Chapter II: hydrocarbons and its principals derivatives

Introduction

The compounds having only **C**, and **H-**atoms are known as Hydrocarbon. Natural gas, Petroleum and coal are major sources of Hydrocarbon.

In the **nineteenth** century, before chemists understood bonding and the structure of organic substances, they experimented with hydrocarbons obtained from heating animal fats and plant oils. They classified these hydrocarbons according to a chemical test in which they mixed each hydrocarbon with **bromine** and then measured how much reacted with the hydrocarbon. Some hydrocarbons would react with a small amount of bromine, some would react with more, and some would not react with any amount of bromine. Chemists called the hydrocarbons that reacted with bromine **unsaturated** hydrocarbons in the same sense that an unsaturated aqueous solution can dissolve more solute. Hydrocarbons that did not react with bromine were said to be saturated.

Present-day chemists can now explain the experimental results obtained 170 years ago. Hydrocarbons that reacted with bromine had double or triple covalent bonds. Those compounds that did not react with bromine had only single covalent bonds. Today, a hydrocarbon having only single bonds is defined as a saturated hydrocarbon. A hydrocarbon that has at least one double or triple bond between carbon atoms is an unsaturated hydrocarbon.

Refining Hydrocarbons

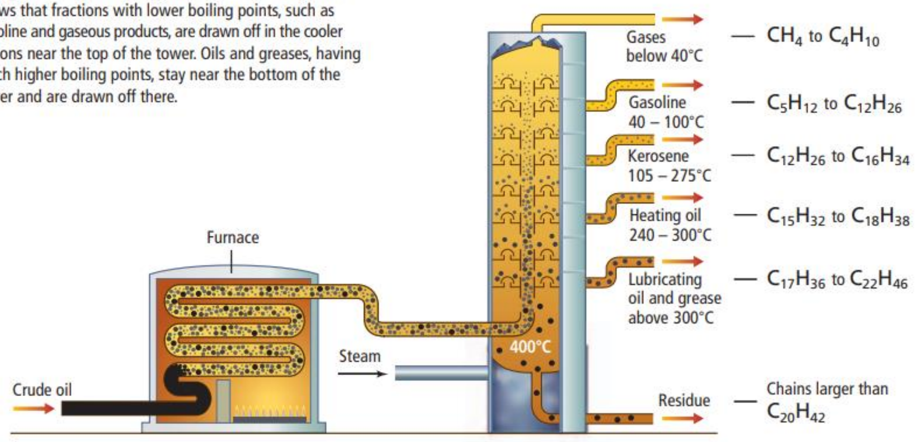
Today, many hydrocarbons are obtained from a fossil fuel called petroleum. Petroleum formed from the remains of microorganisms that lived in Earth's oceans millions of years ago. Over time, the remains formed thick layers of mud like deposits on the ocean floor. Heat from Earth's interior and the tremendous pressure of overlying sediments transformed this mud into oil-rich shale and natural gas. In certain kinds of geological formations, the petroleum ran out of the shale and collected in pools deep in Earth's crust. Natural gas, which formed at the same time and in the same way as petroleum, is usually found with petroleum deposits. Natural gas is composed primarily of methane, but it also contains small amounts of other hydrocarbons that have from two to five carbon atoms.

Fractional distillation Unlike natural gas, petroleum is a complex mixture containing more than a thousand different compounds. For this reason, raw petroleum, sometimes called crude oil, has little practical use. Petroleum is much more useful to humans when it is separated into simpler components or fractions. Separation is carried out in a process called fractional distillation, also called fractionation, which involves boiling the petroleum and collecting components or fractions as they condense at different temperatures. Fractional distillation is done in a fractionating tower similar to the one shown in Figure below.

The temperature inside the fractionating tower is controlled so that it remains near 400°C at the bottom, where the petroleum is boiling, and gradually decreases toward the top. The condensation temperatures (boiling points) generally decrease as molecular mass decreases.

Therefore, as the vapors travel up through the column, the hydrocarbons condense and are drawn off.

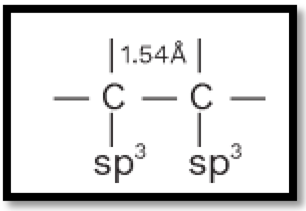
Figure 21.6 This diagram of a fractionating tower shows that fractions with lower boiling points, such as gasoline and gaseous products, are drawn off in the cooler regions near the top of the tower. Oils and greases, having much higher boiling points, stay near the bottom of the tower and are drawn off there.



A furnace heats the crude oil to boiling, and the resulting gases travel to the tower.

The molecular mass of the hydrocarbon determines how high it rises in the tower.

Alkane



The general formula of alkanes is $\mathbf{C_n\ H_{2n+2}}$.

- The main sources of alkanes include petroleum, natural gas and coal.
- Alkanes are also termed as paraffins due to their almost inert nature or reduced activity.
- Bond length of C–C is 1.54 Å and that of C–H bond is 1.11 Å
- Alkanes gives a C–C bond energy of 80 kcal per mole and for C–H bond it is calculated
- as 97 kcal per mole.
- They are non-polar in nature.

- Alkanes show chain, position, and conformational isomerism.
- Liquefied Petroleum Gas (LPG) is composed of propane, butane, and isobutane.

Physical Properties

- From **methane (C1)** to **butane (C4)**, alkanes are in the **gas state**.
- Natural gas is essentially methane. Oils contain a mixture of hydrocarbons (including alkanes ranging from CH_4 to $C_{40}H_{82}$).
- From C5, we find liquids and from C^{17}, solids.
- Liquid or solid alkanes have a fairly low density (about 0.7). They are insoluble in water; on the other hand, they are **miscible** with most organic liquids and are themselves **solvents** for many organic compounds.

Methods of Preparation of Alkanes

By decarboxylation of sodium salts of fatty acids

When R–COOH heated with Sodalime (**4:1** Mixture of **CaO** + **NaOH**) alkane is formed. Here alkane has one **C– atom** less than **R–COOH** as one $\mathbf{CO_2}$ molecule is eliminated.

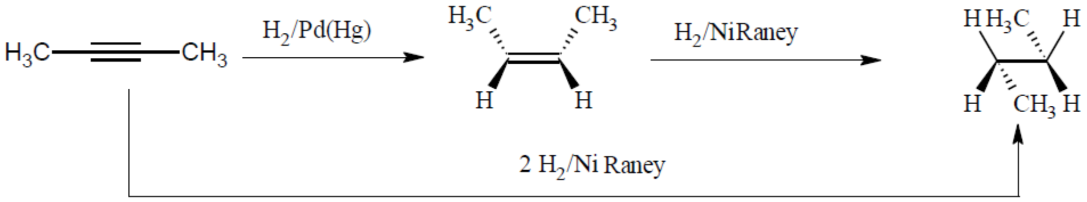
$$R-COOH \xrightarrow[-H_2O]{NaOH} R-COONa \xrightarrow[NaOH+CaO]{\Delta} R-H+Na_2CO_3$$

$$2HCOONa \xrightarrow[CaO]{\Delta} H_2+Na_2CO_3$$

Here **CaO** is used to make the reaction more mild and to keep NaOH dry. It also helps in easy fusion.

By Sabatier and Senderen Reaction

- Here, catalysts used are Raney Ni [An alloy of Ni–Al] and Pd–Pt (Adam's catalyst).
- Temperature range suited for reaction is 300–400°C.
- In case of Raney Nickel reaction is possible at room temperature also.



From the reduction of R–X

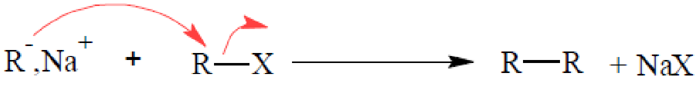
- Here, the reducing agent used is usually Zn + NaOH or HCl or Zn–Cu/acid, Na/alcohol. $LiAlH_4$, $NaBH_4$, $(Ph)_3$ SnH etc

$$R - X + H - H \xrightarrow{Zn/HCl} R - H + HX$$

Using Wurtz Reaction

- In case of **Wurtz reaction**, alkyl halide is treated with **sodium metal** in presence of dry ether to give alkanes.

$$R—X \quad + 2\,Na \longrightarrow R^{-}.Na^{+} + NaX$$



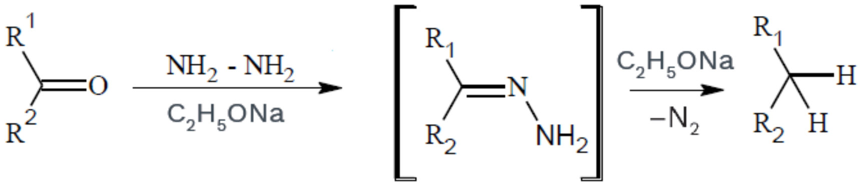
Birch Reduction

In the process, terminal alkenes are reduced to alkanes.

$$R - CH = CH_2 + H_2 \xrightarrow[MeOH]{Na/Liq.NH_3} R - CH_2 - CH_3$$

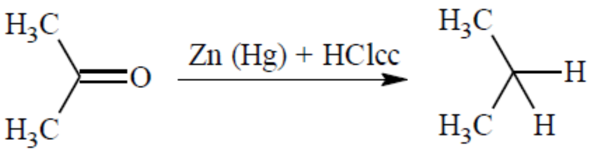
Wolf–Kishner reduction

Carbonyl compounds are reduced into alkanes in presence of hydrazine and a base. The bases used are sodamide, C_2H_5ONa.



Clemmensen reduction

Here, carbonyl compounds are reduced into alkanes by Zn–Hg/HCl as shown below:



Grignard reaction

A compound possessing an active hydrogen atom generally shows this reaction with Grignard reagent.

$$RX + Mg/\text{éther (anhydre)} \longrightarrow RMgX$$

$$RMgX + H_2O \longrightarrow RH + MgXOH$$

Reactivity of alkane

Alkanes are non-reactive towards bases, acids, oxidizing agents etc. due to non-polar nature of C–C and C–H bonds and the inability to donate or accept electrons.

Combustion

Oxidation reactions

(a) Combustion or complete oxidation

$$(C_6H_{2n+2}) + \frac{(3n+1)}{2}O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

$$\text{e.g. } C_2H_6 + \frac{7}{2}O_2 \xrightarrow{\Delta} 2CO_2 + 3H_2O + 1538\,KJ$$

(b) Incomplete combustion

$$CH_4 + O_2 \xrightarrow{\text{Burn}} \underset{\text{Carbon black}}{C} + 2H_2O$$

Carbon black is used in printing ink.

$$2CH_4 + 3O_2 \xrightarrow{\text{Burn}} 2CO + 4H_2O$$

(c) Catalytic oxidation

$$CH_4 + [O] \xrightarrow[\text{100 atm 200°C}]{\text{Cu–tube}} CH_3OH$$

$$CH_3 - (CH_2)_n - CH_3 \xrightarrow[\text{100°C–160°C}]{O_2} (CH_3) - (CH_2)_n - COOH$$

Halogenation

Here H–atoms of alkanes are substituted by X– atom ion.

- Reactivity of halogens(X) is $\mathbf{F_2 > Cl_2 > Br_2 > I_2}$
- Presence of O2 suppresses the reaction.
- Replacement of H-atom is easy and follows the trend: 3° > 2° > 1° > methyl.

For example,

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Final product}}{CCl_4}$$

Mechanism

Initiation

$$Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} \underset{\text{Chlorine free radicals}}{\dot{Cl} + \dot{Cl}}$$

(ii) Propagation

$$\text{(a) } CH_4 + \dot{C}l \xrightarrow{h\nu} \dot{C}H_3 + H-Cl$$

$$\text{(b) } \dot{C}H_3 + Cl-Cl \xrightarrow{h\nu} CH_3-Cl + \underset{\text{Chlorine free radical}}{\dot{C}l}$$

(iii) Termination

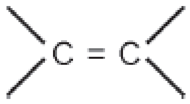
$$\text{(a) } \dot{C}l + \dot{C}l \rightarrow Cl-Cl$$

$$\text{(b) } H_3\dot{C} + \dot{C}H_3 \rightarrow H_3C-CH_3$$

Aromatization

$$\underset{\text{Normal hexane}}{CH_3-(CH_2)_4-CH_3} \xrightarrow[Cr_2O_3-_2Al_2O_3]{\Delta} C_6H_6 + 4H_2\uparrow$$

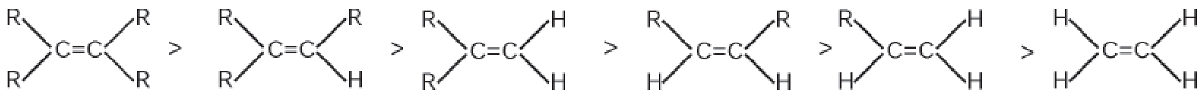
Alkenes Or Olefins



- Alkenes are unsaturated hydrocarbons with a general formula C_nH_{2n}
- The word olefin means making oil. Lower members of the group give oily products on halogenation.
- Unsaturated carbon atoms are sp2 hybridized having a trigonal planar geometry.
- C=C bond has length as 1.34 Å and bond energy is 143.1 kcal per mole.
- Carbon–Hydrogen bond length is 1.1 Å and has bond energy 98.7 kcal per mole.

- Alkenes exhibit chain, ring chain, positional, functional, optical, and geometrical isomerism.

Stability in decreasing order

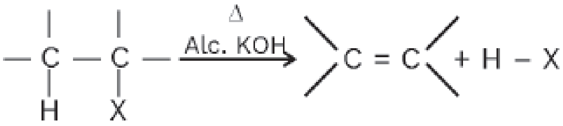


Test of Unsaturation

1. Alkenes decolourize Br_2 in CCl_4 or when in water.
2. They also decolourize 1% of alkaline $KMnO_4$ (Baeyer's Reagent).
3. Ozonolysis gives number and location of double bonds in alkene.

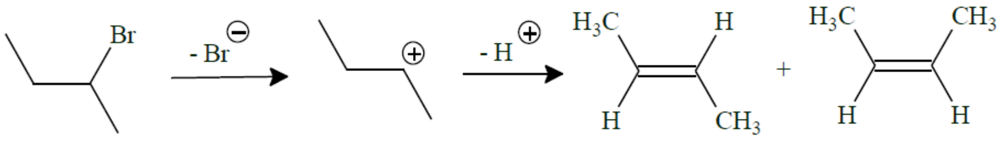
Methods of Preparation of Alkenes

In α, β elimination reactions, By dehydrohalogenation of haloalkanes: Here, reagents used are $C_2H_5O^–$, $(Me)_3COK$, KNH_2, $NaNH_2$, alc. KOH.



By elimination reaction

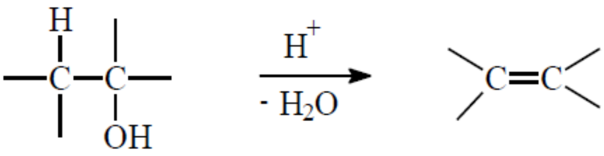
Example: Elimination of HBr from 2-bromobutane.



(E)-But-2-ène **Majoritary**

(Z)-But-2-ène **Minoritary**

Deshydratation of alcohols in acidic conditions



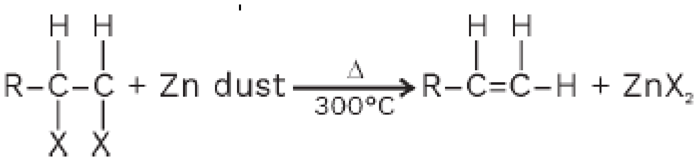
From dehalogenation of dihalogen derivative

From gem dihalides: When gem dihalides are heated with Zn dust and alcohols alkenes are formed.

$$R-CHX_2+2Zn+X_2CH-R\xrightarrow[-2ZnX_2]{\Delta}R-CH=CH-R$$

From vicinal dihalides

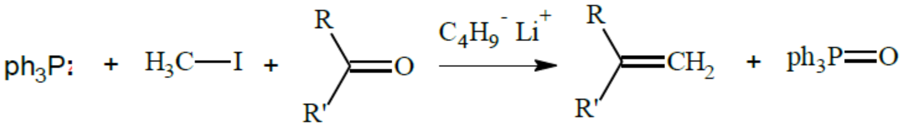
When vicinal dihalides are heated with Zinc dust, alkene having same number of carbon atoms is obtained.



By partial reduction of alkynes

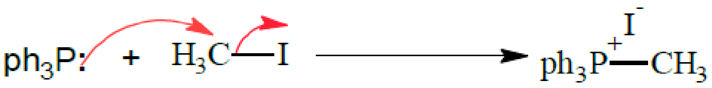
$$R - C \equiv CH + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar}} R - CH = CH_2$$

Wittig reaction: Here, methylene triphenyl phosphorane or phosphorus ylide is treated with a carbonyl compound to prepare an alkene.

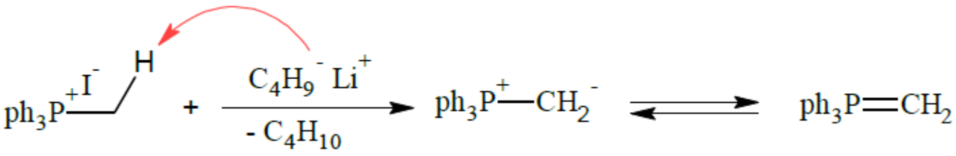


Mechanism

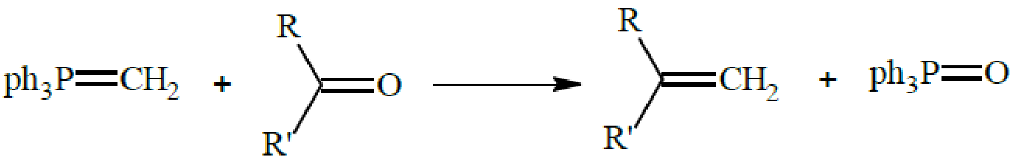
1) Formation of phosphonium salts



2) Action of strong base



3) Action of the ylure with carbonyl



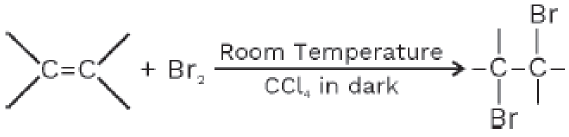
Chemical Properties of Alkenes

Reaction with H2

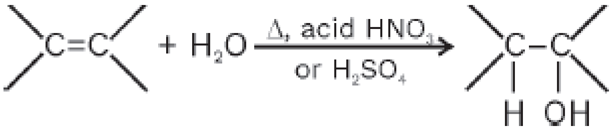
The reaction occurs on surface of catalysts like Ni, Pd or Pt in a cis-syn addition manner.

Reaction with X_2 :

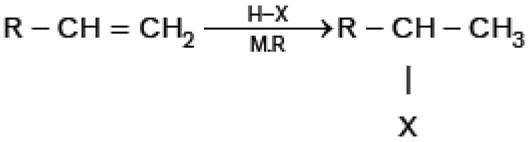
It usually involves trans-addition (Stereospecific)



Reaction with H_2O



Addition with HX

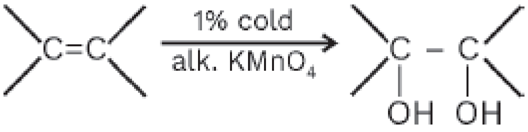


$$R-CH=CH_2 \xrightarrow[M.R]{H-X} R-\underset{\underset{X}{|}}{CH}-CH_3$$

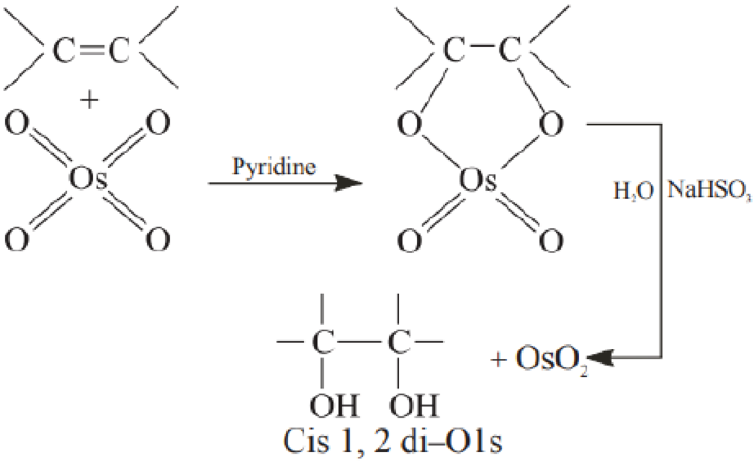
Oxydation or hydroxylation

- Here, hydroxylation occurs by using OsO_4, pyridine or $NaHSO_3/H_2O$, 1% alkaline $KMnO_4$ (Baeyer's reagent).
- On hydroxylation, all of these reagents give syn addition.

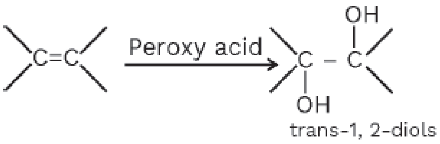
For example



With OsO_4 , pyridine, $NaHSO_3$ /H_2O

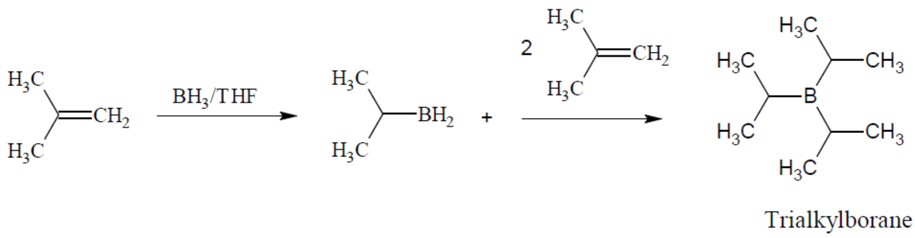


Anti-hydroxylation is not so common and is shown as follows:

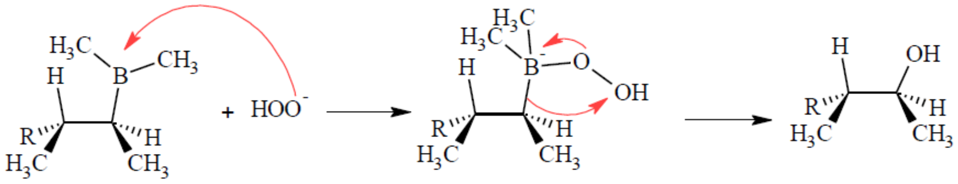


Hydroboration oxidation

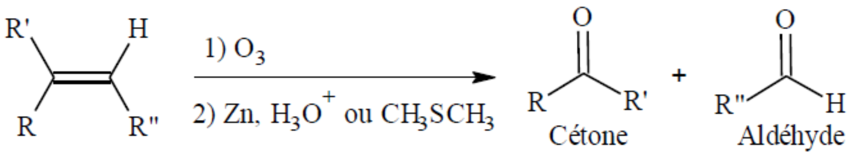
It is used to prepare alcohols following anti- Markovnikov’s rule.



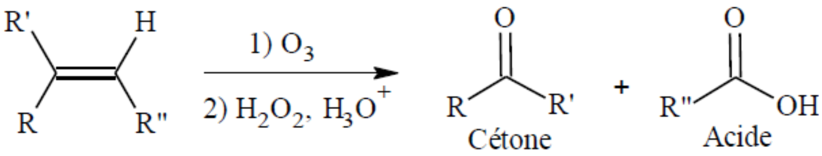
$$H_2O_2 + HO^- \longrightarrow H\text{-}O\text{-}O^- + H_2O$$



Ozonolyse



If Zn is not used, carbonyl compounds get oxidized into acids.



Alkynes

$$\overset{sp}{-C} \equiv \overset{sp}{C-}$$

- Alkynes have a general formula of (C_nH2_{n-2}).
- All the terminal alkynes have weakly acidic nature and acidic nature decreases in following order:

$R{-}C{\equiv}H > R{-}CH{=}CH_2 > R{-}CH_3$

$CH{\equiv}CH > CH_3{-}C{\equiv}CH > CH_3{-}CH_2{-}C{\equiv}CH > .....$

- Alkynes are generally less reactive to electrophilic addition because greater activation energy is needed as formation of a less stable cyclic reaction intermediate species takes place.

Test of Terminal Alkynes

- Terminal alkynes on reaction with with ammonical silver nitrate (AgNO3) give a white precipitate of R–C≡CAg.
- Alkynes give a red precipitate of R–C≡C.Cu with ammonical CuCl.

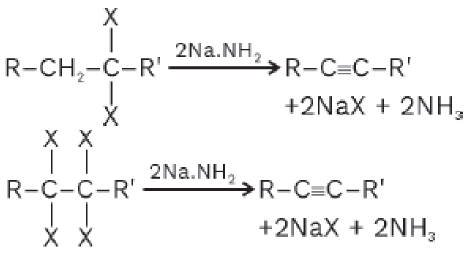
Preparation of Alkynes

Using carbides: Carbides on hydrolysis give alkynes as follows

$$CaO + 3C \xrightarrow[-CO]{1800\text{–}2100^\circ C} CaC_2 \xrightarrow{2H_2O} C_2H_2 + Ca(OH)_2$$

$$Mg_2C_3 \xrightarrow{4H_2O} CH_3 - C \equiv CH = 2Mg(OH)_2$$

By elimination reaction: Here, dihalides undergo α, β-elimination reaction with NaNH2 or alc. KOH to give alkynes.

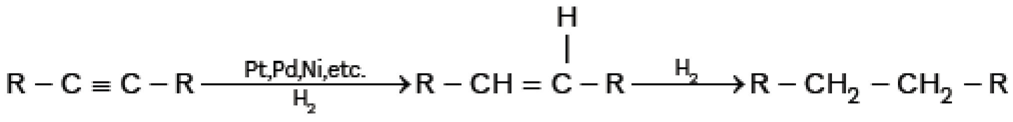


$$R-CH_2-\underset{X}{\overset{X}{C}}-R' \xrightarrow{2Na.NH_2} R-C\equiv C-R' + 2NaX + 2NH_3$$

$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-R' \xrightarrow{2Na.NH_2} R-C\equiv C-R' + 2NaX + 2NH_3$$

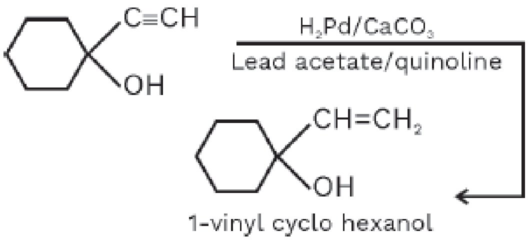
Reactivity of alkyne

Hydrogenation



$$R - C \equiv C - R \xrightarrow[H_2]{Pt,Pd,Ni,etc.} R - CH = \overset{H}{C} - R \xrightarrow{H_2} R - CH_2 - CH_2 - R$$

Lindlar's catalyst ($PdCO_3/BaCO_3$) poisoned with quinoline or lead acetate is generally used for selective hydrogenation in preparation of alkene only.



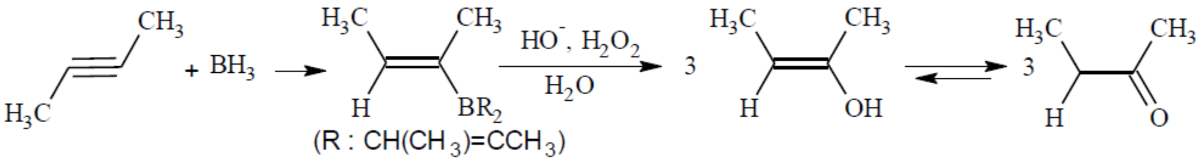
Addition of HX

$$\text{R-C}\equiv\text{C-H} \xrightarrow{\text{HBr}} \text{R-CBr=CH}_2 \xrightarrow{\text{HBr}} \text{R-CBr}_2\text{-CH}_3$$

Addition of X_2

$$\text{R-C}\equiv\text{C-R'} \xrightarrow[\text{CCl}_4]{\text{Br}_2} \text{R-CBr=CBr-R' (E)} \xrightarrow[\text{CCl}_4]{\text{Br}_2\text{ (excès)}} \text{R-CBr}_2\text{-CBr}_2\text{-R'}$$

Hydratation by hydroboration



ozonolyse and oxidation

$$\text{R-C}\equiv\text{C-R'} \xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) KMnO}_4\text{, HO}^-\text{, H}_2\text{O, }\Delta} \text{RCOOH + R'COOH}$$

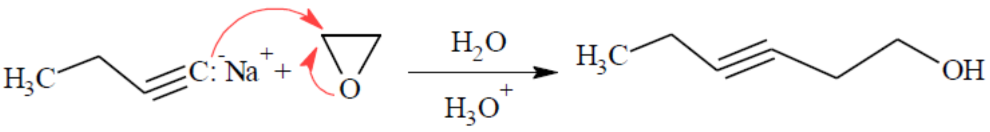
$$\text{R-C}\equiv\text{C-R'} \xrightarrow{\text{O}_3\text{, Zn, CH}_3\text{COOH}} \text{RCOOH + R'COOH}$$

Formation of acetylide

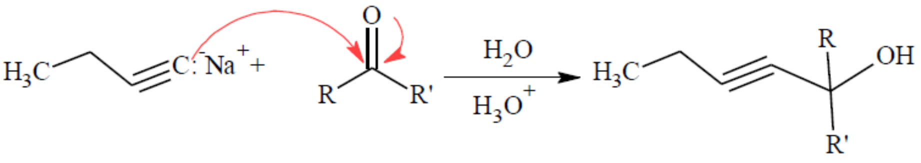
$$\text{CH}_3\text{–C}\equiv\text{C–H + NaNH}_2 \longrightarrow \text{CH}_3\text{–C}\equiv\text{C}^-\text{ Na}^+\text{ + NH}_3$$

$$\text{CH}_3\text{–C}\equiv\text{C–H + Na} \longrightarrow \text{CH}_3\text{–C}\equiv\text{C}^-\text{ Na}^+\text{ + 1/2H}_2$$

Reaction with epoxide



Reaction with ketone or aldehyde



Aromatic Hydrocarbons

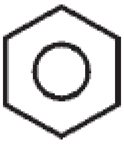
Aromatic word has been derived from Greek word Aroma which generally means pleasant smell. Benzene and compounds which resemble benzene in chemical properties are known as Benzenoid compounds or Aromatic compounds. Aromatic hydrocarbons or Arenes have a general formula **C_nH_{2n6y}** (By represents No. of benzene Rings). and **$n > 6$**. main sources are coaltar coal, Petroleum etc.

Aromaticity and Hunckel (4n + 2)Rule

Aromaticity is defned as “An aromatic compound having a reasonably planar cyclic structure, with **$(4n + 2)\pi$** electron clouds and having unusual stablity because of delocalization of π electron.

Benzene

Benzene is structurally depicted as shown below:

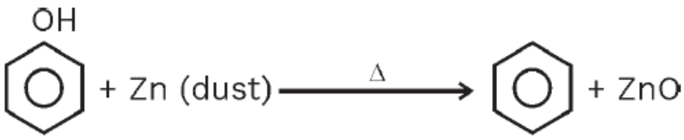


- Benzene was discovered by Faraday in 1825.
- The structure of benzene was given by Kekule in 1865.

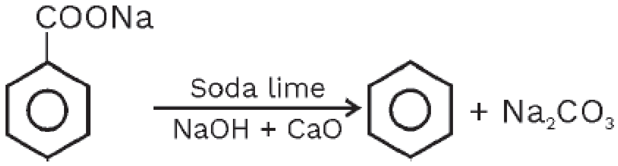
Methods of Preparation of Benzene

From light oil fraction : Light oil fraction of coal-tar consists benzene, xylene, toluene. This mixture on fractional distillation produces benzene as one of the product.

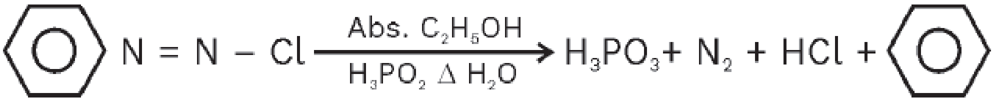
Using acetylene : On passing acetylene through red hot tube polymerizes into benzene.



Using benzoic acid : Chlorobenzene or halobenzene on reduction with alcoholic Na or Ni– Al alloy gives benzene.



Using benzene diazonium chloride: Benzene diazonium chloride on reaction with hypo phophorus acid produces benzene.



Physical Properties

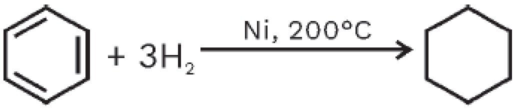
- It is highly inflammable.
- Freezing point of benzene is 5.5°C.
- Its boiling point is 80°C.
- It is immiscible in water.
- A good solvent for resin, rubber and fat.
- Benzene is lighter than water.
- It is colourless volatile, liquid.

Chemical Properties

Benzene has three alternative double bonds; still, it doesn't show usual addition reactions or test of unsaturation with bromine water or Baeyer's reagent. It gives electrophilic substitution reaction due to phenomenon of resonance or complete delocalization of six π electrons.

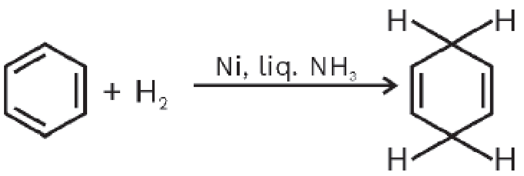
Addition reaction

Hydrogenation



Cyclohexane

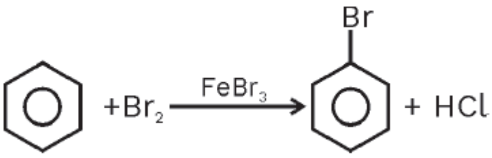
Birch reduction (selective hydrogenation)



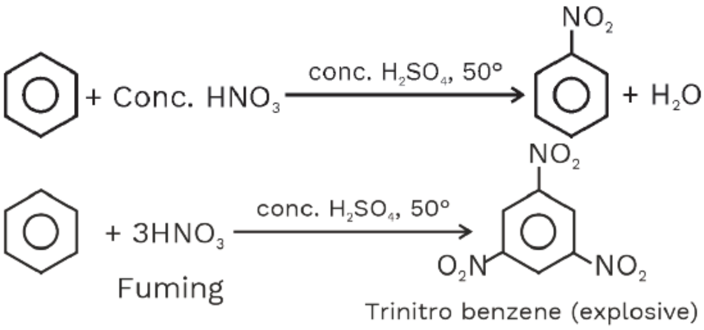
1, 4-dihydrobenzene

Electrophilic substitution reaction

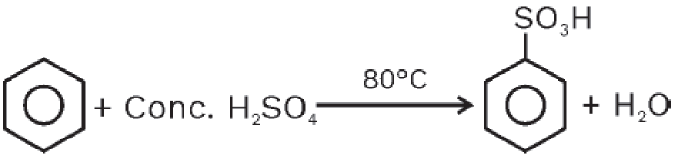
Halogenation



Nitration

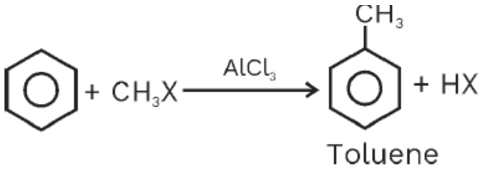


Sulphonation

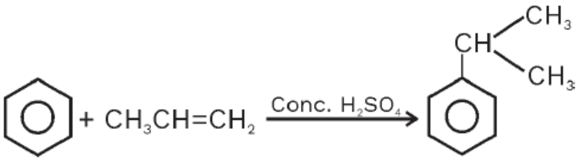


Friedel–Crafts reaction: In this,alkylation or acylation reaction takes place in presence of catalysts like BF_3, $ZnCl_2$, anhyd. $AlCl_3$, $FeCl_3$, or $SnCl_4$.

- **Alkylation:** alkyl halide in presence of anhyd. $AlCl_3$; alcohol alkene in presence of conc.H_2SO_4 can be used.

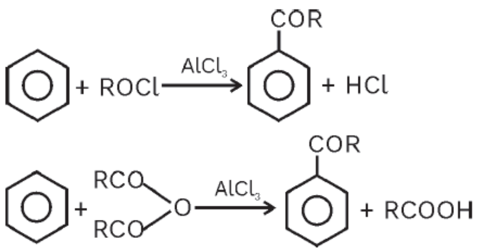


- **By alkene**

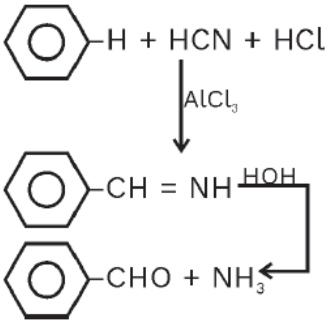


Acylation:

Acid anhydrides or acid halides can be used with anhyd. $AlCl_3$.



Gatterman aldehyde reaction



Halogen-derivatives

Halogenated derivatives are compounds that have a carbon-halogen bond. The general formula of a **monohalogenated** hydrocarbon is **R-X** where **X = I, Br, Cl, F**.

They are used in organic chemistry as reagents and as solvents, chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), carbon tetrachloride (CCl_4).

Halogenated derivatives are classified into primary (**RCH_2X**), secondary (**R_1R_2CHX**), and tertiary (**$R_1R_2R_3CX$**) derivatives.

Preparation of halogen alkane

Radicular Halogenation

$$R\text{-}H + X_2 \xrightarrow{\Delta \text{ ou } h\upsilon} R\text{-}X + H\text{-}X \quad (X = Cl \text{ ou } Br)$$

Electrophilic Additions to alkene

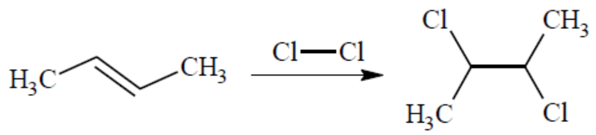
Addition of H-X: MARKOVNIKOV rule

$$CH_3CH_2CH{=}CH_2 \xrightarrow{HBr} CH_3CH_2CHBrCH_3$$

Anti MARKOVNIKOV rule

$$CH_3CH_2CH{=}CH_2 \xrightarrow[ROOR]{HBr/h\upsilon} CH_3CH_2CH_2CH_2Br$$

Addition of (X-X)



Electrophilic Additions to alkyne

MARKOVNIKOV rule

$$CH_3CH_2C\equiv CH \xrightarrow{2\ HBr} CH_3CH_2CBr_2CH_3$$

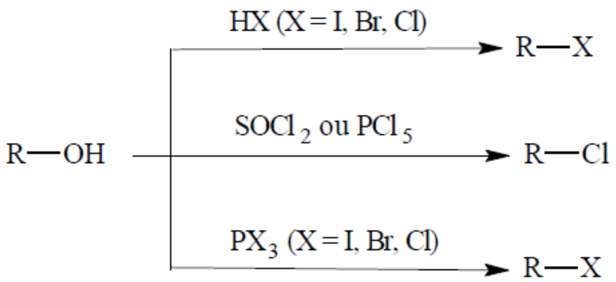
Anti MARKOVNIKOV rule

$$CH_3CH_2C\equiv CH \xrightarrow[ROOR]{2\ HBr/h\upsilon} CH_3CH_2CH_2CH_2Br_2$$

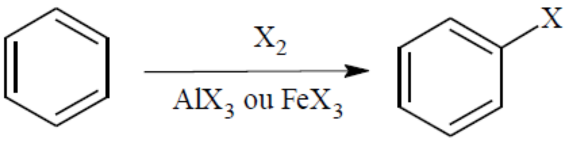
Addition of (X-X)

$$R\text{-}C\equiv C\text{-}R' \xrightarrow[CCl_4]{Br_2} R\text{-}CBr{=}CBr\text{-}R'\ (E) \xrightarrow[CCl_4]{Br_2} R\text{-}CBr_2\text{-}CBr_2\text{-}R'$$

Nucleophilic substitution from alcohols



Halogenation of aromatic compounds



Reactivity

Nucleophilic Substitution

Nucleophile + RX $\longrightarrow$ **Product**

(H_2O, HO-) + RX $\longrightarrow$ ROH (**Alcohol**) + (HX, X^-)

(R'OH, RO- **alcoholate**) + RX $\longrightarrow$ R'OR (Ether) + (HX, X^-)

NH_3 + RX $\longrightarrow$ RNH_2 (Amine) + HX

RNH_2 + R'X $\longrightarrow$ RNHR' (**Secondary amine**) + HX

RNHR' + R"X $\longrightarrow$ RR'NR" (**Tertiary amine**) + HX

HS^- (ion hydrogenosulfure) + RX $\longrightarrow$ RSH (Thiol) + X^-

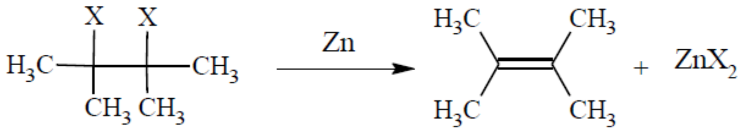
RS^- (thiolate) + R'X $\longrightarrow$ RSR' (Thioether) + X^-

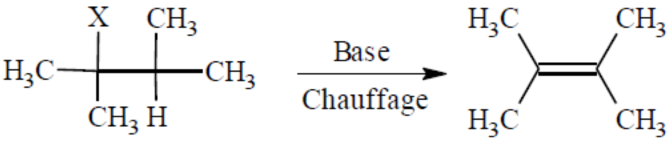
CN^- (**Cyanide**) + RX $\longrightarrow$ RCN (Nitrile) + X^-

$RC{\equiv}C^-$ (**Acetylide**) + R'X $\longrightarrow$ $R'C{\equiv}CR$ (**Alkyne**) + X^-

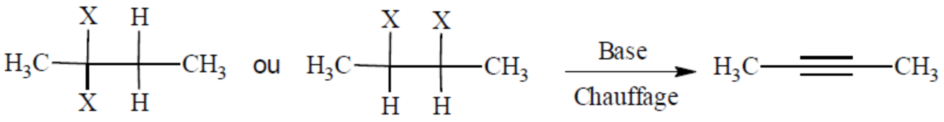
Elimination

Formation of alkene





Formation of alkyne



Wurtz reaction

$$CH_3CH_2CH_2Cl + 2Na \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_3$$

Grignard reaction

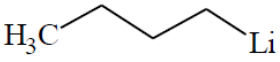
$$R\text{-}X + Mg \xrightarrow[\text{anhydre}]{\text{ether}} R\text{-}MgX$$

Organometallics

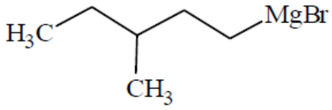
Organometallic compounds are hydrocarbons that have **carbon-metal** bonds. Their general formula is **R-M** where R = alkyl, alkenyl, alkynyl, aryl and M (Metal) = Na, K, Li, Mg, Ca, Al, B, Sn, Pb, Zn, Cd, Ni, Cr, Hg.

Nomenclature

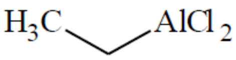
Organometallics are named by the name of the radical **R** followed by that of the **metal**. When the molecule has halogens, they are at the end of the name of compound.



n-Butyllithium



3-méthylpentylmagnesium bromide



ethylaluminium dichloride

Preparation of organometallics

Formation of organomagnesium compounds

$$R\text{-}X + Mg \xrightarrow[\text{anhydre}]{\text{ether}} R\text{-}MgX$$

Formation of organolithium compounds

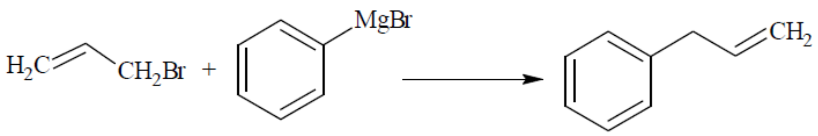
$$R\text{-}X + 2Li \xrightarrow{\text{Hexane}} R\text{-}Li + LiX$$

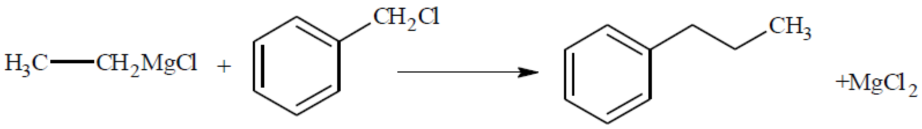
Reactivity

Acido-basic reaction

$$CH_3CH_2CHBrCH_3 + \xrightarrow{Mg} CH_3CH_2CH(MgBr)CH_3 + \xrightarrow{H_2O} CH_3CH_2CH_2CH_3$$

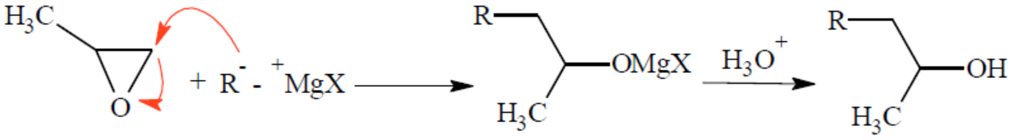
Nucleophilic Substitution



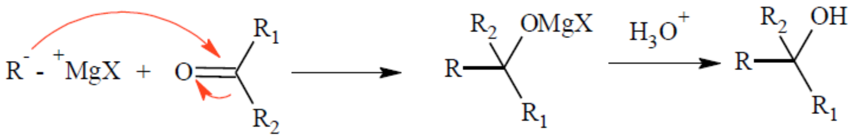


Electrophilic Additions

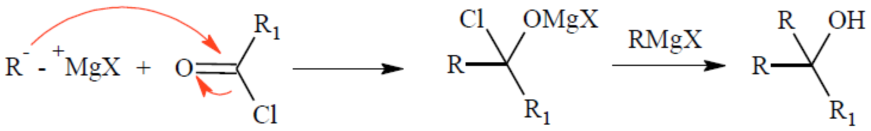
With epoxides



With carbonyles compounds



With acetyl chloride



With nitrile