

CHEMISTRY OF HYDROCARBONS

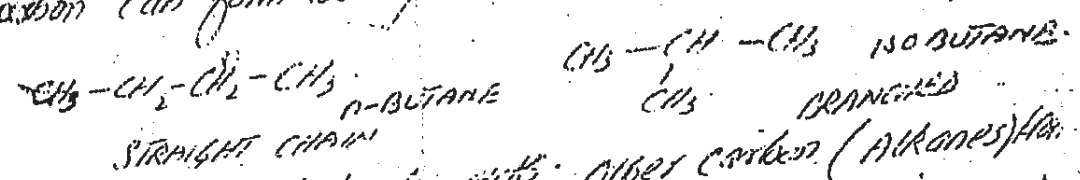
WHAT ARE HYDROCARBONS? EXPLAIN WHY THEY ARE PRESENT IN VERY LARGE NUMBER.

Ans. The simplest organic compounds containing only carbon and hydrogen are called hydrocarbons. The hydrocarbons are widely distributed due to following reasons.

Carbon is a member of group IV in periodic table. It can form four covalent bonds. The four bonds of carbon are directed towards corners of regular tetrahedron.

Carbon has property to catenate with itself to form chains and rings. (The ability of an element to form long chains is called catenation).

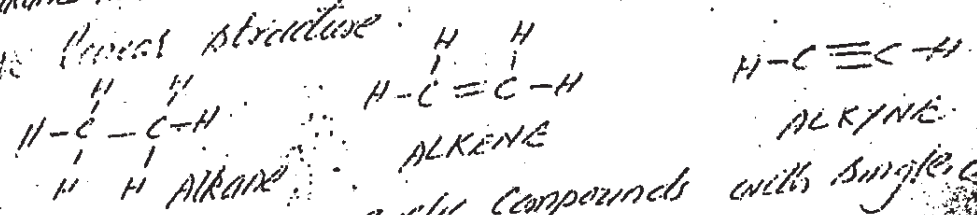
Carbon can form straight chains as well as branched chains



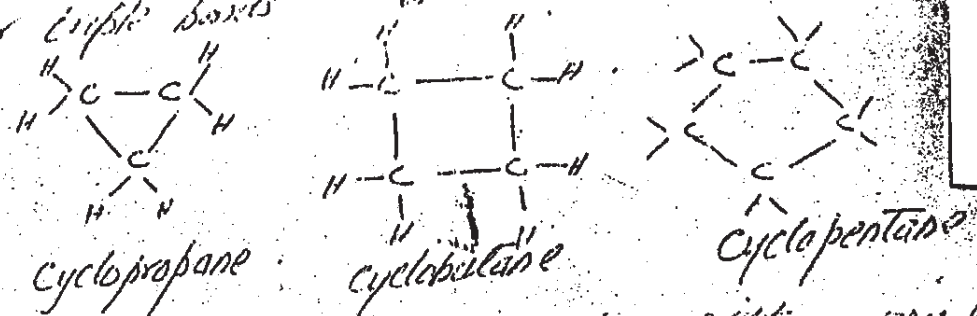
It can form single bonds with other carbon (Alkanes) or double bonds with other carbon (Alkenes)

Carbon can form triple bond with other carbon (Alkyne)

Alkanes have tetrahedral, alkenes have planar and alkynes have linear structure.

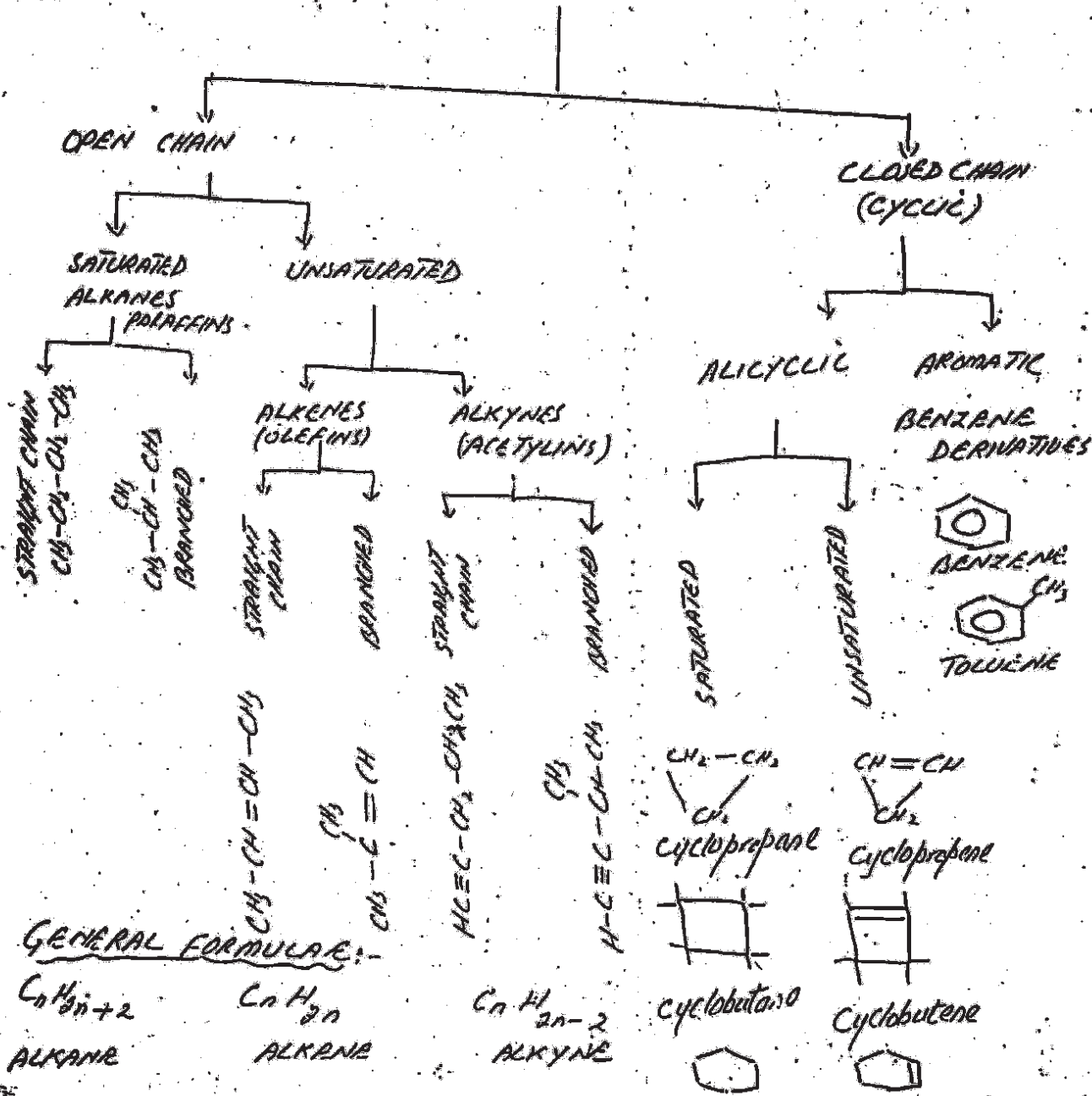


Carbon can form cyclic compounds with single, double or triple bonds



Due to these reasons hydrocarbons exist in very large number. The hydrocarbons are classified as follows.

# CLASSIFICATION OF HYDROCARBONS



GENERAL FORMULAE:-

$C_n H_{2n+2}$   
ALKANE

$C_n H_{2n}$   
ALKENE

$C_n H_{2n-2}$   
ALKYNE

The details of each class of hydrocarbons are given below.

# CLASSIFICATION OF HYDROCARBONS.

(3)

Hydrocarbons are basically divided into two general groups.  
 (i) OPEN CHAIN HYDROCARBONS (ii) CLOSED CHAIN HYDROCARBONS.

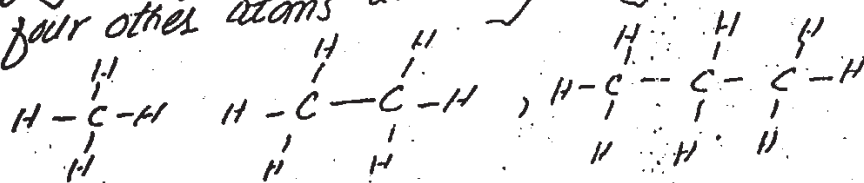
## OPEN CHAIN HYDROCARBONS:-

The open chain hydrocarbons are further divided into two categories.

(i) Saturated and (ii) Unsaturated hydrocarbons

## SATURATED HYDROCARBONS:-

These are also called alkane or Paraffins. In these hydrocarbons tetravalency of carbon is fully satisfied as the carbon is directly attached with four other atoms all through single bonds.



methane

Ethane

Propane

$C_n H_{2n+2}$

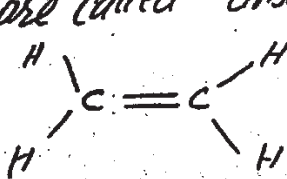
Alkane  
general formula

Alkanes show very little reactivity thus these are also called PARAFFINS mean little affinity. These hydrocarbons can undergo only substitution reaction, these are ampar and have very low m.p. & B.P. These are further divided into straight chain and branched hydrocarbons.

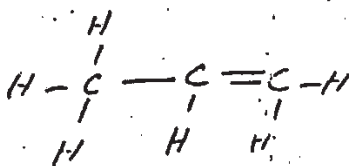
## UNSATURATED HYDROCARBON

These are hydrocarbons which can undergo addition reactions. These are further divided into ALKENES (having d.b.) and ALKYNES (having triple bond).

ALKENES | carbon In these hydrocarbons there is at least one carbon to carbon double bond. The double bonded carbon is directly attached with ~~two~~ three atoms so it has ability to attach another atom. So these are called unsaturated.



Ethene



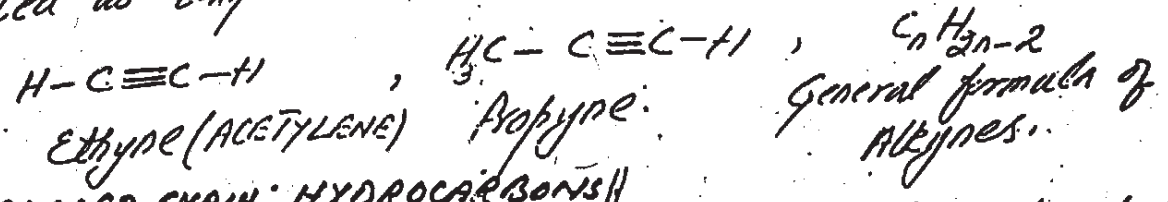
Propene

$C_n H_{2n}$

General formula  
of Alkene

These are further divided into a straight chain & branched.

ALKYNES // These are unsaturated hydrocarbons having a triple bond between two carbons. The carbon is attached with ~~one~~ two other atoms directly hence it can pick up two more atoms. Hence these are more unsaturated as compared to alkenes.

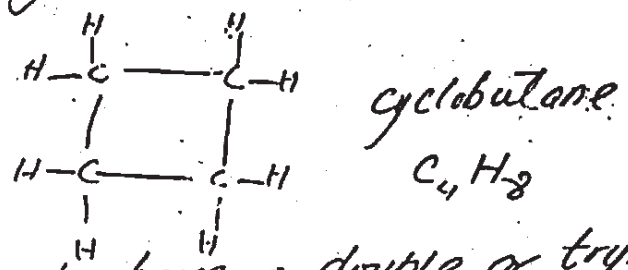
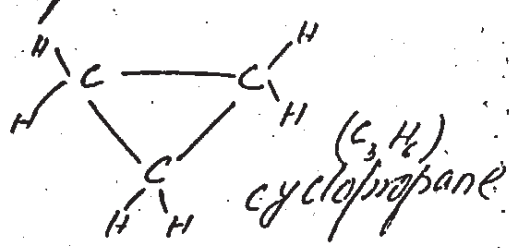




CLOSED CHAIN HYDROCARBONS

These are further divided into two categories. viz (i) ALICYCLIC (ii) AROMATIC

ALICYCLIC HYDROCARBONS

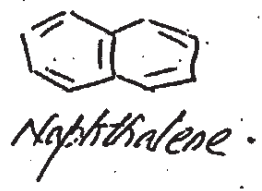
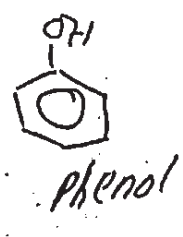
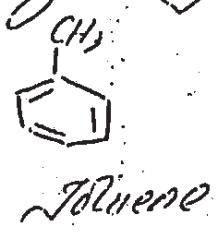
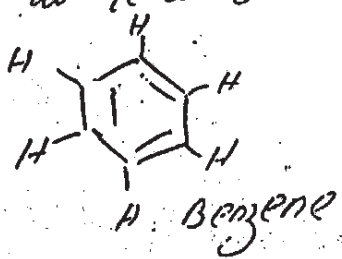
An alkane hydrocarbon on cyclization would produce an alicyclic compound. These saturated alicyclic compounds are analogous to alkane, thus they have chemical & physical properties similar to alkanes. However their general formula corresponds an alkane having same number of carbons.



Alicyclic compounds may also have a double or triple bond. e.g.  cyclopentene  cyclohexene.

AROMATIC COMPOUNDS // (BENZENE AND COMPOUNDS)

A six membered ring having three alternate double bonds is called BENZENE. The compounds having at least one benzene ring are called aromatic compounds.



# RULES OF NAMING ALKANE ACCORDING TO

## I. I.P.A.C. NOMENCLATURE.

The branched alkanes are named according to following rules of nomenclature.

Select longest carbon chain and name it as alkane.

Number the chain so that substituent gets smallest possible number.

Mention position of substituent by carbon number to which substituent is attached.

If same substituent is attached at two or more different carbons, number of each carbon is written before name of substituent.

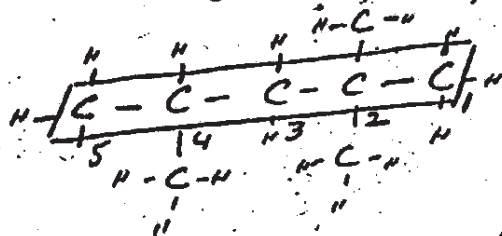
Prefix di, tri or tetra is used for two, three and four identical substituents.

The substituents are written alphabetically.

If two chains of equal length compete for selection, then select that carbon chain which has maximum number of substituents.

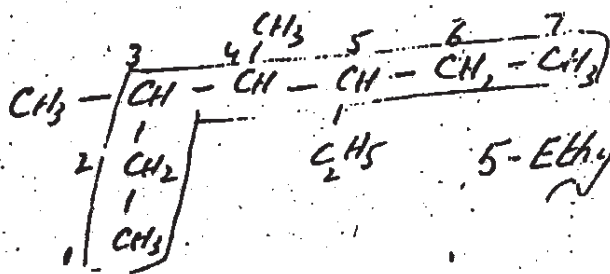
If numbering is possible from two ends then number chain in such way that sum of the numbers of substituents is smallest.

Some examples are given below.



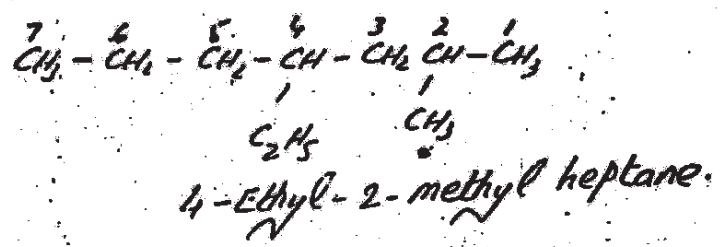
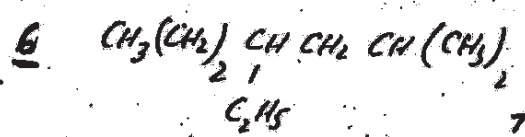
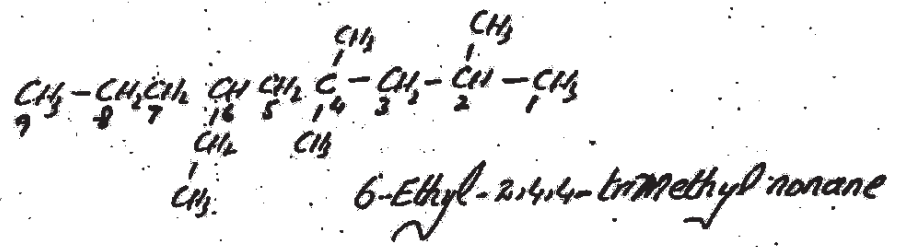
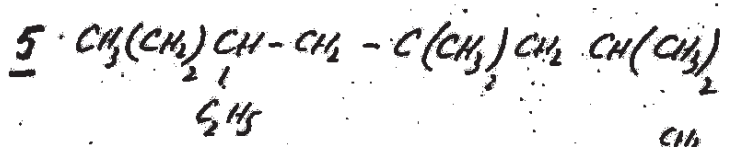
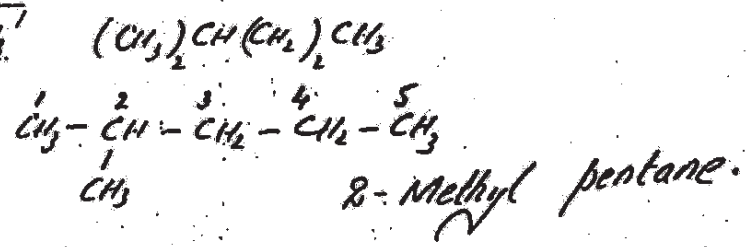
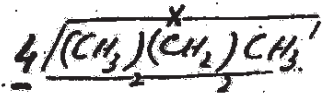
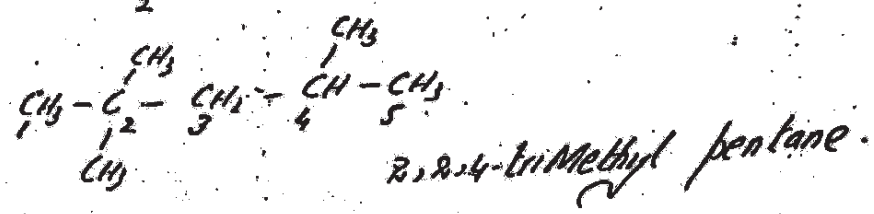
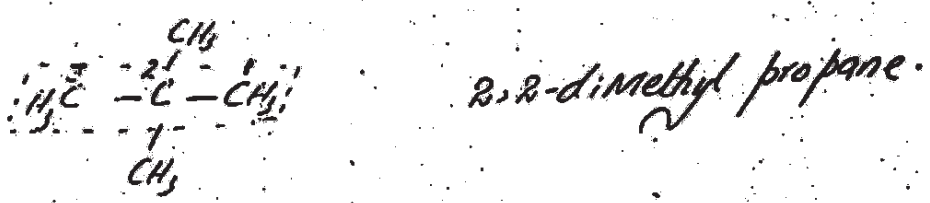
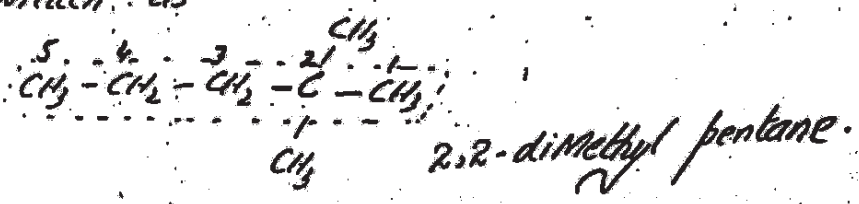
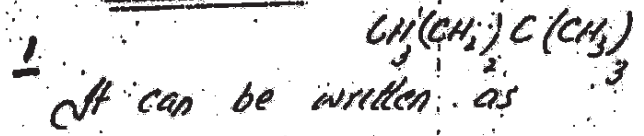
longest C-chain = 5C.

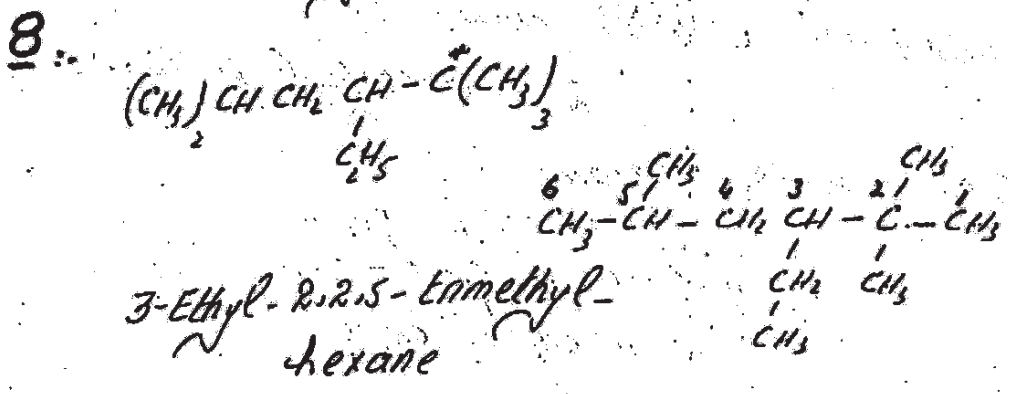
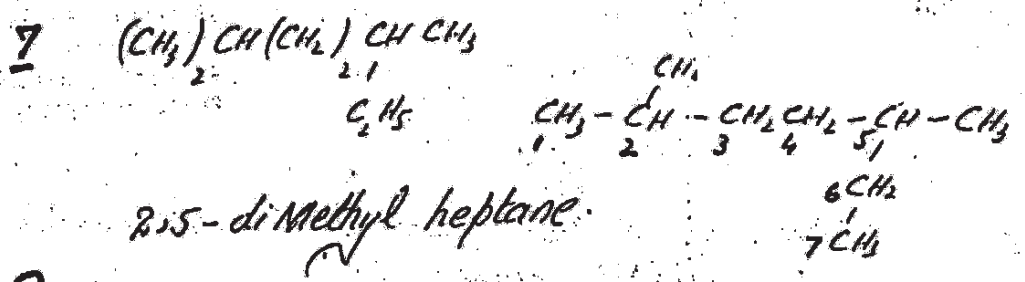
2,2,4-trimethyl pentane.



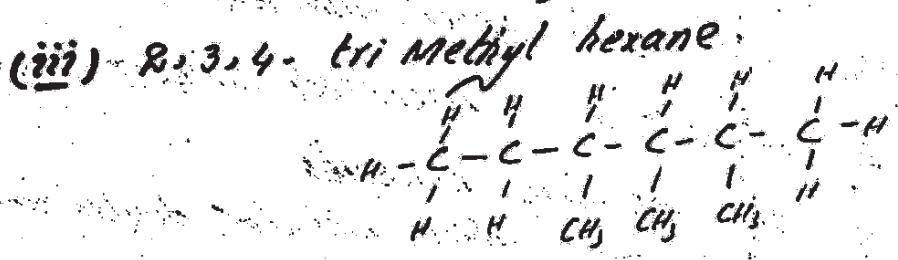
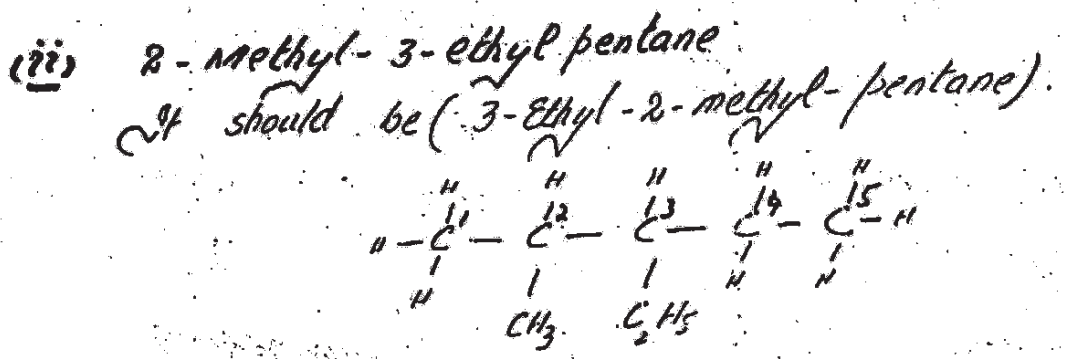
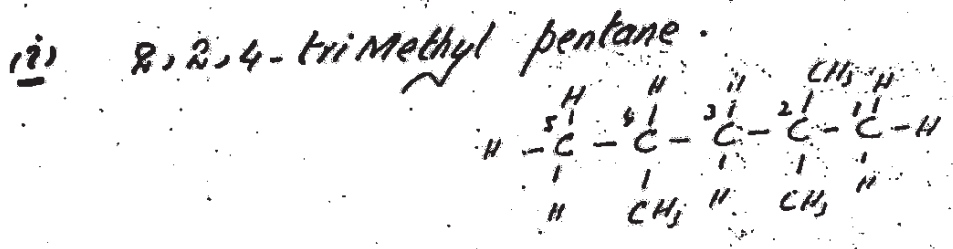
5-Ethyl-3,4-dimethyl heptane.

Write names of following alkanes according to IUPAC nomenclature.

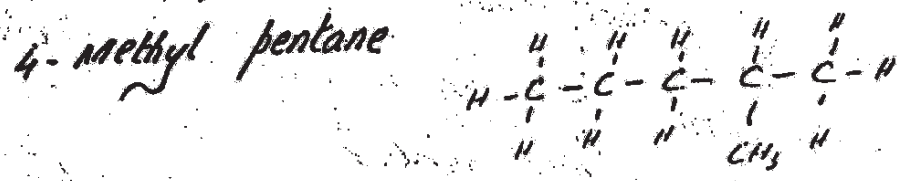




WRITE STRUCTURES OF FOLLOWING COMPOUNDS.

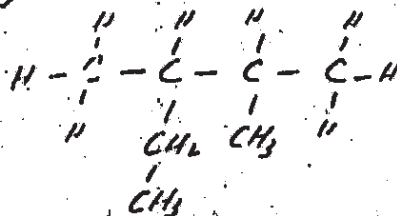


Q.: FOLLOWING NAMES ARE IN-CORRECT. WHY?



WRONG CHAIN NUMBERING  
 It should be :- "2-Methyl pentane."

2-methyl-3-ethyl-butane.

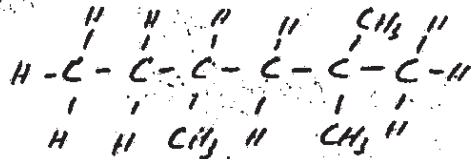


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PO 5, BARGODHA.

WRONG CHAIN SELECTION. LONGEST CARBON CONTAIN 5-CARBONS. CORRECT NAME IS

2,3-dimethyl pentane.

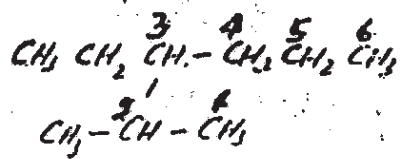
3,5,5-trimethyl hexane.



INCORRECT NUMBERING.

It should be 2,2,4-trimethyl hexane.

Q:- WHICH NAME IS CORRECT.



Correct Name:- 3-Ethyl-2-methyl hexane.

INCORRECT NAMES

REASONS.

- a Isopropyl hexane WRONG CHAIN SELECTION
- b 3-ISOPROPYL HEXANE " " "
- d 4-Ethyl-5-methyl hexane INCORRECT NUMBERING
- e 2-methyl-3-propyl pentane INCORRECT LONGEST CHAIN

WRITE RULES OF NAMING ALKENES

- 1- Select longest carbon chain which includes double bond
- 2- The name of parent chain ends with "-ene"
- 3- Number the chain in such a way that double bond gets smallest possible number.
- 4- The position of double bond is indicated by number of carbon forming double bond.

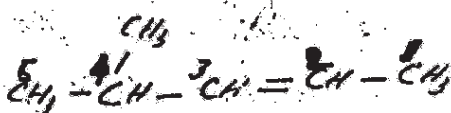
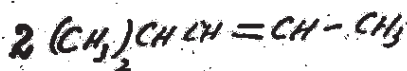


5 - Two double bonds are indicated by respective numbers of carbons forming double bonds. di, or tri is written before "ene"

WRITE NAMES OF FOLLOWING ACCORDING TO IUPAC SYSTEM.

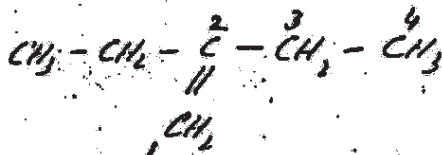


2 - Hexene.



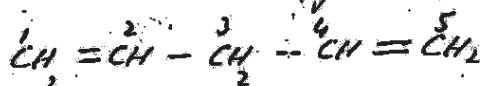
4 - Methyl - 2 - pentene.

3



2 - Ethyl - 1 - butene.

4



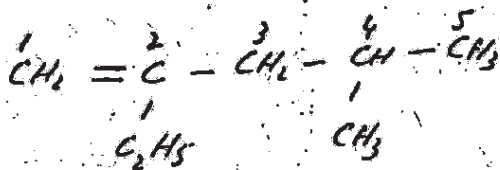
1, 4 - Pentadiene

5



1, 3 - Pentadiene

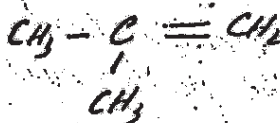
6



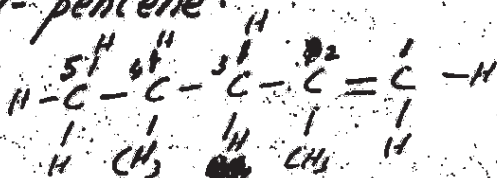
2 - Ethyl - 4 - methyl - 1 - pentene.

WRITE STRUCTURES OF FOLLOWING.

2 - Methyl propene.



2, 4 - dimethyl - 1 - pentene.



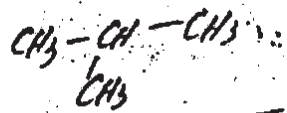


Q No. 4:-

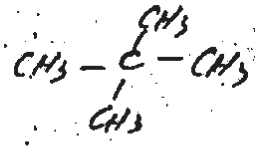
WRITE STRUCTURAL FORMULA OF FOLLOWING COMPOUNDS

(11)

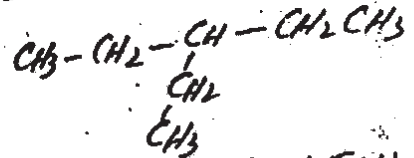
(1) 2-METHYL PROPANE



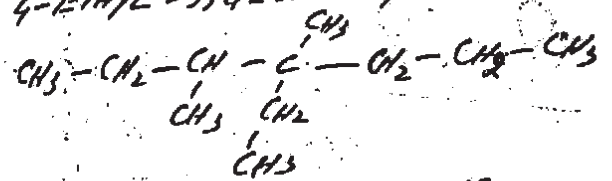
(2) NEOPENTANE



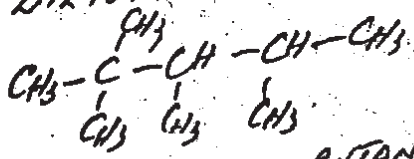
3) 3-ETHYL-PENTANE



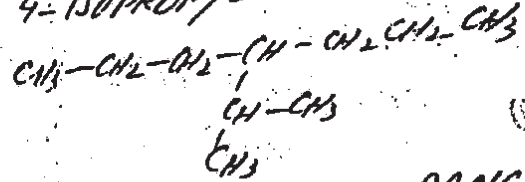
(4) 4-ETHYL-3,4-DIMETHYL HEPTANE



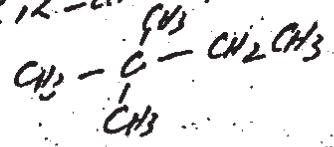
5- 2,2,3,4-tetramethyl PENTANE.



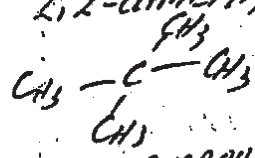
(6) 4-ISOPROPYL HEPTANE



7- 2,2-dimethyl BUTANE

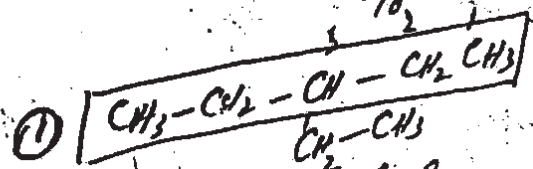


(8) 2,2-dimethyl PROPANE

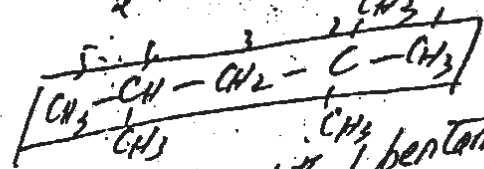


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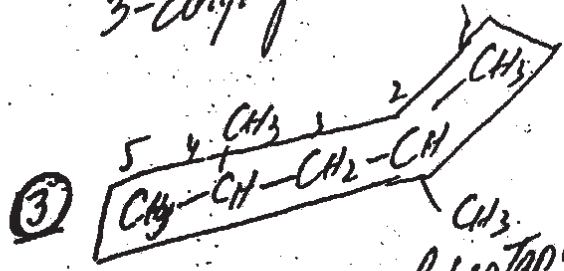
WRITE NAMES OF FOLLOWING COMPOUNDS ACCORDING I.U.P.A.C. NOMENCLATURE



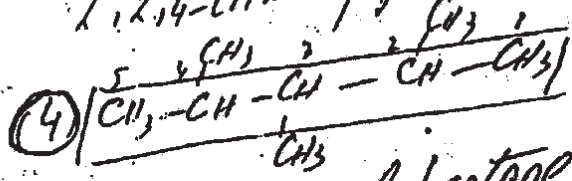
3-Ethyl pentane



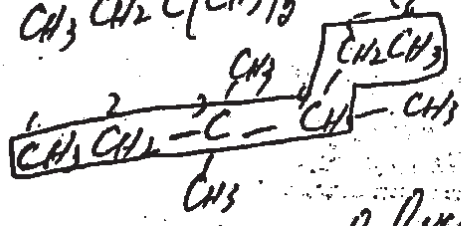
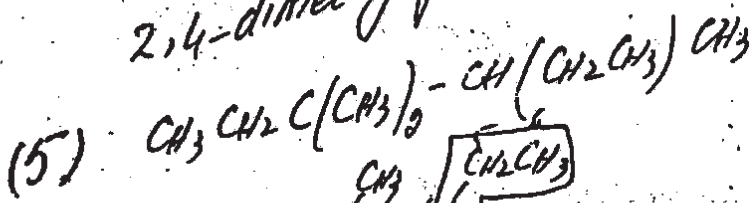
2,2,4-trimethyl pentane.



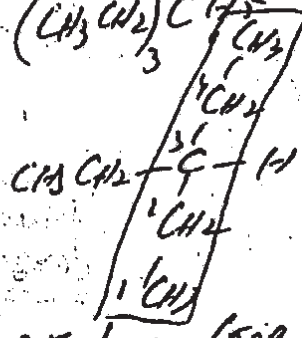
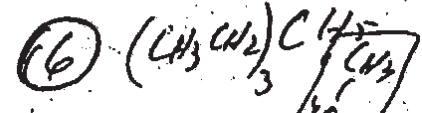
2,4-dimethyl pentane



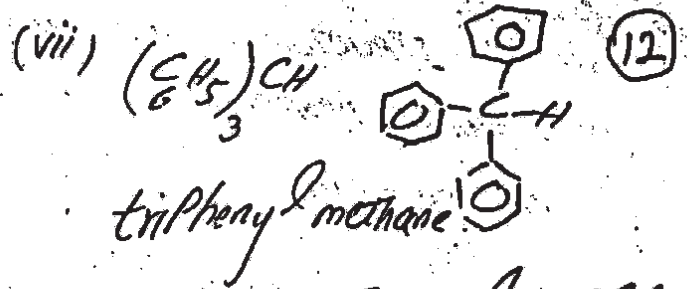
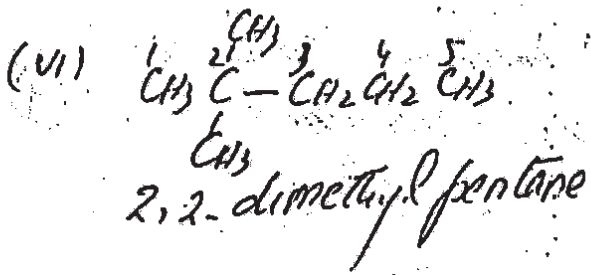
2,3,4-trimethyl pentane



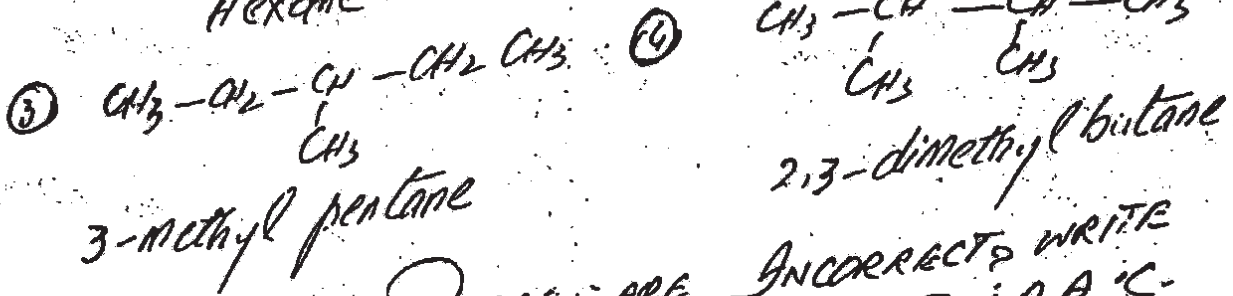
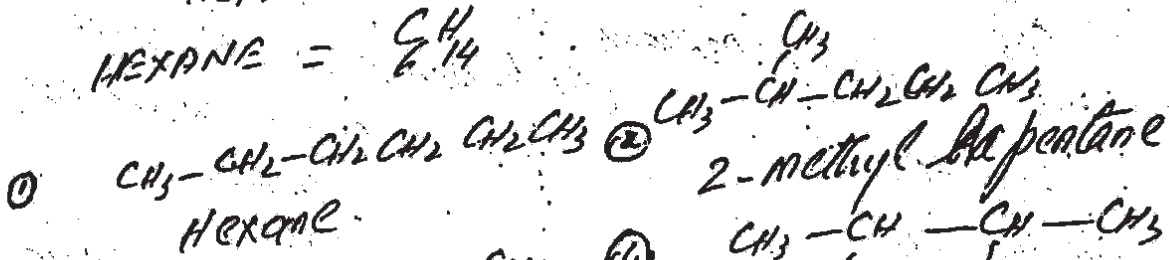
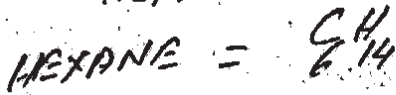
3,3,4-trimethyl hexane



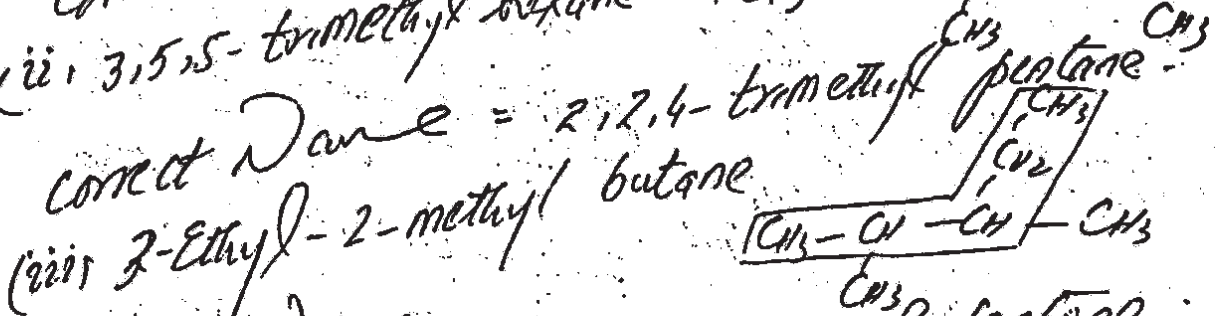
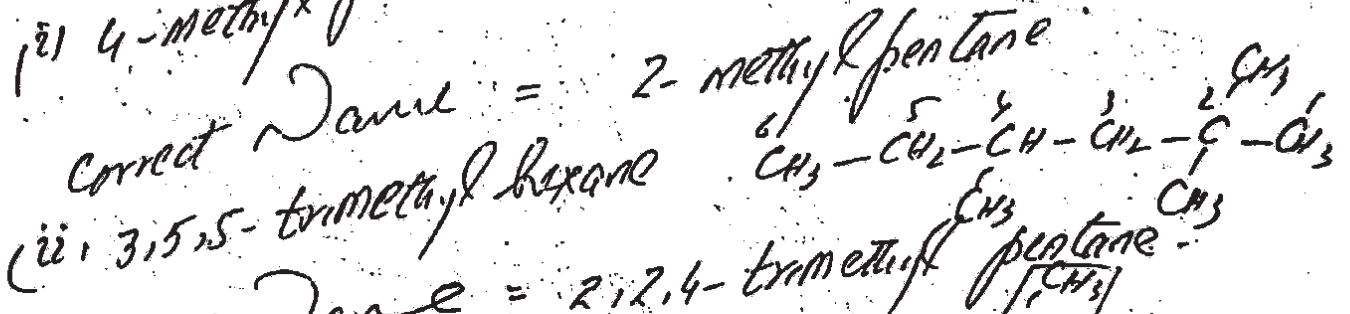
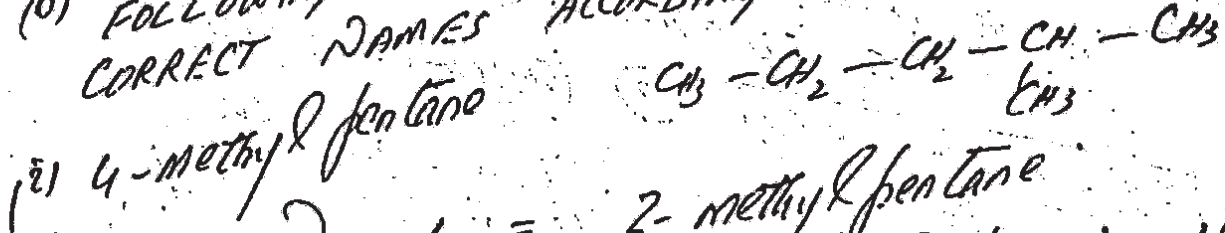
3-Ethyl pentane



Q. NO. 7 WRITE STRUCTURAL FORMULA OF FIVE ISOMERIC HEXANE AND WRITE THEIR NAMES.



(b) FOLLOWING NAMES ARE INCORRECT? WRITE CORRECT NAMES ACCORDING TO I.U.P.A.C.

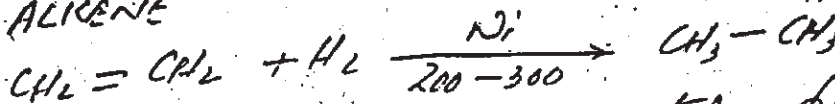
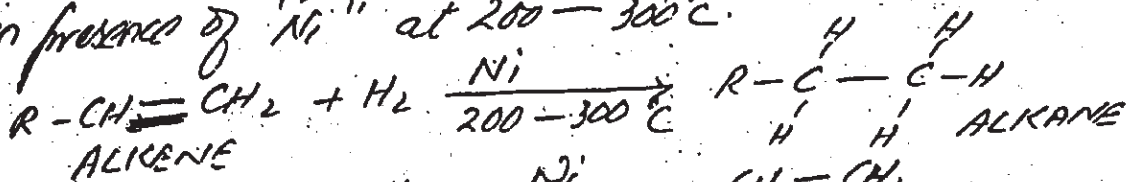


# METHODS OF PREPARATION OF ALKANES.

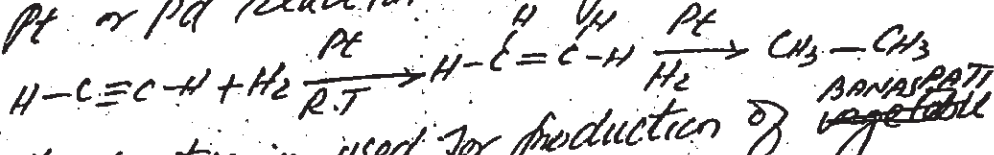
(13)

## SABITIER SENDRENS' REACTION (HYDROGENATION OF UNSATURATED HYDROCARBONS)

The addition of hydrogen to an unsaturated hydrocarbon is called HYDROGENATION. The reaction is carried out in presence of "Ni" at 200-300°C.

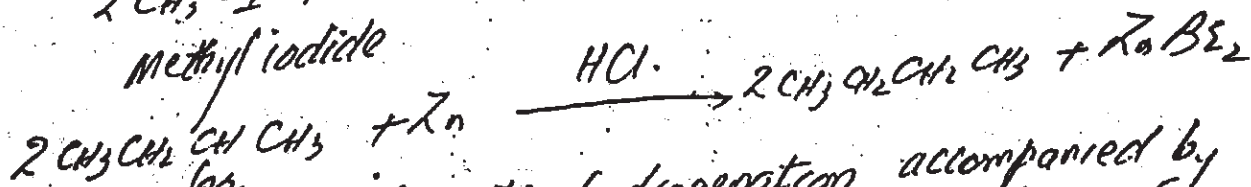
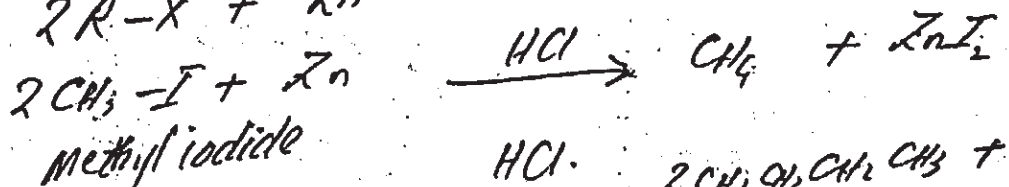
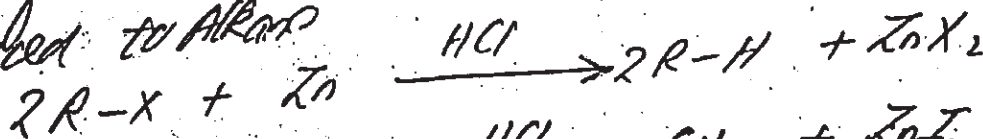


In presence of "Pt" or Pd reaction takes place at room temperature.

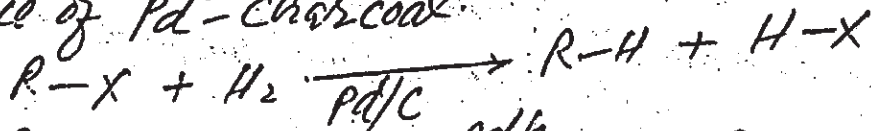


APPLICATION The reaction is used for production of ghee from veg. oil. The oils contains unsaturated fatty acids which are converted into saturated compounds on hydrogenation.

FROM REDUCTION OF ALKYL HALIDES: Alkyl halides are reduced to alkanes in presence of "Zn" and HCl or acetic acid. Zn is a good reducing agent. It transfers electron to carbon. Thus alkyl halide is reduced to alkane.



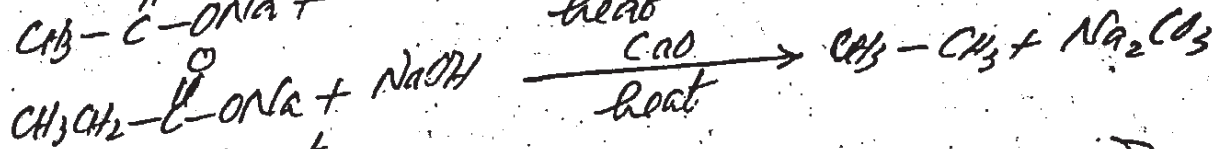
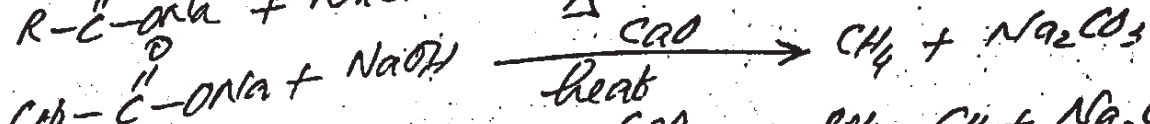
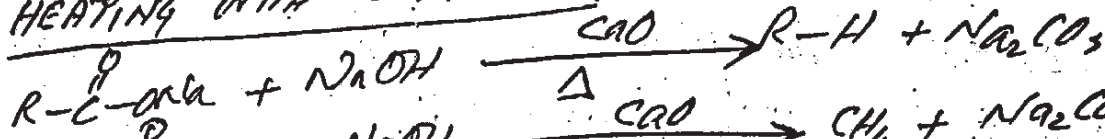
HYDROGENOLYSIS: The hydrogenation accompanied by bond breakage is called HYDROGENOLYSIS. It is carried out by reaction of Alkyl halide with hydrogen in presence of Pd-charcoal.



# DECARBOXYLATION OF MONOCARBOXYLIC ACIDS. (14)

There are two methods for conversion of sodium salts of carboxylic acids into alkanes

(a) HEATING WITH SODALIME

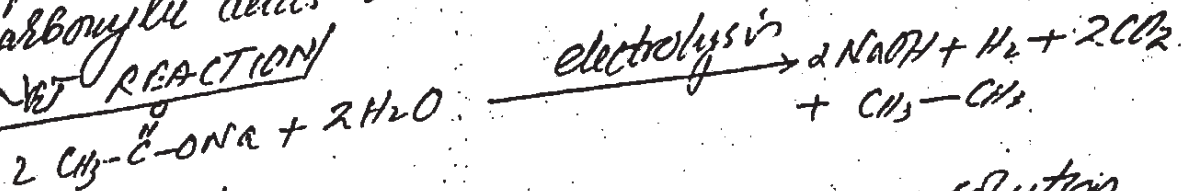


Sodium propionate

2- KOLB ELECTROLYTIC METHOD | The electrolysis of

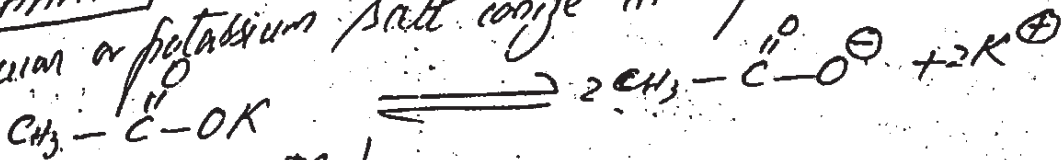
aqueous solution of sodium or potassium salt of carboxylic acids is called Kolb Electrolysis

NET REACTION



MECHANISM

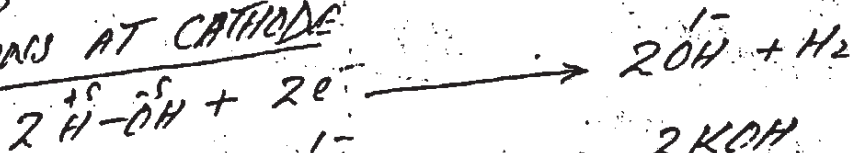
Sodium or potassium salt ionize in aqueous solution



REACTION AT ANODE



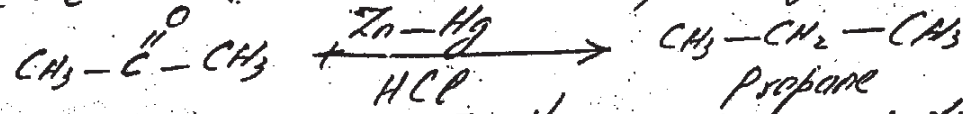
REACTIONS AT CATHODE



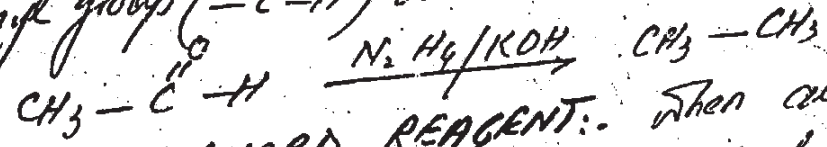
The reaction has limited application because it forms a number of side products.

FROM CARBONYL COMPOUNDS: - The carbonyl comp. (i.e. Aldehydes and Ketones) are reduced to Alkanes by five methods.

CLEMENSON REDUCTION :- Ketones are reduced to alkanes by reaction with Zinc amalgam and HCl. The  $\text{-C(=O)-}$  is reduced to methylene group.  $\text{-CH}_2\text{-}$

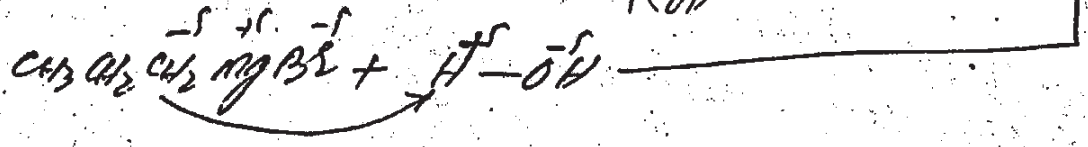
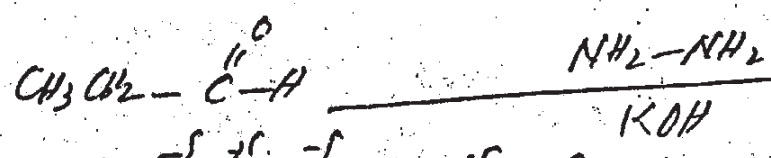
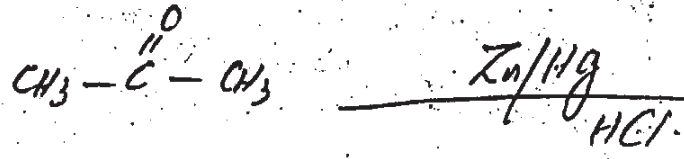
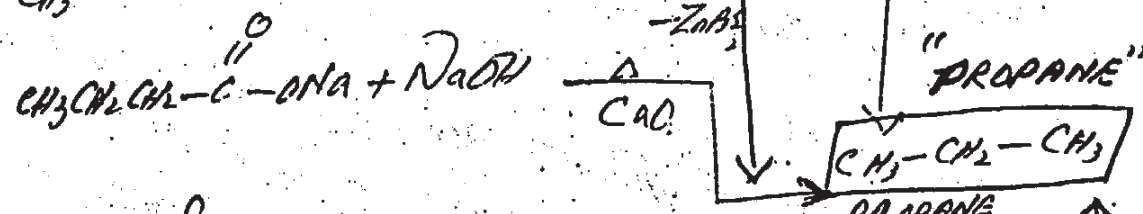
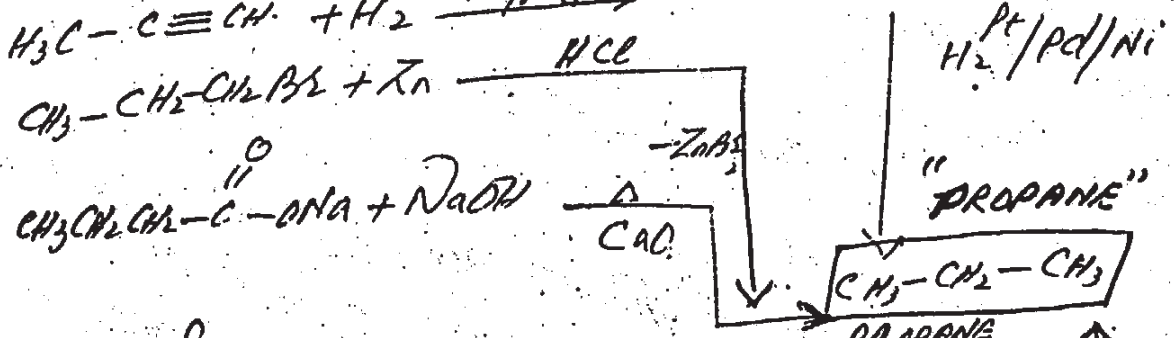
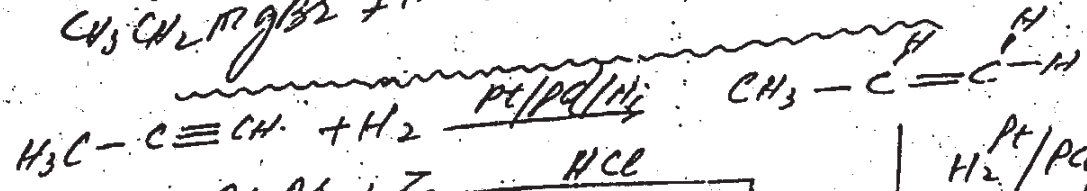
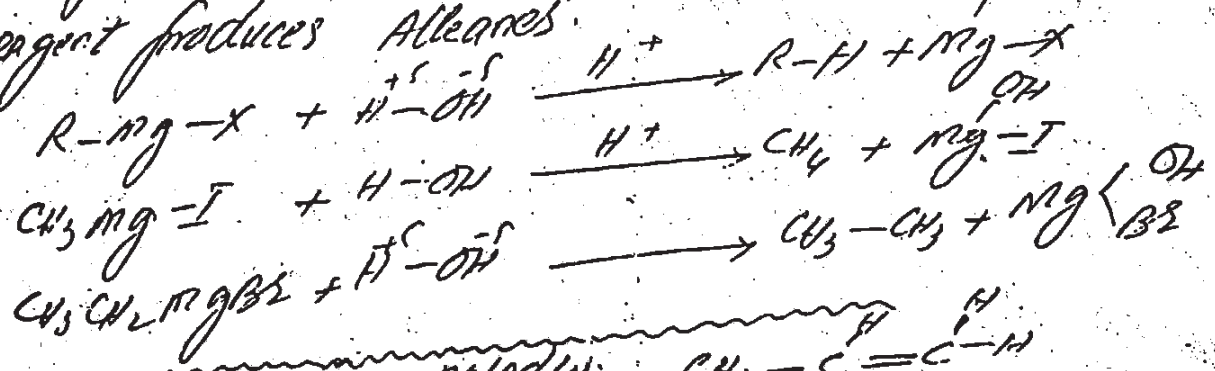


WOLF KISHNER REDUCTION Aldehydes are reduced to alkanes by reaction with KOH and hydrazine. The formyl group ( $\text{-C(=O)-H}$ ) is reduced to  $\text{-CH}_3$ .



FROM GRIGNARD REAGENT :- When alkyl halides are treated with Magnesium in anhydrous ether, alkyl magnesium halide is produced. This is called Grignard reagent.

The hydrolysis of Grignard reagent produces Alkanes.



# PHYSICAL CHARACTERISTICS OF ALKANES

PHYSICAL STATE / Alkane containing  $C_1 - C_4$  atoms = Gases

$C_5 - C_{17}$  atoms = Liquids

$C_{18}$  - onwards = Solids

All hydrocarbons (Alkanes) are colourless odourless liquids or solids

2- SOLUBILITY / All alkanes are non-polar or weakly polar compounds. They are insoluble in water but soluble in non-polar solvents like ether, benzene etc.

3- BOILING POINTS / Their m.p., b.p., density increases with increase in number of carbon atoms. The solubility decreases with increase in number of carbon atoms. Their b.p. increases  $20 - 30^\circ$  per  $CH_2$  group.

The branched alkanes have lower b.p. than straight chain isomeric hydrocarbons. n-Butane has b.p.  $55^\circ$  while isobutane has b.p.  $-102^\circ C$ .

4- MELTING POINTS / The m.p. of alkanes increase with increase in molecular mass but this increase is not regular.

## WRITE NOTE ON REACTIVITY OF ALKANES

The alkanes are saturated compounds. They are also called paraffins (little affinity). They are not attacked by general laboratory reagents like acids, bases, oxidizing agents, reducing agents etc. The inertness of alkanes can be explained on two bases

## NON PLANAR NATURE

Alkanes are non-planar compounds due to v. small A.E.N. between "C" and "H". Thus the ionic reagents find no place to attack on alkane molecule.

INERTNESS OF SIGMA BOND :- These C-C sigma bond between two carbon atoms. Sigma bond is quite

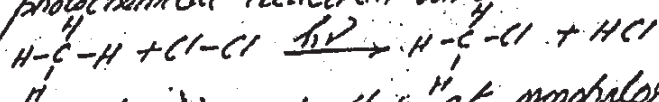


strong bond. The shared electron pair is tightly held<sup>17</sup> by two atoms. A lot of energy is required to break it. The electrons present in a  $\sigma$ -bond can neither attack on any electrophile nor a nucleophile can attack on them. Both these facts make alkanes less reactive.

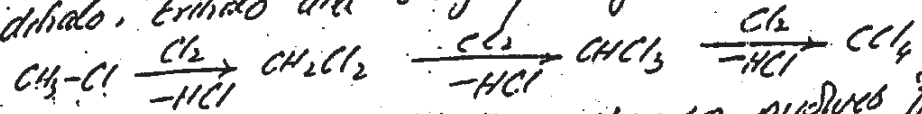
However under suitable conditions alkanes undergo two types of reactions.

1) SUBSTITUTION REACTIONS (2) THERMAL & CATALYTIC REACTIONS  
These reactions take place at high temp. or in presence of sunlight. The reaction proceeds through free radical mechanism.

HALOGENATION: Alkanes react with halogens (Cl<sub>2</sub>) in presence of sunlight to produce chloroalkanes. This is a photochemical reaction which involves free radical mechanism.

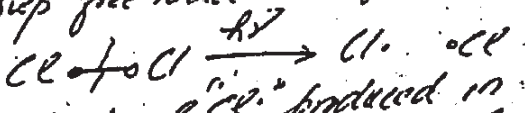


The reaction does not stop at monohalogenated state and dihalo, trihalo and tetrahalogenated compounds are formed.

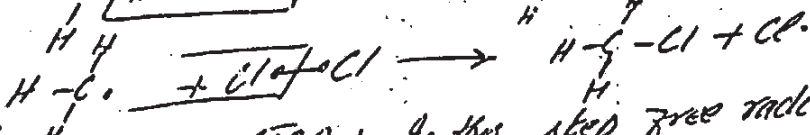
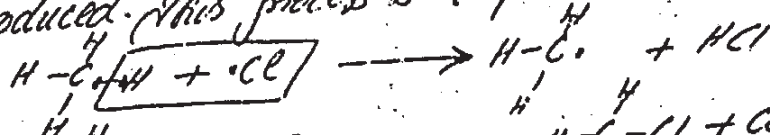


MECHANISM: Free radical mechanism involves following steps

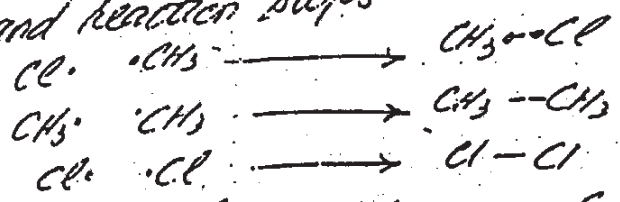
(i) INITIATION STEP: In this step free radicals are produced due to action of sunlight.



(ii) PROPAGATION STEP: Chlorine radical 'Cl·' produced in first step reacts with methane and abstracts methyl radical from molecule of 'CH<sub>4</sub>'. Methyl radical abstracts 'Cl' from another molecule of 'Cl<sub>2</sub>' and methyl chloride and another 'Cl·' is produced. This process is repeated over and over again.



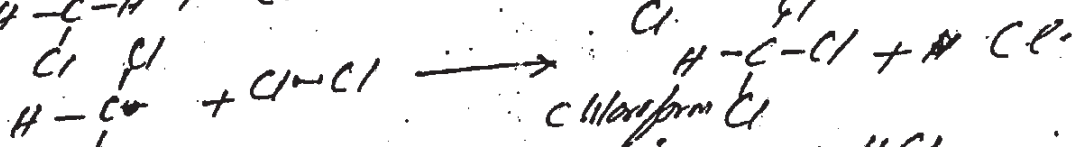
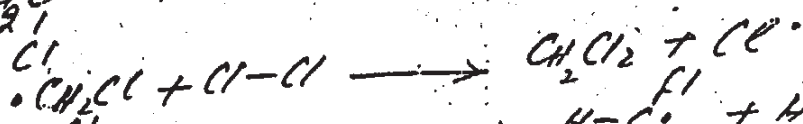
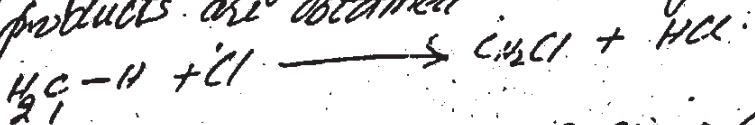
TERMINATION STEP: In this step free radicals are annihilated and reaction stops.



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3, S.B. SANGHINA

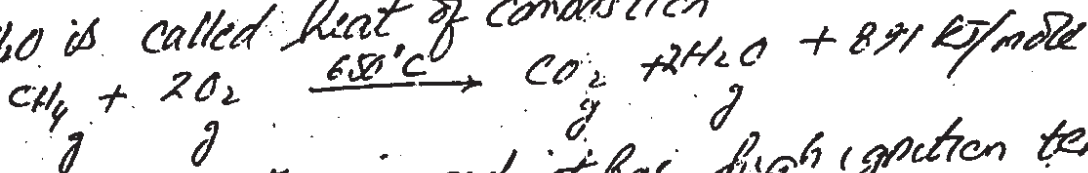
The order of reactivity of halogens is F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub>.  
Iodine does not react.

By repetition of above steps polyhalogenated products are obtained.



COMBUSTION  
REACTIONS OF ALKANES

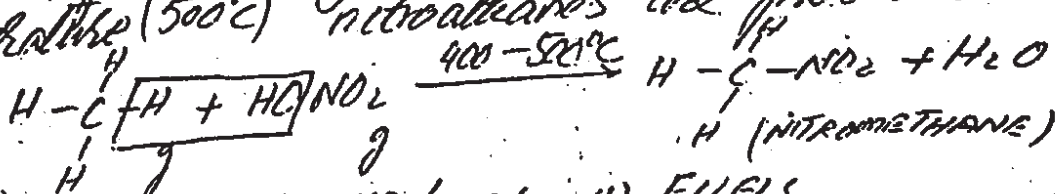
Burning of Alkanes in presence of oxygen is called Combustion. Complete combustion produces  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and heat. The amount of heat evolved when 1 mole of hydrocarbon burns into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is called heat of combustion.



The reaction is exothermic and it has high ignition temp. Thus it is initiated by heat or flame or spark.

APPLICATION The reaction takes place in internal combustion engine of Automobiles. A compressed mixture of alkane and  $\text{O}_2$  burns smoothly in internal combustion engine and increases its efficiency.

NITRATION OF ALKANES: The replacement of hydrogen of alkane by nitro group is called nitration. When vapours of alkane and nitric acid are passed through a glass tube at high temperature ( $500^\circ\text{C}$ ) nitroalkanes are produced.

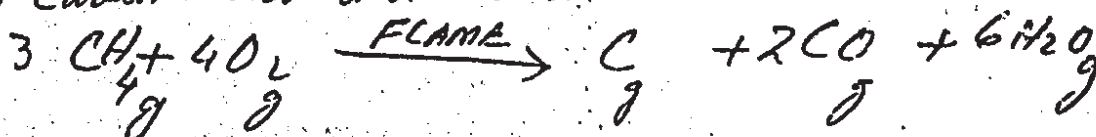


Nitroalkanes are used as

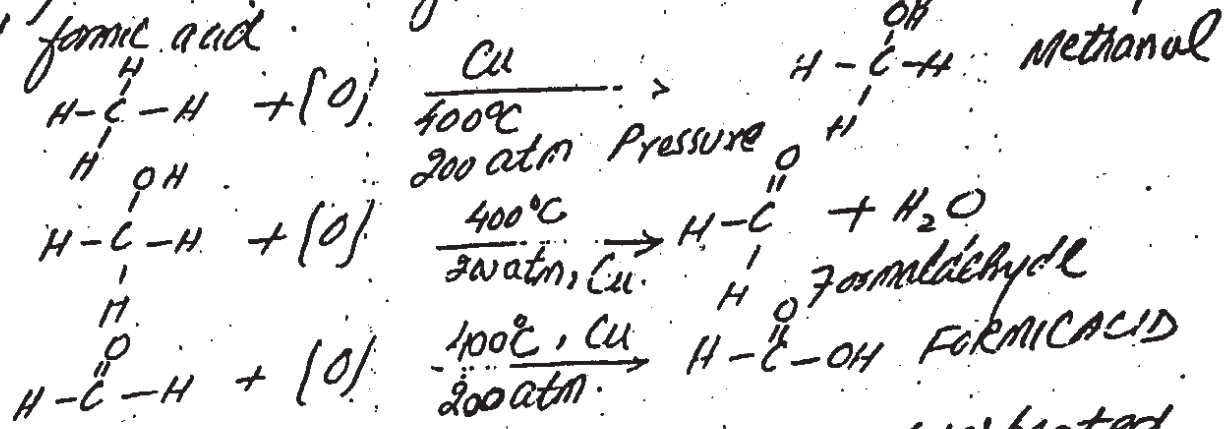
- 1) FUELS
- 2) SOLVENT
- 3) IN ORGANIC SYNTHESIS

OXIDATION OF METHANE: The oxidation of methane under different conditions produces different products.

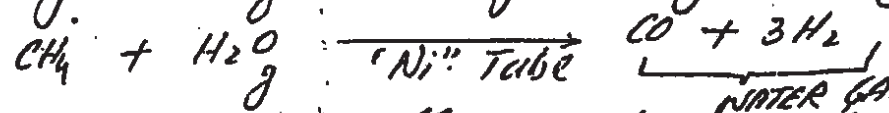
"INCOMPLETE OXIDATION" The incomplete oxidation in presence of limited supply of oxygen or Air produces  $\text{CO}$ , carbon black and steam.



CATALYTIC OXIDATION: - Methane when burnt in presence of copper at 400°C and 200 atm. pressure, undergoes catalytic oxidation. It produces Methanol, formaldehyde and formic acid.

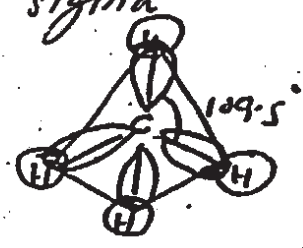


ACTION OF STEAM: - Methane reacts with superheated steam in presence of nickel producing water gas.



This method is commercially used for preparation of H<sub>2</sub> gas.

STRUCTURE OF METHANE: - Methane has a tetrahedral structure. Carbon is sp<sup>3</sup> hybridized. Four C-H sigma bonds are formed due to sp<sup>3</sup>-1s overlap. H-C-H bond angle is 109.5°. It's a non planar structure.



USES OF METHANE:

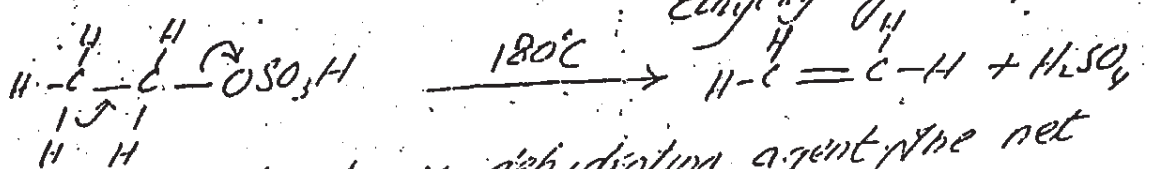
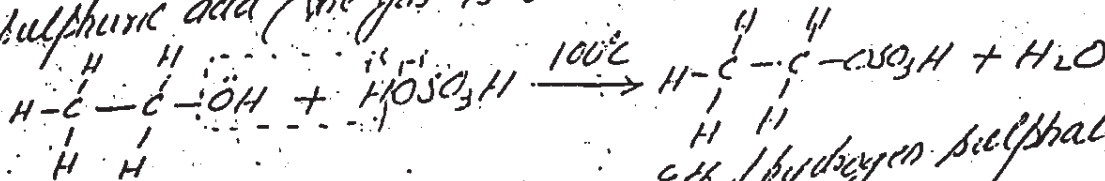
- 1) It's an important fuel and illuminating gas.
  - 2) Pyrolysis of CH<sub>4</sub> produces carbon black which is an important raw material for paints and automobile tyres.
  - 3) It is used to prepare chloroform, formaldehyde, tetra-chloromethane etc.
  - 4) It is used to prepare hydrogen on commercial scale.
- $$\text{CH}_4 + \text{H}_2\text{O} \xrightarrow{\text{Ni}} \text{CO} + 3\text{H}_2$$
- 5) Urea fertilizer is prepared by using CH<sub>4</sub> as one of raw materials.

# PREPARATION OF ETHENE (ETHYLENE).

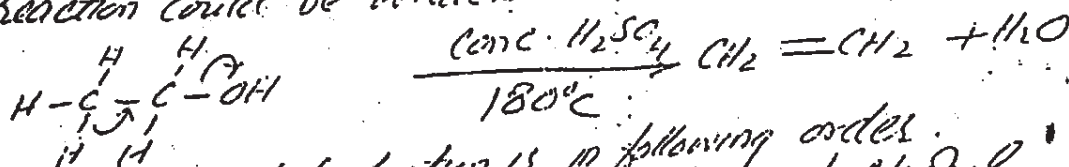
Ethene or ethylene is an important alkene. It is present in wood gas or coal gas. It can also be prepared by following methods.

## Laboratory methods - DEHYDRATION OF ALCOHOL:

Ethylene can be prepared on a small scale by heating together ethyl alcohol and sulphuric acid. The gas is collected over water.



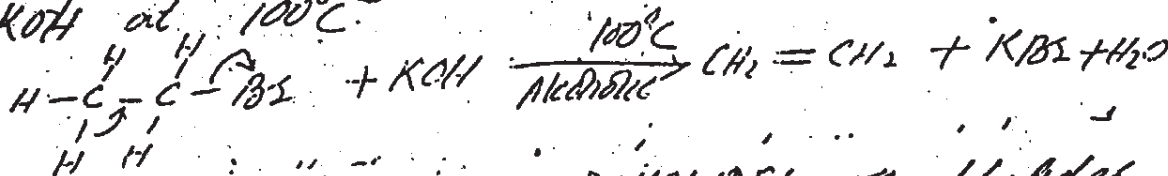
Sulphuric acid acts as dehydrating agent. The net reaction could be written as



The ease of dehydration is in following order:  
 tert alcohol > sec alcohol > 1° alcohol.  
 20% H<sub>2</sub>SO<sub>4</sub>, 85°C      60% H<sub>2</sub>SO<sub>4</sub>, 160°C      75% H<sub>2</sub>SO<sub>4</sub>, 140-170°C

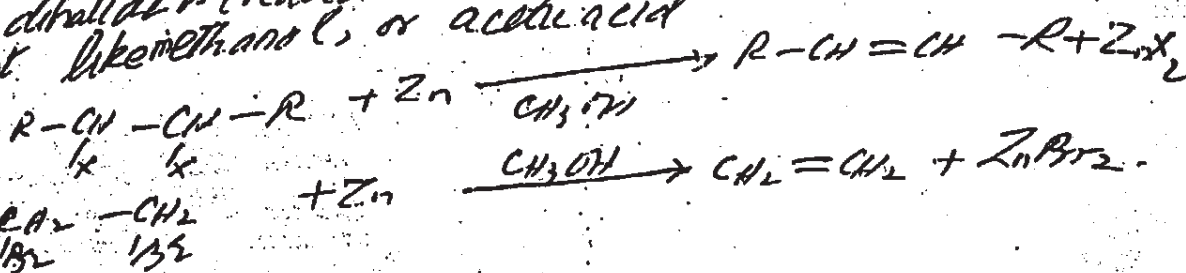
## 2. DEHYDROHALOGENATION OF ALKYL HALIDES.

The removal of hydrogen and halogen from two adjacent carbons is called dehydrohalogenation. It is also called β-elimination reaction. Dehydrohalogenation takes place when alkyl halides is treated with alcoholic KOH at 100°C.



## 3. DEHALOGENATION OF VICINAL DIHALIDES: The dihalides

having two halogen atoms on two adjacent carbon atoms are called vicinal dihalides. Dehalogenation occurs when dihalide is treated with zinc dust in anhydrous solvent like methanol, or acetic acid.



FROM ACETYLENE:-(Hydrogenation of Acetylene)

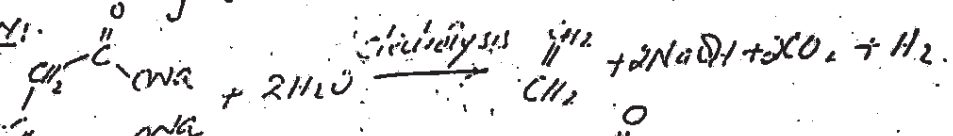
When hydrogen is added to acetylene in presence of palladium over  $\text{BaSO}_4$ , reaction can be stopped at ethene stage.



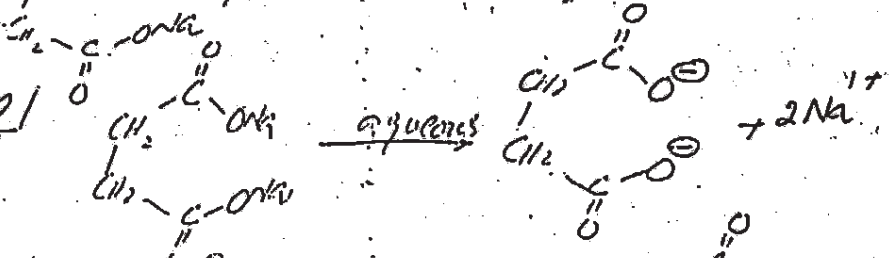
In presence of Ni, Pt or Al reaction cannot be stopped at ethene stage.

KOLB ELECTROLYSIS: The electrolysis of aqueous solution of disodium succinate produces ethene. This is called Kolb electrolysis.

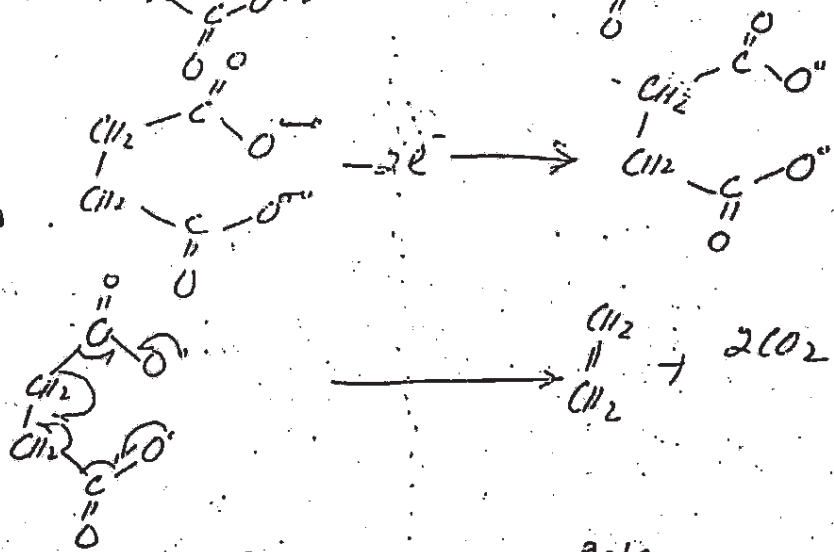
NET REACTION:



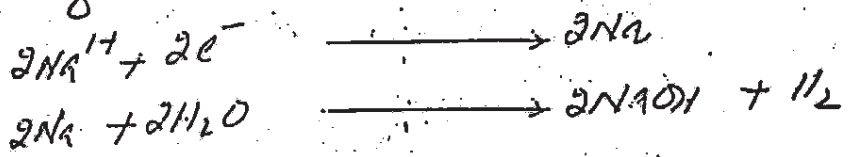
MECHANISM:



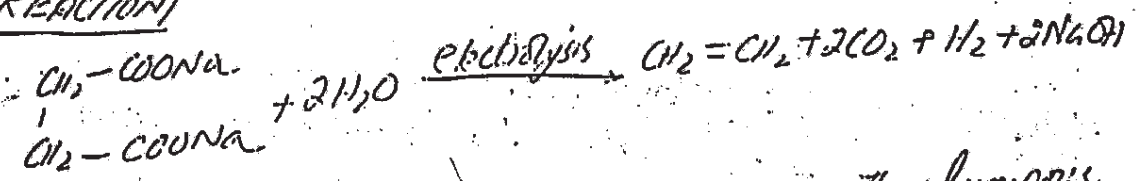
ANODE



CATHODE

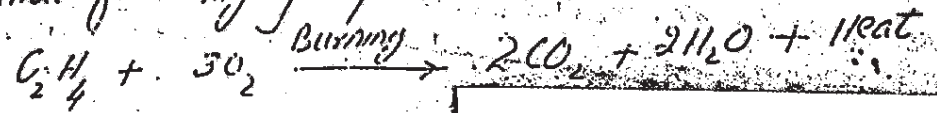


NET REACTION:



COMBUSTION OF ETHENE:

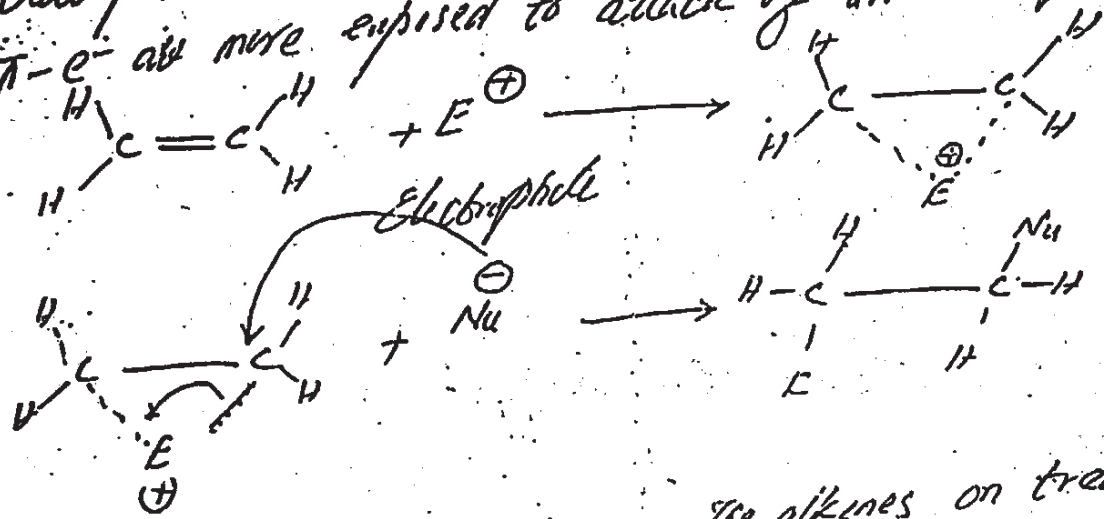
Ethylene burns with luminous flame and forms highly explosive mixture with air or oxygen.



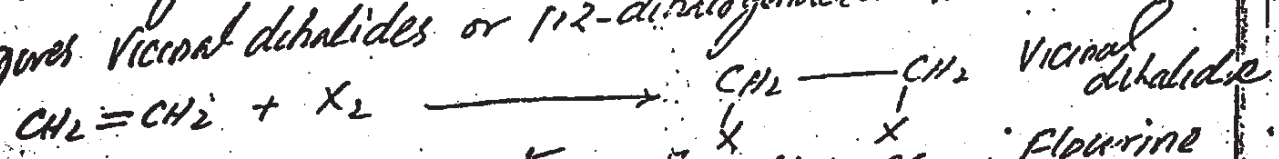
WRITE GENERAL MECHANISM OF ELECTROPHILIC 2,3

ADDITION REACTIONS OF ALKENES:

Alkenes have a C-C double bond between two carbon atoms. In a double bond there is a sigma and a pi bond between two atoms. pi bond is formed by parallel overlap of p-orbitals. The e<sup>-</sup> in pi bond are less firmly bonded to carbon atoms. Thus an electrophile can easily attack these pi-electrons. Thus alkenes undergo electrophilic addition reactions more quickly. The pi-e<sup>-</sup> are more exposed to attack of an electrophile.

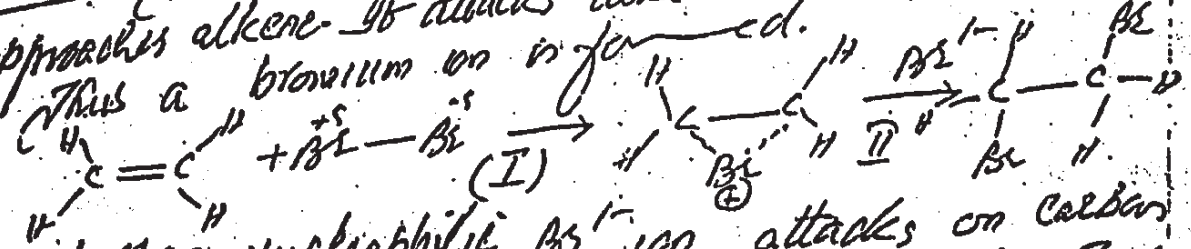


MECHANISM OF HALOGENATION: The alkenes on treatment with halogen in an inert solvent like CCl<sub>4</sub> at room temp. gives vicinal dihalides or 1,2-dihalogenated Alkanes.



The order of reactivity is  $F_2 > Cl_2 > Br_2$ . Fluorine is too reactive and iodine fails to react.

MECHANISM The bromine molecule becomes polarized as it approaches alkene. It attacks alkene as an electrophile.



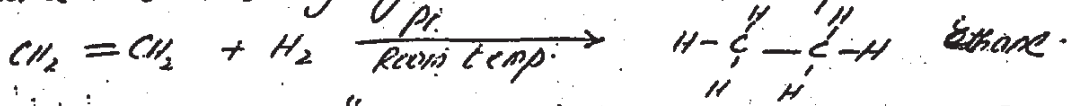
In second step nucleophilic Br<sup>-</sup> ion attacks on carbons of bromonium ion to form vicinal dibromide. The color of bromine is discharged. This test is used for identification of double bond in a compound.

ADDITION REACTIONS

Ethylene undergoes electrophilic addition reacts to form addition products which are saturated compounds.

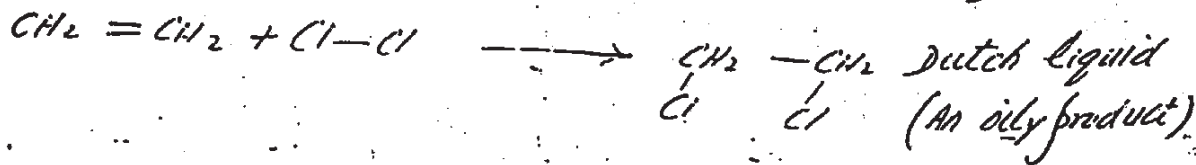
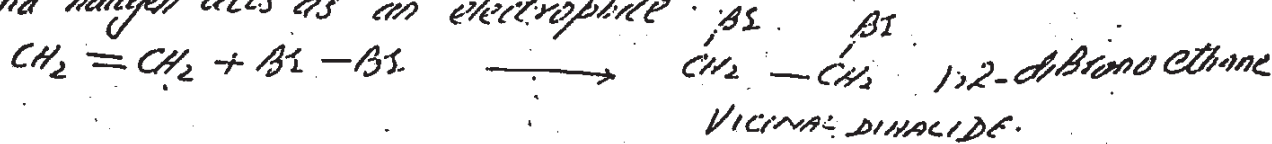
HYDROGENATION:- (ADDITION OF HYDROGEN)

When mixture of ethene and H<sub>2</sub> is passed over Platinum. Ethane is produced due to hydrogenation. at room temperature.



However in presence of "Ni" reaction takes place at 250° to 300°C. This process is important in industry. It is used to convert vegetable oil to solid fats.

ADDITION OF HALOGENS:- The addition of halogens to alkenes produces vicinal dihalide. The alkene behaves like a nucleophile and halogen acts as an electrophile.

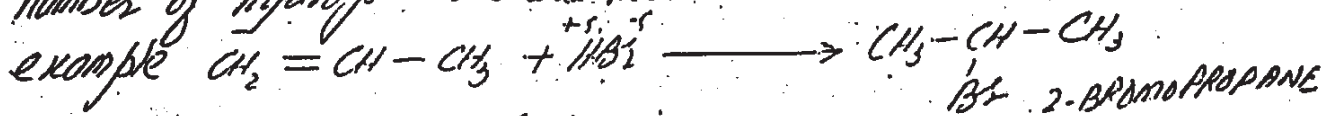


ADDITION OF HALOGEN ACIDS:-

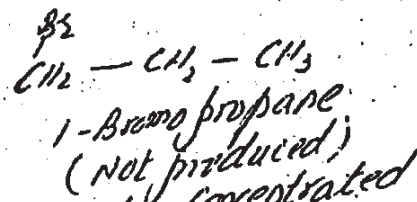
The addition of halogen acids to an alkene produces an alkyl halide. The order of reactivity is HI > HBr > HCl.



MARKOVNIKOFF'S RULE:- It states that, when an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of reagent will attach to that carbon atom which has least number of hydrogen atoms attached to it. Consider following example

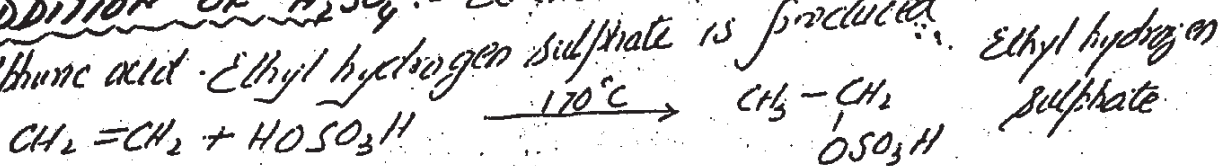


Thus according to Markovnikoff's Rule 2-Bromopropane is produced.



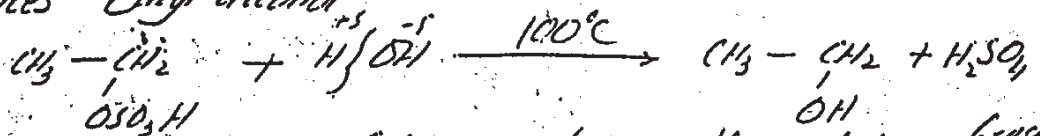
and NOT 1-Bromo propane.

ADDITION OF H<sub>2</sub>SO<sub>4</sub>:- Ethene is absorbed by Sulphuric acid. Ethyl hydrogen sulphate is produced.

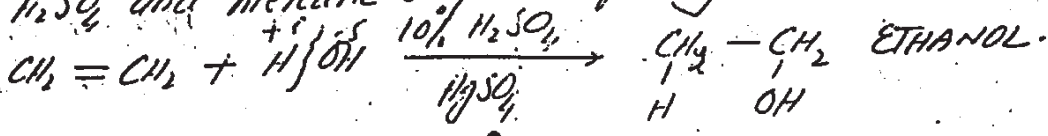




Ethyl hydrogen sulphate on hydrolysis with boiling water produces Ethyl alcohol.



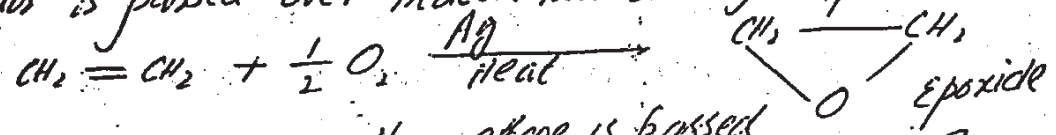
ADDITION OF WATER: Ethene combines with water in presence of 10% H<sub>2</sub>SO<sub>4</sub> and Mercuric Sulphate forming ethanol



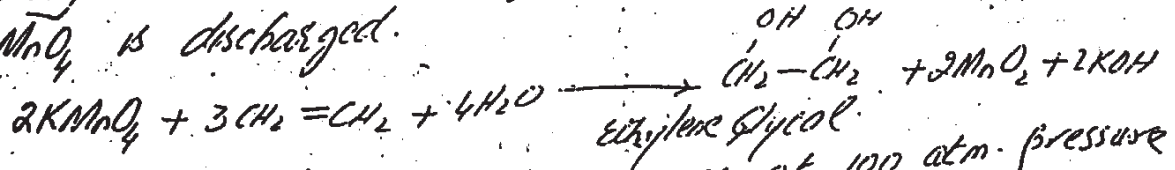
ADDITION OF HYPOCHLOROUS ACID:-

Ethene reacts with hypochlorous acid to produce ethylene chlorohydrin (2-chloro ethanol).

ADDITION OF OXYGEN:- When a mixture of ethene and air is passed over heated silver ethylene epoxide is formed

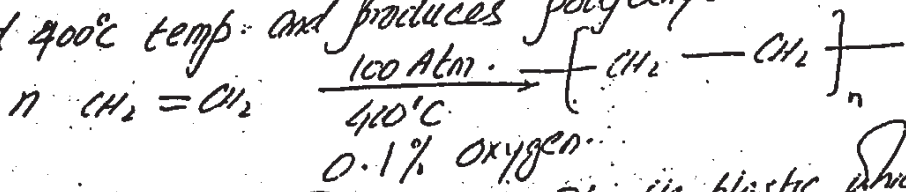


HYDROXYLATION:- When ethene is passed through dilute alkaline of KMnO<sub>4</sub>, pink colour of KMnO<sub>4</sub> is discharged.



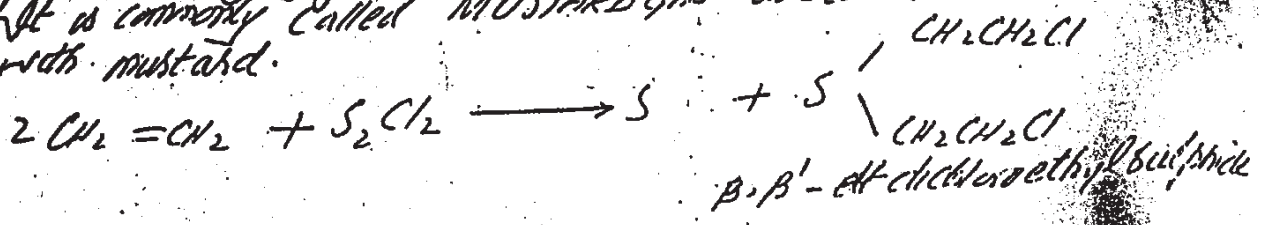
POLYMERIZATION:-

Ethylene polymerizes at 100 atm. pressure and 400°C temp. and produces polyethylene.

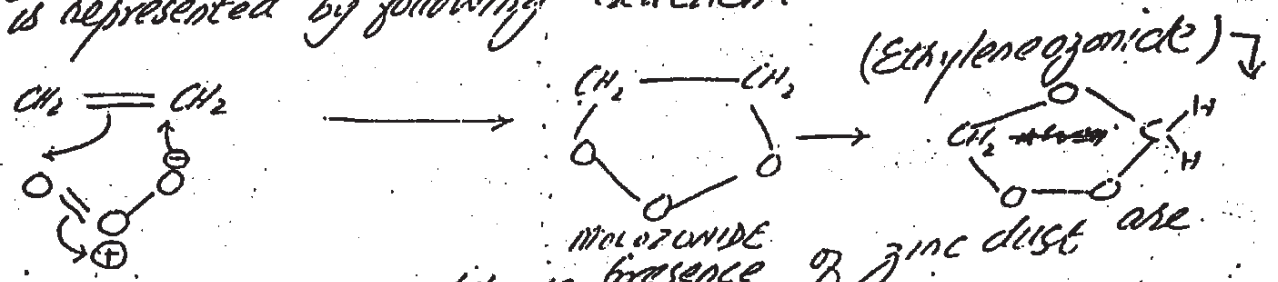


Polyethylene is a white tough flexible plastic which softens near 140°C. Polyethylene produced in presence of (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>Al and Titanium chloride catalyst has improved qualities. For example it softens at high temperature, greater rigidity and low permeability.

ADDITION OF SULPHUR MONOCHLORIDE: Ethene on treatment with sulphur monochloride form β, β-dichloroethyl sulphide. This product is highly poisonous. It was used in first world war. It is commonly called MUSTARD GAS due to its resemblance with mustard.

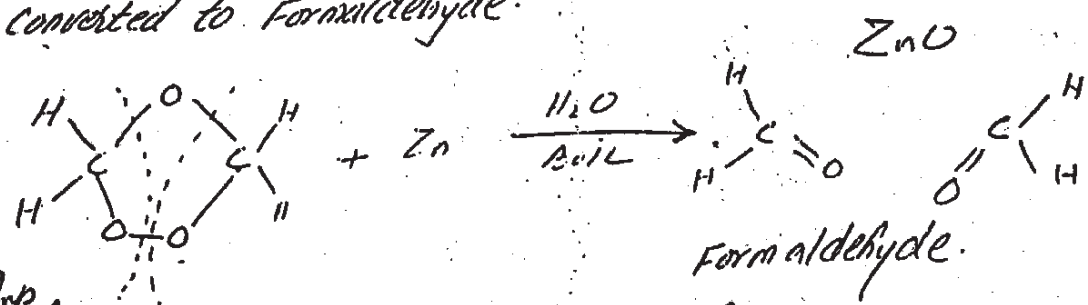


OZONOLYSIS: When ozone is passed through solution of alkene in ether solvent, ozonide is formed. The ozonolysis is represented by following reaction.



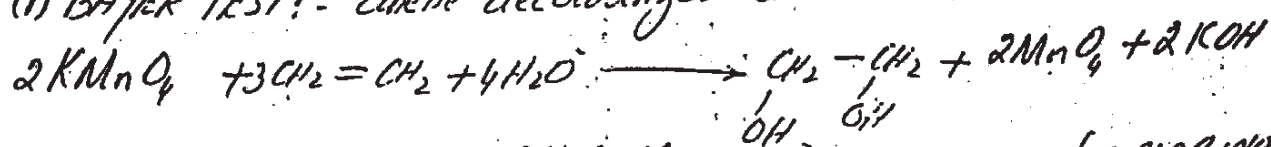
Ozonide on boiling water is converted to Formaldehyde.

in presence of zinc dust are



IDENTIFICATION OF ETHENE (ETHYLENE) cold <sup>KMnO<sub>4</sub></sup>

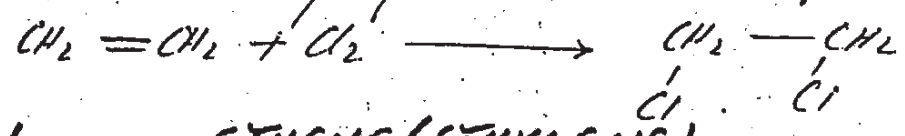
(1) BAYER TEST: Ethene decolorizes dilute alkaline solution of



(2) DECOLORIZATION OF BROMINE Ethene decolorizes bromine water



(3) FORMATION OF DUTCH LIQUID Ethene reacts with chlorine and produces an oily liquid called Dutch liquid (Ethylene dichloride)



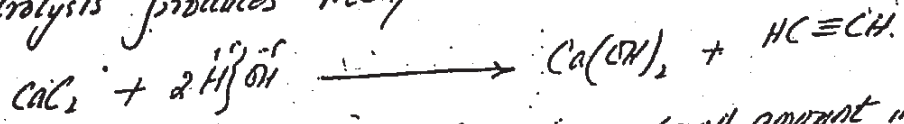
USES OF ETHENE (ETHYLENE)

1. It is used for manufacture of a plastic material polyethylene.
2. It is used to produce mustard gas which is poisonous gas.
3. It is applied as general anaesthetic.
4. It is used in artificial ripening of green citrus fruit.
5. It is used for welding purposes because it can be used stored in cylinders under high pressure. There is no danger of explosion in this case.

- 6 It is used to prepare a large number of other chemicals like ethylene oxide, Ethanol, Glycol, ethylhalides
- 7 It is used to manufacture ethyl benzene. Ethyl benzene is used to produce styrene. Styrene is an important monomer to produce plastics & rubber.

ETHYNE OR ACETYLENE

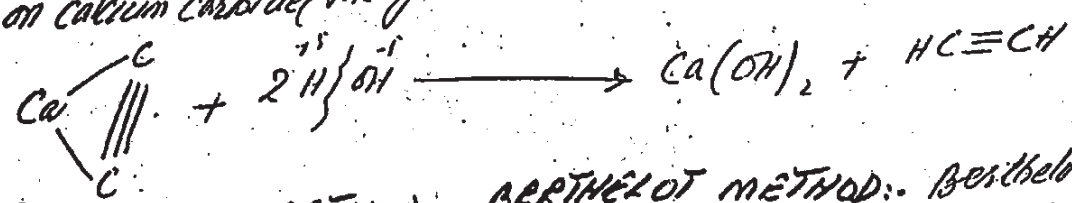
DISCOVERY:- Acetylene was discovered accidentally by Wilson in 1899. He was interested to get calcium from  $CaCO_3$  by using coke as reducing agent. He heated mixture of  $CaCO_3$  and coke for long time but calcium was not produced. He threw the entire mixture into water. A gas was given out. It was found to be acetylene. Actually when  $CaCO_3$  and coke are heated, calcium carbide is produced. Calcium carbide  $CaC_2$  on hydrolysis produces Acetylene



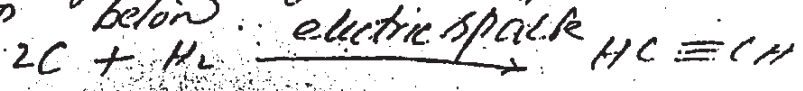
NATURAL SOURCE Acetylene is present in small amount in coal gas. It is also produced as side product in destructive distillation of many organic substances.

PREPARATION OF ACETYLENE:-

1 LABORATORY METHOD:- HYDROLYSIS OF CALCIUM CARBIDE. Acetylene is produced in laboratory by dropping water on calcium carbide. The gas is collected over water.

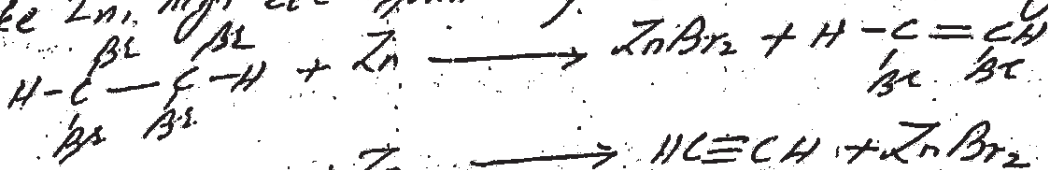


2 INDUSTRIAL METHOD:- BERTHELOT METHOD:- Berthelot prepared acetylene by direct reaction of carbon and hydrogen in presence of electric sparks. Carbon rods are used as electrodes and hydrogen gas is passed between these two electrodes in presence of electric sparks. The reaction is shown below:

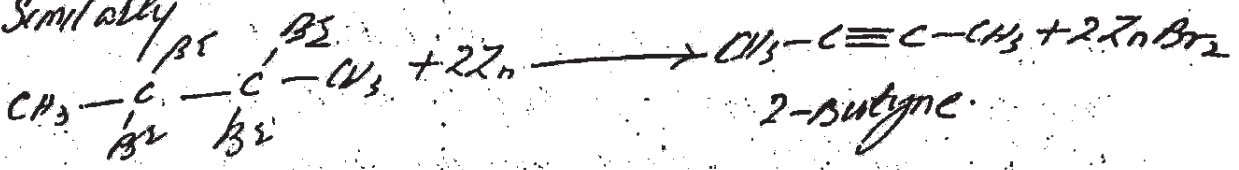


DEHALOGENATION OF TETRAHALIDES

tetrahaloalkanes on treatment with active metals like Zn, Mg, etc. form alkynes. It is called dehalogenation.

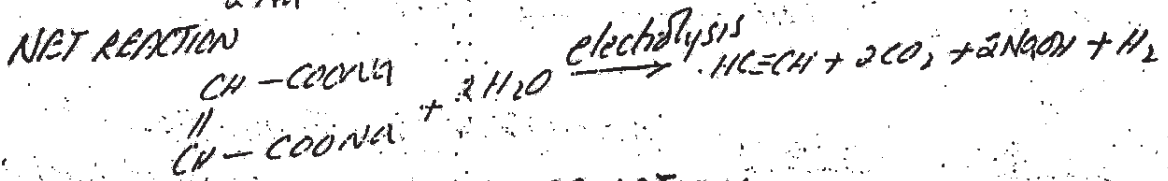
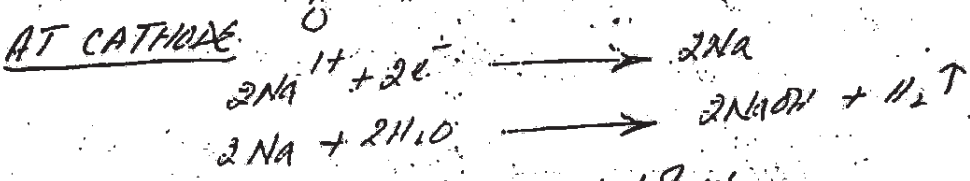
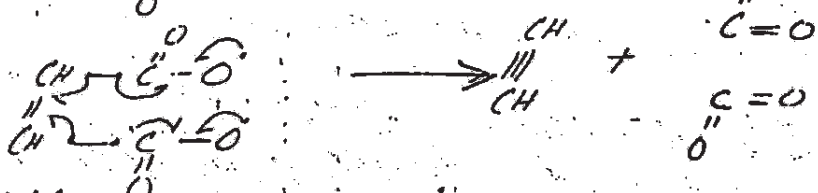
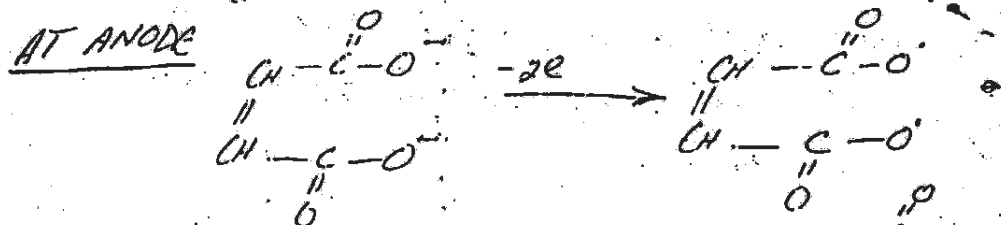
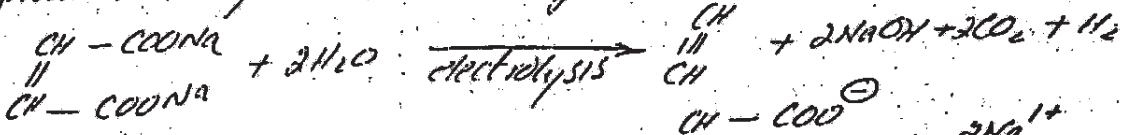


Similarly



3 GENERAL METHOD OF PREPARATION

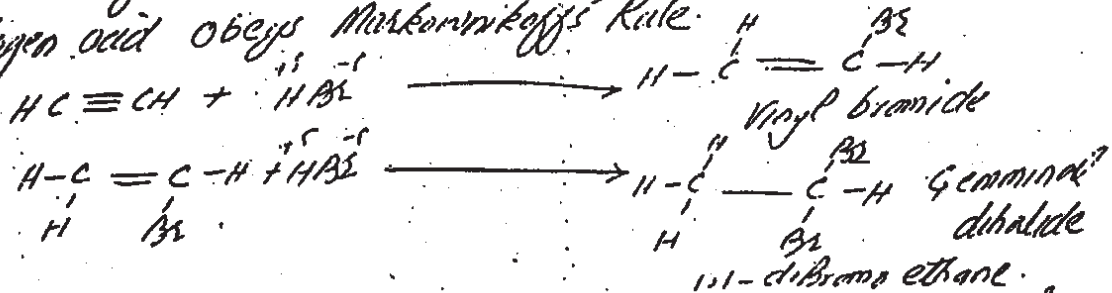
(a) KOLB ELECTROLYSIS: dibromide molecule in aqueous solution produces acetylene on electrolysis. It is called Kolb Electrolysis.



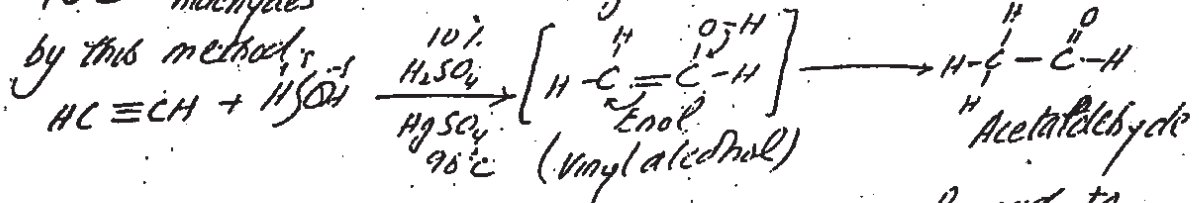
DOUBLE DEHYDROHALOGENATION:

Vicinal and Geminal dihalide on treatment with alcoholic KCN produce acetylene. The reaction is called double dehydrohalogenation. (Two times removal of hydrogen and halogens)

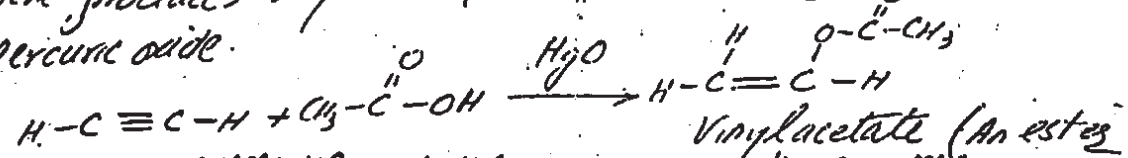
**ADDITION OF HALOGEN ACIDS:** - Each molecule of acetylene adds two molecules of halogen acids. In first step vinyl halide ( $C_2=CH$ ) is formed which reacts with another molecule of halogen acid and forms a Geminal dihalide. The addition of second halogen acid obeys Markovnikov's Rule.



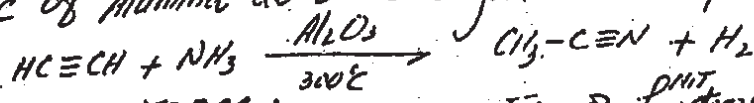
**ADDITION OF WATER:** - Acetylene on treatment with 10%  $H_2SO_4$  &  $HgSO_4$  adds one molecule of water to produce "ENOL" (The enol rearranges to form acetaldehyde). The reaction takes place at  $98^\circ C$ . Aldehydes and ketones are produced on commercial scale by this method.



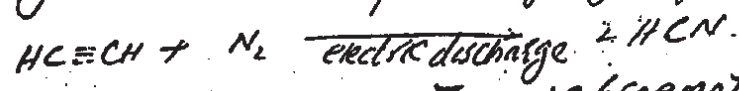
**VINYLATION:** - The addition of carboxylic acid to acetylene produces vinyl ester. The reaction takes place in presence of mercuric oxide.



**ADDITION OF AMMONIA:** - Acetylene combines with ammonia in presence of Alumina at  $300^\circ C$  to produce methyl nitril.

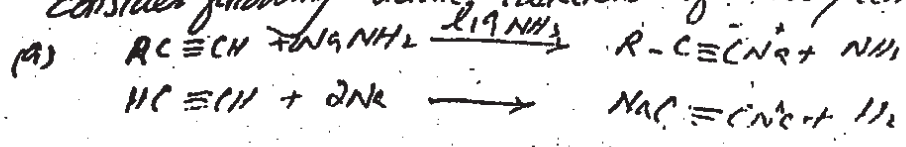


**ADDITION OF NITROGEN:** When a mixture of hydrogen and acetylene is subjected to electric sparks, hydrogen cyanide ( $HCN$ ) is produced.

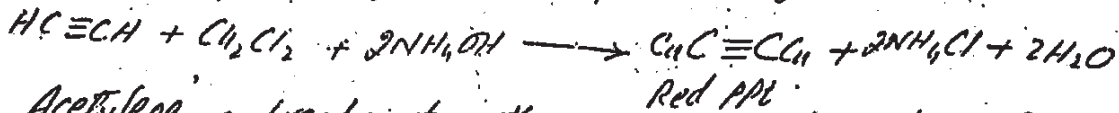


**ACIDIC CHARACTER OF ACETYLENE (FORMATION OF METALLIC ALKYNIDES)**

The hydrogen which can be replaced by a metal atom is called acidic hydrogen. When hydrogen of acetylene is replaced by metal the resulting salt is called metal acetylide. Let us consider following acidic reactions of acetylene.



(b) When acetylene is shaken with ammoniacal cuprous chloride, a red precipitate of copper acetylide is produced.



(c) Acetylene on treatment with ammoniacal silver nitrate produces white precipitate of Silver acetylide.



Metallic acetylides are highly explosive in dry state.

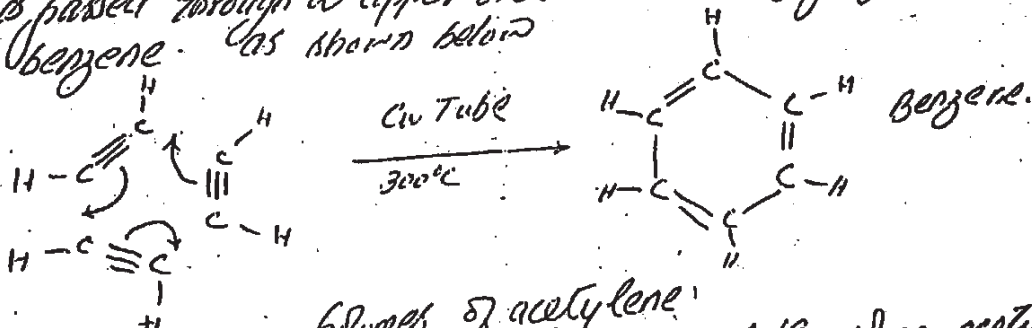
On treatment with dilute acids, acetylene is regenerated



IDENTIFICATION | The above two reactions are used for identification of acetylene. Ethene does not react with ammoniacal  $\text{AgNO}_3$  or  $\text{Cu}_2\text{Cl}_2$ .

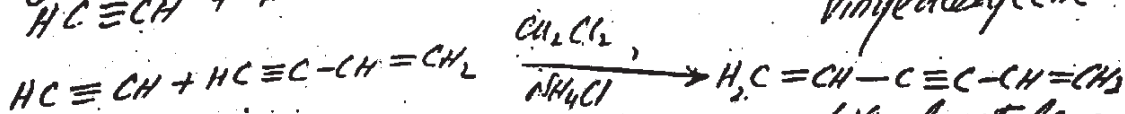
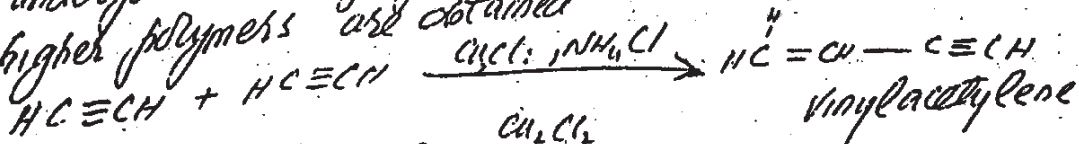
POLYMERIZATION OF ACETYLENE :- The process of formation of a large molecule of high MW by combination of small molecules is called polymerization.

(i) CONVERSION OF ACETYLENE INTO BENZENE :- When acetylene is passed through a copper tube at  $300^\circ\text{C}$  it polymerizes to benzene. As shown below



Thus benzene is a polymer of acetylene.

2. LINEAR POLYMERIZATION OF ACETYLENE When acetylene is passed through cuprous chloride and ammonium chloride it undergoes linear polymerization. Divinyl acetylene and higher polymers are obtained



IMPORTANCE Vinylacetylene is quite important.

It combines with  $\text{HCl}$  to form Chloroform (2-Chloro-1,3-butadiene)



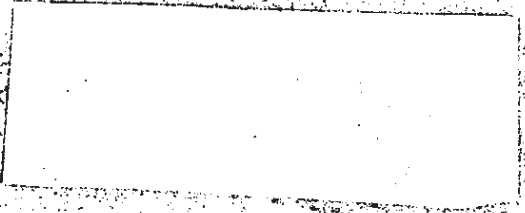
Synthetic rubber is made by polymerization of Chloroprene.  
2. USES OF ACETYLENE:-

- (1) Acetylene is used to cut and weld the metals. When acetylene is burnt in oxygen, oxyacetylene flame has a temp. of about 3000°C. For welding the proportion of oxygen and acetylene are so controlled that carbon monoxide and water is produced. Thus oxidation of metal is avoided. For cutting purposes an excess of oxygen is used. Thus oxyacetylene flame is able to cut nickel chrom. plates.
- (2) Acetylene is used to prepare acetaldehyde and acetic acid.
- (3) It is used to prepare, ethanol, rubber, plastics, fabrics.
- (4) It is used to prepare acetylene tetrachloride which is a good solvent for varnishes, resins and rubber.
- (5) It is used for artificial ripening of fruit.

SOME IMPORTANT CONVERSIONS FOR PRACTICE (TRY YOURSELF)

- ETHENE  $\longrightarrow$  ETHANOL
- "  $\longrightarrow$  ETHANE
- "  $\longrightarrow$  ETHYNE
- "  $\longrightarrow$  FORMALDEHYDE
- "  $\longrightarrow$  GLYCOL
- "  $\longrightarrow$  VICINAL DIBROMIDE
- "  $\longrightarrow$  MUSTARD GAS
- "  $\longrightarrow$  DUTCH LIQUID
- ETHYNE  $\longrightarrow$  PROPYNE
- "  $\longrightarrow$  ETHENE
- "  $\longrightarrow$  ALDEHYDE
- "  $\longrightarrow$  1,1-DIBROMIDE
- "  $\longrightarrow$  ETHANE
- "  $\longrightarrow$  METHYL CYANIDE
- "  $\longrightarrow$  HCN.

- ETHYNE  $\longrightarrow$  BENZENE
- "  $\longrightarrow$  CHLOROPRENE
- HOW WILL YOU DISTINGUISH BETWEEN
- ETHANE & ETHENE
- ETHENE & ETHYNE
- HOW WILL YOU PREPARE ETHENE FROM
- ETHYL BROMIDE
- ETHANOL
- SODIUM BUCONATE
- ETHYNE



24

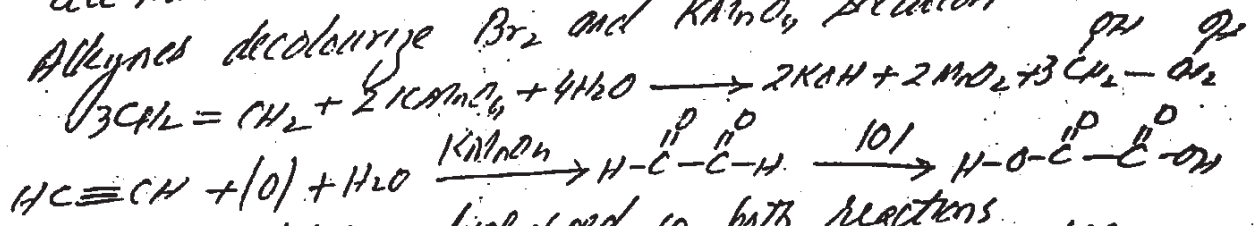
## COMPARISON OF REACTIVITIES OF ALKANE, ALKENE AND ALKYNES.

The general decreasing order of reactivities of Alkanes, alkenes and alkynes is Alkene > Alkyne > Alkane.

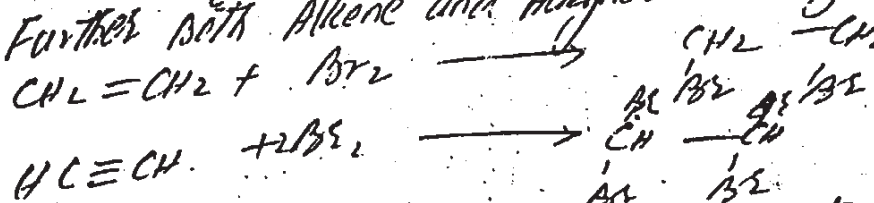
In alkene there is a  $\sigma$  and a  $\pi$ -bond between two atoms. The electrons of  $\pi$ -bond are more exposed to an attack of an electrophile. Further  $\pi$  bond is a weak bond. Thus an electrophile can very easily attack on alkene. In alkynes the bond distance between triply bonded carbon atoms is very small and  $\pi$ -e<sup>-</sup> are not available to be attacked by electrophilic reagent. Thus alkynes are less reactive than Alkenes but they are more reactive than Alkane.

### Q:- HOW TO DISTINGUISH BETWEEN ALKANE, ALKENE AND ALKYNES BY CHEMICAL TESTS

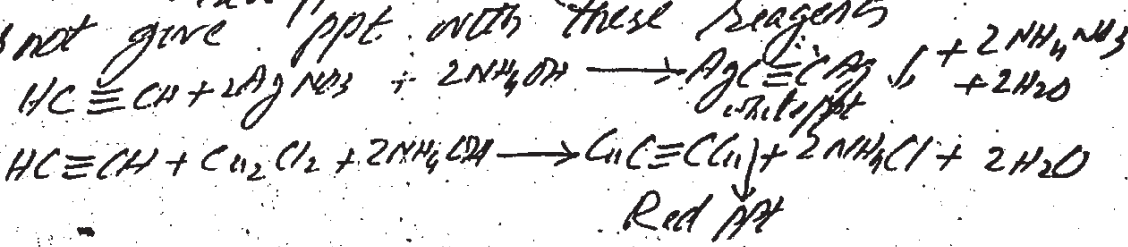
1) ALKANES do not decolourize Br<sub>2</sub> water or dil Alkaline KMnO<sub>4</sub> solution but alkene and Alkynes decolourize Br<sub>2</sub> and KMnO<sub>4</sub> solution



Colour of KMnO<sub>4</sub> is discharged in both reactions. Further both Alkene and Alkynes decolourize Br<sub>2</sub> water



However Alkyne give white ppt with silver Ammonical nitrate and red ppt with (Cu<sub>2</sub>Cl<sub>2</sub> and NH<sub>4</sub>OH) Alkene does not give ppt with these reagents

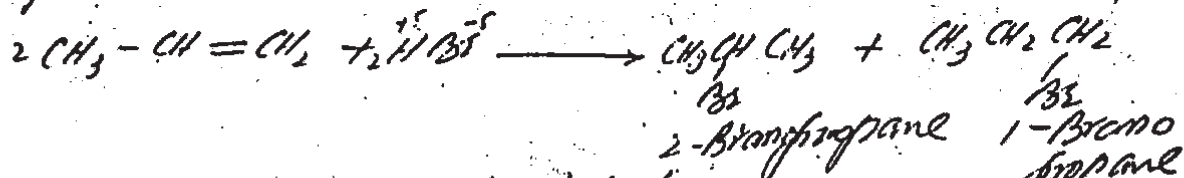




Q.1

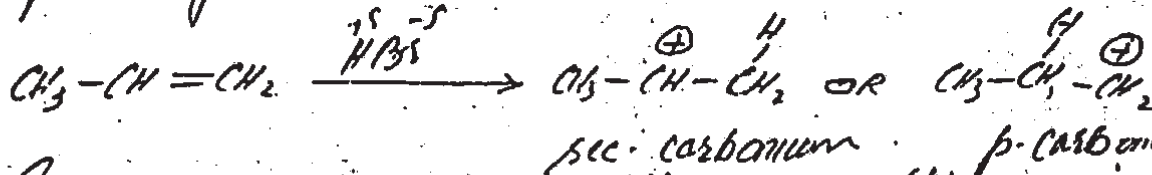
WHAT IS MARKOVNIKOFF'S RULE EXPLAIN ?

When an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of reagent will add to that carbon atom which has least number of hydrogen atoms. For example consider addition of HBr to propene. Two possible products are expected to form



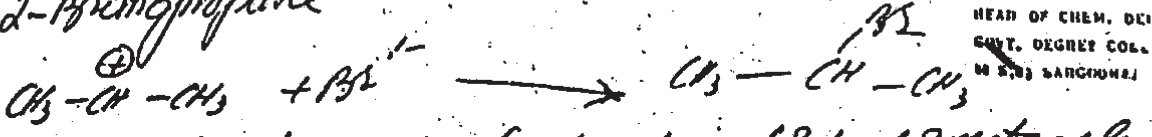
According to Markovnikoff's rule 2-Bromopropane will be formed.

EXPLANATION The reaction proceeds through formation of carbocation ion. This electrophilic addition of HBr will proceed. Carbocation ion in first step. Two possible carbocation ions can be formed

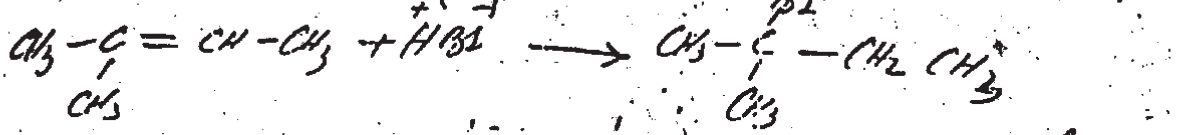


Since sec. carbocation ion is more stable than p. carbocation ion so (a) will be formed in first step.

In second step Br<sup>-</sup> ion will attack (a) to form 2-Bromopropane



Since carbocations are produced in polar solvent only so Markovnikoff's rule is obeyed in polar solvent only.



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