

VIVEKANANDA COLLEGE
THAKURPUKUR
KOLKATA-700063

NAAC ACCREDITED 'A' GRADE



Topic: Organic Chemistry: Alkanes, Alkenes and Alkynes

Course Title: GE2/CC2

Paper: GE2/CC2

Unit: NA

Semester: 2 (Gen)

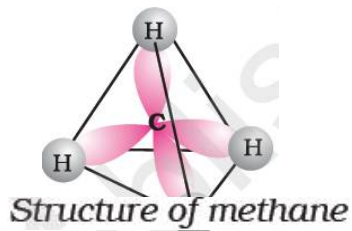
Name of the Teacher: Yasin Nuree

Name of the Department: Chemistry

ALKANES

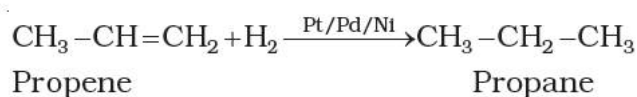
Alkanes are saturated open chain hydrocarbons

containing carbon - carbon single bonds.

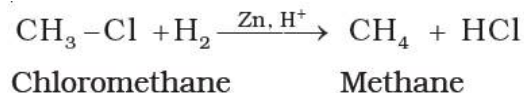


Preparation

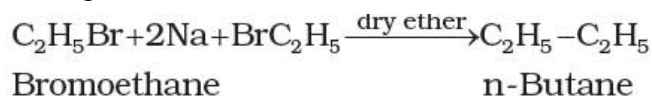
1. Dihydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes.



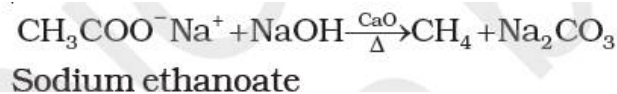
2. Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes.



3. Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as **Wurtz reaction** and is used for the preparation of higher alkanes containing even number of carbon atoms.



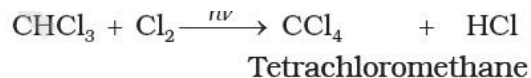
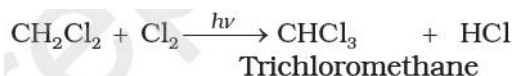
4. Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid.



Reactions:

1. *Substitution reactions:* One or more hydrogen atoms of alkanes can be replaced by halogens, nitro group and sulphonic acid group. Halogenation takes place either at higher temperature (573-773 K) or in the presence of diffused sunlight or ultraviolet light.

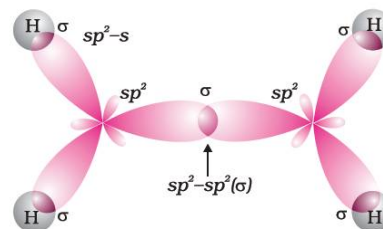
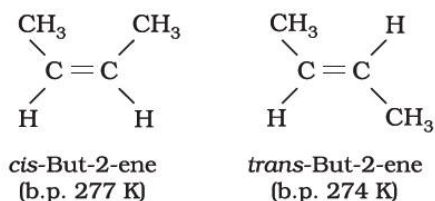




- Oxidation: Ordinarily alkanes resist oxidation but alkanes having tertiary H atom can be oxidized to corresponding alcohols by potassium permanganate.
- Pyrolysis of alkanes is believed to be a free radical reaction. Preparation of oil gas or petrol gas from kerosene oil or petrol involves the principle of pyrolysis. For example, dodecane, a constituent of kerosene oil on heating to 973K in the presence of platinum, palladium or nickel gives a mixture of heptanes and pentene.

ALKENES:

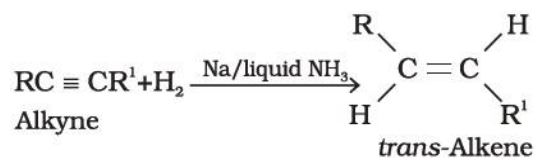
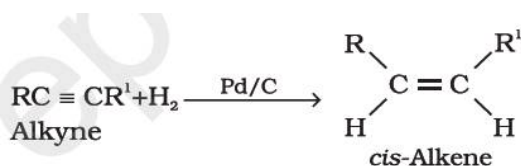
Unsaturated hydrocarbons containing at least one double bond having general formula for alkenes is C_nH_{2n} . Alkenes are also known as olefins (oil forming).



Orbital picture of ethene depicting σ bonds only

Preparation

- Alkynes on partial reduction with calculated amount of dihydrogen in the presence of *palladised* charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as *Lindlar's catalyst*.

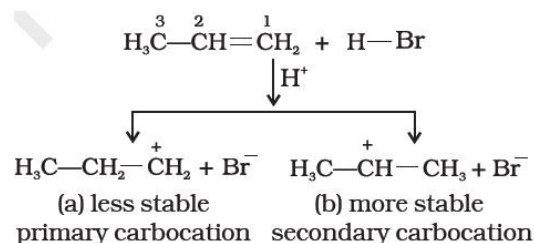


- Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol).

3. Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule. Since a water molecule is eliminated from the alcohol molecule in the presence of an acid, this reaction is known as acidic dehydration of alcohols.

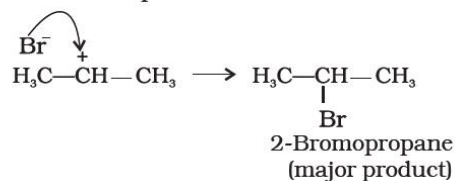
Reactions:

1. hydrogen halides is $\text{HI} > \text{HBr} > \text{HCl}$. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction. How will $\text{H} - \text{Br}$ add to propene ? The two possible products are I and II.



(i) The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.

(ii) The carbocation (b) is attacked by Br^- ion to form the product as follows :

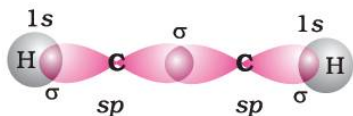


Markovnikov rule. The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus according to this rule, product I *i.e.*, 2-bromopropane is expected. In actual practice, this is the principal product of the reaction. This generalisation of Markovnikov rule can be better understood in terms of mechanism of the reaction.

Anti Markovnikov addition or peroxide effect or Kharash effect In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This happens only with HBr but not with HCl and HI . This addition reaction was observed by M.S. Kharash and F.R. Mayo in 1933 at the University of Chicago. This reaction is known as *peroxide* or *Kharash* effect or addition reaction anti to Markovnikov rule.

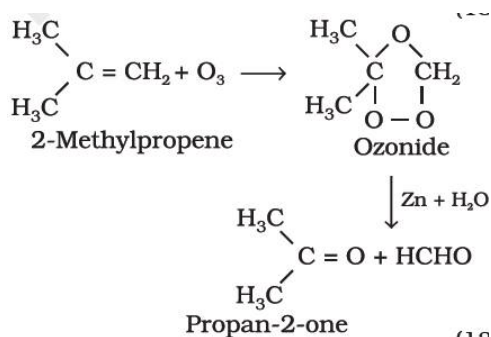
2. **Addition of water :** In the presence of a few drops of concentrated sulphuric acid alkenes react with water to form alcohols, in accordance with the Markovnikov rule.

3. **Ozonolysis :** Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by $\text{Zn-H}_2\text{O}$ to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.



ALKYNES:

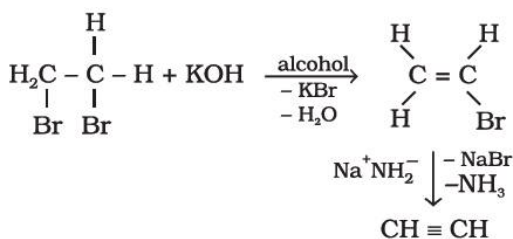
Their general formula is C_nH_{2n-2} containing at least one triple bond between two carbon atoms.



Preparation

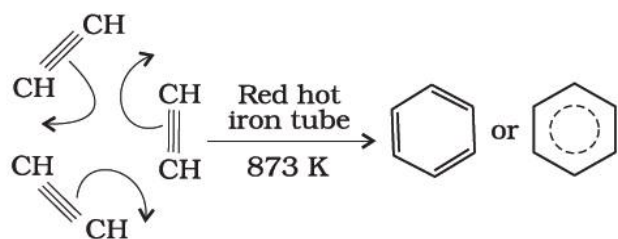
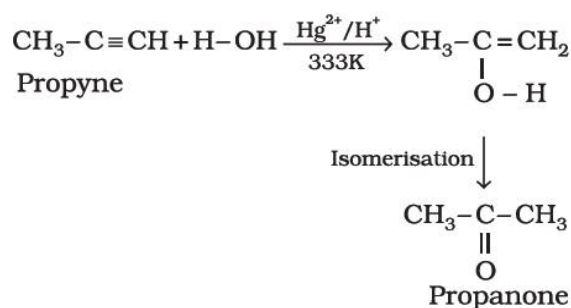
1. Ethyne is prepared by treating calcium carbide with water.

2. Vicinal dihalides on treatment with alcoholic potassium hydroxide undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.



Reactions

- One molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333 K to form carbonyl compounds.
- Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene.



References:

- Organic Chemistry by I. L. Finar
- Advanced Organic Chemistry by Graham Solomon.
- Advanced Organic Chemistry by P Y Bruice
- Organic Chemistry by R L Madan