

Aliphatic Hydrocarbons.

Q.1 What do you mean by saturated and unsaturated hydrocarbons? How these are distinguished chemically?

BWP – 2014, DGK - 2014

Ans: **Saturated Hydrocarbons:**

Define:- "There are the compounds of carbon and hydrogen in which all the valencies of carbon are fully utilized and there is single bonds between carbon and carbon atoms."

There general formula in C_nH_{2n+2} , eg:



Methane

Propane

n – pentane

Due to their least chemical reactivity, the saturated hydrocarbons are also known as '**Paraffins.**' The name '**Paraffins**' comes from the combination of Latin word '**parum**' and "**affin**".

Parum = Little

Affin = Affinity

Unsaturated hydrocarbons:

Define:- "Compounds of carbon and hydrogen, in which all valencies of carbon is not fully utilized and they contain either double or triple bond in them, are called unsaturated hydrocarbon." e.g.
 $CH_2 = CH_2$ (ethane) $CH \equiv CH$ (ethyne) etc.

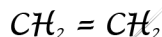
Unsaturated hydrocarbons are of two types.

i. Alkenes or Olefins

ii. Alkynes or Acetylenes

i. Alkenes or Olefins:

Define:- Those hydrocarbons in which there is double bond between carbon and carbon atoms are called alkenes or olefins. Their general formula is C_nH_{2n} , e.g.

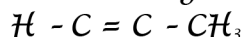
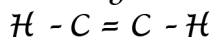


Ethene

Propene

ii. Alkynes or Acetylenes:

Define:- "Those hydrocarbons in which there is a triple bond between carbon and carbon atoms are called alkynes or acetylenes." Their general formula is C_nH_{2n-2} e.g.



(Ethyne) Acetylene

Propyne

Continue.....p/2.....

Q.2 Write rules for naming alkanes. Explain with examples.

RWP – 2010

Ans: **Rule for Naming Alkanes:**

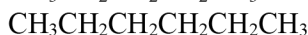
Straight chain alkanes are called normal alkanes and represented by “n” e.g.



n-butane



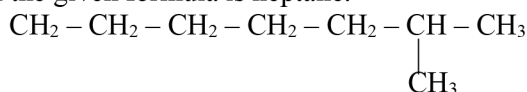
n-pentane



n-hexane

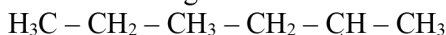
Branched – chain alkanes are named according to the following rules.

1. Select longest possible chain of carbon atoms. Length of chain determines the parent name e.g. the longest chain in the given formula is heptane.

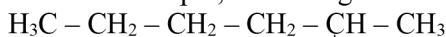


The carbon atoms which are not part of the continuous chain, are called substituents.

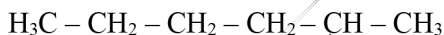
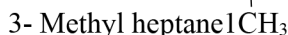
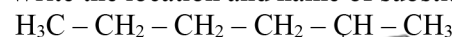
2. Start numbering from that end which is near to the substituent.



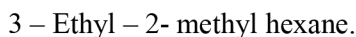
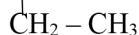
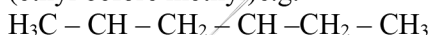
In above example, chain length of seven carbon atoms (heptane) and one CH_3 is substituent.



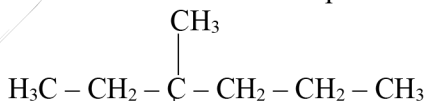
3. Write the location and name of substituent before the parent name or stem name e.g.



4. If more than one substituents of different types are present, they should be named in alphabetic order. (ethyl before methyl) e.g.

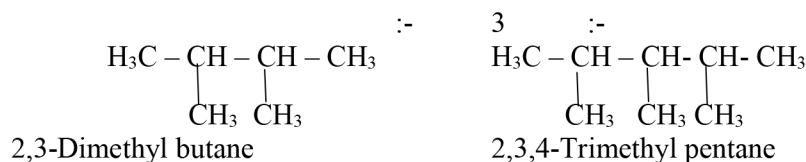


5. When two substituents are present at the same carbon, write that number twice.



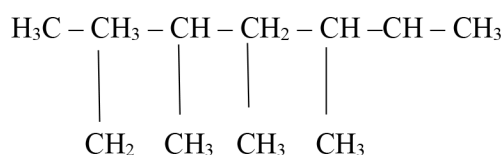
6. If similar substituents are present more than, once, the number of carbon atom to which substituent is attached given each time, Prefixes di, tri, tetra, etc. are used for the same type of substituents. Commas are placed between number and hyphen at the end of number.

Continue.....p/3.....



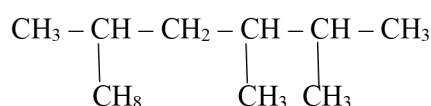
Application of these six rules allows us to name most of the alkanes that we shall encounter. Two other rules, however, may be required occasionally.

7. When two chains of equal length compete for selection as the parent chains, choose the chain with greater number of substituents.



Right selection of chain (Four branches)

8. When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.



2,3,5-Trimethylhexane (not 2,4,5 trimethylhexane)

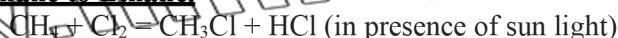
Q.3

Convert: (i) methane to ethane (ii) Ethane to methane.

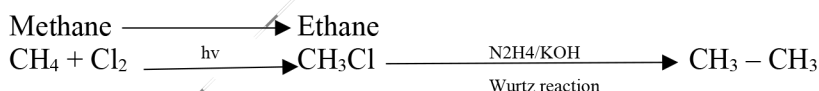
BWP-2015, DGK-2017, LHR-2018

Ans:

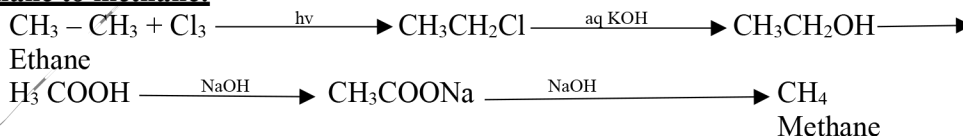
(i) Methane to Ethane:



$\text{CH}_3\text{Cl} + \text{Na/ether} \rightarrow \text{CH}_3 - \text{CH}_3 + \text{NaCl}$ (ethane) this reaction is called wurtz reaction.....



(ii) Ethane to methane:



Continue.....p/4.....

Q.4 Write four methods for preparation of alkanes.

LHR – 2008, 2014, GRW-2015, FBD-2018

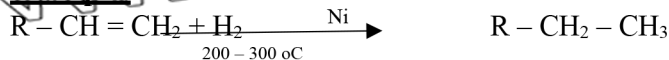
Ans:

General Methods for preparations.

1. **Hydrogenation of unsaturated hydrocarbons (Sabatier's and sendrn's reaction)**

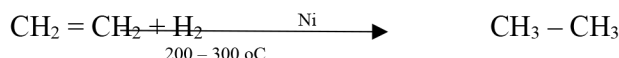
Hydrogenation of alkenes or alkynes in the presence of Nickel catalyst at $200 - 300^{\circ}\text{C}$ yields alkanes.

Example:



Alkene

Alkane



Ethene

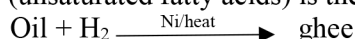
Ethane

Other Catalysts for hydrogenation:

The hydrogenation can also be carried out with platinum or palladium at room temperature but they are expensive than Nickel.

Importance of hydrogenation:

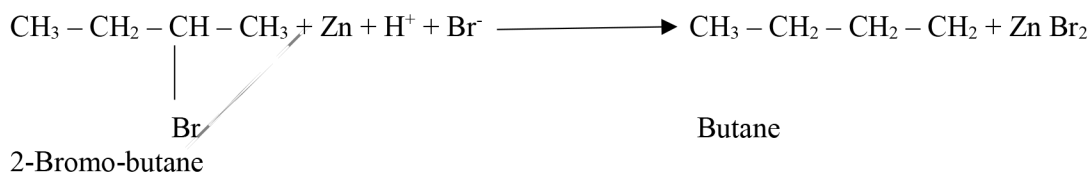
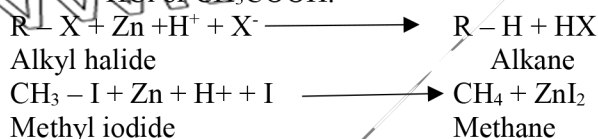
This method is of industrial importance. Production of vegetable ghee by the catalytic hydrogenation of vegetable oil (unsaturated fatty acids) is the application of this method on industrial scale.



2. **From Alkyl Halides:**

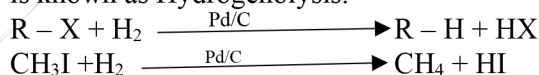
Reduction in the presence of Zn and halogen acid.

An alkane is produced when an alkyl halide reacts with zinc in the presence of an aqueous acid such as HCl or CH_3COOH .



Hydrogenolysis:

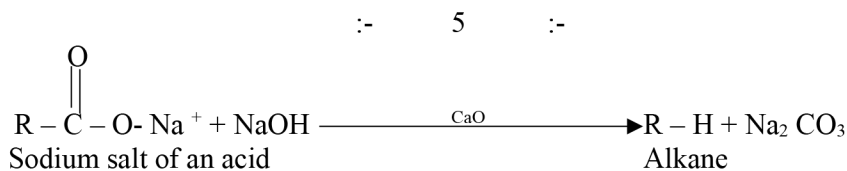
Alkanes can also be prepared from alkyl halides using palladium –charcoal as a catalyst. This method is known as Hydrogenolysis.



3. **Decarboxylation of mono-carboxylic acids:**

1. When sodium salt of fatty acids are heated with soda-lime alkane are form. Soda lime is prepared by soaking quick lime (CaO) with caustic soda solution and drying the product. They eliminate a molecule of CO_2 to form alkanes.

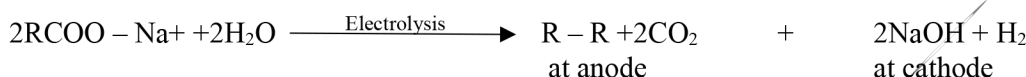
Continue.....p/5.....



ii. **Kolbe's electrolytic method:**

SGD-2009, DGK-2015

When a concentrated solution of sodium or potassium salt of a monocarboxylic acid is electrolyzed, an alkane is produced. This method is only suitable for the preparation of symmetrical alkanes. Those of the type R-R Methane cannot be prepared by this method.



Mechanism:

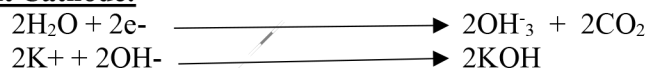
When potassium salt of acetic acid is electrolyzed, acetate ions (CH_3COO) migrate towards the anode gives up one electron to produce acetate free radical ($\text{CH}_3\text{COO}^\cdot$), which decomposes to give a methyl free radical ($\text{CH}_3^\cdot$) and CO_2 . Two such methyl radical combine to give ethane.



At Anode:



At Cathode:



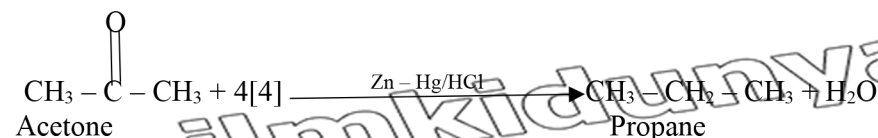
Limitation:

This reaction has limited synthetic applications as it forms a number of side products.

4. Formaldehyde and ketones (Carbonyl compounds):
Carbonyl group of aldehyde or ketones is reduced to methyl (CH_3-) or methylene ($-\text{CH}_2-$) by either Clemmensen or Wolff-Kishner's reduction.

Clemmensen Reduction:

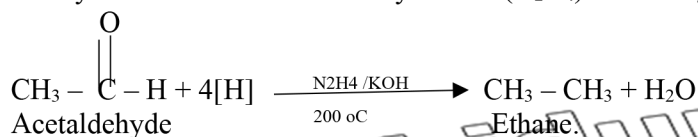
In this reaction, ketones react with zinc amalgam and hydrochloric acid to form alkanes (mixture of a metal with mercury is called amalgam).



Continue.....p/6.....

Wolf Kishner's Reduction:

Aldehyde reacts with KOH and hydrazine (N₂H₄) and changes to alkane.



Q.5 Explain with equation how alkenes can be prepared from Grignard's reagent.

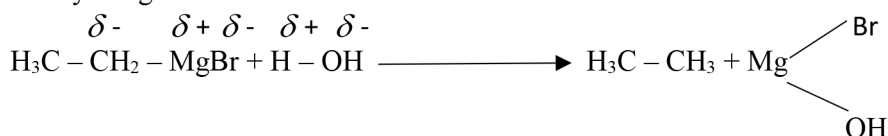
MTN-2016

Ans: Alkyl halides react in anhydrous ether with magnesium to form alkyl magnesium halides, known as Grignard Reagent. They decompose on treatment with water or dilute acid to give alkanes.



Methyl magnesium bromide

Methane



Ethyl magnesium bromide

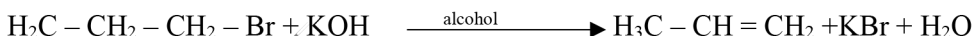
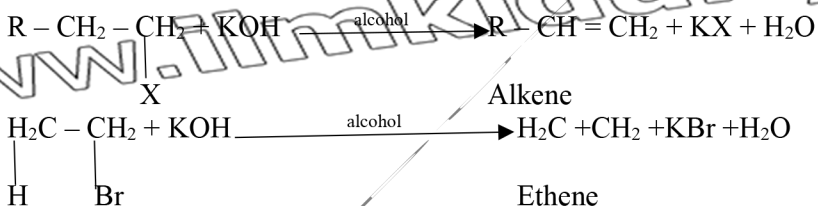
Ethane

Q.6 Write two methods of preparation and two properties of alkene.

RWP - 2009, SWL-2016, LHR -2017

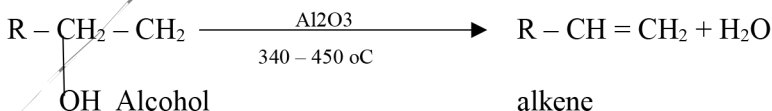
Ans: 1. **Dehydrohalogenation of Alkyl Halides (Elimination reaction):**

Alkyl halides on heating with alcoholic potassium hydroxide undergo dehydrohalogenation i.e. elimination of a halogen atom together with a hydrogen atom from adjacent carbon atoms.



2. **Dehydration of Alcohols:**

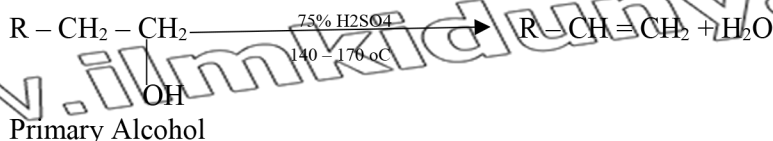
Alcohols when dehydrated in the presence of a catalyst give alkenes. The best procedure is to pass vapours of alcohol over heated alumina (Al₂O₃).



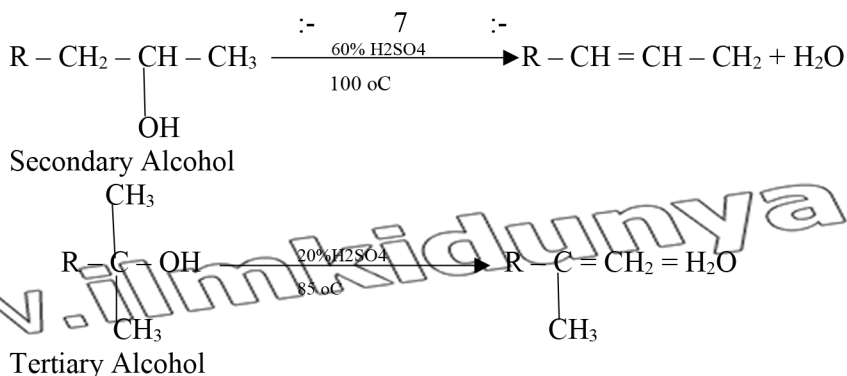
Al₂O₃, P₄O₁₀, H₂SO₄ (conc.) and H₃PO₄ are dehydrating agent used for preparation of alkene. The ease of dehydration of various alcohols is in the order.

Ter. Alcohol > Sec. alcohol > Pri-alcohol

Thus



Continue.....p/7....



Q.7 Explain free radical mechanism for the reaction of chlorine with methane in the presence of sunlight. OR Write note on halogenation of alkane. **LHR – 2014,2015,SGD-2017**

Ans: 1. **Halogenation (substitution reaction):**

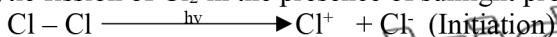
Successive replacement of hydrogen atoms of alkanes with halogen atoms is called halogenation. Halogenation takes place in the presence of sunlight or UV light or at high temperature. Extent of halogenation depends upon the amount of halogen used and its nature.

- If halogen and alkanes are taken with 1:1 ration CH_3Cl is formed. If greater amount of halogen is used, further substitution of halogen will also takes place and Cl_4 is formed.
- Reaction of alkanes with fluorine is highly violent results in a mixture of carbon, fluorinated alkanes and hydrofluoric acid. Iodine does not substitute directly because the reaction is too slow and reversible.

Mechanism:

Free radical formation or Initiation:

Homolytic fission of Cl_2 in the presence of sunlight produces chlorine radical. It is called initiation step.



Q.8 Compare the reactivity of alkane and alkene.

Ans: **Reactivity of alkanes:**

In alkanes, single bond is present between $\text{C}-\text{C}$ or $\text{C}-\text{H}$ bonds. They are non-polar bonds and high energy is required to break the bonds. Due to greater bond strength and non-polarity, neither nucleophile nor electrophile attach on it, so alkanes are less reactive.

Reactivity of alkenes:

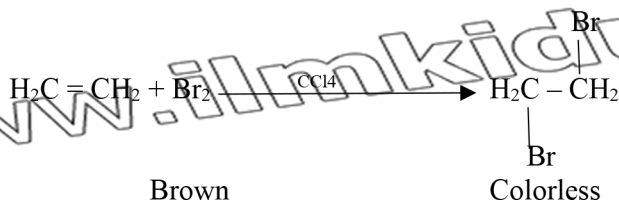
In alkenes, double bond is present between two carbon atoms, one is sigma and other is pi-bond- σ bond is formed by linear overlapping of partially filled sp^2 hybrid orbitals and electron density is maximum between two nuclei or at bond axis. π -bond is formed by the parallel overlapping of p-orbitals of carbon atoms. In π -bond, electrons density is maximum above and below the bond axis. Due to less overlapping, π electrons are not firmly attached. Due to less overlapping region, π bonds are weaker bond than sigma easily on π electrons are more exposed electrons and an electrophile can attached easily on π -electrons. Thus the compounds containing π -bond are more reactive or one can say alkenes are more reactive than alkane. Alkenes usually undergo addition reactions.

Continue.....p/8.....

Q.9 Give any two method of preparation of alkene (Ethene) and also mention two test of establish double bond is alkenes. **LHR,SGD - 2014**

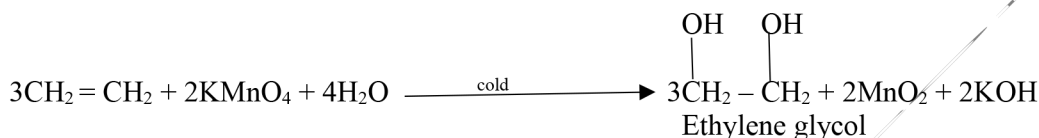
Ans: **Alkenes can be identified by following tests:**

(i) Alkenes decolorize brown color of bromine.



(ii) Alkenes decolorize color of Baeyer's reagent.

FBD - 2014



Q.10 Write reactions of alkene with:

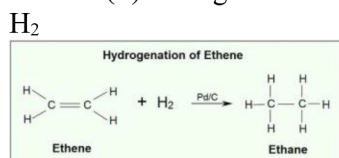
(i) H_2

(ii) Halogen

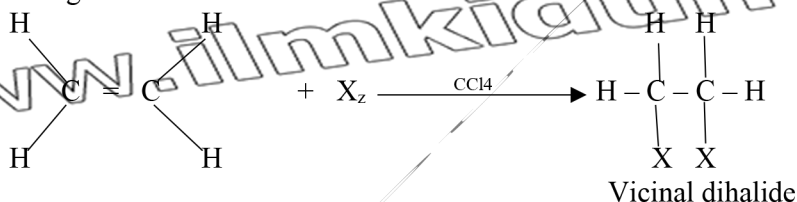
(iii) Halogen acid

(iv) H_2O

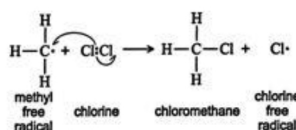
Ans: (i)



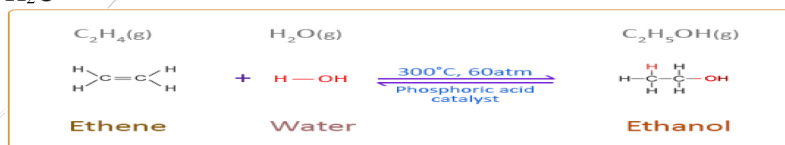
(ii) Halogen



(iii) Halogen acid



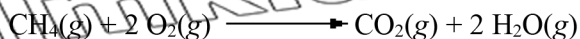
(iv) H_2O



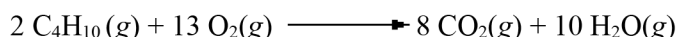
Continue.....p.9.....

Q.11 Reaction with alkanes, alkenes, alkynes.

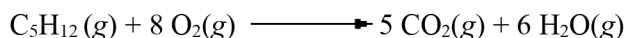
Ans: In the absence of a spark or a high-intensity light source, alkanes are generally inert to chemical reactions. However, anyone who has used a match to light a gas burner, or dropped a match onto charcoal coated with lighter fluid, should recognize that alkanes burst into flame in the presence of a spark. It doesn't matter whether the starting material is the methane found in natural gas,



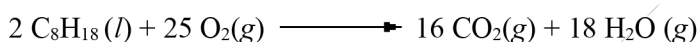
the mixture of butane and iso butane used in disposable cigarette lighters,



the mixture of C_5 to C_6 hydrocarbons in charcoal lighter fluid,



or the complex mixture of C_6 to C_8 hydrocarbons in gasoline.

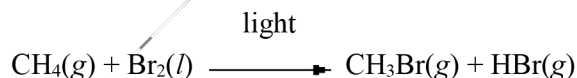


Once the reaction is ignited by a spark, these hydrocarbons burn to form CO_2 and H_2O and give off between 45 and 50 kJ of energy per gram of fuel consumed.

In the presence of light, or at high temperatures, alkanes react with halogens to form **alkyl halides**. Reaction with chlorine gives an **alkyl chloride**.

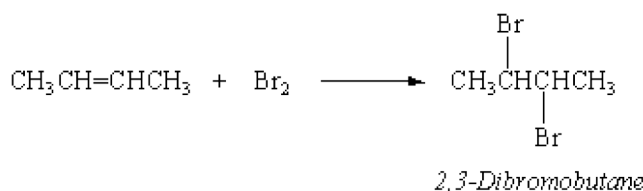


Reaction with bromine gives an **alkyl bromide**.



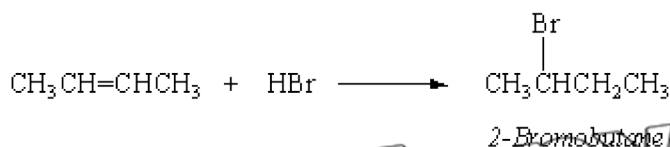
Alkenes and Alkynes:

Unsaturated hydrocarbons such as alkenes and alkynes are much more reactive than the parent alkanes. They react rapidly with bromine, for example, to add a Br_2 molecule across the $\text{C}=\text{C}$ double bond.

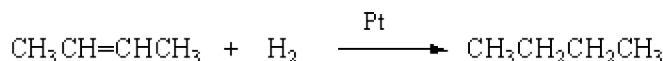


This reaction provides a way to test for alkenes or alkynes. Solutions of bromine in CCl_4 have an intense red-orange color. When Br_2 in CCl_4 is mixed with a sample of an alkane, no change is initially observed. When it is mixed with an alkene or alkyne, the color of Br_2 rapidly disappears.

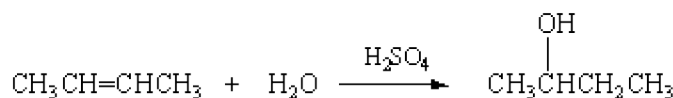
The reaction between 2-butene and bromine to form 2,3-dibromobutane is just one example of the addition reactions of alkenes and alkynes. Hydrogen bromide (HBr) adds across a $\text{C}=\text{C}$ double bond to form the corresponding alkyl bromide, in which the hydrogen ends up on the carbon atom that had more hydrogen atoms to begin with. Addition of HBr to 2-butene, for example, gives 2-bromobutane.



H_2 adds across double (or triple bonds) in the presence of a suitable catalyst to convert an alkene (or alkyne) to the corresponding alkane.

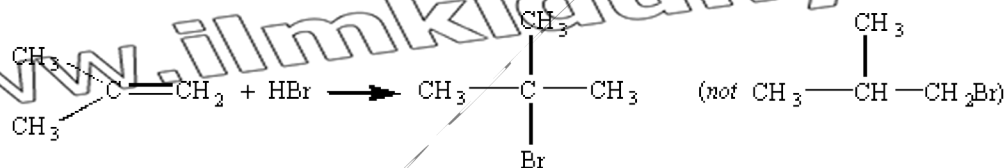


In the presence of an acid catalyst, it is even possible to add a molecule of water across a $\text{C}=\text{C}$ double bond.

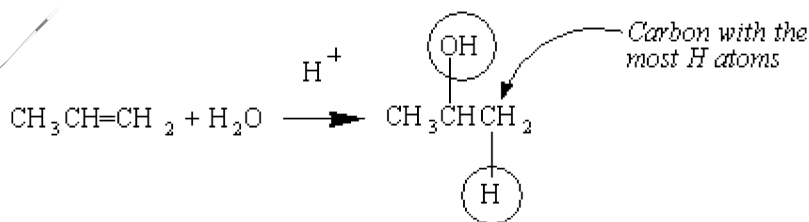


Addition reactions provide a way to add new substituents to a hydrocarbon chain and thereby produce new derivatives of the parent alkanes.

In theory, two products can form when an unsymmetric reagent such as HBr is added to an unsymmetric $\text{C}=\text{C}$ double bond. In practice, only one product is obtained. When HBr is added to 2-methylpropene, for example, the product is 2-bromo-2-methylpropane, not 1-bromo-2-methylpropane.



In 1870, after careful study of many examples of addition reactions, the Russian chemist Valdimir Markovnikov formulated a rule for predicting the product of these reactions. Markovnikov's rule states that the hydrogen atom adds to the carbon atom that already has the larger number of hydrogen atoms when HX adds to an alkene. Thus, water ($\text{H} - \text{OH}$) adds to propene to form the product in which the OH group is on the middle carbon atom.



Continue.....p/H.....

Q.12

Give uses of Methane

SGD – 2014

Ans:

Uses of Methane:

1. Methane is used for the preparation of methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), Chloroform (CHCl_3) and carbon tetrachloride (CCl_4)
2. Methane is important constituent of natural gas and used as fuel.
3. Methane is used for the industrial preparation of methyl alcohol, formaldehyde and formic acid.
4. Methane is used for preparation of carbon black used in paint, printing inks and automobile tyres.
5. By cracking of methane hydrogen gas is produced. This gas is used for the manufacture of vegetable ghee and fertilizers.

Q.13

Explain the polymerization of Acetylene (Linear).

Ans:

Polymerization is self – addition reaction of alkynes to give linear unsaturated compounds. The alkynes also give cyclic unsaturated compounds.

Linear polymerization:

Acetylene polymerizes to vinyl acetylene when two molecules join with each other. The catalyst used is Cu_2Cl_2 and NH_4Cl , vinyl acetylene give chloroprene by reacting with HCl . When third molecule of acetylene joins with vinyl acetylene, divinyl acetylene is produced.

Cyclic polymerization:

Acetylene and higher alkynes gives cyclic compounds, especially the derivative of benzene under various conditions. When acetylene gas is passed through cu-tubes at 300°C , then benzene is produced.

Q.14

Write reaction of alkyne with.

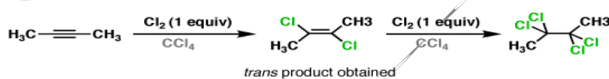
SGD – 2010

- (i) Cl_2 (ii) H_2O (iii) HCN (iv) HBr

Ans:

(i) Cl_2

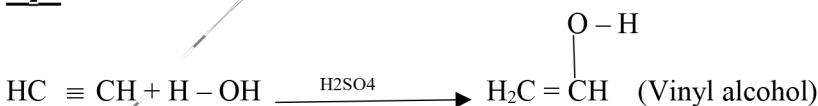
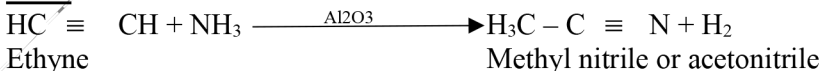
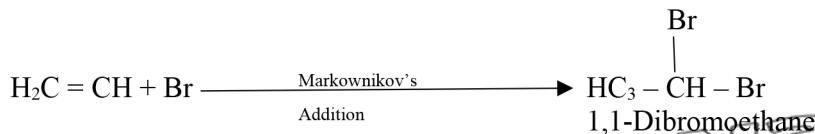
Chlorination of alkynes gives the *trans* alkene
A second equivalent of Cl_2 gives the tetrachloro alkane



CCl_4 (carbon tetrachloride) is solvent

Also works for Br_2 and I_2

* interesting to note that alkynes are not as reactive as alkenes in this reaction

(ii) H_2O (iii) HCN (iii) HBr 

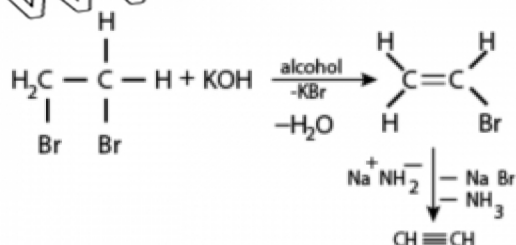
Continue.....p/12.....

Q.15 How alkene and alkyne can be prepared from vicinal dihalides?

FBD - 2014

Ans: Dihalides are obtained from corresponding alkenes by the addition of halogens (Group 17 elements). Alkynes are obtained from vicinal dihalides by dehydro halogenation which is carried out in two steps:

The first step is to prepare the unsaturated halides. The halides formed have a halogen attached to a double-bonded carbon. These halides are called vinylic halides which are not reactive in nature. These halides are made to react with the strong base which results in the formation of alkynes. Metal acetylides are used to convert small alkynes into large ones.



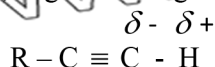
Q.16 Write a note on the acidity of ethyne.

Explain acidic characters of alkynes with examples. Write main use of alkynides.

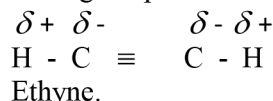
GRW-2009, LHR 2013, SWL, MTN -2014, 2015, SWL 2015, DGK -2015, FBD, SGD, BWP, LHR -2016, MTN -2018

Ans: **Acidic Nature of Alkynes:**

Alkynes differ from alkanes and alkenes in that, they have acidic hydrogen in them. The hydrogen atom attached to triple bonded carbon atom or sp hybridized carbon atom is acidic in nature. In ethyne and other terminal alkynes s-orbitals of hydrogen is overlapped with sp-hybrid orbital of carbon which has 50% s characters. Due to greater s-characters of hybrid orbital of carbon, it attracts the electron to itself and behaves as more electronegative than sp³ or sp² carbon atoms. Due to greater attraction of sp carbon, slightly negative charge is present on carbon and slightly positive charge is present on hydrogen.



Terminal alkyne or 1-alkyne

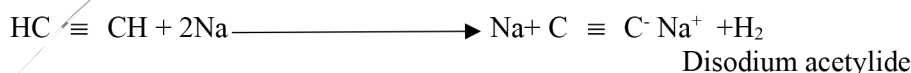
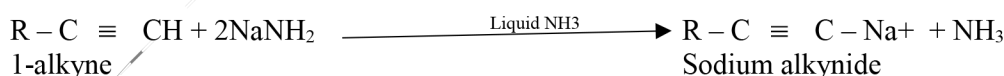


Ethyne.

This acidic hydrogen can be replaced by a metal ion to form salts called alkynides. Acetylene has two acidic hydrogens while 1-alkynes have one acidic hydrogen while 2-alkynes have no acidic hydrogen.

Example:

1. When 1-alkyne or ethyne is treated with soda lime in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained respectively.



Sodium acetylide is a very valuable reagent used for chemical synthesis and is essentially ionic in nature.

2. Acetylides of copper and silver are obtained by passing acetylene in the ammoniacal solution of cuprous chloride and silver nitrate respectively.



Continue.....p/13.....

Conversion of acetylides to acetylene:

Silver or copper acetylides react with acids to regenerate alkynes.

**Uses of alkynides:**

These alkynides are used for the preparation, purification separation and identification of alkynes

Q.17 Give comparison of reactivities of ethane, ethene and ethyne.

LHR – 2010,2014,2018

Ans: **Comparison of Reactivity of Alkanes, Alkenes and Alkynes.**

- Alkanes are the least reactive hydrocarbons. Alkanes have all sigma bonds in them which are strong bonds. In sigma bonds, electrons are very tightly held between the nuclei and makes them stable. A lot of energy is required to break C – C or C – H bond in alkanes. Electrons of the sigma bonds of alkane are not attracted by any nucleophile or electrophile. So alkanes do not react with ionic reagents, acids, alkalis, oxidizing or electrophile. So alkanes do not react with ionic reagents, acids, alkalis, oxidizing agent or reducing agents. However, under suitable conditions, alkanes undergo some substitution, combustion and thermal or catalytic reactions. Alkanes do not go addition reactions.
- Alkenes are the most reactive hydrocarbons. Alkenes have one sigma and one pi-bond between C – C atoms. Each carbon atom of double bond is sp^2 hybridized. Pi-bond in alkene is weak and can easily be broken by any electrophile. Pi bond of alkene is weak than sigma bond, pi-electrons of alkene are more exposed and can easily be attached by any electrophilic reagent. Due to these factors alkenes are more reactive than alkane as well as alkynes.
- Alkynes are less reactive than alkenes but more reactive than alkanes. Alkynes have one sigma and two pi-bond between C – C atoms. Alkynes are less reactive than alkenes. This is because the bond distance between the two triple bonded carbon atoms is very short. So the pi-electrons of alkynes are not available to be attacked by electrophilic reagents. Alkynes are, however, more reactive than alkenes towards nucleophilic reagents.

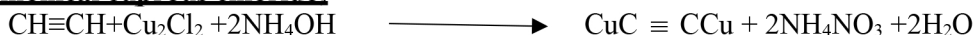
Q.18 How does ethyne reacts with:

SGD -2008,LHR -2011, GRW -2011

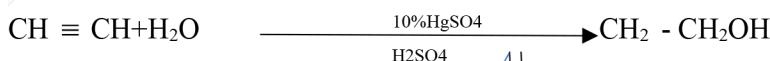
- Ammonical cuprous chloride
- Alkaline KMnO_4

- 10% H_2SO_4 in the presence of HgSO_4
- Halogen acid

Ans: (i) **Ammonical cuprous chloride:**

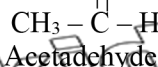


(ii) **10% H_2SO_4 in the presence of HgSO_4**



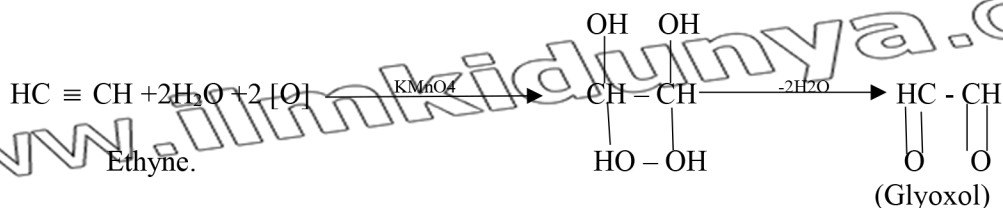
Acetylene

Tautomerisation

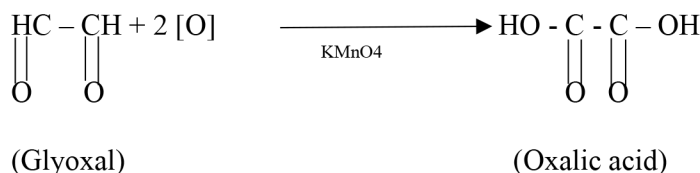
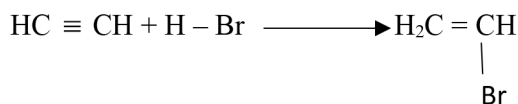


Acetaldehyde

Continue.....p/14.....

(iii) **Alkaline KMnO_4** 1. Ethyne on oxidation with strong alkaline KMnO_4 . Give glyoxal.

- Glyoxal on further oxidation changes to oxalic acid.

(iv) **Halogen acid:**Alkynes react with HCl or HBr to form dihaloalkanes. Addition of second molecule in vinyl bromide take place according to Marknikov's rule.

Q.19 How will you prepare following compounds from ethyne.

FBD -2008, MTN -2014, RWP -2015, SGD -2014

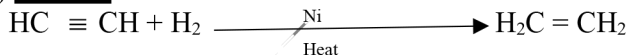
(i) Ethane

(ii) Oxalic acid

(iii) Chloroprene

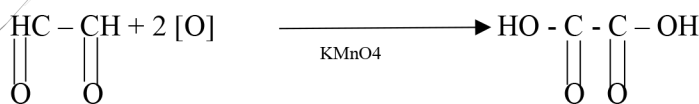
(iv) Benzene

Ans:

(i) **Ethane.**

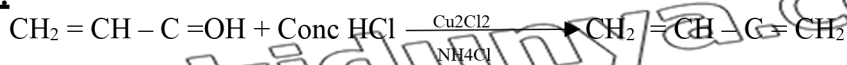
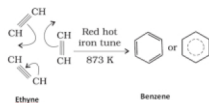
Ethyne

Ethene

(ii) **Oxalic Acid.**

(Glyoxal)

(Oxalic acid)

(iii) **Chloroprene:**(iv) **Benzene**Ethyne $\longrightarrow$ Benzene

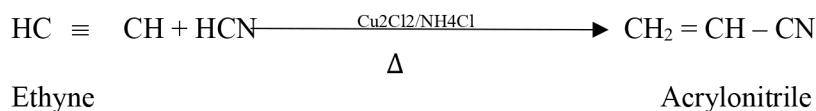
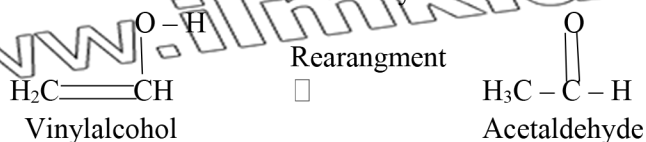
Q.20 How will you prepare following compounds from ethyne.

- (i) Acetaldehyde (ii) Acrylonitrile

RWP-2008, 2015, LHR -2008,2012, GRW -2008,MTN -2014

Ans: (i) **Acetaldehyde**

Vinyl alcohol is an unstable enol. The enol has the hydroxyl group attached to a double bonded carbon atom and isomerises to acetaldehyde.

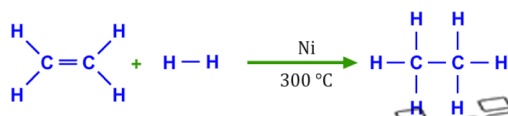


Q.21 Starting from ethane. Prepare the following compounds.

DGK - 2009

- (i) Ethene (ii) Ethyne (iii) 1,2-dibromoethane (iv) Ethyl chloride

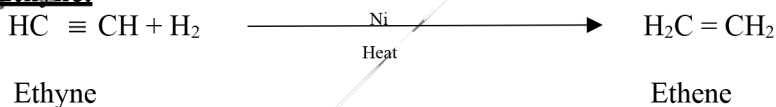
Ans: (i) **Ethene**



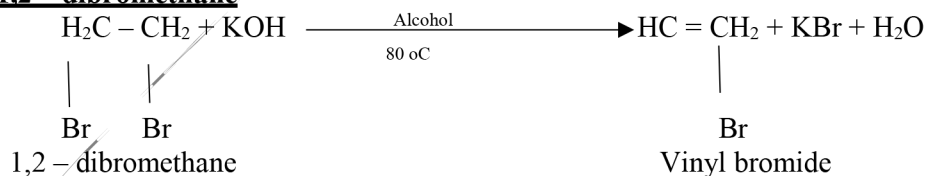
Ethene

Ethane

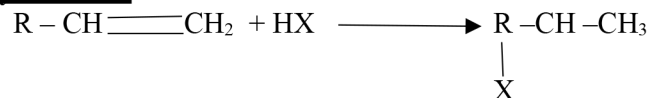
(ii) **Ethyne:**



(iii) **1,2-dibromomethane**



(iv) **Ethyl chloride**



Q.22

How will you make following conversion from an alkene:

LHR – 2017

i) 2-Bromopropane

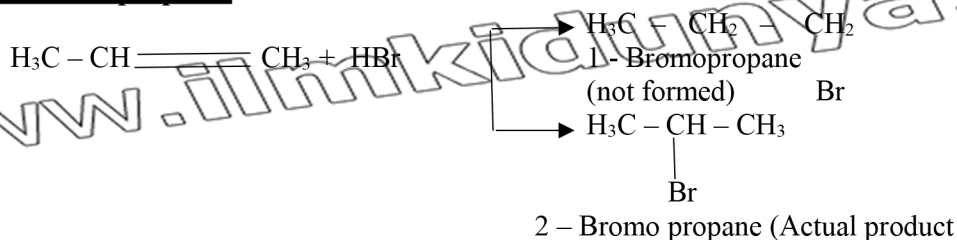
ii) 2-Bromo-2-methyl propane

iii) 2-Propanol

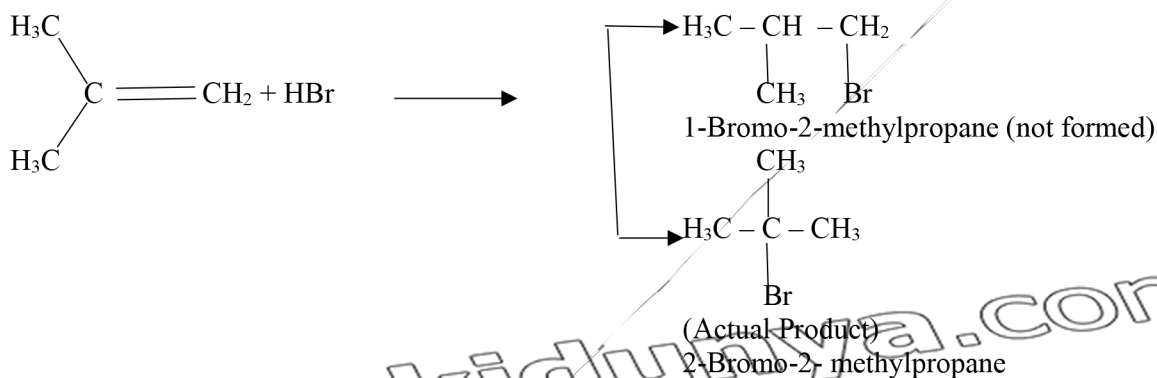
iv) Propylene oxide.

Ans:

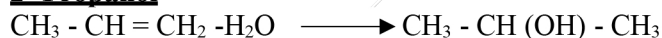
i) **2- Bromopropane:**



ii) **2- Bromo -2- methyl propane**



(iii) **2- Propanol**



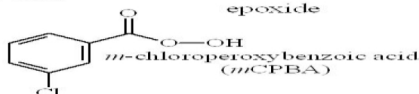
(iv) **Propylene oxide:**

III. Other Reactions of Alkenes

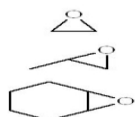
B. Epoxidation



peroxyacetic acid



m-chloroperoxybenzoic acid (*m*CPBA)



epoxyethane (ethylene oxide)

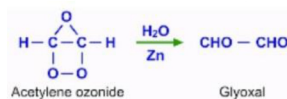
1,2-epoxypropane (propylene oxide)

1,2-epoxycyclohexane (cyclohexene oxide)

Continue.....p/17....

:- 17 :-

Ans: First react Ethyne($\text{H}-\text{C}\equiv\text{C}-\text{HH}-\text{C}\equiv\text{C}-\text{H}$) (Acetylene) with ozone(O_3) to get Acetylene ozonide.


$$\text{CH}_2 = \text{CH} - \text{C} = \text{OH} + \text{Conc HCl} \xrightarrow[\text{NH}_4\text{Cl}]{\text{Cu}_2\text{Cl}_2} \text{CH}_2 = \text{CH} - \text{C} = \text{CH}_2$$

D GK -2014, SGD -2015

$$\text{CH} \equiv \text{CH} \xrightarrow{\text{Na}} \text{CH} \equiv \text{CNa} \xrightarrow{\text{CHI}_2} \text{CH} = \text{C} - \text{CH}_3$$

Acetylen monosodium acetylide Propyne

$$\begin{array}{ccc} \text{H} & \text{O} & \\ & \diagup \quad \diagdown & \\ & \text{C} = \text{C} & \\ & \diagdown \quad \diagup & \\ \text{H} & \text{O} & \end{array} \xrightarrow[\text{Zn}]{\text{H}_2\text{O}} \text{CHO} - \text{CHO}$$

Acetylene oxide Glyoxal

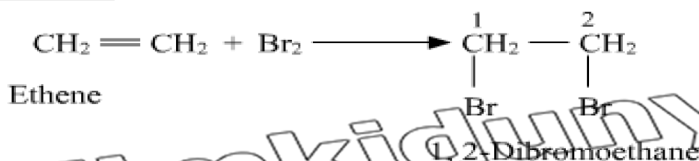
acetylene
 $2\text{CH}\equiv\text{CH} \xrightarrow{\text{Cu}_2\text{Cl}_2, \text{NH}_4\text{Cl}} \text{CH}\equiv\text{C}-\text{CH}\equiv\text{CH}_2$
 acetylene monovinylacetylene
 $\xrightarrow{\text{HCl}, \text{Cu}^{2+}} \text{CH}_2=\text{C}(\text{Cl})-\text{CH}=\text{CH}_2$
 chloroprene

LHR – 2009, FBD -2015

(i) **Ethyl alcohol:**


$$\text{H}_2\text{C}-\text{CH}_2-\text{OSO}_3\text{H} + \text{H}-\text{OH} \xrightarrow{100\text{ }^\circ\text{C}} \text{H}_3\text{C}-\text{CH}_2-\text{OH}$$
$$3\text{CH}_2=\text{CH}_2 + 2\text{KMnO}_4 + 4\text{H}_2\text{O} \longrightarrow \begin{array}{c} \text{OH} \quad \text{OH} \\ | \quad | \\ 3\text{CH}_2 - \text{CH}_2 \end{array} + 2\text{KOH} + 2\text{MnO}_2$$

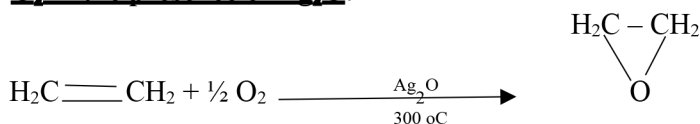
Continue.....p/18.....

(iv) **Vinyl chloride:**

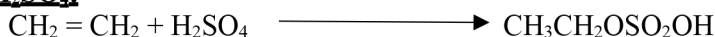
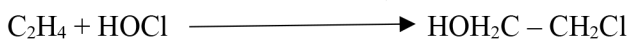
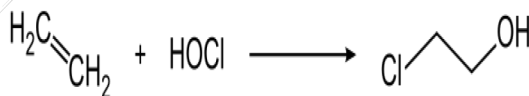
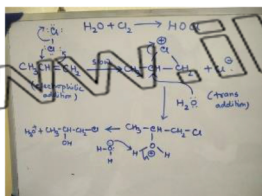
Q.26 Give reaction of ethane with:

LHR - 2017a) O_2 in the presence of Ag_2O b) Conc. H_2SO_4 c) S_2Cl_2 d) HOCl

Ans:

a) **O_2 in the presence of Ag_2O :**

Ethylene oxide or ethylene epoxide

b) **Conc. H_2SO_4 :**c) **S_2Cl_2** d) **HOCl** 

Q.27

How can you convert?

BWP -2009, LHR -2013

(i) 2,3 - dibromobutane into 2-butene

(ii) Ethene into ethylene glycol

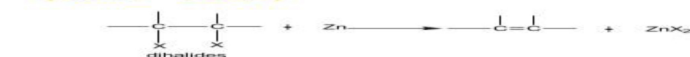
(iii) Acetylene into chloroprene

(iv) Aceton into propane

(v) Acetylene to disilver acetylide

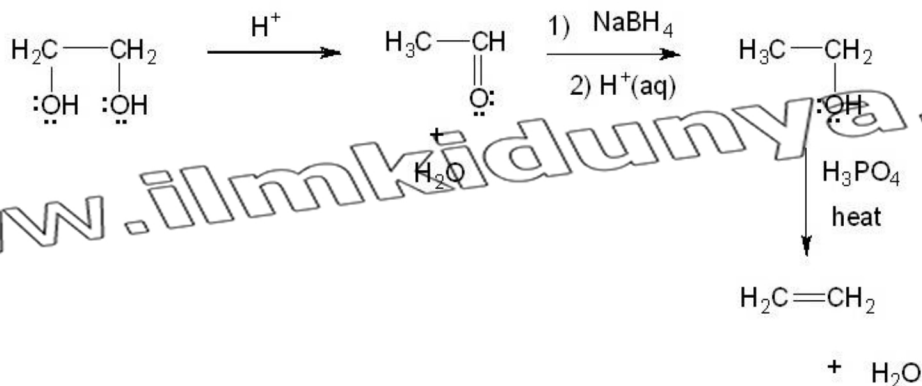
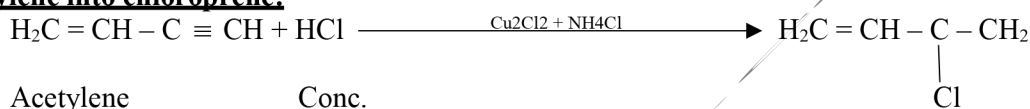
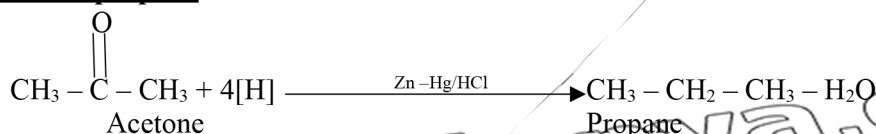
Ans:

(i) 2,3 - dibromobutane into 2-butene

The Conversion of 2,3 dibromobutane to 2 butene with zinc and alcohol is $\beta\beta$ elimination.**3. Dehalogenation of vicinal dihalides (same side)**

Example :

2, 3- dibromobutane 2-butene

(ii) **Ethene into ethylene glycol:**(iii) **Acetylene into chloroprene:**(iv) **Acetone into propane**(v) **Acetylene to disilver acetylide:**

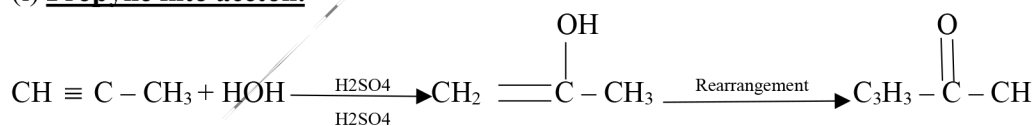
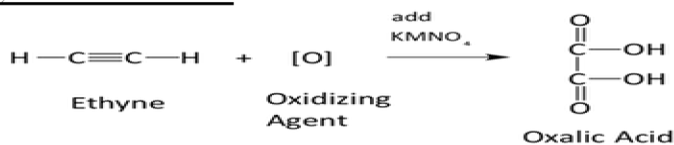
Q.28

Convert the following (i) Propyne into acetone

(ii) Ethyne in to oxalic acid.

LHR -2011, GRW -2011

Ans:

(i) **Propyne into acetone.**(ii) **Ethyne in to oxalic acid.**

Continue.....p/20.....

Q.29

How will you distinguish between ethane, ethane and ethyne chemically?

LHR – 2014

Ans:

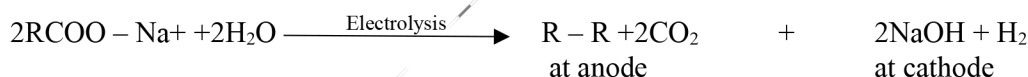
Reagent	Ethane	Ethylene	Acetylene
Alkaline KMnO ₄ Soln.	No Reaction	Decolourized $3\text{CH}_2 = \text{CH}_2 + 4\text{H}_2\text{O} + 2\text{KMnO}_4 \rightarrow \text{CH}_2(\text{OH}) - \text{CH}_2(\text{OH}) + 2\text{MnO}_2 + 2\text{KOH}$	Decolourized $3\text{CH} \equiv \text{CH} + 4\text{H}_2\text{O} + 8\text{KMnO}_4 \rightarrow 3\text{H}_2\text{C}_2\text{O}_4 + 8\text{MnO}_2 + 8\text{KOH}$
Bromine Water	No Reaction	Decolourized $\text{CH}_2 = \text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_2\text{Br} - \text{CH}_2\text{Br}$	Decolourized $\text{CH} \equiv \text{CH} + \text{Br}_2 \rightarrow \text{CHBr} = \text{CHBr}$ $\xrightarrow{\text{Br}_2} \text{Br}_2\text{CH} - \text{Br}_2\text{CH}$
Ammonical AgNO ₃	No Reaction	No Reaction	White ppt. of silver acetylide $\text{CH} \equiv \text{CH} + 2\text{AgNO}_3 + 2\text{NH}_4\text{OH} \rightarrow \text{AgC} \equiv \text{Cag} + 2\text{NH}_4\text{NO}_3 + 2\text{H}_2\text{O}$
Ammonical Cu ₂ Cl ₂	No Reaction	No Reaction	Raddish brown ppt. of copper acetylide $\text{CH} \equiv \text{CH} + \text{Cu}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{CuC} \equiv \text{CCu} + 2\text{NH}_4\text{Cl} + \text{H}_2\text{O}$
10% H ₂ SO ₄ + HgSO ₄	No Reaction	Ethyl alcohol is formed $\text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} \xrightarrow[10\% \text{H}_2\text{SO}_4]{\text{HgSO}_4} \text{CH}_3 - \text{CH}_2\text{OH}$	Acetaldehyde is formed $\text{CH} \equiv \text{CH} + \text{H}_2\text{O} \xrightarrow[10\% \text{H}_2\text{SO}_4]{\text{HgSO}_4} \text{CH}_3 - \text{CHO}$

Q.30 Explain Kolbe's electrolytic method with mechanism for preparation of alkanes.

DGK -2008, BWP -2014,2017, LHR -2015

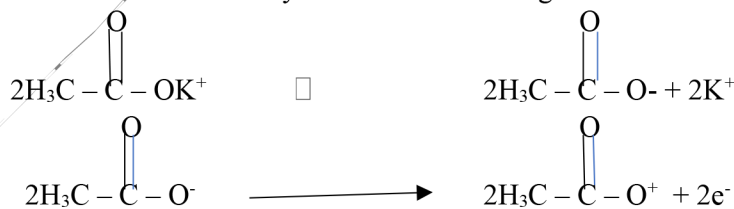
Ans: **Kolbe's electrolytic method:**

When a concentrated solution of sodium or potassium salt of a monocarboxylic acid is electrolyzed, an alkane is produced. This method is only suitable for the preparation of symmetrical alkanes. I.e.e. those of the type R – R Methane cannot be prepared by this method.



Mechanism:

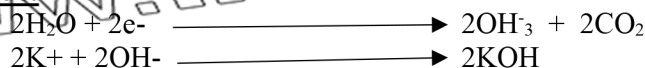
When potassium salt of acetic acid is electrolyzed, acetate ions (CH₃COO⁻) migrate towards the anode gives up one electron to produce acetate free radical (CH₃COO[•]), which decomposes to give a methyl free radical (CH₃[•]) and CO₂. Two such methyl radical combine to give ethane.



At Anode:



At Cathode:



Q.31 How alkanes are prepared by Wolf – Kishner and Clemenson reduction for preparation of alkanes. **SGD -2014**

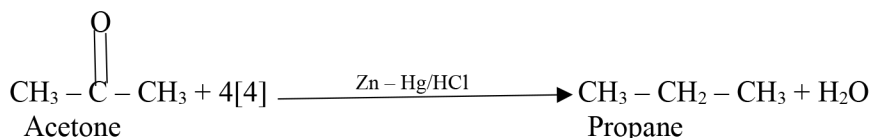
Ans: **Wolf – Kishner:**

Aldehyde reacts with KOH and hydrazine (N₂H₄) and changes to alkane.



Clemenson Reduction:

In this reaction, ketone react with zinc amalgam and hydrochloric acid to form alkane (mixture of a metal with mercury is called amalgam).



Q.32 How following compounds are obtained from methane.

(i) Methyl chloride (ii) Nitromethane

Ans: (i) **Methyl chloride:**



(ii) **Nitromethane:**



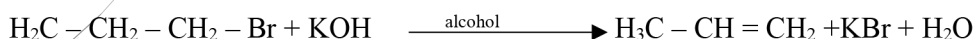
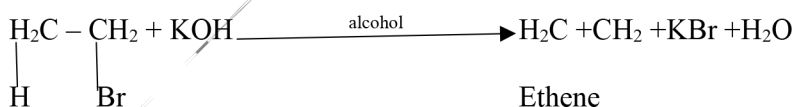
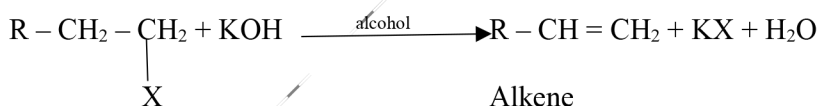
BWP - 2014

Q.33 Write two methods for preparation of alkenes.

SWL -2014, GRW -2015

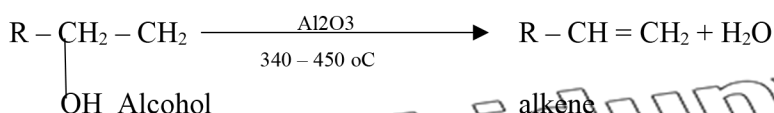
Ans: 1. **Dehydrohalogenation of Alkyl Halides (Elimination reaction):**

Alkyl halides on heating with alcoholic potassium hydroxide undergo dehydrohalogenating i.e. elimination of a halogen atom together with a hydrogen atom from adjacent carbon atoms.



2. **Dehydration of Alcohols:**

Alcohols when dehydrated in the presence of a catalyst give alkenes. The best procedure is to pass vapours of alcohol over heated alumina (Al₂O₃).

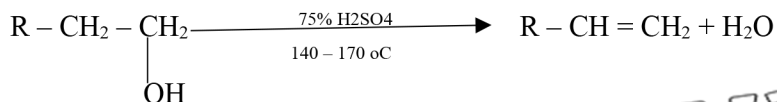


Al₂O₃, P₄O₁₀, H₂SO₄ (conc.) and H₃PO₄ are dehydrating agent used for preparation of alkene. The ease of dehydration of various alcohols is in the order.

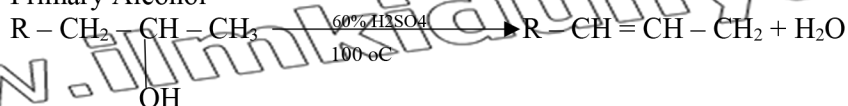
Ter. Alcohol > Sec. alcohol > Pri-alcohol

Continue.....p/22...

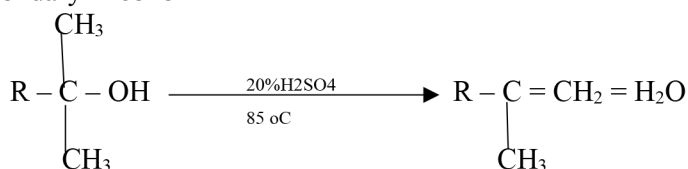
Thus



Primary Alcohol



Secondary Alcohol



Tertiary Alcohol

Q.34

State Markownikov's rule. Give reaction of HBr with:

(i) Propene

(ii) 1 - Butene

(ii) 2- Butene

SWL – 2014

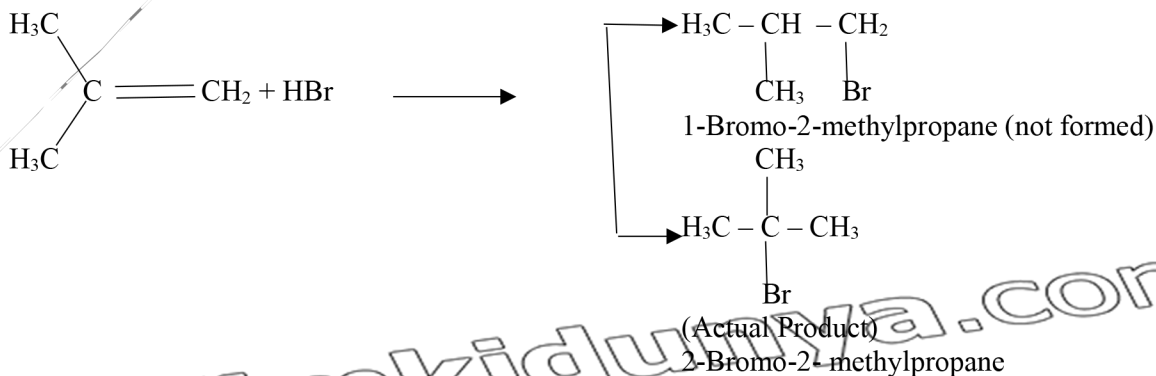
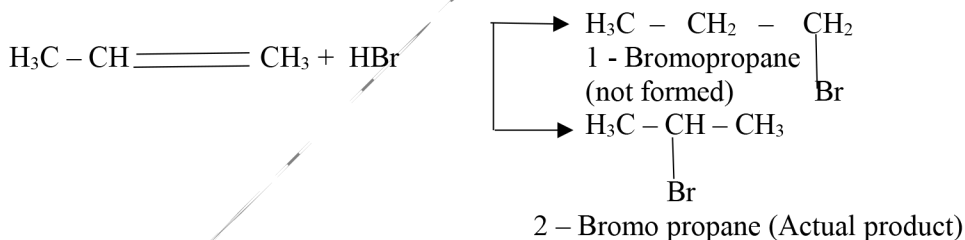
Ans:

Markownikov's Rules:

"If unsymmetrical reagent is added to unsymmetrical alkene, the negative part of reagent will be added to that carbon which have least number of hydrogen atoms."

Unsymmetrical alkenes are those which have different number of hydrogen atoms on both side of double bond.

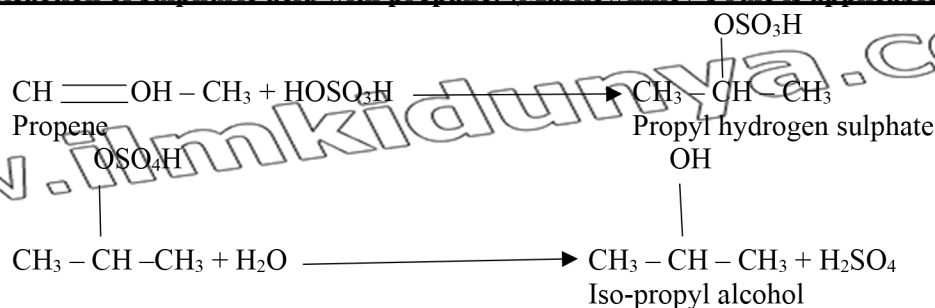
Examples:



Continue.....p/23.....

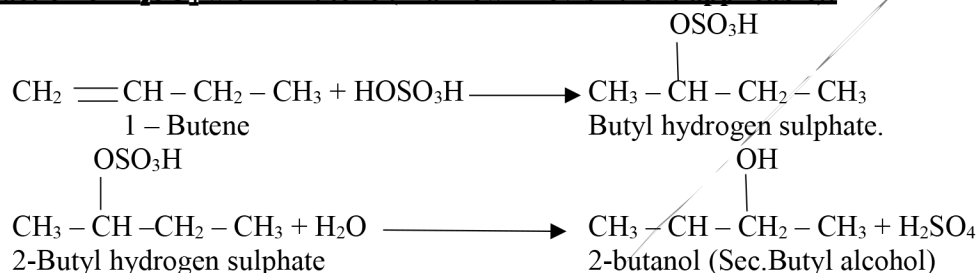
(i) **Propene**

1. Reaction of sulphuric acid with propene: (Markownikov's rule is applicable):



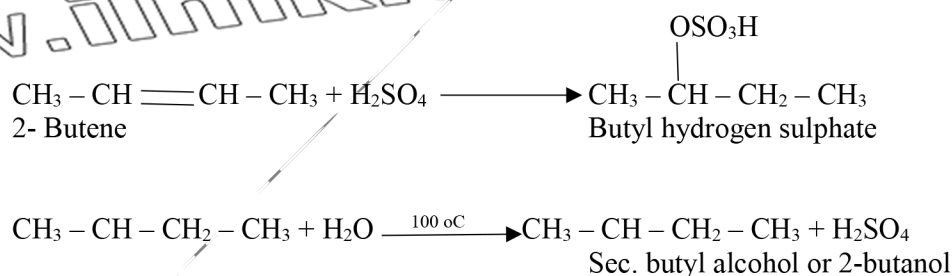
(ii) **1-Butene**

2. Reaction of H₂SO₄ with 1-Butene (Markownikov's rule is applicable):



(iii) **2-Butene**

Reaction of H₂SO₄ with 2-butene: (Markownikov's rule is applicable):



Q.35 How does propyne react with the following reagents?

MTN - 2017

i) AgNO₃/NH₄OH ii) Cu₂Cl₂/NH₄OH iii) H₂O/H₂SO₄, HgSO₄

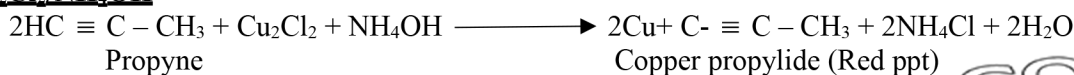
iv) NaNH₂

Ans: **Reaction of Propyne:**

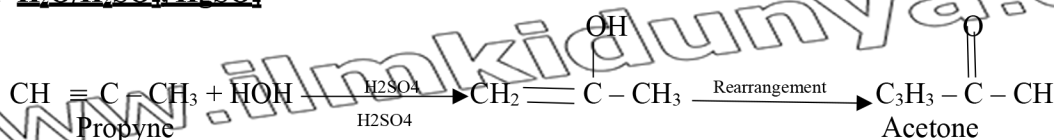
1. AgNO₃/NH₄OH



2. Cu₂Cl₂/NH₄OH



3. H₂O/H₂SO₄, HgSO₄



THE END: