HYDROCARBON

Types of organic reactions: There are mainly four types of organic reactions.

1. Substitution reaction
2. Addition reaction
3. Elimination reaction
4. Rearrangement reaction

① Substitution reaction:

A reaction in which an atom or group of atom is replaced by another atom or group of atoms without causing any change in the structure of remaining part of molecule is known as substitution reaction. for eg.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3-Cl + HCl$$
(chloromethane)

$$CH_3-Cl + KOH_{(aq.)} \longrightarrow CH_3-OH + KCl$$
(methanol)

$$CH_3-CH_2-Br \xrightarrow{aq.\ KOH} CH_3-CH_2-OH + KBr$$
ethanol

② Addition reaction:

A reaction in which atom or group of atoms are added to substrate to give single product is known as addition reaction. for eg.

$CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$

$CH \equiv CH + H_2 \longrightarrow CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$

$CH_2 = CH_2 + HCl \longrightarrow CH_3 - CH_2 - Cl$

$CH_2 = CH_2 + Cl_2 \longrightarrow$ $ClCH_2 - CH_2Cl$

1, 2 - dichloro ethane.

(3.) Elimination reaction:

A reaction in which product is formed by the removal of small molecules such as H_2O, NH_3, HCl etc. from the organic compounds is known as elimination reaction, for e.g

$$CH_3 - CH_2 - Cl + KOH \longrightarrow CH_2 = CH_2 + KCl + H_2O$$

$$CH_3 - CH_2 - OH + H_2SO_4 \xrightarrow[\text{conc.}]{} CH_2 = CH_2 + H_2SO_4 \cdot H_2O$$

(4) Rearrangement reaction

A reaction in which product is formed by the rearrangement of reactant is known as rearrangement of reactant. for e.g.

$$CH_3 \cdot CH_2 CH_2 CH_3 \xrightarrow[\Delta]{AlCl_3} CH_3 - \overset{CH_3}{\underset{|}{C}}H - CH_3$$

$$NH_4CNO \xrightarrow{\text{rearr.}} NH_2 - CO - NH_2$$

Cracking :-

The process of decomposition of higher boiling point hydrocarbons into lower B.P. hydrocarbons or strong heating is called cracking (Pyrolysis). for e.g. heating of dodecane at (500 to 700)°C gives mixture of alkane and alkene

Dodecane ($C_{12}H_{26}$) →
- Decane ($C_{10}H_{22}$) + ethane (C_2H_4)
- Nonane (C_9H_{20}) + Propene (C_3H_6)
- Octane (C_8H_{18}) + Butene (C_4H_8)
- Heptane (C_7H_{16}) + Pentene (C_5H_{10})
- Hexane (C_6H_{14}) + Hexene (C_6H_{12})
- Pentane (C_5H_{12}) + Heptene (C_7H_{14})

example 2.

$CH_3-(CH_2)_8-CH_3 \longrightarrow CH_3-(CH_2)_6-CH_3 + CH_2=CH_2$

decane → octane + ethene

Types of cracking :

(1.) Thermal cracking :-

The cracking of hydrocarbon by the application of heat only is called thermal cracking.

(2.) catalytic cracking :-

The cracking of hydrocarbon at low temperature in the presence of suitable catalist such as, Alumino - Silico (Al$_2$O$_3$ - SiO$_2$) is known as catalytic cracking.

(3.) Steam cracking :-

The cracking of hydrocarbon in which

mixture of steam and hydrocarbon is heated for short time followed by immediate cooling is called steam cracking.

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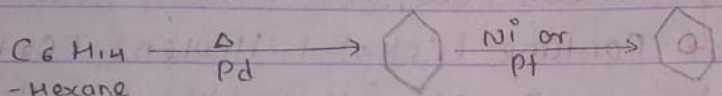
Aromatization or Reforming:-

The process of conversion of acyclic or and alicyclic compounds into aromatic compounds in the presence of suitable catalyst is known as reforming or aromatization. It involves cyclization dehydro-genation and sometimes isomerism

for eg



Cyclohexane Benzene

Bergius Process:-

The process of heating powdered coal with hydrogen at 450°c temp' and 300 atm pressure in the presence of catalyst Fe_2O_3 to give mix. of alkanes and arenes is known as Bergius process.

$$C + H_2 \xrightarrow[Fe_2O_3]{450^\circ C,\ 300\ atm} \text{mix. of alkane + arenes}$$

powdered coal

Fischer:-

In this process steam is passed over hot coke to form water gas which is heated at 300°c and 5-10 atm pressure in the presence of Ni catalyst to give mix. of alkanes.

$$\underset{\text{(coke)}}{C} + \underset{\text{(Steam)}}{H_2O} \xrightarrow{\Delta} \underset{\text{water gas}}{[CO + H_2]} \xrightarrow[5\text{-}10\ atm]{300^\circ C,\ Ni} \text{alkane} + H_2O$$

Quality of gasoline and octane number :-

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Gasoline burn in internal engines but some low quality gasoline burns with unusally producing metallic sound which is known as knocking; knocking decreases efficiency of engines gasoline that knocks badly is called low quality gasline and that causes no knocking is called high quality gasoline. Quality of gasoline is expressed in terms of octane number.

Two extreme compounds are taken such as n-Heptane and iso-octane. n-Heptane knocks badly and its octane number is taken as zero while iso-octane burns without knocking and it's octane number taken as 100.

The octane no. of other fuels is defined as the Percentage of iso-octane in the mixture of iso-octane and n-Heptane that causes some knocking as the fuel. e.g octane number of a fuel is 80, it means that the fuel causes some knocking as a mixture of 80% iso-octane and 20% n-Heptane.

* Anti knocking agent :-

Those chemical substances that reduces knocking property of gasoline or improves octane no. are called anti knocking agents (gasoline additives).

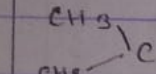
e.g $Fe(CO)_5$ (Iron carbonyl), $Pb(C_2H_5)_4$ (tetraethyl lead).

Nomenclature of organic compound

1. Alkane :- (C_nH_{2n+2})

Formula	IUPAC name	common name
CH_4	methane	marsh gas
CH_3-CH_3	ethane	ethane
$CH_3-CH_2-CH_3$	Propane	propane
$CH_3-CH_2-CH_2-CH_3$	Butane	n-Butane
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$	2-methyl Propane	ISO-butane
$CH_3-CH_2-CH_2-CH_2-CH_3$	Pentane	n-Pentane
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$	2-methyl butane	ISO-Pentane
$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$	2,2-dimethyl Propane	Neo-Pentane
$CH_3-\underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$	3-methyl hexane	Sec-heptane

2. Alkene (C_nH_{2n})

Formula	IUPAC name	Common name
C_2H_4	ethane	ethylene
C_3H_6	propene	propxlene
$H_2C-CH=CH-CH_3$	But 2-ene	β - butxlene
$H_2C=CH-CH_2-CH_3$	But 1-ene	α - butxlene
	2-methyl propane	Iso butxlene
$CH_2=CH-CH_2-CH_2-CH_3$		
$CH_3-CH=CH-CH_2-CH_3$		
$CH_2=CH-CH=CH_2$	1,3-Butandiene But-1,3-diene	

3. Alkyne (C_nH_{2n-2})

Formula	IUPAC name	Common name
C_2H_2, $CH\equiv CH$	ethyne	Acetxlene
C_3H_4, $CH\equiv C-CH_3$	propxne	methyl acetxlene
$HC\equiv C-CH_2-CH_3$	But-1-yne	ethxlacetxlene
$H_3C-C\equiv C-CH_3$	But-2-yne	dimethyl acetxlene

4. Alkyl halides $(C_nH_{2n+1})X$ (where X = Cl, Br, I etc)

Compounds	IUPAC name	Common name
CH_3-Cl	Chloro methane	methyl chloride
CH_3-CH_2-Br	bromo - ethane	ethyl bromide
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Cl$	1-chloro-2-methyl Propane	Iso-butxl chloride
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2-Br$	1-bromo-2,2-dimethyl Propane	Neopentxl bromide

5. Alcohol ($C_nH_{2n+1}OH$)

Compounds	IUPAC name	Common name
CH_3OH	methanol	methyl alcohol
C_2H_5OH	ethanol	ethyl alcohol
$CH_3-CH_2-CH_2-OH$	1 - propanol	n - propyl alcohol
$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$	2 - Propanol	Iso propyl alcohol
$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$	2 - propanol	Sec butxl alcohol
$\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$	Ethane-1,2-diol	Ethxlene glycol
$\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$	Propan-1,2,3-triol	Glycerol / Glycerin

6. Ether ($C_nH_{2n+1}OC_nH_{2n+1}$)

Compounds	IUPAC name	common name
CH_3-O-CH_3	methoxy methane	Dimethyl ether
$CH_3-O-CH_2-CH_3$	methoxy ethane	ethyl methyl ether
$CH_3-CH_2-O-CH_2-CH_3$	ethoxy ethane	Die ether
$CH_3-CH_2-CH_2-O-CH_2-CH_3$	1-ethoxy propane	ethyl-n-propyl ether
$CH_3-\underset{\underset{CH_3}{|}}{CH}-O-CH_2-CH_3$	2-ethoxy propane	ethyl isopropyle ther

7. Aldehyde ($C_nH_{2n+1}CHO$)

Compounds	IUPAC name	common name
$HCHO$	methanal	formaldehyde (formalin)
CH_3CHO	ethanol	Acetaldehyde
CH_3-CH_2-CHO	propanol	propional dehyde
$CH_3-CH_2-CH_2-CHO$	bulanal	~~Butyral~~ Butyral dehyde
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CHO$	2 methyl propanol	Iso-butylad dehyde
$CH_3-CH_2-CH_2-CH_2-CHO$	Pentanal	n-valerala dehyde

8. Ketones ($C_nH_{2n+1}COC_nH_{2n+1}$)

Compounds	IUPAC	Common
CH_3COCH_3	Propanone	Acetone
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$	2-butanone	ethyl methyl ketone
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$	3-Pentanone	dimethyl ketone
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$	2-Pentanone	methyl n propyl ketone
$CH_3-\underset{CH_3}{\underset{\|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3$	3-methyl butan-2-one	methyl isopropyl ketone

9. Carboxylic acids ($C_nH_{2n+1}COOH$)

Compounds	IUPAC	Common
$H-COOH$	methanoic acid	formic acid
CH_3-COOH	ethanoic acid	Aceticacid (vinega)
$CH_3-CH_2-CH_2-COOH$	Butanoic acid	n-Butyreic acid
CH_3-CH_2-COOH	propanoic acid	propionic acid
$CH_3-\underset{OH}{\underset{\|}{CH}}-COOH$	2-hydroxy propanoic acid	2-hydroxy propanoic acid
$\begin{matrix}COOH\\\|\\COOH\end{matrix}$	ethan dioic acid	Oxylic acid

Derivatives of carboxylic acid

10. Esters ($C_nH_{2n+1}COOR'$)

Compounds	IUPAC name	Common name
$H-COOR'$	Alkyl methanoate	Alkyl formate
CH_3-COOR'	Alkyl ethanoate	Alkyl acetate
CH_3-CH_2-COOR'	Alkyl propanoate	Alkyl propionate
$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5$	Ethyl ethanoate	Ethyl acetate

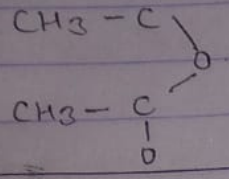
11. Acid halide ($C_nH_{2n+1}COX$)

Compound	IUPAC name	Common name
$H-COX$	methanoyl halide	formyl halide
CH_3-COX	ethanoyl halide	acetyl halide
CH_3-CH_2-C-X	propanoyl halide	propion halide

12. Amide ($C_nH_{2n+1}CONH_2$)

Compound	IUPAC name	Common name
$H-\overset{O}{\overset{\|}{C}}-NH_2$	methan amide	formamide
CH_3-CONH_2	Ethan amide	acetamide
$CH_3-CH_2-CONH_2$	Propan amide	Propionamide

13. Anhydride C_nH_{2n+1}

Compound	IUPAC name	Common name
	ethanoic anhydride	acetic anhydride

14. Amines ($C_nH_{2n+1}NH_2$)

Compound	IUPAC name	Common name
CH_3-NH_2	methan amine	methyl amine
$CH_3-CH_2-NH_2$	ethan amine	ethyl amine
$CH_3-CH_2-CH_2-NH_2$	1-propan amine	cimine propane
$CH_3-\underset{CH_3}{CH}-NH_2$	2-amino propane	Iso-propyl amine

15. Nitro compound ($C_nH_{2n+1}NO_2$)

Compound	IUPAC name	Common name
CH_3NO_2	Nitro methane	–
$CH_3CH_2NO_2$	Nitro ethane	–
$CH_3-CH_2-CH_2-NO_2$	1-Nitro propane	–
$CH_3-\underset{NO_2}{CH}-CH_3$	2-nitro propane	–

(Alkane)

General method of Preparation of alkane

① By the addition of hydrogen to unsaturated hydrocarbons:

When unsaturated hydrocarbon heated with hydrogen in the presence of catalyst (Ni or Pt or Pd etc) gives corresponding alkanes. The process of addition of hydrogen is known as hydrogenation. for e.g

$$R-CH=CH-R \xrightarrow[\Delta]{H_2/Ni} R-CH_2-CH_2-R$$

$$CH_2=CH_2 \xrightarrow[\Delta]{H_2/Ni} CH_3-CH_3$$

$$CH_2CH=CH_2 \xrightarrow[\Delta]{H_2/Ni} CH_3-CH_2-CH_3$$

$$CH_3-CH=CH_2-CH_3 \xrightarrow[\Delta]{H_2/Ni} CH_3-CH_2-CH_2-CH_3$$

By the reduction of Haloalkanes:-

When haloalkane treated with Zn in the presence of HCl or Lithium Aluminium Hydride ($LiAlH_4$), alkanes are formed.

$$CH_3-Cl + 2[H] \xrightarrow{Zn/HCl} CH_4 + HCl$$

$$CH_3CH_2-Cl + 2[H] \xrightarrow{LiAlH_4} CH_3-CH_3 + HCl$$

$$CH_3-\underset{Br}{CH}-CH_3 + 2[H] \xrightarrow{LiAlH_4} CH_3-CH_2-CH_3 + HBr$$

(3) Wurtz reaction:

When haloakane or alkyl halide are heated with Na, in the presence of dry ether, alkanes are formed. This reaction is known as wurtz reaction. for e.g

$$2CH_3-CH_2-Cl \xrightarrow{\text{dry ether/Na}} CH_3-CH_2-CH_2-CH_3 + 2NaCl$$

$$2CH_3-Cl + 2Na \xrightarrow{Na/\text{dry ether}} CH_3-CH_3 + 2NaCl$$

$$2CH_3-\underset{Br}{\underset{|}{CH}}-CH_3 \xrightarrow{Na/\text{dry ether}} CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3 + 2NaBr$$

(4) From Grignard reagent:

Alkyl magnesium halide ($RMgX$) is known as Grignard reagent. It is prepared by heating alkyl halide with Mg in the presence of dry ether. for e.g

$$R-X + Mg \xrightarrow[\Delta]{\text{dry ether}} RMgX$$

$$CH_3-Cl + Mg \xrightarrow[\Delta]{\text{dry ether}} CH_3-MgCl$$

Alkanes are prepared by the hydrolysis of Grignard reagent

$$CH_3MgCl + H-OH \longrightarrow CH_4 + Mg(OH)Cl$$

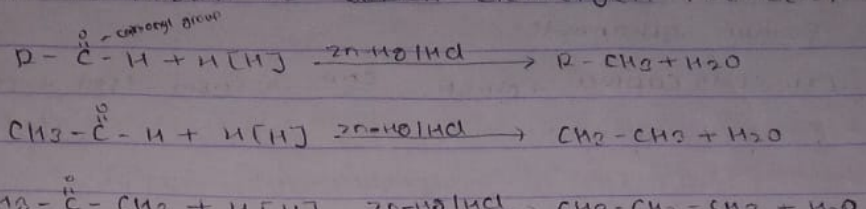
$$CH_3CH_2MgI + H-OH \longrightarrow CH_3-CH_3 + Mg(OH)I$$

(5) By the reduction of aldehyde and ketones:

(a) By clemensen reduction:

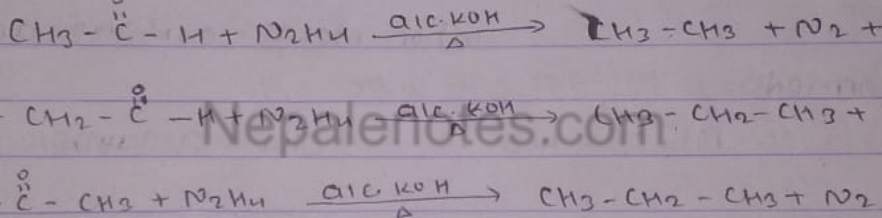
When aldehyde and ketones are treated with Zn-Hg in the presence of HCl, alkanes are formed.

This reaction is known as ~~clemmen~~ clemeryen reduction.



(b) Wolf-kishner reduction :-

When aldehyde and ketone are heated with hydrazine (NH_2-NH_2) in the presence of alcoholic KOH, alkanes are formed. This reaction is known as wolf-kishner reduction.



(b) From salt of carboxylic acid :

(a) By soda-lime method (Decarboxylation) :-

The mixture of NaOH and CaO (lime) in 3:1 ratio is called soda-line. When salts of carboxylic acid are heated with soda-lime alkanes are formed. This reaction is known as decarboxylition because it involves removal of carboxyal group from the molecule or CO_2 from organic compound.

$CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$

Sodium ethanoate

$CH_3CH_2COONa + NaOH \xrightarrow[\Delta]{CaO} CH_3-CH_3 + Na_2CO_3$

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(b) By Kolbe's electrolytic method :-

When salt of mono carboxylic acids are electrolysed, alkanes are formed.

$CH_3COONa + H_2O \xrightleftharpoons{\text{electrolysis}} CH_3-CH_3 + CO_2\uparrow + NaOH$

(7) By hydrolysis of carbide :-

When metal carbides are hydrolised, alkanes are formed.

$Al_4C_3 + H_2O \longrightarrow CH_4 + Al(OH)_3$

* Physical properties of alkanes :-

1. Physical state:

First four members of alkane are colourless gases next 11 members are colourless liquid and higher members are waxy solid.

2. Solubility:

Alkanes are insoluble in water but soluble in organic solvents such as ether, benzene, alcohol etc.

3. melting and boiling point:

m.p and B.P of alkanes increases with increase in molecular mass, due to increase in vander waal's force of attraction.

- For isomeric alkanes, melting and boiling points decrease with increasing branching. As branching increases molecule takes spherical shape and surface area decrease. So, van der wall's force also decreases.

* Chemical Properties of alkane:-

1. Halogenation:

The reaction in which one hydrogen atom of alkan

is replaced by halogen atom is called halogenation. for e.g

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3-Cl + HCl$$

$$CH_3-Cl + Cl_2 \xrightarrow{h\nu} CH_2-Cl_2 + HCl$$

$$CH_2-Cl_2 + Cl_2 \xrightarrow{h\nu} CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

2. Nitration:

The reaction in which one hydrogen atom of alkane is replaced by NO_2 group is called nitration. Nitration specially carried out in the presence of fuming HNO_3. (conc. HNO_3 + conc. H_2SO_4). for e.g

$$CH_4 + HNO_3 \xrightarrow[\text{fuming}]{} CH_3-NO_2 + H_2O$$

$$C_6H_{14} + HNO_3 \longrightarrow C_6H_{13}-NO_2 + H_2O$$

3. Sulphonation:

The reaction in which one hydrogen atom of alkane is replaced by sulphonic acid is called sulphonation.

$$C_7H_{16} + H_2SO_4 \xrightarrow[\text{fuming}]{\Delta} C_7H_{15}-SO_3H + H_2O$$

4. Oxidation:

Alkanes on complete oxidation gives CO_2 and H_2O with the release of energy.

$CH_4 + O_2 \xrightarrow{\text{burn}} CO_2 + H_2O + E$

5. Reforming:

The reaction Produces Branched Alkanes and so is use ful in improving octane number. Reforming is the process of increasing the amount of cycloakanes and Hydrocarbons containing Benzene Rings, to improve octane number. This can produce Branched and cyclic Hydrocarbons and is used to improve octane number.

(Alkenes)

Isomerism in alkene:-

Alkene shows chain and position isomerism.

(i) Chain isomerism :- $CH_3 - CH_2 - CH = CH_2 \longrightarrow$ 1- Butene

$CH_3 - \underset{CH_3}{\overset{|}{C}} = CH_2 \longrightarrow$ 2-methyl-1- Propene

(ii) Position isomerism :- $CH_3 - CH_2 - CH = CH_2 \longrightarrow$ 1- Butene

$CH_3 - CH = CH - CH_3 \longrightarrow$ 2-Butene

General methods of Preparation of alkenes:-

① By dehydration of alcohol:

When alcohols are heated with dehydrating agents such as conc. H_2SO_4 or anhydrous P_2O_5 (Phosphorus Pentoxide), alkenes are formed as a result of dehydration. for e.g

$$\underset{\text{Conc}}{CH_3 - CH_2 - OH} + H_2SO_4 \xrightarrow{160^\circ - 170^\circ C} CH_2 = CH_2 + H_2O \quad \text{Ethene}$$

$$\underset{\text{Conc}}{CH_3 - CH_2 - CH_2 - OH} + H_2SO_4 \xrightarrow{160^\circ - 170^\circ C} CH_3CH = CH_2 + H_2O \quad \text{Propene}$$

② By dehydrohalogenation of alkyl halide:

When alkyl halides are heated with alcoholic KOH, alkenes are formed. This reaction is known as dehydrohalogenation.

$$CH_3CH_2-Cl + KOH \xrightarrow[\text{alc.}]{\Delta} CH_2=CH_2 + KCl + H_2O$$

$$CH_3CH_2CH_2-Br + KOH \xrightarrow[\text{alc}]{\Delta} CH_3CH=CH_2 + KBr + H_2O$$

(3.) From vicinal dihalides:

1,2-dihalo alkanes are also known as ~~vicinal~~ vicinal dihalides. Then vicinal dihalides heated with zinc in the presence of methanol gives alkene. for e.g

$$CH_2(Cl)-CH_2(Cl) + 2Zn \xrightarrow[\Delta]{CH_3-OH} CH_2=CH_2 + ZnCl_2$$

$$CH_3-CH(Cl)-CH_2(Cl) + 2Zn \xrightarrow[\Delta]{CH_3-OH} CH_3-CH=CH_2 + ZnCl_2$$

(4.) By catalytic hydrogenation of alkyne:

Alkanes are formed by catalytic hydrogenation of alkynes in the presence of H_2/Ni or $Pb/BaSO_4$ (Lindler's catalyst). for e.g

$$CH\equiv CH + H_2 \xrightarrow[\Delta]{Ni} CH_2=CH_2$$

$$CH_3-C\equiv CH + H_2 \xrightarrow[\Delta]{Ni} CH_3CH=CH_2$$

$$CH\equiv CH + H_2 \xrightarrow[\Delta]{Ni} CH_2=CH_2$$

(5.) By Kolbe's electrolytic method:

Ethane is prepared by the electrolysis of sodium succinate.

$$\underset{\text{Sodium succinate}}{CH_2-COONa \atop CH_2-COONa} \xrightarrow[+2H_2O]{} \underset{\text{anode}}{CH_2=CH_2} + 2CO_2 + 2NaOH + H_2$$

* Chemical Properties of Alkene:

1. Addition of hydrogen (hydrogenation):

$$CH_2 = CH_2 + H_2 \xrightarrow[\Delta]{Ni} CH_3 - CH_3$$

$$CH_3 - CH = CH_2 + H_2 \xrightarrow[\Delta]{Ni} CH_3 - CH_2 - CH_3$$

$$CH_3 - CH = CH - CH_3 + H_2 \xrightarrow[\Delta]{Ni} CH_3 - CH_2 - CH_2 - CH_3$$

When alkenes are heated with hydrogen in the presence of Ni or catalyst, alkenes are formed.

2. Addition of halogens (halogenation):

$$CH_2 = CH_2 - Cl_2 \xrightarrow{CCl_4} CH_2 - CH_2 Cl Cl$$

$$CH_3 - CH = CH_2 + Cl_2 \xrightarrow{CCl_4} CH_3 - \overset{Cl}{\underset{|}{C}}H - \overset{Cl}{\underset{|}{C}}H_2$$

$$CH_3 - CH = CH_2 + Br_2 \xrightarrow{CCl_4} CH_3 - \overset{Br}{\underset{|}{C}}H - \overset{Br}{\underset{|}{C}}H_2$$

When alkenes are treated with halogens haloede alkenes are formed.

3. Addition of haloacide (HX):

Al Symmetrical alkenes reacts with haloacids to give haloalkenes.

$$CH_2 = CH_2 + HCl \longrightarrow CH_3 - CH_2 - Cl$$

$$CH_3 - CH = CH - CH_3 + HCl \longrightarrow CH_3 - CH_2 - \underset{Cl}{CH} - CH_3$$

2-Chloro butane

* Markovnikov's rule:

It states that "when an unsymmetrical reagent added to unsymmetrical alkene, the positive part of unsymmetrical reagent goes to that double bonded carbon having greater number of hydrogen and negative part of unsymmetrical reagents goes to that double bonded ~~atom~~ carbon having lesser number of hydrogen. for e.g

$$CH_3-CH=CH_2 + HCl \longrightarrow CH_3-\underset{Cl}{CH}-CH_3 \quad (2\text{-chloro propane})$$

$$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{Br}{CH}-CH_3 \quad (2\text{-Bromopropane})$$

* Anti-markonikov's rule (Peroxide effect) or Kharasch effect:

for e.g

$$HBr + CH_3-CH=CH_2 \xrightarrow{\text{Peroxide}} CH_2-CH_2-CH_2-Br$$

4. Addition of sulphuric acid:

when alkenes are treated with sulphuric acid, ethyl hydrogen sulphate are formed which on hydrolysis with boiling water gives alcohol.

$$CH_3=CH_2 + H_2SO_4 \longrightarrow CH_3-CH_2-HSO_4 \xrightarrow[H_2O]{boil} CH_3-CH_2-OH + H_2SO_4$$

5. Addition of water:

when water is added to alkene in the Presence of 1% $HgSO_4$, 2% H_2SO_4 at 60 to 70°C alcohol are formed.

$$CH_2 = CH_2 + H_2O \xrightarrow[4\text{ gt. } H_2SO_4]{1\text{ gt. } HgSO_4} CH_3 - CH_2 - OH$$
(60-70°C)

$$CH_2 - CH = CH_2 + H_2O \xrightarrow[4\text{ gt. } H_2SO_4]{1\text{ gt. } HgSO_4} CH_3 - \overset{OH}{\overset{|}{C}}H - CH_3$$
(60-70°C)

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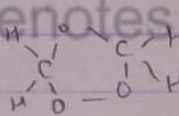
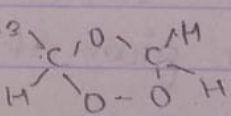
6. Addition of ozone (Ozonolysis):

When alkene is added to ozone in the presence of some inert solvents such as CCl_4, an unstable intermediate compound called ozonide is formed which on hydrolysis in the presence of Zn dust gives aldehyde or mixture of aldehyde and ketone.

(1.) $CH_2 = CH_2 + O_3 \xrightarrow{CCl_4}$  $\xrightarrow[+H_2O]{Zn}$ $H-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H$

(Ozonide (unstable))

(2.) $CH_3CH = CH_2 + O_3 \xrightarrow{CCl_4}$  $\xrightarrow[+H_2O]{Zn}$ $CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H + H_2O_2$

(ethanol)

(3.) $CH_3 - \overset{CH_3}{\overset{|}{C}} = CH_2 - O_3 \xrightarrow{CCl_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H-\overset{O}{\overset{\|}{C}}-H + H_2O$

propanone, methanol

(4.) $CH_3 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 - O_3 \xrightarrow{CCl_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_2-\overset{O}{\overset{\|}{C}}-H + H_2O_2$

(5.) $CH_3-\overset{CH_3}{\overset{|}{C}} = \overset{CH_3}{\overset{|}{C}} - CH_3 + O_3 \xrightarrow{CCl_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O_2$

7. Oxidation with aqueous alkaline Potassium Permanganate solution (Baeyer's reagent):

Alkaline Potassium Permanganate solution is Boyer's reagent. When alkene Pass through Baeyer's reagent. Pink colour of Baeyer's reagent gets discharged and diol formed.

$$KMnO_4 + KOH \longrightarrow K_2MnO_4 + H_2O + [O]$$

$$CH_2 = CH_2 + [O] + H_2O \xrightarrow{OH^-} \underset{\text{1,2 ethanediol}}{CH_2(OH)-CH_2(OH)}$$

$$CH_3CH = CH_2 + [O] + H_2O \xrightarrow{OH^-} \underset{\text{1,2 - Propanediol}}{CH_3-CH(OH)-CH_2(OH)}$$

NOTE:- Baeyer's test is used to detect the presence of double bond or alkene.

8. Reaction with Bromine:

When ethene is passed through bromine. dark brown colour of bromine gets discharged for e.g

$$\underset{\text{(dark brown)}}{CH_2 = CH_2 + Br_2} \xrightarrow{CCl_4} \underset{\text{(colourless)}}{CH_2(Br)-CH_2(Br)}$$

This reaction is also known as Bromine test for alkenes.

* Polymerization:

Polymers are very large molecules which are formed by the combination of large number of small molecules called monomers. The process of formation of Polymers by the combination of their monomers is called Polymerization. Polymerization is of two types:

(a) Addition Polymerization:

The Polymers which are formed by the combination of large number of monomers without removal of small molecules such as H_2O, HCl, NH_3 etc. are called addition Polymers and this phinomenon is called addition Polymerization.
for e.g Polyvinyl chloride, Polythene, Polystyrene etc.

(b) condensation Polymerization:

The Polymers which are formed by the combination of large number of monomers with the removal of small molecules like HCl, H_2O, NH_3 etc are called condensation Polymers and this phenomenon is called condensation Polymerization. for e.g nylon, bakelite etc.

Uses of alkenes:-

(i) Alkenes are used for making PVC, Polythene, Polystnene etc.
(ii) They also help in the ripening of fruits.

(Alkynes)

* General Method of Preparation of alkynes:

(1.) From vicinal dihalids:

When vicinal dihalids heated with alcoholic KOH. haloalkenes are formed which on further reaction with alc. KOH gives alkyne.

$$CH_2(Br)-CH_2(Br) + KOH \xrightarrow[-HBr]{\Delta} CH_2=CH(Br) \xrightarrow[\Delta]{alc.KOH} CH\equiv CH + KBr + H_2O$$

(2.) From haloform:

When haloform heated with silver powder ethyne is formed.

$$CH(I)_3 + Ag + I-CH(I)_2 \xrightarrow{\Delta} CH\equiv CH + 6AgI$$

i.e $2CHI_3 + 6Ag \xrightarrow{\Delta} CH\equiv CH + 6AgI$.

(3.) From Kolbe's electrolytic Method:

$$\begin{matrix} CH-COOK \\ \| \\ CH-COOK \end{matrix} + 2H_2O \rightleftharpoons \begin{matrix} CH \\ \| \\ CH \end{matrix} + KOH + H_2\uparrow + CO_2\uparrow$$

(Potassium meleate)

* Chemical Properties:

1. Addition of hydrogen:

$$CH \equiv CH + H_2 \xrightarrow[\Delta]{Ni} CH_2 = CH_2 \xrightarrow{H_2/Ni} CH_3 - CH_3$$

$$CH_3C \equiv CH + H_2 \xrightarrow[\Delta]{Ni} CH_3CH = CH_2 \xrightarrow{H_2/Ni} CH_3CH_2CH_2$$

2. Additions of halogens:

$$CH \equiv CH + Cl_2 \xrightarrow{CCl_4} \underset{Cl}{\overset{Cl}{CH}} = \underset{Cl}{\overset{Cl}{CH}} \xrightarrow{CCl_4} \underset{Cl}{\overset{Cl}{CH}} - \underset{Cl}{\overset{Cl}{CH}}$$

$$CH_3C \equiv CH + Br_2 \xrightarrow{CCl_4} \underset{Cl}{\overset{Cl}{CH_3C}} = \underset{Cl}{\overset{Cl}{CH}} \xrightarrow{CCl_4} \underset{Cl}{\overset{Cl}{CH_3C}} - \underset{Cl}{\overset{Cl}{CH}}$$

Propene

1,1,2,2- tetraBromo propane

3. Addition of haloacids:

(According to Markovikov's rule)

$$CH \equiv CH + HCl \longrightarrow CH_2 = CH - Cl$$ 1- Chloro ethene

$$CH_3 - C \equiv CH + HCl \longrightarrow CH_3 - \underset{Cl}{\overset{}{C}} = CH_2$$

2-chloro propene

4. Catalytic hydration of alkynes:

$$CH \equiv CH + H_2O \xrightarrow[4\%\ HgSO_4,\ H_2SO_4]{1\%\ HgSO_4,\ 4\%\ H_2SO_4,\ \Delta} CH_2 = \underset{\vdots}{\overset{\overset{OH}{|}}{C}} - H \quad \text{(ethenol)}$$

$$CH_2 - \overset{\vdots}{\underset{\vdots}{C}} - H \quad \text{(ethanal)}$$

$$CH_3C \equiv CH + H_2O \xrightarrow[4\%\ HgSO_4,\ H_2SO_4]{1\%\ HgSO_4,\ 4\%\ H_2SO_4} CH_3\overset{\overset{OH}{|}}{C} = CH \longrightarrow \text{(Rearrangement)}$$

$$CH_3 - \overset{\vdots}{\underset{\vdots}{C}} - CH_3 \quad \text{(Propanone)}$$

5. Addition of ozone:

$$CH \equiv CH + O_3 \xrightarrow{CCl_4} H - \underset{\vdots}{\overset{\overset{O}{/}}{C}} - \underset{\vdots}{\overset{\overset{O}{/}}{C}} - H \xrightarrow[+H_2O_2]{Zn/H_2O} H - \overset{\vdots}{\underset{\vdots}{C}} - \overset{\vdots}{\underset{\vdots}{C}} - H$$

$+H_2O$ (ethane-dial)

$$CH_3C \equiv CH + O_3 \xrightarrow{CCl_4} CH_3 - \overset{\vdots}{\underset{\vdots}{C}} - \overset{\vdots}{\underset{\vdots}{C}} - H \xrightarrow[+H_2O_2]{Zn/H_2O} \text{2-ketopropanal}$$

6. Reaction with Baeyer's reagent:

Ethyne reacts with Baeyer's reagent to give ethane 1,2-diol which on further oxidation gives ethane 1,2-dioic acid.

$$CH \equiv CH + [O] + H_2O \xrightarrow{OH^-} H - \overset{\vdots}{\underset{\vdots}{C}} - \overset{\vdots}{\underset{\vdots}{C}} - H \xrightarrow{[O]} HO - \overset{\vdots}{\underset{\vdots}{C}} - \overset{\vdots}{\underset{\vdots}{C}} - OH$$

Ethane 1,2-diol — Ethane 1,2-dioic acid

(7) Reaction that shows acidic nature of ethyne:

x^{n} with Na metal

(a) Reaction with ammonical silver nitrate solution:

When ethyne is passed through ammonical silver nitrate solution white ppt. of silver acetylide is obtained which indicate acidic nature of ethyne.

$$CH \equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow AgC \equiv CAg + 2H_2O + 2NH_4NO_3$$

Silver acetylide (white ppt.)

(b) Reaction with ammonical cuprous chloride:

When ethyne is passed through ammonical cuprous chloride solution, red ppt. of copper acetylide is obtained which indicate acidic natur of ethyne.

$$CH \equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow CuC \equiv CCu + 2H_2O + 2NH_4Cl$$

(copper acetylide) (red ppt.)

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* Polymerization of ethyne:

Three molecules of ethyne when heated with red hot iron tube at 1450 - 500°C, benzene is formed as a result of polymerization.

$$3CH \equiv CH \xrightarrow[1450^{\circ}C - 500^{\circ}C]{\text{Red hot fe tube,}} C_6H_6$$

(Benzene)

Uses of ethynes:

(i) It is used for ripening of fruits.
(ii) mixture of ethyne and oxygen is used for welding and cutting metals in the form of oxyacetylene.
(iii) It is used for the preparation of benzene.

Laboratory Preparation of ethene (ethylene

Ethene gas is labratory by heating ethanol with conc. H_2SO_4 at 170°c

Principle

$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH \xrightarrow[\Delta\,(170^\circ C)]{\text{conc } H_2SO_4} H-\underset{H}{C}=\underset{H}{C}-H + H_2O$$

When alcohol is heated in presence of conc. H_2SO_4 alkene produced if ethyl alcohol is used and temperature is made 160°c - 170°c

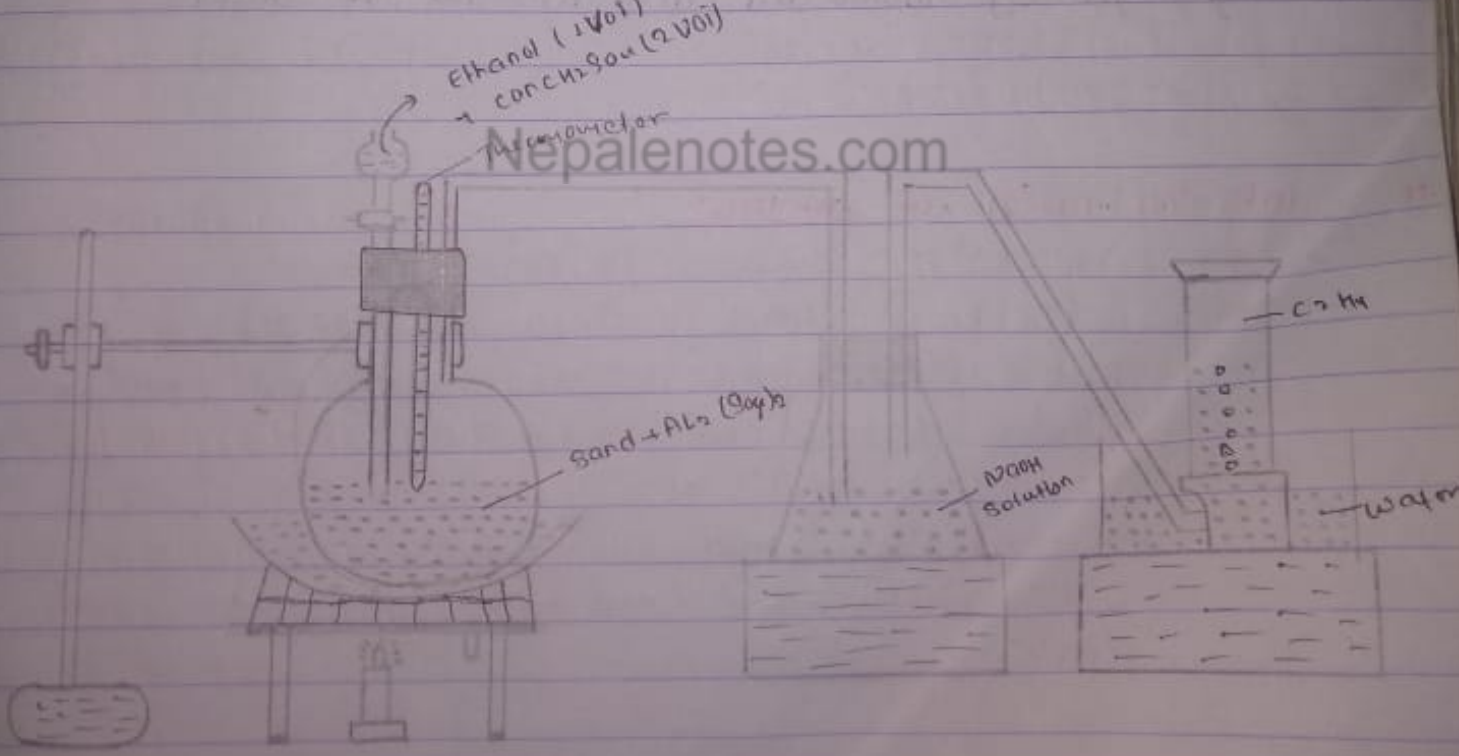

fig: Laboratory preaparation of ethene

Procedure:

A mixture of 1 volume of ethyl alcohol and 1 volume of conc. H_2SO_4 is taken in a round bottom flask with a dropping funnel fitted with a thermometer and delivery tube. Small amount of sand + Aluminium sulphate $[Al_2(SO_4)_3]$ are added to a flask to prevent frothing then flask is heated to about 160° to 170°c on sand bath ethene gas is produced, the gas thus proceduced which contains SO_2, CO_2 impurites Then the gas is passed through a soln containing ag. NaOH where the impurities are absorbed. Finally the pure gas is collected in to gas jar by downward displacement of water.

Lab Preparation of alkyne:

Principle:

Ethyne is prepared in laboratory by droping water on calcium carbide.

$$CaC_2 + 2H_2O \longrightarrow CH \equiv CH + Ca(OH)_2$$

Calcium carbide → Ethyne

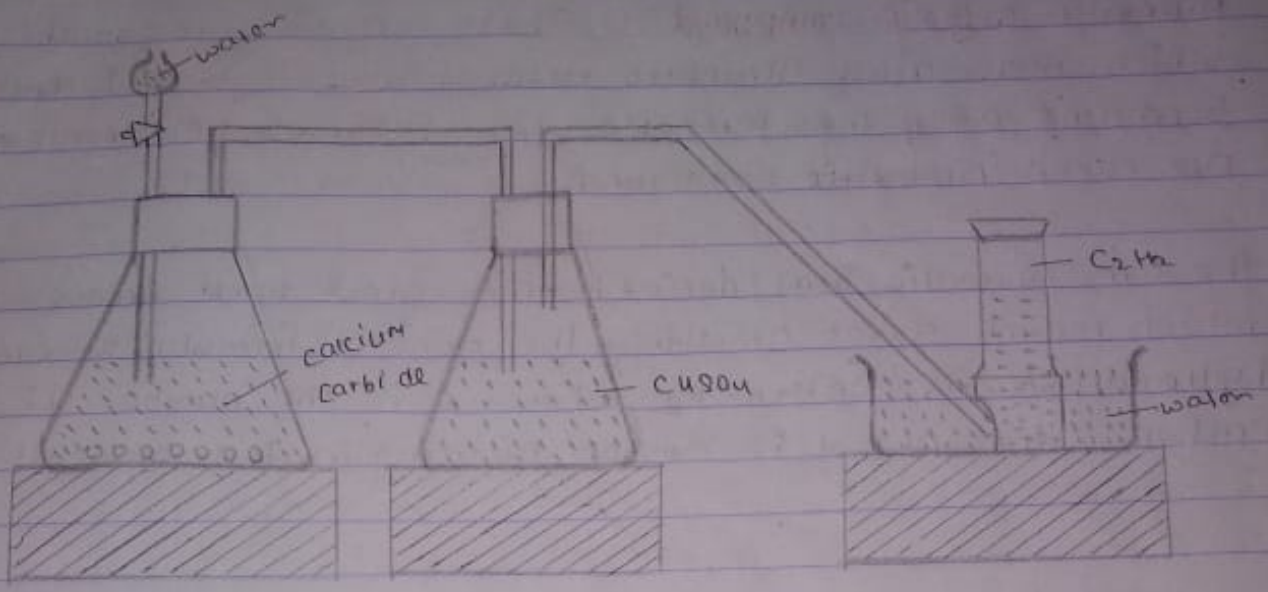

fig: Laboratary preparation of ethyne (Acelytene)

Theory:

Some pieces of calcium carbide are taken in a flask fitted with delivery tube & dropping funnel. water is taken in a dropping funnel and allowed to fall in dropwise. then ethyne gas is produced. which is passed through acidified $CuSO_4$ solution to remove impurities like NH_3, H_2S, PH etc. finally Pre ethyne gas is collected by downward displacement of water.