example, zinc and acetic or hydrochloric acid, zinc and sodium hydroxide, zinc-copper couple and ethanol.

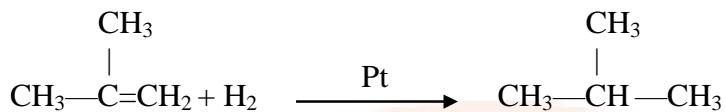


(ii) Reduction by reducing agents like LiAlH₄, NaBH₄ etc

(iii) Using organometallic compounds like Grignard Reagent

(II) Hydrogenation of alkenes in the presence of Pd or Pt:

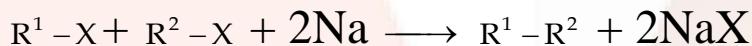
This addition is an example of heterogeneous catalysis involving syn-addition.



The stereospecificity of the reaction is that the addition of hydrogen to the double bond occurs in syn fashion without disturbing the configuration at the chiral carbon.

(a) Wurtz Reaction:

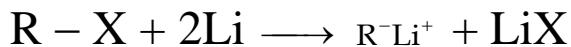
An ethereal solution of an alkyl halide (preferably the bromide or iodide) is treated with sodium, when alkane is obtained. *For example,*

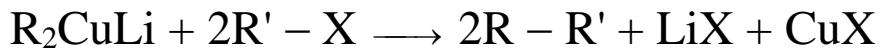
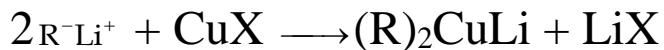


(b) Corey-House Synthesis:

A superior method for coupling is the *Corey-House Synthesis* which could be employed for obtaining alkanes containing odd number of carbon atoms (unsymmetrical alkanes).

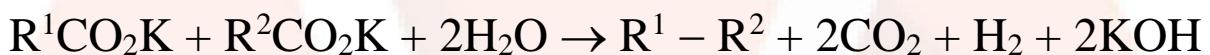
For example,





(c) Kolbe's electrolytic method:

A concentrated solution of the sodium or potassium salt of a carboxylic acid or a mixture of carboxylic acids is electrolysed. *For example,*



Decarboxylation of carboxylate salts:

By heating a mixture of the sodium salt of a carboxylic acid and soda-lime, alkanes can be obtained.

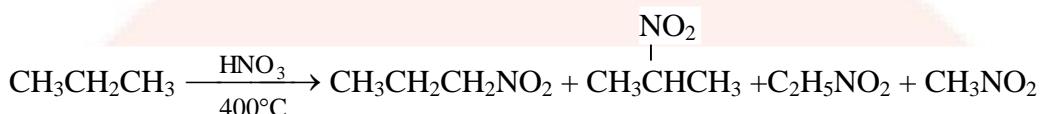


PHYSICAL PROPERTIES

- (I) The first four alkanes (methane to butane) are colourless gases, the next thirteen (pentane to heptadecane) are colourless liquids and those containing 18 carbon atoms or more are solids at ordinary temperatures.
- (II) Their boiling point show gradual rise as the carbon content increases.

CHEMICAL PROPERTIES

(I) Nitration: Under certain conditions alkanes react with nitric acid, when a hydrogen atom will be replaced by a nitro-group, NO_2 . This process is known as *nitration*.



(II) Sulphonation: It is the process of replacing hydrogen atom by a sulphonic acid group, SO_3H . Sulphonation of a normal alkane from hexane onwards may be carried out by treating the alkane with oleum (fuming sulphuric acid).



(III) Oxidation: All alkanes readily burn in excess of air or oxygen to form carbon dioxide and water.



On the other hand, controlled oxidation under various conditions, leads to different products.

(IV) Halogenation: Chlorination may be brought about by photo irradiation, heat or catalysts, and the extent of chlorination depends largely on the amount of chlorine

used. A mixture of all possible isomeric monochlorides is obtained, but the isomers are formed in unequal amounts, due to difference in reactivity of primary, secondary and tertiary hydrogen atoms.

The order of ease of substitution is

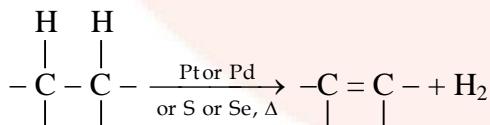
Tertiary Hydrogen > Secondary Hydrogen > Primary Hydrogen

ALKENES

Alkenes are hydrocarbons whose molecules contain the carbon–carbon double bond. They are also called as *olefins*.

METHODS OF PREPARATION OF ALKENES

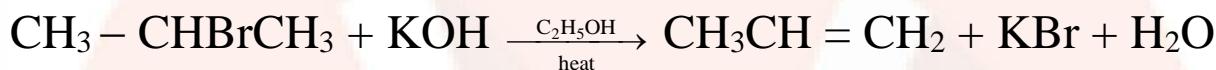
(I) Cracking of Petroleum: Cracking of petroleum hydrocarbons is the source of commercial alkenes.



(II) Partial Hydrogenation of Alkynes: Alkynes can be partially reduced to alkenes by the use of reagents like Lindlar's catalyst, P–2 catalyst with H_2 , Na in liquid NH_3 etc.

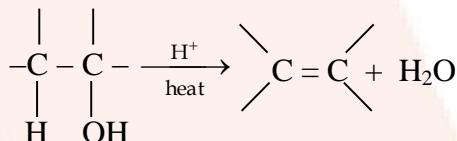
(III) Dehydrohalogenation of Alkyl Halides (1, 2 – Elimination):

When isopropyl bromide is treated with hot concentrated alcoholic solution of a strong base like potassium hydroxide, propylene is obtained.



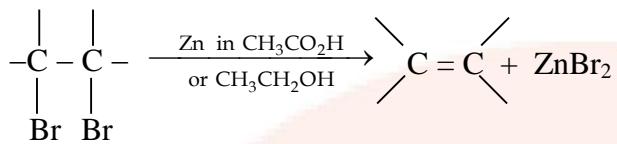
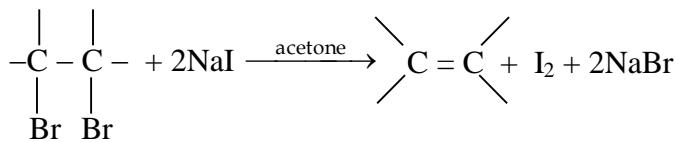
(IV) Acid Catalysed Dehydration of Alcohols:

Heating an alcohol with a strong acid like H_2SO_4 causes elimination of water and form an alkene. Elimination of water is called *dehydration*.



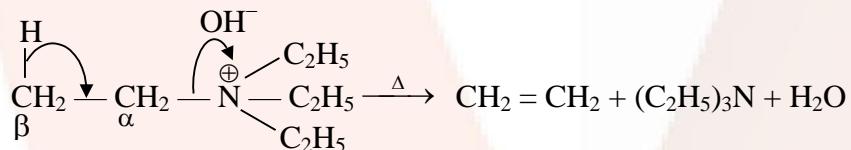
(V) Debromination of Vicinal Dibromides:

Vic-dibromides undergo debromination when they are treated with a solution of sodium iodide in acetone or a mixture of Zn dust in acetic acid (or ethanol).



(VI) Heating Quaternary (tetra alkyl) Ammonium Hydroxides:

Alkenes can also be formed by heating tetra alkyl ammonium hydroxides with the simultaneous elimination of trialkyl amine. This reaction involves Hoffmann's elimination and product will be governed by Hoffman's rule.



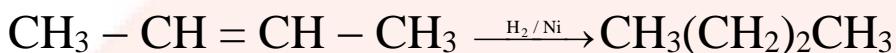
PHYSICAL PROPERTIES

The first three members are gases, the next fourteen members are liquids and the higher ones are solids. They are colourless and odourless (except ethylene which has a faint sweet smell), practically insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether, etc.

GENERAL CHEMICAL PROPERTIES OF THE ALKENE

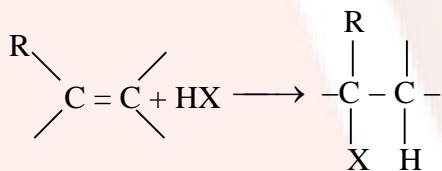
(I) Hydrogenation

The addition of hydrogen to unsaturated compounds normally involves heterogeneous catalysis by finely divided metals such as Ni, Pt, Pd, Ru, Rh etc.



(II) Addition of Hydrogen Halides

Hydrogen halides (HCl, HBr and HI) add to the double bond of alkenes.



The addition of HX to alkenes follow Markownikov's rule, according to which "*the negative part of the unsymmetrical reagent goes to that carbon atom which bears lesser number of hydrogen atoms*".

(III) Addition of Hydrogen Bromide In Presence of Peroxides

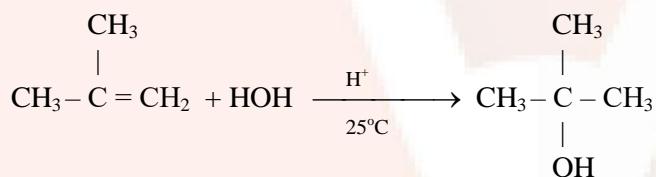
The addition of HBr to propene, $\text{MeCH} = \text{CH}_2(1)$, under polar conditions (in absence of peroxide) yields 2–bromopropane. However, in the presence of peroxides (or under other conditions that promote radical formation) however, the addition proceeds via a rapid chain reaction to yield

1-bromopropane. This addition of HBr in presence of peroxide is generally referred to as the *peroxide effect leading to anti-Markownikov addition*.

(IV) Addition of Water

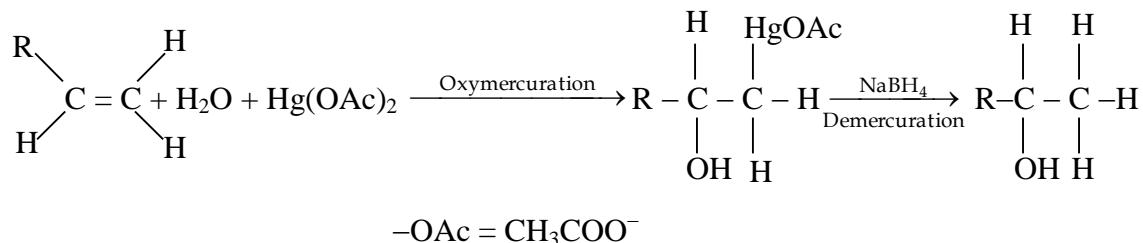
(a) Acid Catalyzed Hydration

The acid catalyzed addition of water to the double bond of an alkene is a method of preparation of low molecular weight alcohols. The addition of water to the double bond follows Markovnikov's rule in those case where rearrangement is not involved.



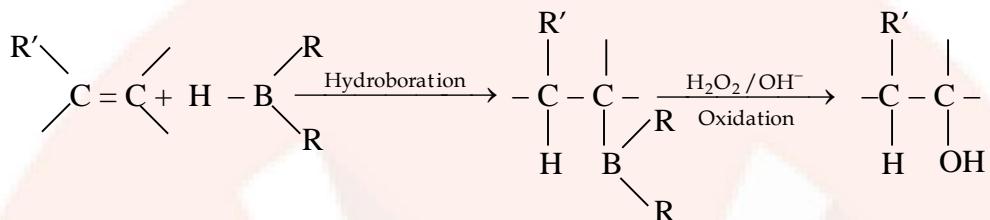
(b) Oxymercuration-Demercuration

Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds which on reduction yield alcohols.



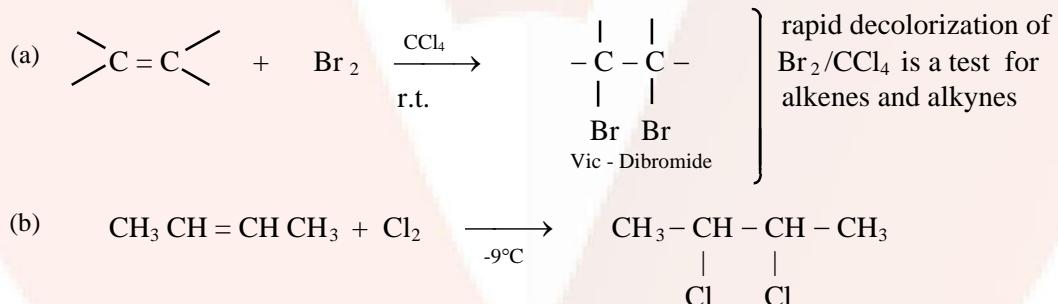
(c) Hydroboration-Oxidation

With the reagent diborane, $(BH_3)_2$ or disubstituted borane (R_2BH) alkenes undergo hydroboration to yield trialkylboranes, R_3B , which on oxidation gives alcohols. *For example,*



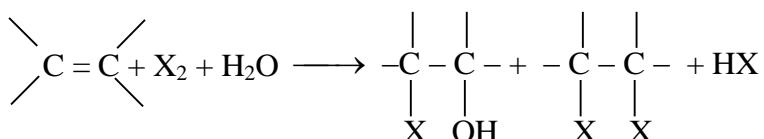
(V) Addition of Bromine and Chlorine

Alkenes react rapidly with bromine at room temperature and in the absence of light.



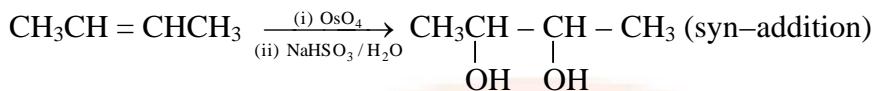
(VI) Halohydrin Formation

If the halogenation of an alkene is carried out in aqueous solution (rather than in CCl_4),



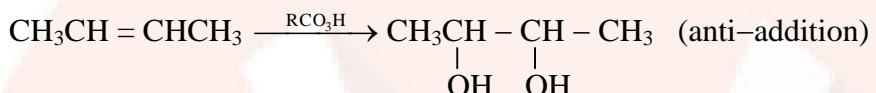
(VII) Hydroxylation

(a) *Syn* hydroxylation:

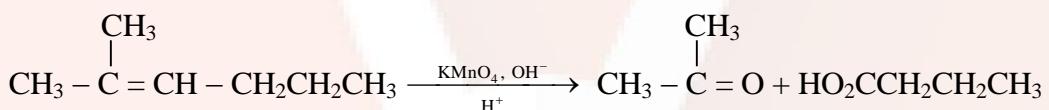


KMnO_4 can also be used for *syn* hydroxylation.

(b) *Anti* hydroxylation:

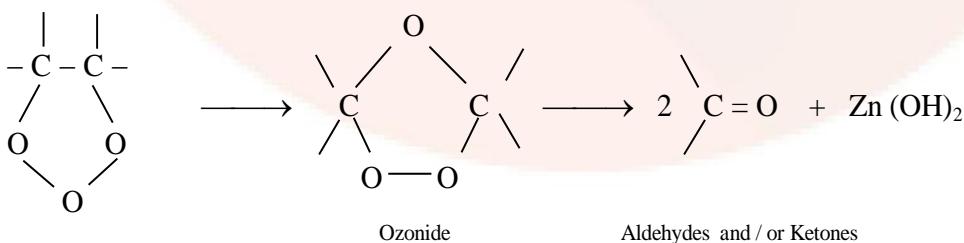


(VIII) Oxidative Cleavage By Hot Alkaline KMnO_4



(IX) Ozonolysis

A more widely used method for locating the position of double bond in an alkene involves the use of ozone (O_3).



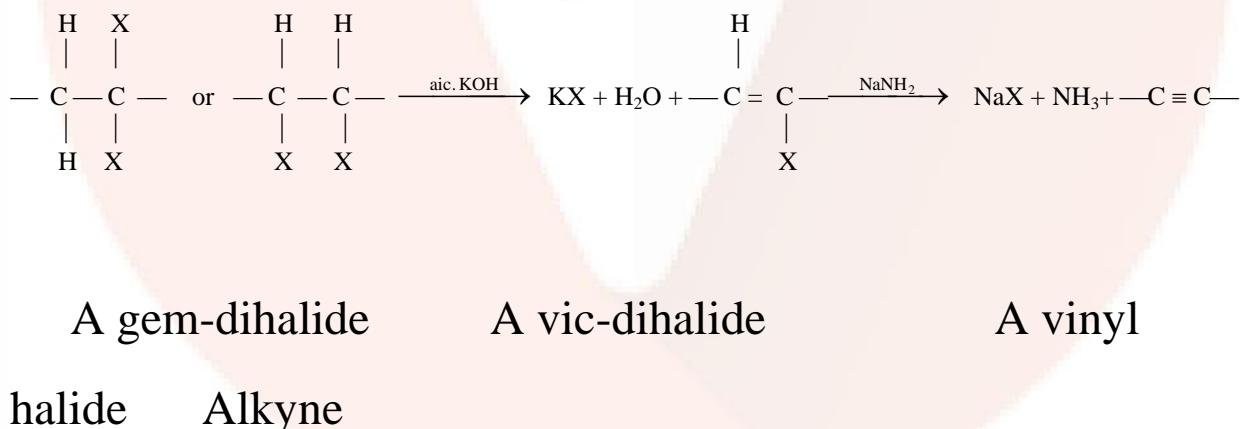
Ozonolysis can be of either of reductive type or of oxidative type.

ALKYNES

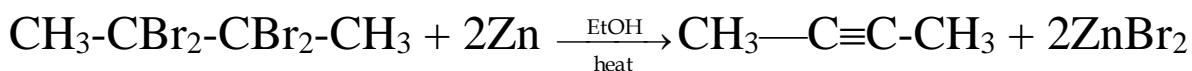
The alkynes are unsaturated hydrocarbons that contain one triple bond. They have the general formula C_nH_{2n-2} and the triple bond is known as the '*acetylenic bond*'..

METHODS OF PREPARATION OF ALKYNES

1. Dehydrohalogenation of vic-Dihalides or gem-Dihalides



2. Dehalogenation of vic-Tetrahalogen Compounds

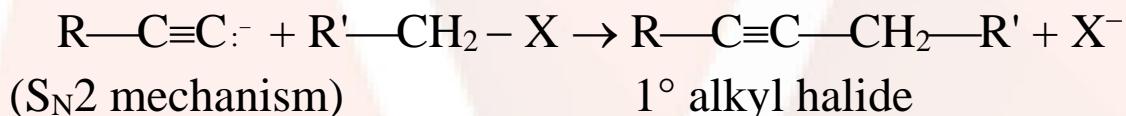
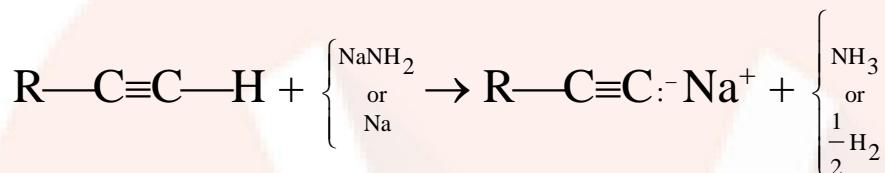


2,2,3,3-Tetrabromobutane

2-Butyne

This reaction has the drawback that the halogen compound is itself prepared by halogen addition to alkynes. The mechanism for dehalogenation has been taken up in the topic “*alkenes*”.

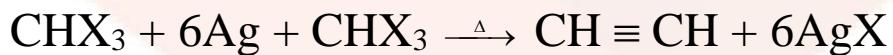
3. Alkyl Substitution in Acetylene or 1–alkynes



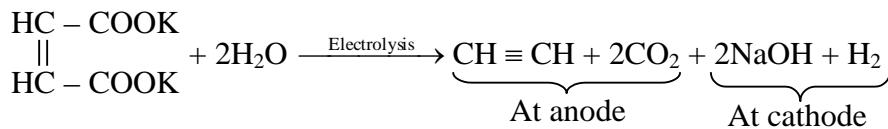
4. By the action of water on calcium carbide



5. By Heating chloroform or iodoform with silver metal



6. Kolbe's electrolytic methods



PHYSICAL PROPERTIES

The physical properties of alkynes are similar to those of the corresponding alkenes. The lower members are gases with boiling points somewhat higher than those of the corresponding alkenes. Terminal alkynes have lower boiling points than isomeric internal alkynes and can be separated by careful fractional distillation.

GENERAL CHEMICAL PROPERTIES

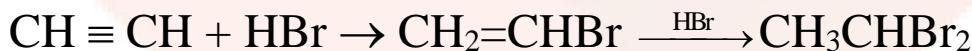
(I) Hydrogenation

Acetylene adds on hydrogen in the presence of a catalyst, the reaction proceeding in two stages.



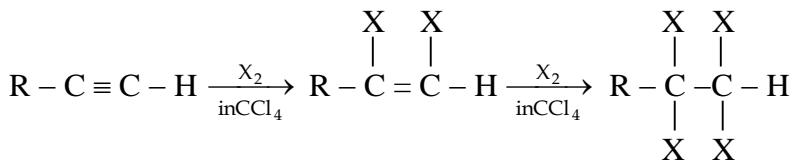
(II) Addition of HX

Acetylene combines with hydrogen bromide to form vinyl bromide first and then ethylidene dibromide.



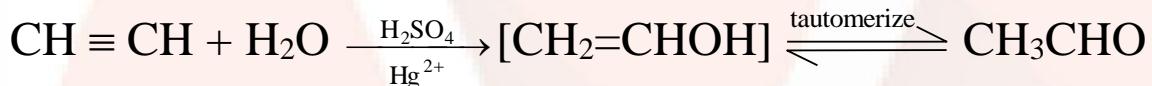
Peroxides have the same effect on the addition of hydrogen bromide to acetylene as they have on alkenes.

(III) Addition of Halogen (Br₂, Cl₂)

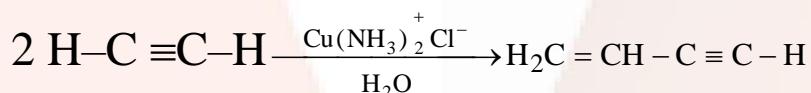


(IV) Addition of H₂O

When passed into dilute sulphuric acid at 60°C in the presence of mercuric sulphate as catalyst, acetylene adds on a molecule of water to form acetaldehyde.

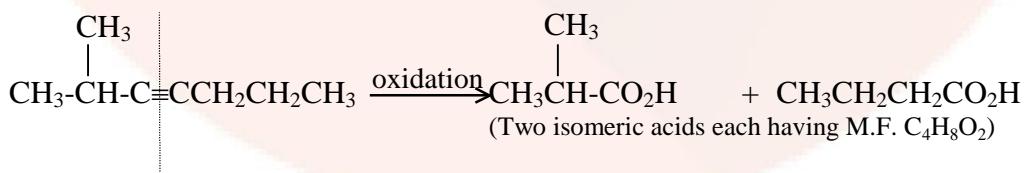


(VI) Dimerization



Vinylacetylene

(VII) Oxidation to Carboxylic Acids



(VIII) Ozonolysis



2-Pentyne

Acetic acid Propanoic acid

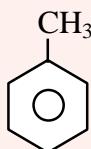
(IX) Polymerization Reactions

When acetylene is passed into dilute hydrochloric acid at 65°C in the presence of mercuric ions as catalyst, vinyl chloride is formed.

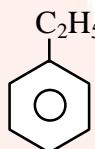


ARENES

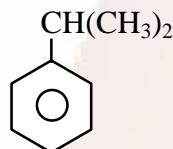
Hydrocarbons that consists of both aliphatic and aromatic groups are known as *arenes*. Toluene, ethyl benzene and isopropyl benzene are *alkyl benzenes* while vinyl benzene (styrene) is an *alkenyl benzene*. The aliphatic portion of these compounds is commonly called the *side chain*.



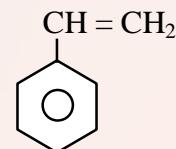
Methyl benzene
Phenyl ethene



Ethyl benzene



Isopropyl benzene



(toluene)
(styrene or vinyl benzene)

(cumene)

METHODS OF PREPARATION OF ARENES

Preparation of Alkyl Benzenes

(a) Friedel–Craft's Alkylation

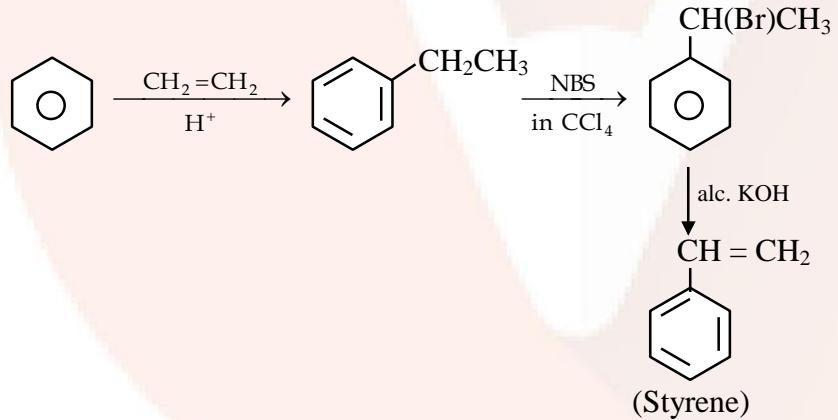
Substitution of hydrogen by alkyl group in aromatic compound is known as Friedel–Crafts alkylation.

(b) Friedel–Craft's Acylation

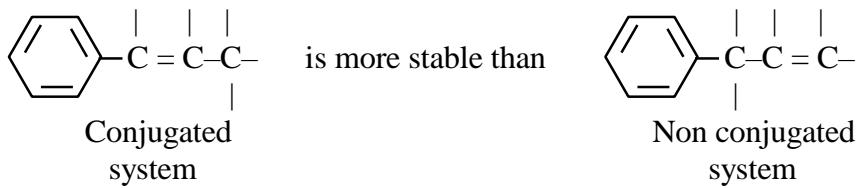
Substitution of hydrogen by acyl group in aromatic compound is known as *Friedel–Crafts Acylation*.

Preparation of Alkenyl Benzenes

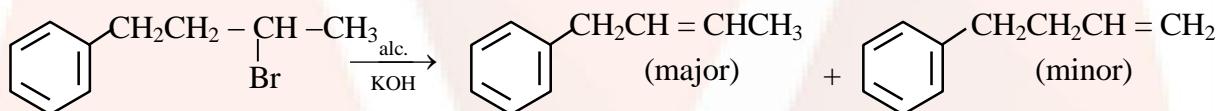
(a) Styrene (vinyl benzene) can be prepared as



(b) Alkenyl benzenes that have their side-chain double bond conjugated with the benzene ring are more stable than those that do not have.



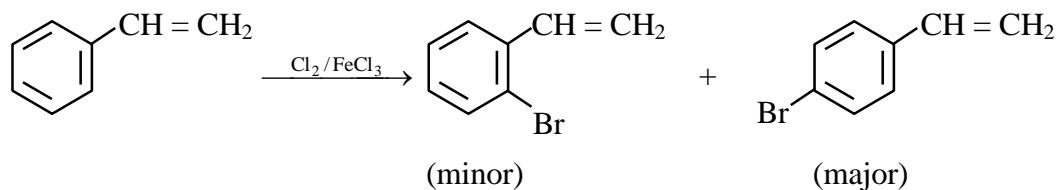
(c) Alkenyl benzenes can also be obtained by the dehydrohalogenation of haloalkyl groups attached to benzene ring. The elimination is governed by Saytzeff rule i.e. more substituted alkene is formed in greater amount.



GENERAL CHEMICAL PROPERTIES

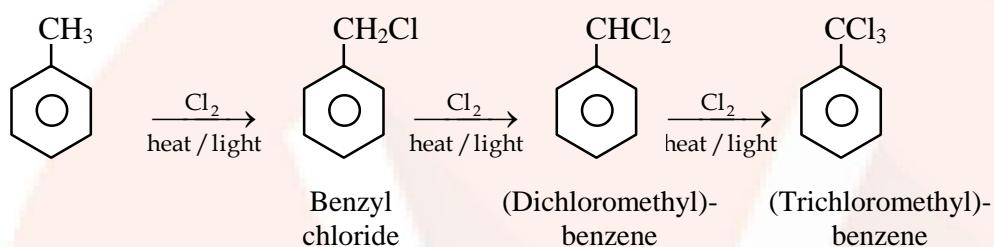
Halogenation of the Ring

When halogenation of the alkyl or alkenyl benzenes is to be carried out in ring, a lewis acid catalyst is required. Since alkyl and alkenyl groups are ortho and para directing, so the incoming electrophile (Cl^+ or Br^+ in chlorination and bromination respectively) will be oriented at either ortho or para position.



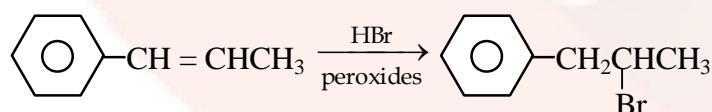
Halogenation of the Side Chain

Chlorine and bromine can also be made to replace hydrogens of the methyl group of toluene. Side chain halogenation takes place when the reaction is carried out in the absence of Lewis acids and under conditions that favour the formation of radicals.

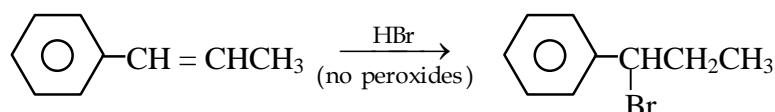


Additions to the Double Bond of Alkenyl Benzenes

In the presence of peroxides, hydrogen bromide adds to the double bond of 1-phenyl propene to give 2-bromo-1-phenyl propane as the major product.

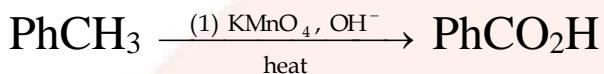


In the absence of peroxides, HBr adds in just the opposite way.

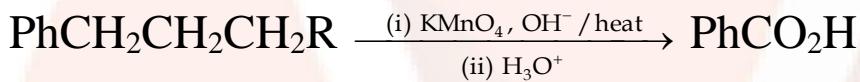


Oxidation of the Side Chain

Strong oxidizing agents oxidize toluene to benzoic acid. The oxidation can be carried out by the action of hot alkaline potassium permanganate. This method gives benzoic acid in almost quantitative yield.



Benzoic acid



An alkylbenzene

Benzoic acid

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