

SATYA SANKAR RAY
SENIOR LECTURER (CHEMICAL)
U.C.P.-ENGINEERING SCHOOL
BERHAMPUR
ORGANIC CHEMISTRY NOTES

Methane — Marsh Gas.
Coal Miner — Fire damp.

classmate

Date _____

Page _____

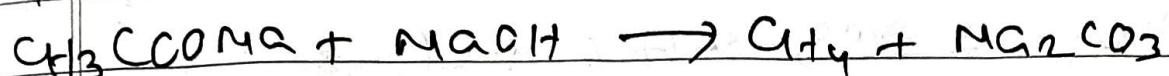
10-90%

Source - Natural gas from Petroleum crude oil.

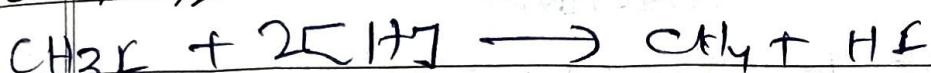
Coal Gas - upto 35%.

Method of Preparation:-

① Heating sodium Acetate with Sodium.



② Reduction of methyl iodide using nascent hydrogen, C from ethanol or zinc copper couple.



Zn-Cu Couple - ZnC in a solution of Zinc Copper sulphate.

→ Round bottom flask - $\text{CH}_3\text{I} + 95\% \text{C}_2\text{H}_5\text{OH}$.

③ By treating with aluminium carbide with water or dilute acid.



④ By hydrolysis of methyl magnesium iodide.



→ use for small scale preparation.

large quantity from natural gas crude oil.

or by round off remains of petroleum product.

Physical Properties:-

1) colourless gas soluble in water.

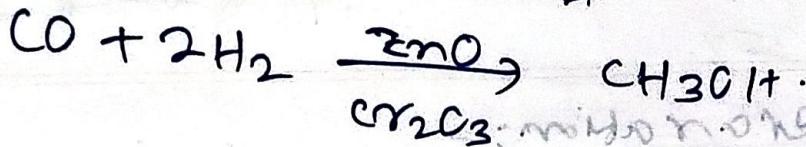
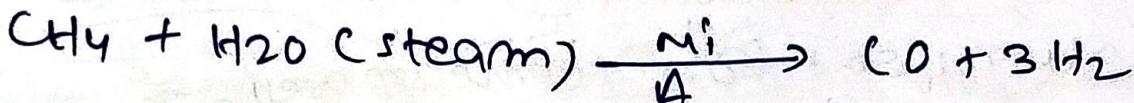
3) soluble in organic solvent like acetone, ethanol, ether and benzene.

Chemical Properties:-

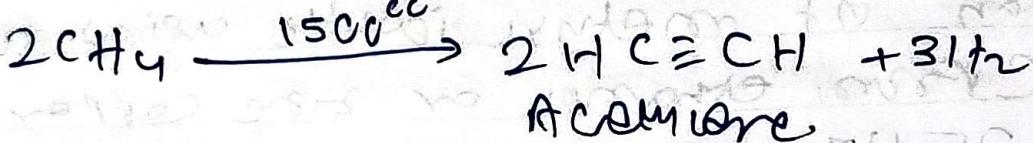
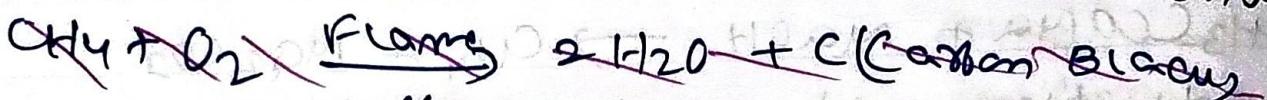
① $\text{CH}_4 + 2\text{Cl}_2 \xrightarrow{\text{U.V.}} \text{C} + 4\text{HCl}$, explosion to form, or ignition.

In presence of UV light or ignition,

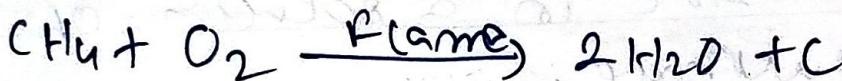
② When methane is treated with steam.



③ Heated in absence of air (or) oxygen at 1500°C.



④ When burnt in limited supply of air



Uses:-

1) domestic fuel 2) methanol

3) carbon black - prints ink, shoe polish, rubber etc.

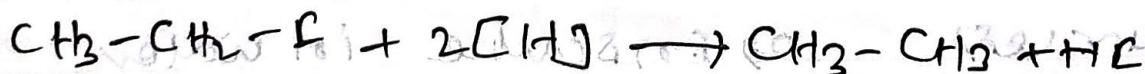
Ethane - 10-20% along with methane in natural gas.

Method of Production:

① Heating sodium propionate with soda lime.



② Reaction of ethyl iodide using nascent hydrogen

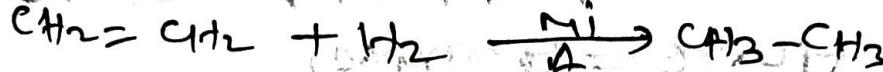


③ Wurtz reaction, similar to ethane.

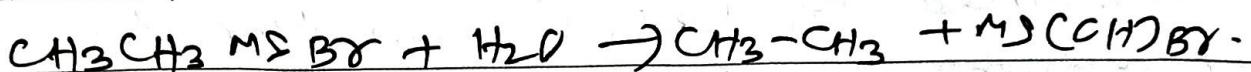
By action of sodium metal on methyl iodide in dry ether solution.



(1) By passing a mixture of ethyne and hydrogen over heated nickel catalyst.



(5) By hydrolysis of ethyl magnesium bromide.



Physical Properties:- (Page - 207)

1. colourless gas
2. sparingly soluble in water, but dissolve in organic solvent like ethanol, ether and benzene.

Assignment - 01

(1) What is carbon black? Name 5 industries produces carbon black? write industrial application.

(2) write a short note on shoe polish which include major industry, Brand, composition, manufacturing process.

(3) write a short note on Tyre industry? Key material, composition, Brand, type, design parameters.

(4) what is petroleum, write a brief note on petroleum producing country. Manufacture it, natural gas, LPG.

(5) write a note on composition of Petroleum country available in different

(6) Explain petroleum drums.

(7) Explain fractional distillation of petroleum.

(8) write the composition and uses of Petroleum fraction.

(9) Explain cracking with example.

(10) Explain manufacture of synthetic petrol by using Boron process, and Fisher-Tropsch process.

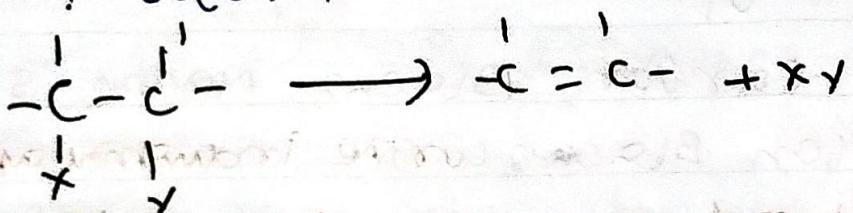
⑤ Alkene - carbon carbon double bond $C=C$

Content - commonly known as olefins
(oleum-oil, H₂carb = to make)

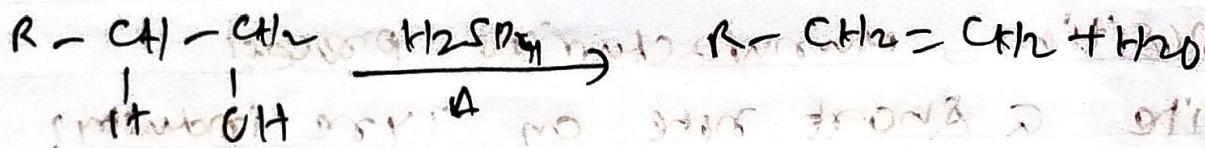
- Alkene fiber seldom occurs in nature.
- Produced in large number by cracking of Petroleum.

Method of Preparation

Preparation of alkene involves elimination of atoms or group from two adjacent carbon atoms.



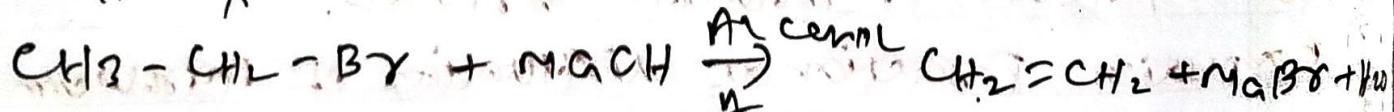
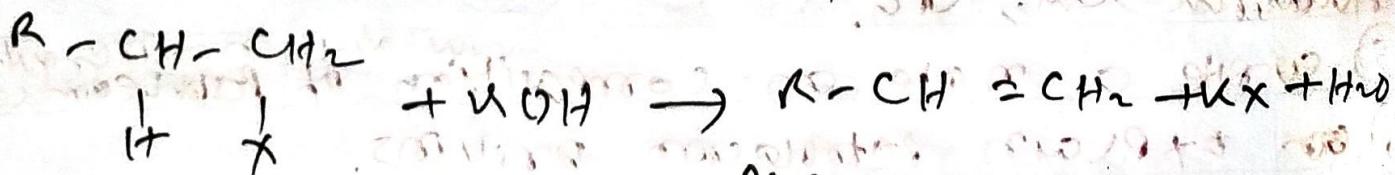
① Dehydration of alcohol.



The ease of dehydration of alcohol is

* 3° alcohol > 2° alcohol > 1° alcohol.

② Dehydrohalogenation of Alkyl halide



Alkyl halide is heated with an aqueous

solution of sodium (or) potassium hydroxide

* Dehydration of alcohol may be brought by passing the alcohol vapour over heated calcium (Al₂O₃) at 900°C. Other dehydrations are b. P₂O₅/H₃P₄

The ease of dehydrohalogenation of alkyl halide is
 3° alkyl halide $> 2^{\circ}$ alkyl halide $> 1^{\circ}$ alkyl halide.

classmate of

Date 6

Page

③ De halogenation of vicinal dihalides



$\boxed{Br \text{ or } Br}$

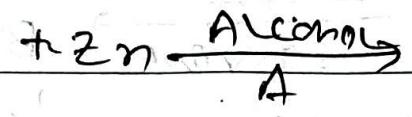
Vic-Dihalide



Alkene



$\boxed{Br} \quad \boxed{Br}$



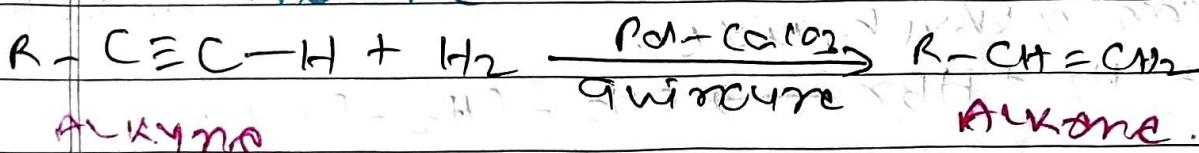
Propane

1,2-Bisbromo Propane

④ By controlled hydrodehalogenation of Alkyne.

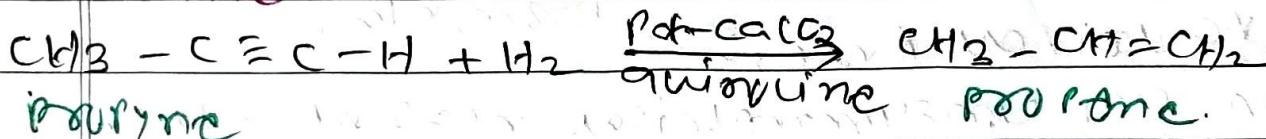
Lindlar catalyst - Pd poisoned with $CaCO_3$

plus quinoline.



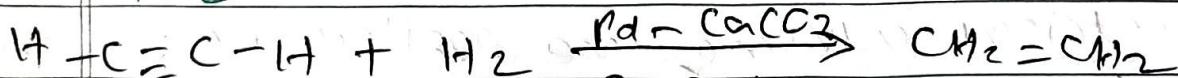
Alkyne

Alkene



Purine

Propane



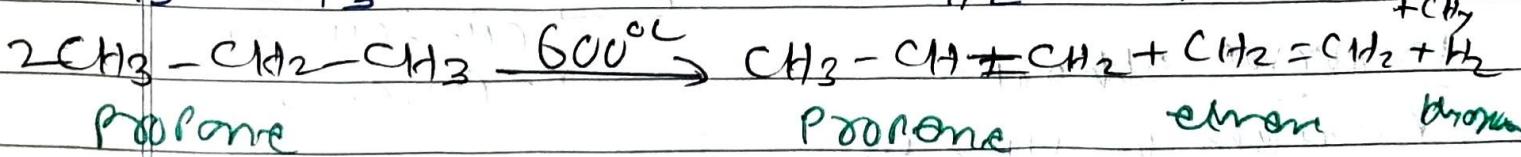
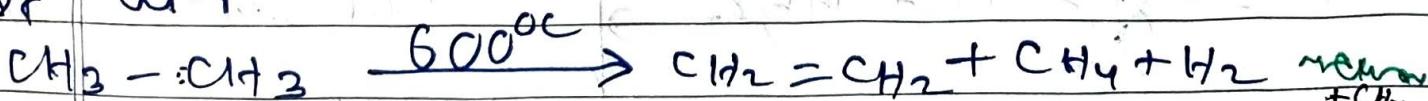
Acetylene

Ethene/Ethyne

⑤ By cracking of alkanes.

When alkane heated at $500-600^{\circ}C$ in absence

of air.



Propane

Propane

Ethene

Ethyne

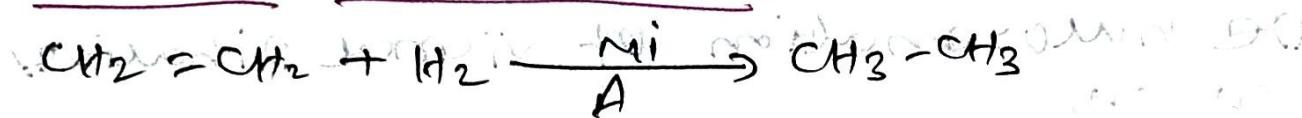
PHYSICAL PROPERTIES:

- ① Let three gas (ethene, propane, ethyne) at room temperature - Ethene is colourless, odourless & soluble in water, forms solns in solvents.

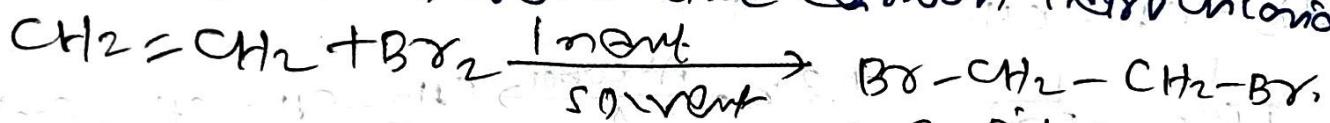
SPECIAL PROPERTIES OF ALKENES

(1) Addition of hydrogen \rightarrow under pressure and in presence of Ni, Pt, rd catalyst.

Catalytic hydrogenation:-



(2) Addition of Halogens (Cl₂ or Br₂) in presence of solvent like carbon tetrachloride.

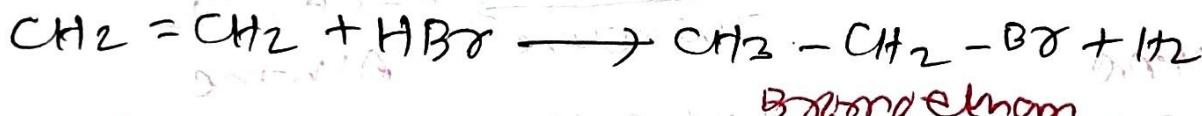


Test of unsaturation \rightarrow 1, 2-Dibromoethane.

Red colour of bromine is discharged as colourless dibromo compound.

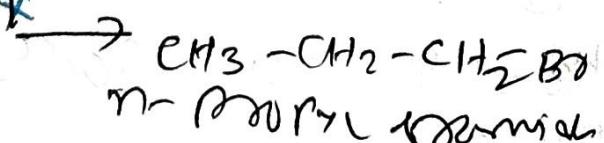
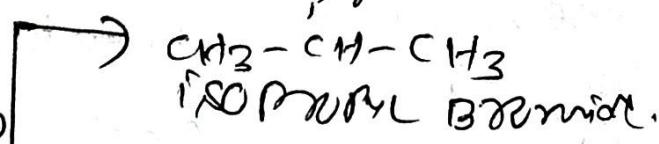
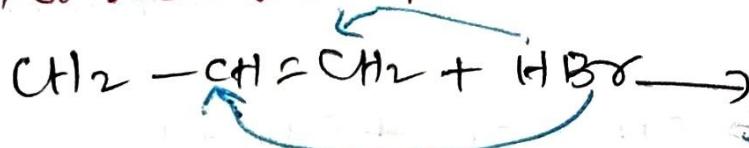
(3) Addition of Halogen Acid:-

Alkene react with halogen acids (HCl, HBr, HI) to form alkyl halide.



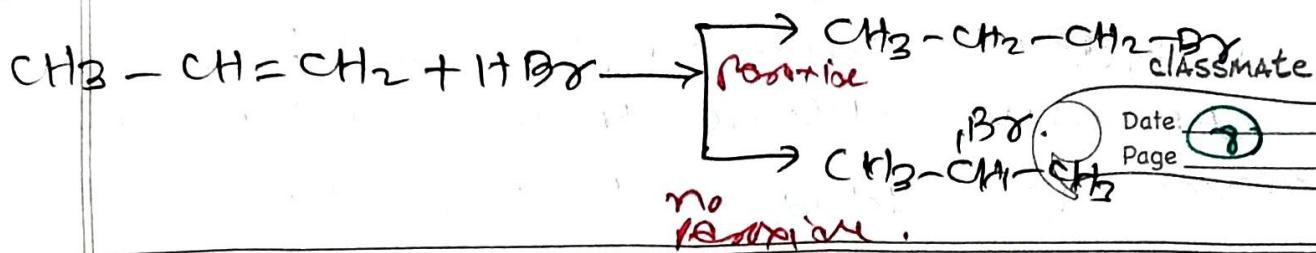
MARKOVNIKOV'S RULE

When an unsymmetrical reagent add to an unsymmetrical alkene, the positive part of the reagent becomes attached to the double bond carbon which bears the greatest number of hydrogen atoms.

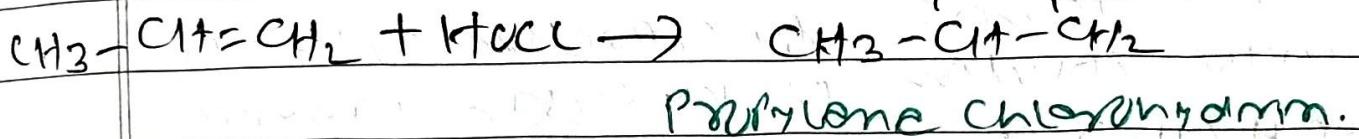
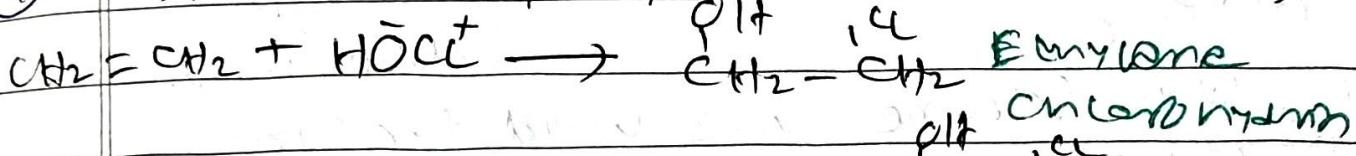


Peroxide effect

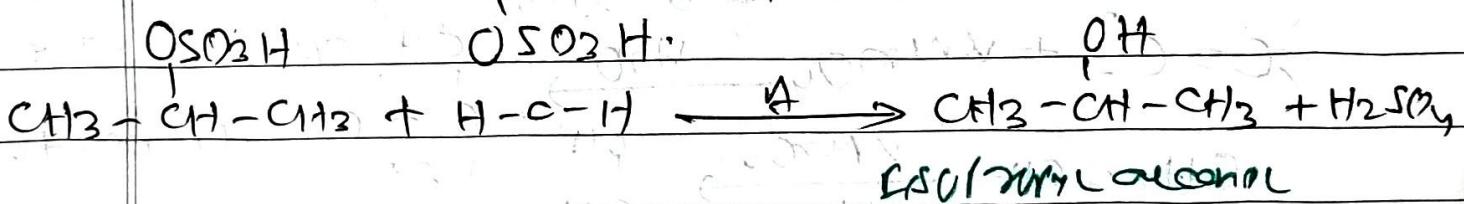
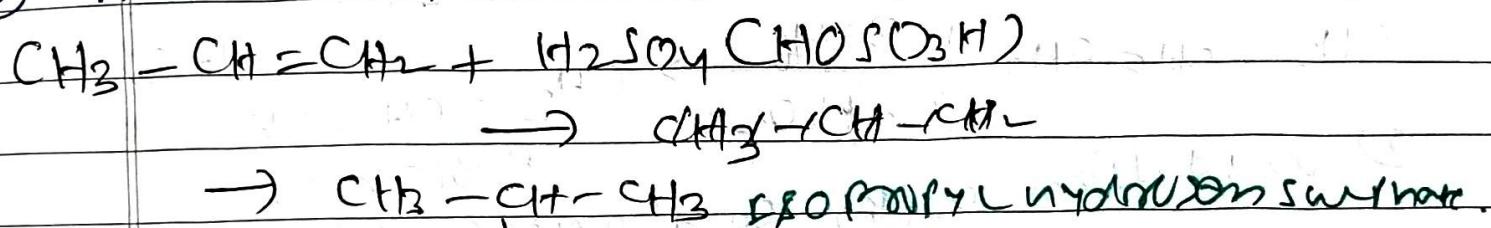
Addition of HBr to unsymmetrical alkene in presence of organic peroxide ($R-C-O-R'$) takes a course opposite to Markovnikov Rule known as peroxide effect or Antimarkovnikov rule.



(4) Addition of Hypohalous Acid (HOX)



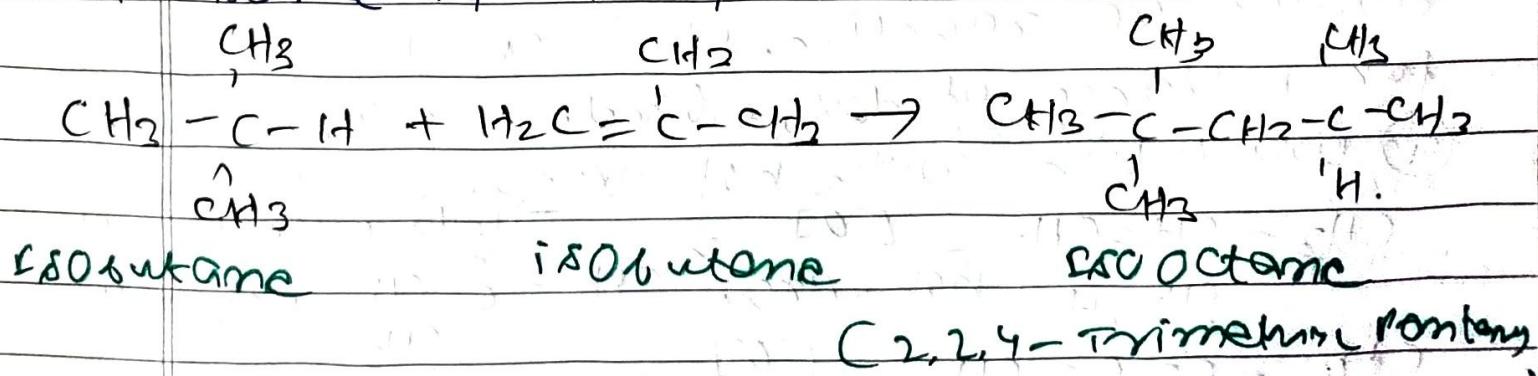
(5) Addition of sulfuric acid and hydration



Overall reaction



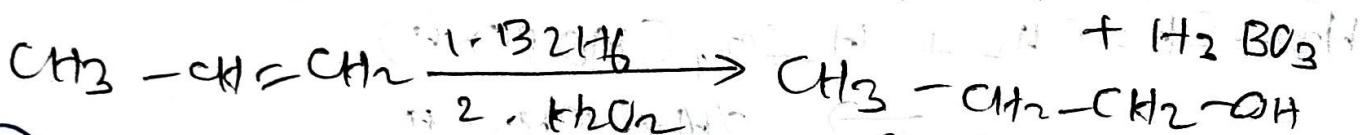
(6) Alkylation : some alkylates added to alkene in presence of H_2SO_4 or HF .



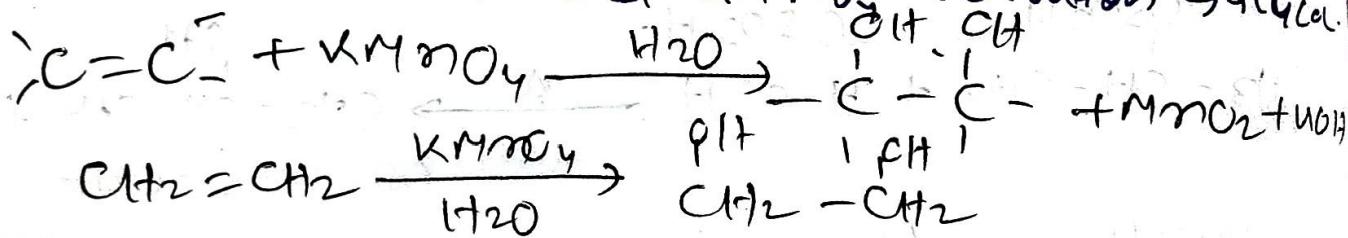
⑨ ⑦ Hydroboration : diborane (B_2H_6) reacts with alkene to form trialkylborane. Borane is added as borane (BH_3)



Trialkyl borane are used for synthesis of primary alcohols by reaction with alkene aqueous solution of hydrogen peroxide



⑧ Oxidation with cold KMnO_4 solution \rightarrow glycol.

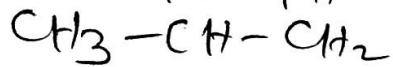


$\text{CH}_2=\text{CH}_2$



Propylene

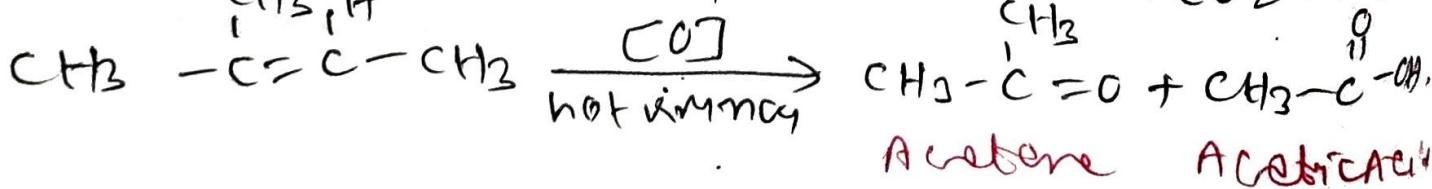
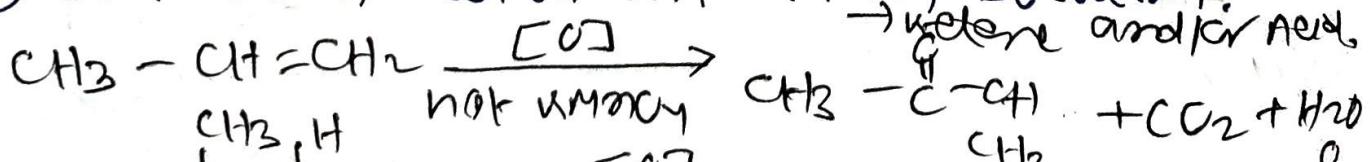
Ethylene glycol.

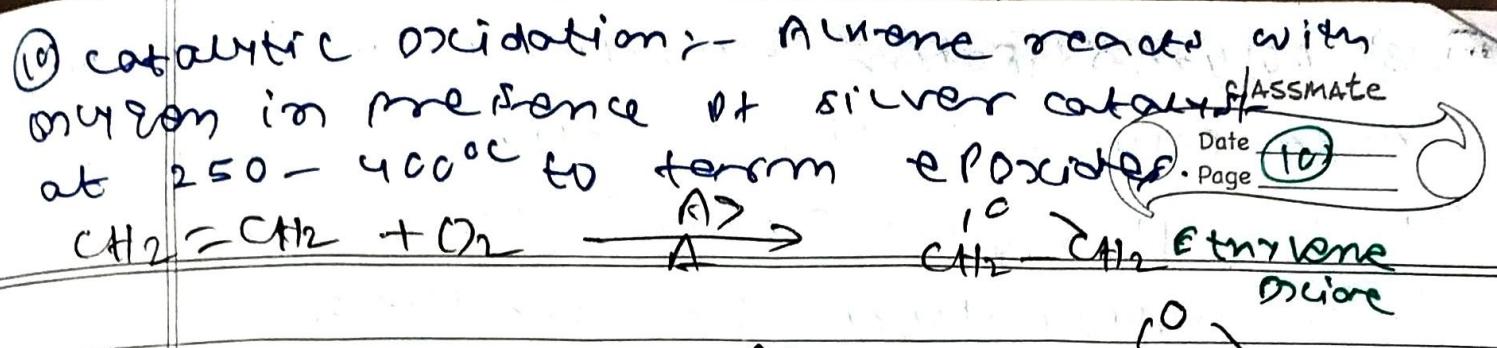


Propylene glycol.

Bright purple colour of KMnO_4 disappear during the reaction. It is used as a test for presence of double bond. (Bauyer's test)

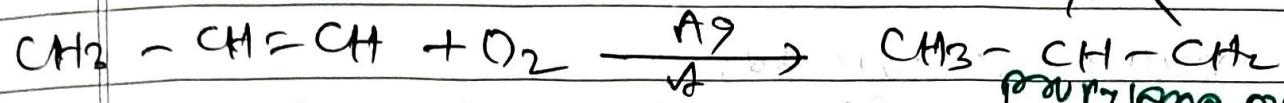
⑨ Oxidation with hot KMnO_4 solution.





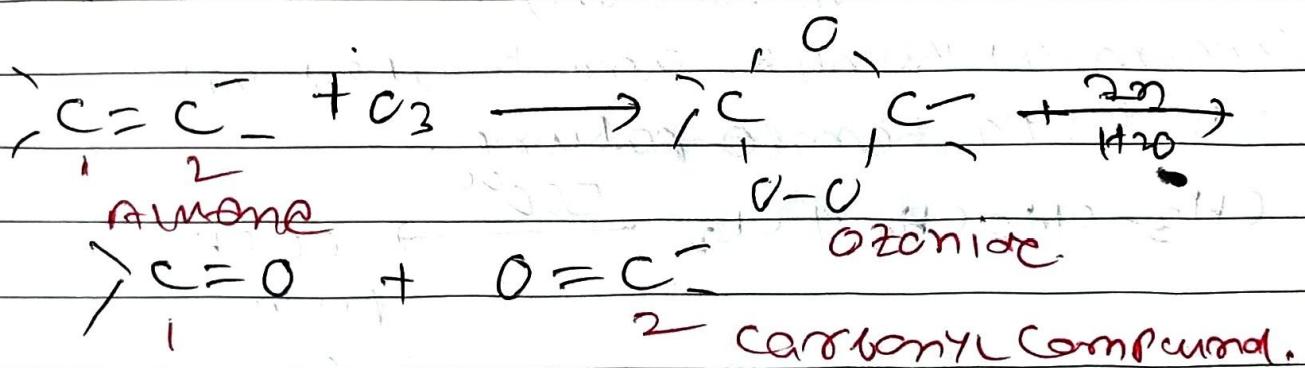
Date _____
Page _____

10

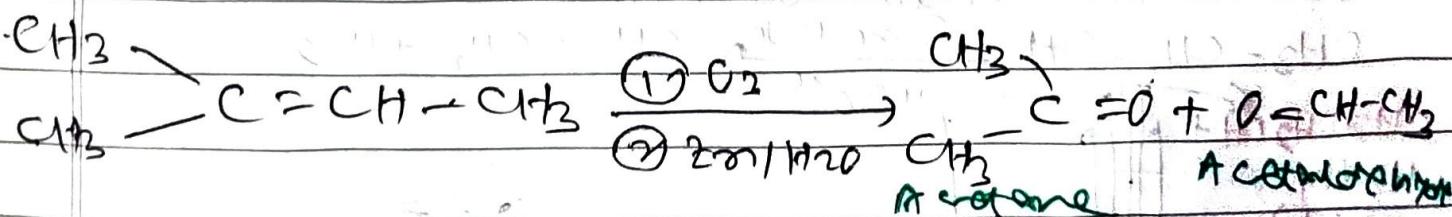
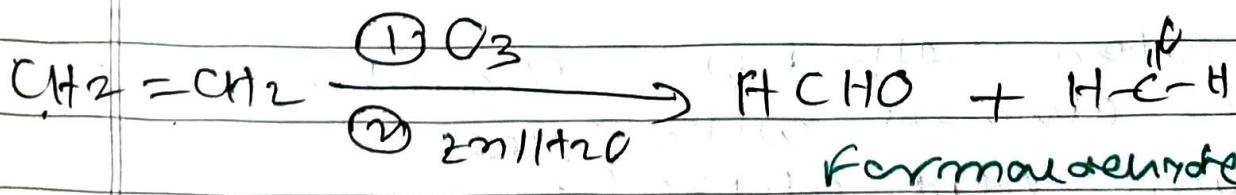


⑪ oxidation with ozone (ozonide)

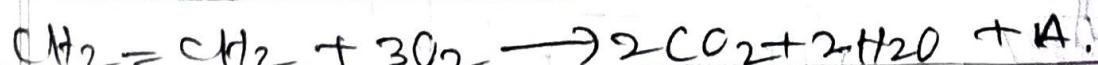
Ozone is passed through an alkene across the double bond to form ozonide. Ozonides are explosive compounds. They are not isolated. On warming with zinc and water aldehyde, ketone.



The two step process of preparing the ozonide and decomposes it to get carbonyl compound is called ozonolysis.

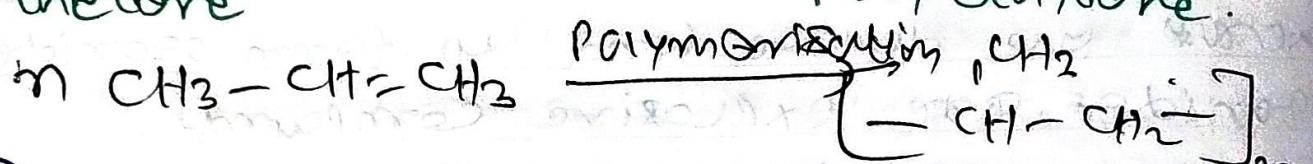
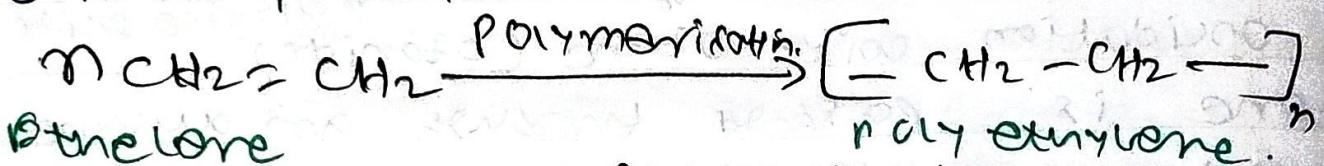


⑫ combustion reaction:



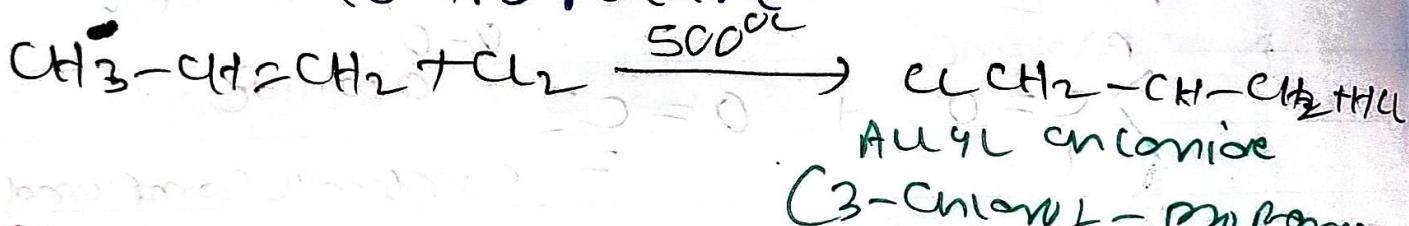
(13) Polymerization reaction (Addition Polymerization)

These polymerisation reactions are catalysed by HF , H_2SO_4 or organic peroxides. High temperature or high pressure are generally required.



(14) Substitution of alkene by halogen. (Allylic substitution)

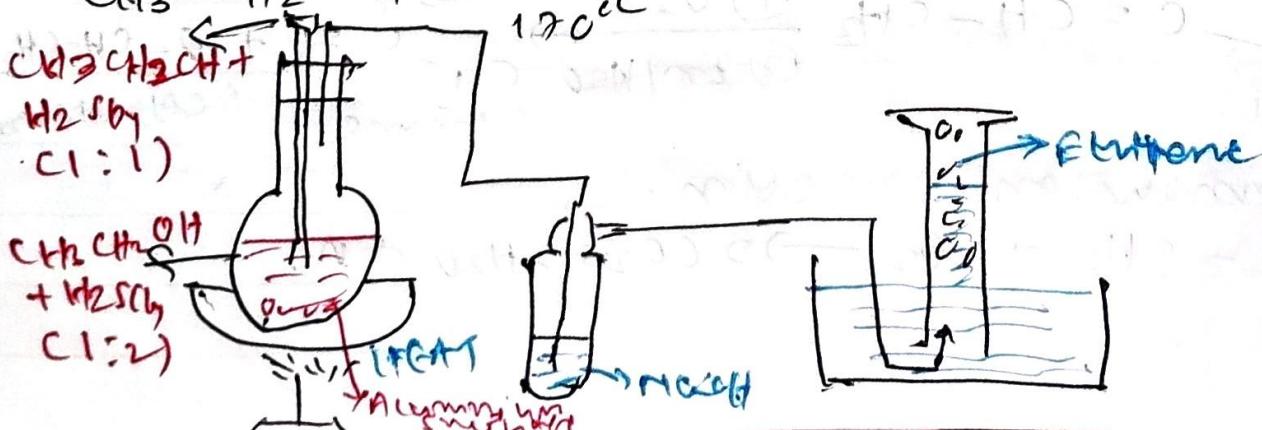
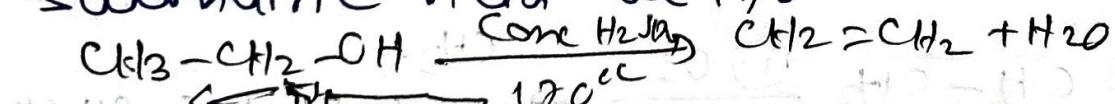
When alkenes are treated with Cl_2 or Br_2 at high temperature.



Ethylene (Ethene) $\text{CH}_2=\text{CH}_2$

source \rightarrow large amount by cracking of Petroleum.

(1) Laboratory method of Preparation: Heating ethanol with excess concentrated sulphuric acid at 170°C .



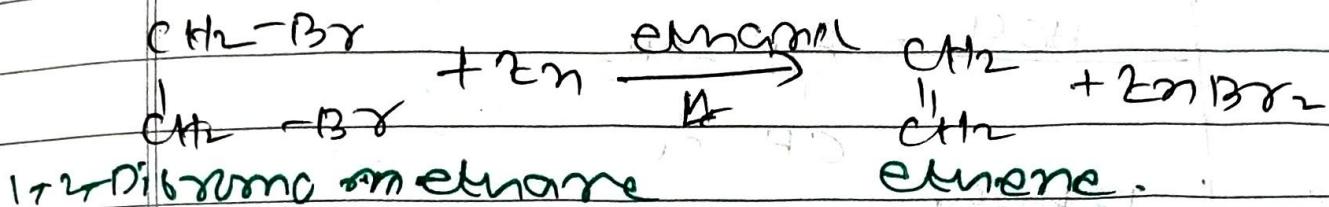
② By heating ethyl iodide with alcoholic KOH

$$\text{CH}_3\text{-CH}_2\text{-I} + \text{KOH} \xrightarrow[\text{ethanol}]{\Delta} \text{CH}_2=\text{CH}_2 + \text{KI}$$

CLASSMATE
Date _____
Page 13

roodo ethene

③ By heating 1,2-dibromoethane with zinc dust in ethanol

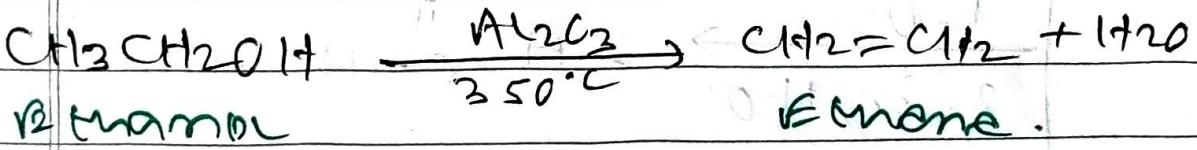


④ By controlled addition of hydrogen to acetylene in presence of Lindlar catalyst

$$\text{H}_2\text{C} \equiv \text{CH} + \text{H}_2\text{O} \xrightarrow[\text{quinine}]{\text{Pd/CeCO}_3} \text{CH}_2 = \text{CH}_2$$

AcetyleneEthene.

⑤ By passing ethanol vapour over alumina catalyst at 350°C



PHYSICAL PROPERTIES:-

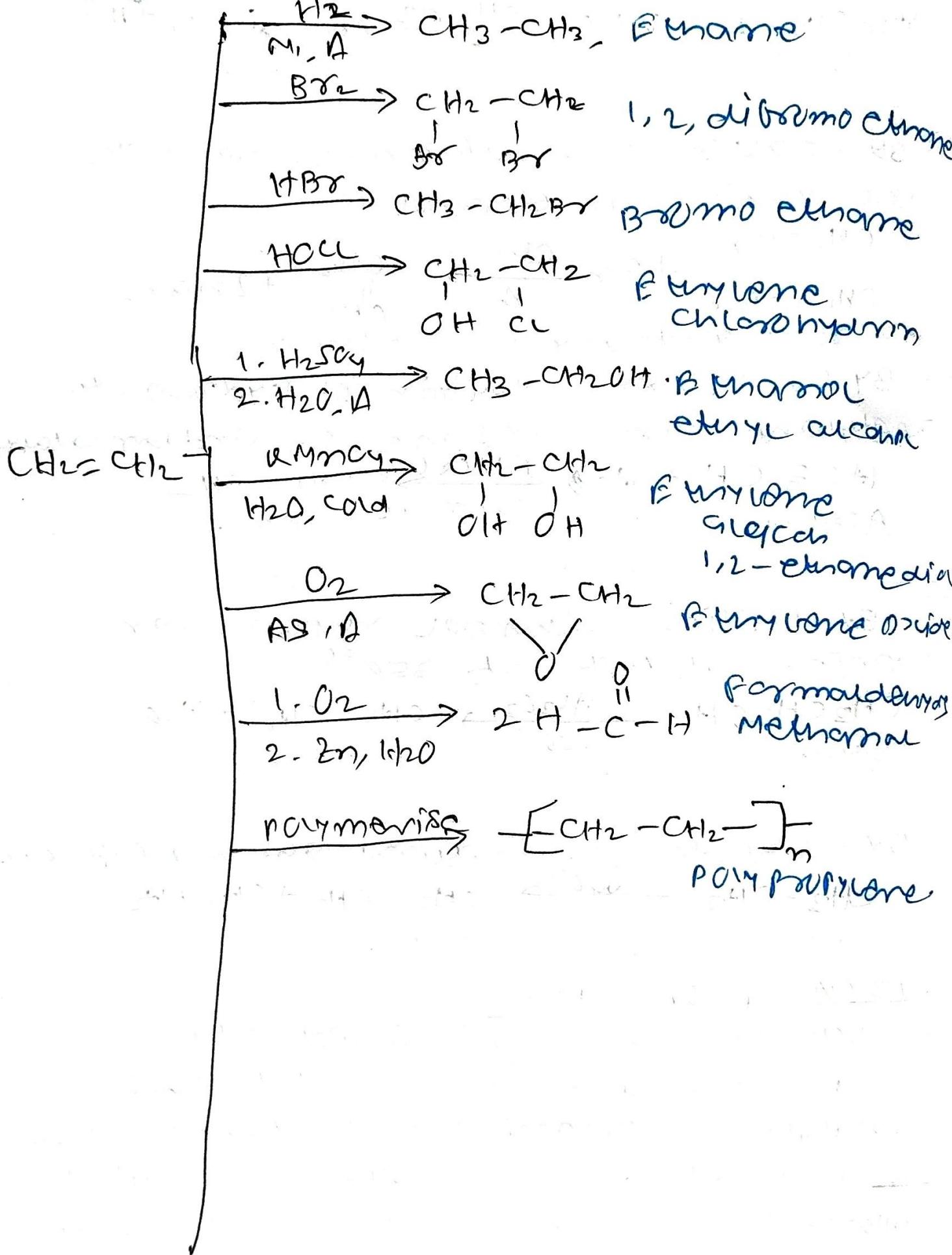
1. colourless gas with sweet odour.
 - 2 - slightly soluble in water but easily soluble in organic solvent- ethanol, ether.

Uses:- 1. used for manufacture of medicines

Important polymer use PVC, EPR (Ethylene
Polypropylene rubber), SARAN, polyethylene.

Floor tiles made from synthetic fiber, ceramic tiles

(13) CHEMICAL PROPERTIES OF ETHYLENE



2.3 ALKYNES:-

Methods of preparation, properties
use of acetylene.

classmate _____
Date _____
Page _____

(14)

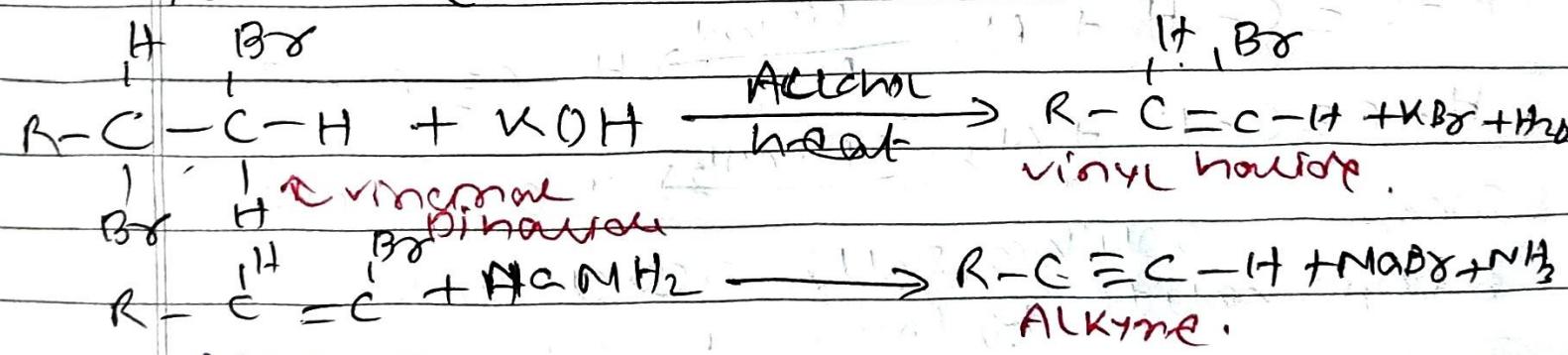
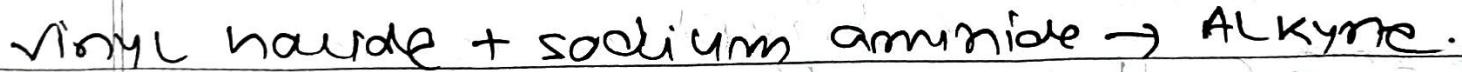
- Alkyne are highly unsaturated as

compared to alkyne.

- First member is $\text{HC}\equiv\text{CH}$, ethyne,
Acetylene.

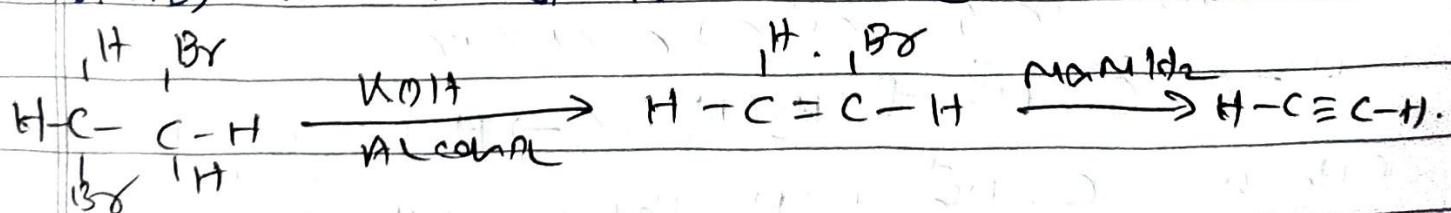
Method of Preparation:-

① Dehydrohalogenation of vicinal Dihalides;
compounds that contains halogen atoms on
adjacent carbon atom are called **Vicinal
dihalide**.

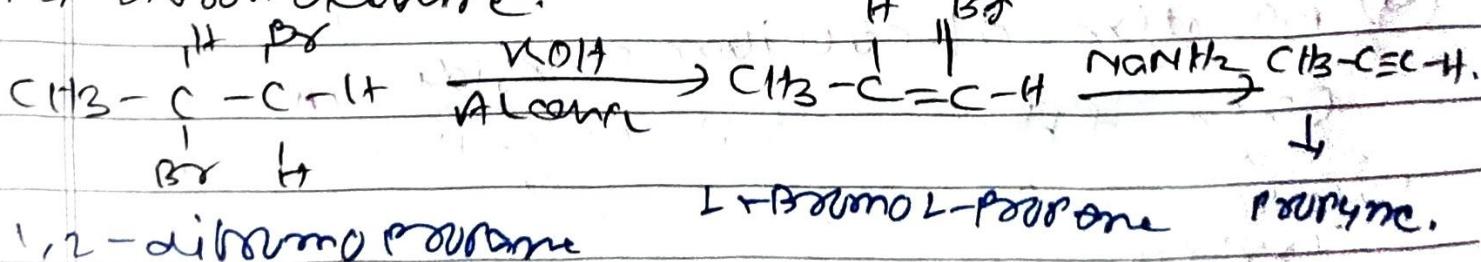


Halides are unreactive so a strong base

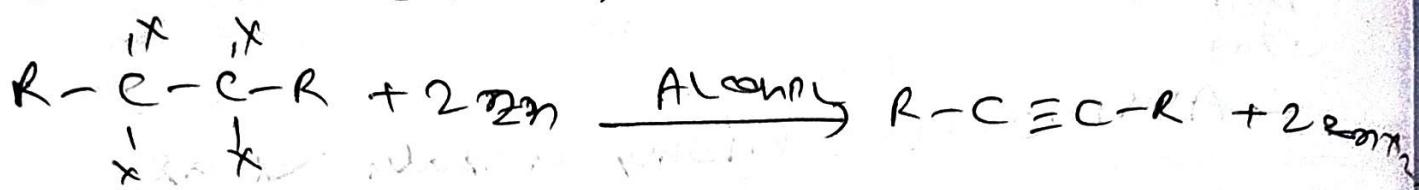
$\text{NaBH}_4(\text{H}_2)$ is used to remove 2nd HBr .



1,2-Dibromoethane.



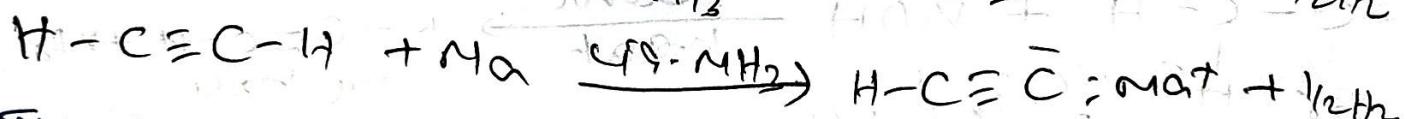
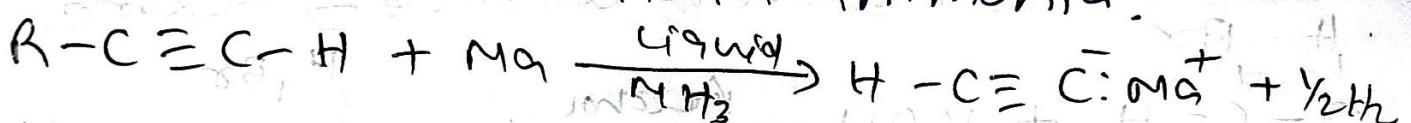
⑤ Dehalogenation of tetrahalides



This reaction is not of great utility for preparing alkynes, because tetrahalides are themselves made by addition of halogen to alkynes.

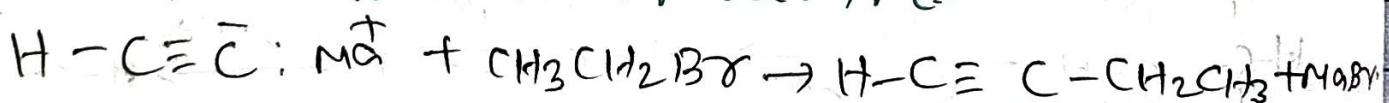
③ Reaction of sodium Acetylide with LO_2 alkyl halides.

Sodium acetylides are prepared by treatment of acetylene or 1-alkynes with sodium in liquid ammonia.

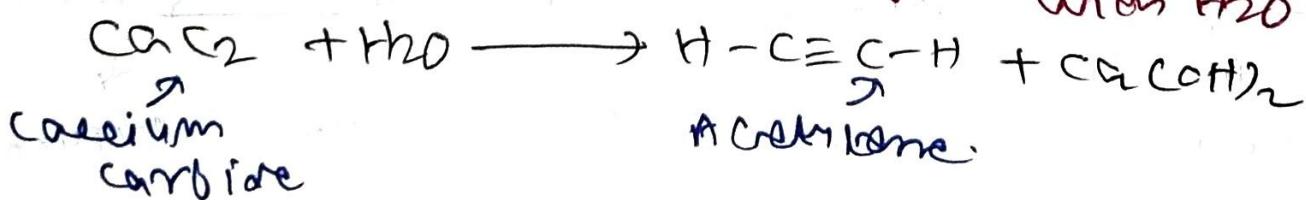


These sodium salts react with primary alkyl halide to form alkynes.

The main advantage of this method is that it can be used to convert lower alkynes into higher alkynes.



④ Reaction of calcium carbide with H_2O



PHYSICAL PROPERTIES:-

- CLASSMATE
Date 16
Page

 1. Let 3N - HgO , next - a liquid, higher ΔH_{vap}
 2. A ~~alkyne~~ has garlic odour, next ~~one~~ ~~but~~ ~~another~~ = Odourless.
 3. Slightly soluble in water but dissolve in organic & solvent - Benzene Acetone Ethanol,
 4. BP and M.P. and $\Delta r\text{-}$ grants by increase in no.
 5. Alkyne have higher ΔH_{vap} as compared to alkenes.

CHMICAL PROPERTIES :-

- ① Addition of Hydrogen: - (Ni, Pt, Pd)

$$R-C\equiv C-H + H_2 \xrightarrow{Ni} R-CH=CH_2 \xrightarrow{H_2} R-CH_2-CH_3$$

$$CH_3-C\equiv CH + H_2 \xrightarrow{Ni} CH_3-CH=CH_2 \xrightarrow{H_2} CH_3-CH_2-CH_3$$

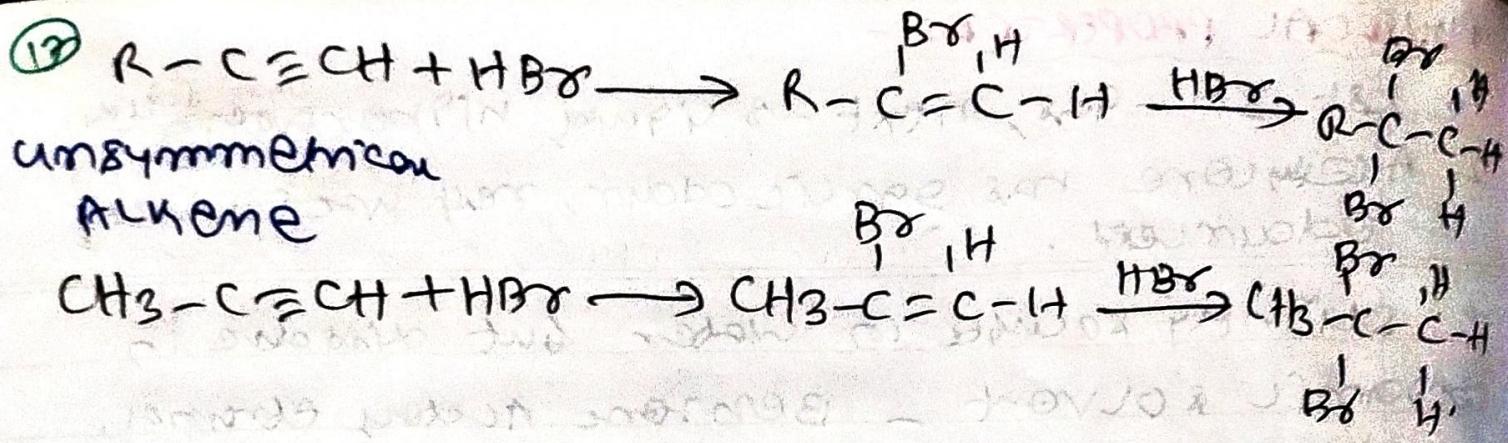
- ③ Addition of Halogen Acids - Markovnikov Rule.

$\text{R}-\text{C}\equiv\text{C}-\text{R} + \text{H}X \longrightarrow \text{R}-\overset{\text{X}}{\underset{\text{X}}{\text{C}}}=\overset{\text{H}}{\underset{\text{R}}{\text{C}}}-\text{R} \xrightarrow{\text{H}X} \text{R}-\overset{\text{H}}{\underset{\text{X}}{\text{C}}}-\overset{\text{X}}{\underset{\text{R}}{\text{C}}}-\text{R}$

Symmetrical Alkyne $\text{H}-\overset{\text{H}, \text{Br}}{\underset{\text{C}}{\text{C}}}-\text{H} + \text{HBr} \longrightarrow \text{H}-\overset{\text{H}}{\underset{\text{Br}}{\text{C}}}-\overset{\text{H}}{\underset{\text{C}}{\text{C}}}-\text{H}$

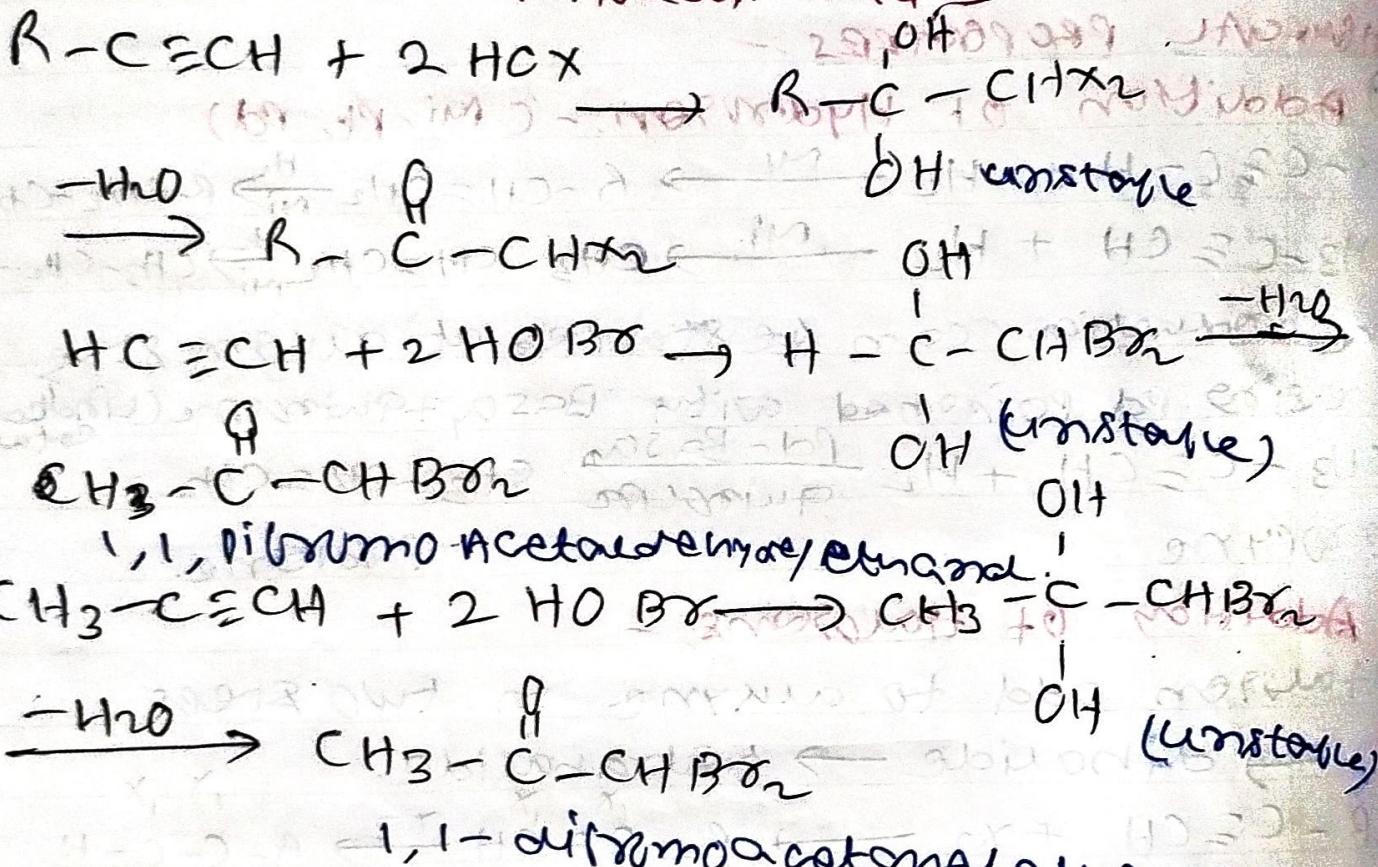
1-Bromoethane $\text{H}-\overset{\text{H}, \text{Br}}{\underset{\text{C}}{\text{C}}}-\text{H} \xrightarrow{\text{HBr}}$

1,1-Dibromoethane $\text{H}-\overset{\text{H}}{\underset{\text{Br}}{\text{C}}}-\overset{\text{H}}{\underset{\text{C}}{\text{C}}}-\text{H}$



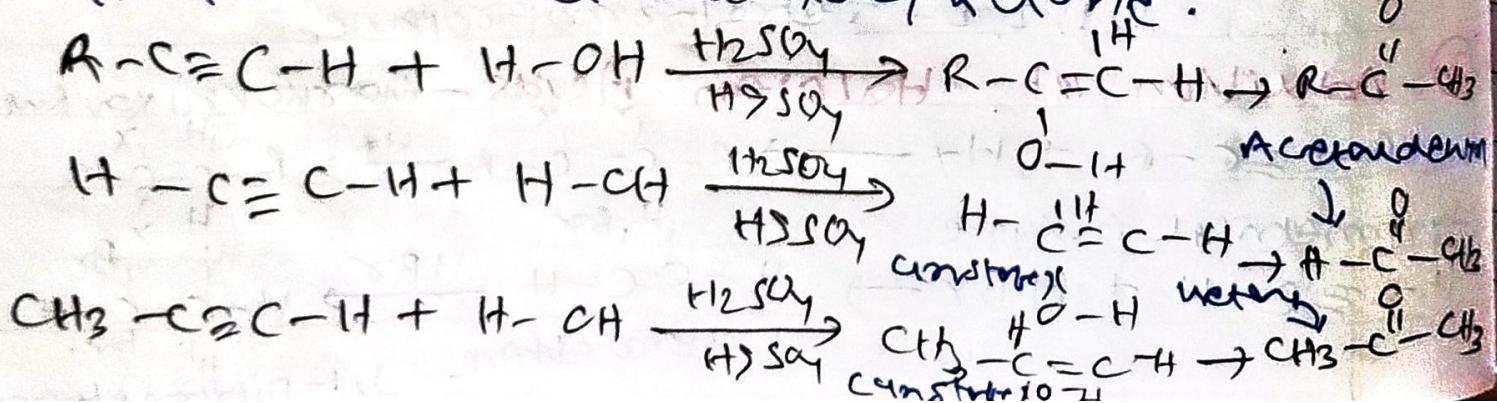
2,2-Dibromo
Propane

(4) Addition of Hydrohalic Acid.

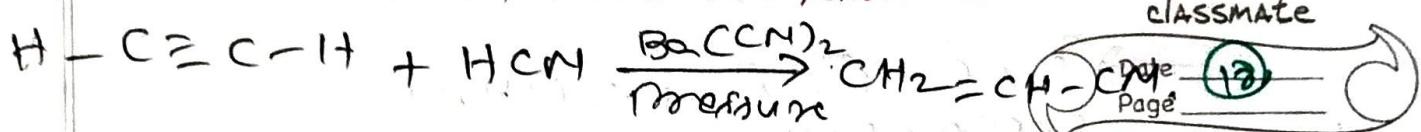


(5) Hydrogenation (Addition of Water)

reacts with water in presence of mercuric sulphate and sulphuric acid to form aldehydes/ketone.



⑥ Addition of Hydrogen cyanide.



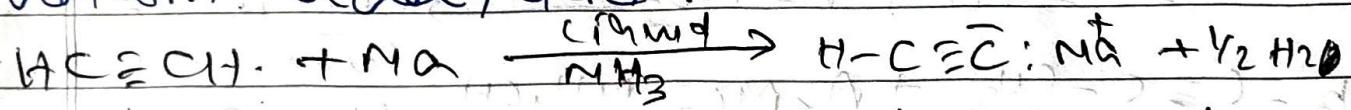
React with HCN in presence of Boron cyanide as catalyst.

Acetone yields vinyl cyanide or acrylonitrile from which synthetic fiber orlon is made.

⑦ salt Formation :- $\text{C}\equiv\text{C}-\text{H}$) are acidic can be replaced by metal to form salts known as **Acetylides**.

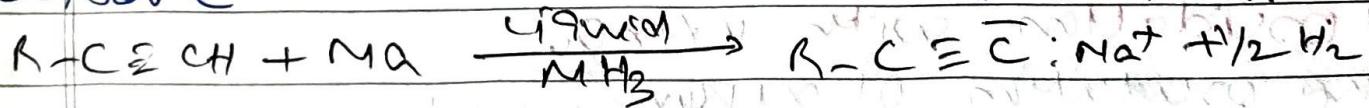
④ formation of sodium Acetylide

Acetylene or $\text{L}\text{-}\alpha\text{lyne}$ reacts with ~~soot~~ sodium with liquid ammonia or sodium amide (NaNH_2) to form sodium acetylide.



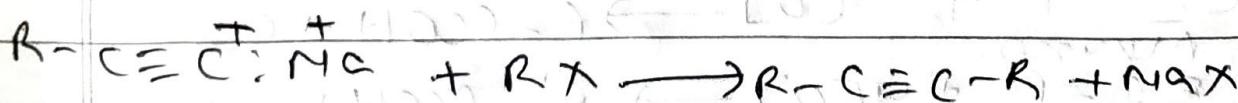
A Crosby varne

Sodium Acetylate



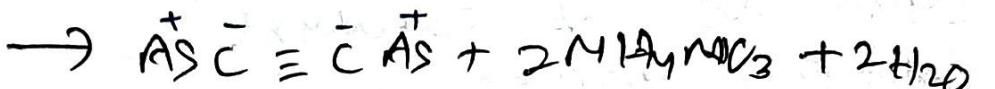
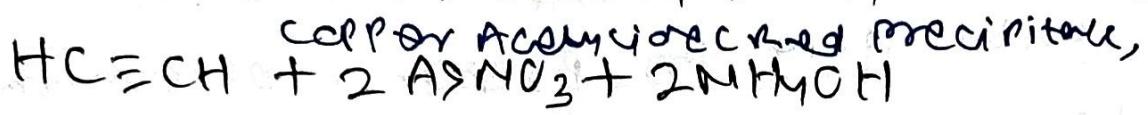
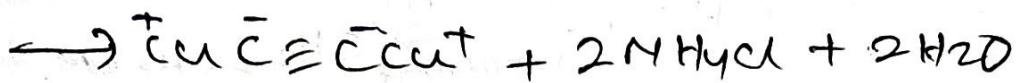
L-Aukyne

Sodium Acetylide reacts with primary alkyl halide to yield higher alkynes.



⑥ Formation of copper and silver Acetnides :-

A cycloone and 1-alkynes react with ammonical solution of cuprous chloride and silver nitrate to form acetylide of

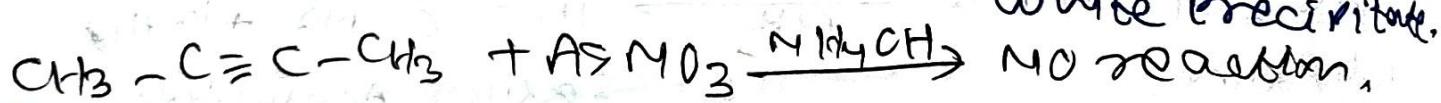
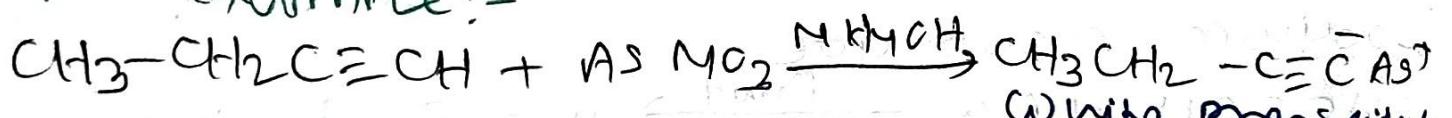


Silver Acetylide (white precipitate)

Copper and Silver Acetylides are very sensitive to shock when dry and may explode violently.

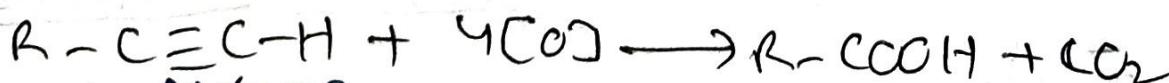
However they can be decomposed by acids ($\text{CH}_3\text{CO}_2\text{H}$) to resonance alkynes. Since 2-alkynes do not form acetylides, this reaction may be used to distinguish 2-alkyne from 1-alkyne.

For example:-



⑰ OXIDATION WITH KMnO_4

The oxidation of alkanes with alkane potassium permanganate to form carboxylic acids and CO_2 .



1- Alkyne.



2- Alkyne



Propane

Acetic Acid.

