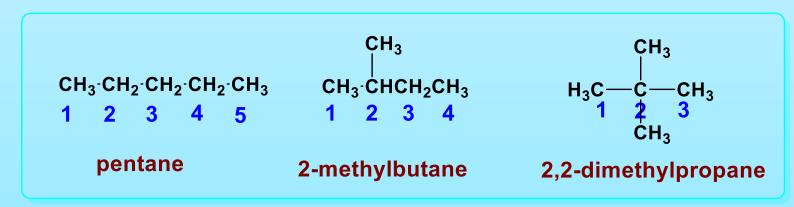
Isomerism

- ➤ There are many organic compounds that have the same molecular formula but have different physical and chemical properties they are therefore different compounds
- > Such compounds are said to be *isomers*
- So far we have seen compounds that are constitutional (or structural) isomers, e.g.
- In this topic, we will learn about structural isomers, however; in the second year we will learn about other types of isomers

Isomerism

- > So what are constitutional isomers?
- ➤ Constitutional isomers are isomers that differ because their atoms are connected in a different order, i.e. they have different connectivity
- There are a number of different types
- 1. Chain isomers (C₅H₁₂)



Isomerism

2. Positional isomers (C₃H₇CI)

3. Functional group isomers

Natural occurrence

- Alkanes, alkenes and alkynes can be obtained from nature in the form of natural gas
- ➤ Methane, for example, is the main constituent of natural gas (often more than 90% by volume)
- Crude petroleum gives rise to much higher straight-chain alkanes, branched and cycloalkanes
- ➤ Individual components in crude oil can be isolated using fractional distillation

PNG Liquified Natural Gas Project with Hides Gas Conditioning Plant through a 700-kilometre pipeline



Hides Gas Conditioning Plant at Hela Province, Southern Highlands

The plant processes up to 1 billion standard cubic feet of gas gathered from eight wells each day





LNG Processing Plant at Caution Bay on the South Coast of Central Province, with the capacity of producing 8.3 million tonnes of LNG annually





Turning Natural Gas into Liquid Natural Gas



- Some of these compounds can be prepared in the laboratory using specific reactions:
- ➤ Hydrogenation of alkenes for example provides one of the most important methods for preparing specific alkanes (This is an example of an addition reaction or reduction)
- Here a mixture of the alkene and hydrogen is passed over a finely divided catalyst, usually platinum, palladium or nickel

$$C_nH_{2n} + H_2 \xrightarrow{Pt, Pd} C_nH_{2n+2}$$

Specific example

$$H_2C = CH_2 + H_2 \xrightarrow{Pt, Pd} H_3C - CH_3$$

ethene ethane

Similarly, alkynes can also be hydrogenated (initially) to alkenes and then to alkanes

$$C_nH_{2n-2} + H_2 \xrightarrow{Pt, Pd} C_nH_{2n} + H_2 \xrightarrow{Pt, Pd} C_nH_{2n+2}$$
alkyne alkene alkane

HC
$$=$$
 CH + H₂ $\xrightarrow{\text{Pt, Pd}}$ H₂C $=$ CH₂ + H₂ $\xrightarrow{\text{Pt, Pd}}$ H₃C $=$ CH₃ ethene ethane

- Reduction of haloalkanes alkyl halides are alkanes in which one of the hydrogen atoms has been replaced by a halide atom
- Most of these compounds react with zinc metal and aqueous acid to produce an alkane
- > A general and specific reaction are as follows:

- Grignard reaction the Grignard reaction is an organomagnesium halide, which has great application in organic chemistry
- ➤ In this reaction it is reacted with water (in the presence of an acid) to produce an alkane
- A general and specific reaction are as follows:

R-X + Mg
$$\longrightarrow$$
 R-MgX $\xrightarrow{H_2O}$ R-H + Mg(OH)X

$$CH_3-CH_2-Br \xrightarrow{Mg} CH_3-CH_2-MgBr \xrightarrow{H_2O} CH_3-CH_2-H + Mg(OH)Br$$

- Cracking of alkanes this is an industrial source of alkene
- Large hydrocarbons in crude petroleum are broken down (cracked) into smaller fragments
- ➤ The technique used here is called *pyrolysis* (using heat)

$$R - \begin{matrix} H & H \\ | & | \\ C - C - R \end{matrix} \xrightarrow{heat} \begin{matrix} H & H \\ | & | \\ R \end{matrix} \xrightarrow{heat} \begin{matrix} C = C \\ | & | \\ R \end{matrix} \xrightarrow{H} \begin{matrix} H & H \end{matrix}$$

- ➤ In laboratories, a number of methods have been used to prepare specific alkenes
- ➤ A greater majority of alkenes are produced using ELIMINATION reactions, i.e. removal of atoms from adjacent carbon atoms resulting in the formation of a double bond
- ➤ The main compounds used in these reactions are alcohols and haloalkanes we will learn more about these in (Haloalkanes) and (Alcohols and ethers) topics

- Dehydrohalogenation of haloalkanes is a very popular method for preparing alkenes
- ➤ Here the haloalkane is heated in an alcoholic solution of potassium hydroxide resulting in the production of an alkene

$$R - C - C - R \xrightarrow{\text{heat}} R \xrightarrow{\text{loc. KOH}} R \xrightarrow{\text{loc. KO$$

- Another method for preparing alkenes involves the dehydration of alcohol
- ➤ When most alcohols are heated in the presence of concentrated (excess) sulfuric acid at elevated temperatures, the molecule loses a water molecule and forms an alkene

$$R - C - C - R \xrightarrow{\text{conc. H}_2SO_4} R \xrightarrow{\text{h}} C = C + H_2O$$

As in the preparation of alkenes, reactions required for the formation of triple bonds also involve elimination reactions, i.e. atoms are removed from adjacent carbon atoms

$$R \xrightarrow{H} \xrightarrow{H} \xrightarrow{H} \xrightarrow{R} \xrightarrow{\text{heat}} \xrightarrow{\text{heat}} \xrightarrow{\text{leat}} \xrightarrow{\text{leat}$$

➤ Ethyne, for example, can be prepared by boiling 1,2-dibromoethane with an alcoholic solution of potassium hydroxide

Basic reaction mechanisms

- You would have realized now that alkanes are considered to be generally classed as being inert (i.e. unreactive)
- This is because the carbon-carbon and carbon-hydrogen bonds are very strong and therefore do not break easily
- As we have seen, they will break only when heated at very high temperatures (pyrolyzed)

Basic reaction mechanisms

- One reaction of alkanes that does not require high temperatures is the halogenation reaction
- This reaction requires light (UV or sunlight) to proceed and follows a radical mechanism

H—C—H +
$$CI_2$$
—hv + CI_2 —C—CI + HCI
H

- Alkenes are highly reactive compounds in comparison to alkanes
- The pi electrons in the double bond act as a source of electrons, i.e. it functions as a base or a nucleophile
- ➤ They react with electron-deficient species such as acids or electrophiles
- ➤ Their reactions are characterized as electrophilic addition across the double bond

These reactions can proceed through ionic or free radical mechanisms

Ionic addition

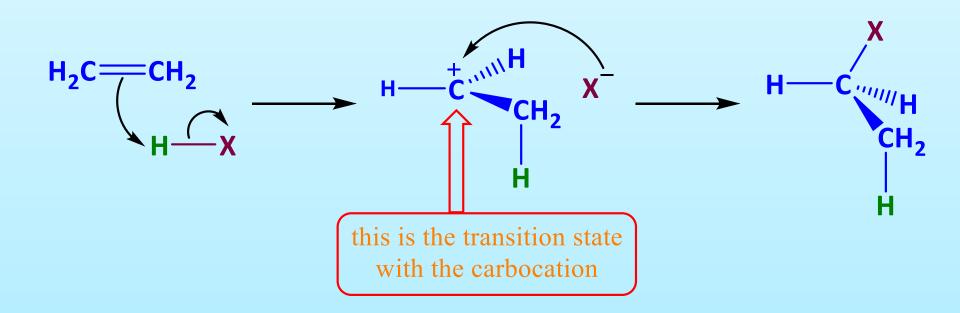
- ➤ lonic addition across the double bond is initiated by the more electropositive component of the attacking reagent
- It attaches itself to one of the unsaturated carbon atoms and induces a positive charge on the other carbon atom

- ➤ The resulting transition state contains a positively charged "three valent carbon" which is referred to as a *carbocation* (*carbonium* ion)
- > See the following example

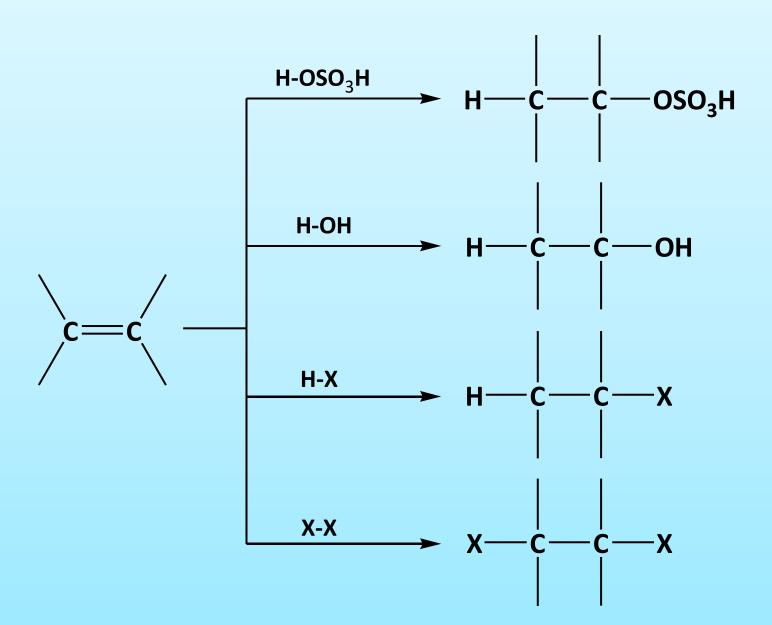
$$H_2C = CH_2 + H - X \rightarrow H_2C - CH_2$$

In theory there are two possible products depending on where the H attaches itself

> The resulting transition state

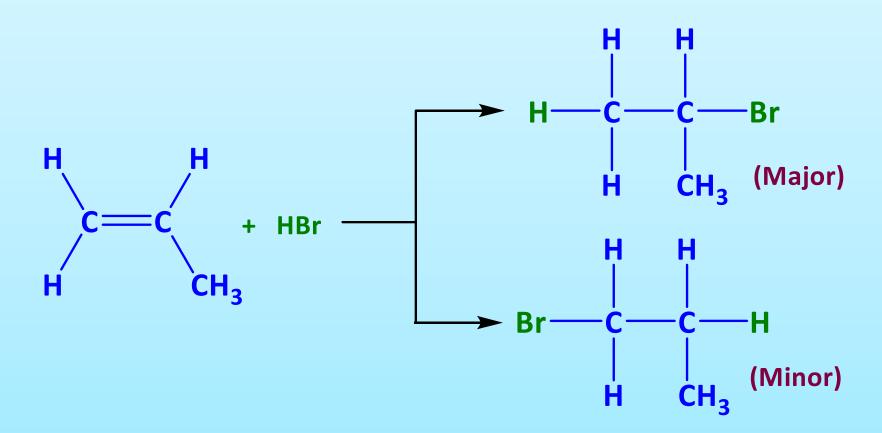


Given below are the generic representation of the general ionic addition reactions:

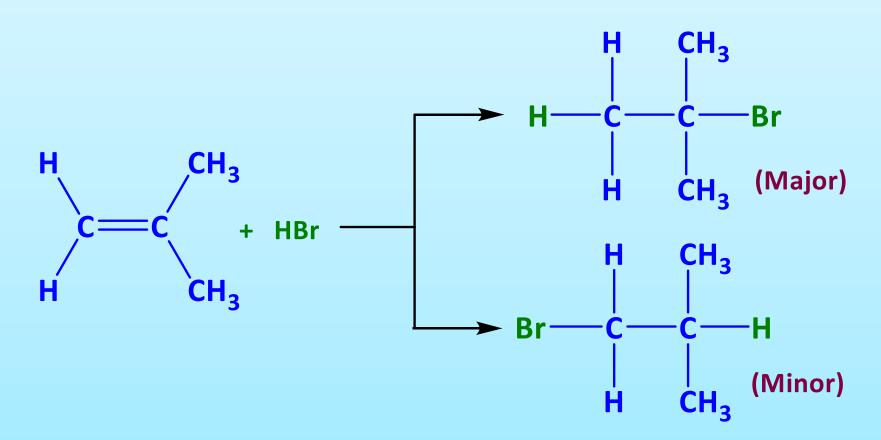


- Hydrogen halides (HCI, HBr, HI, HF) add to double bonds of alkenes as shown above
- ▶ If one of these is added to an unsymmetrical alkene (like propene), the hydrogen atom (of the H-X) will add to the carbon atom of the double bond that already has the greater number of hydrogen atoms
- This addition is said to be following Markovnikov's rule

The Markovnikov's addition – example 1



➤ The Markovnikov's addition – example 2



Addition of bromine and chlorine to alkenes

➤ Alkenes react rapidly with bromine and chlorine in non-nucleophilic solvents to form vicinal dihalides, i.e. two halide atoms on adjacent carbons

H
C=C
H
$$Cl_2$$
H
 Cl_2
H
 Cl_2
H
 Cl_2
 Cl_2
H
 Cl_2
 Cl_2

➤ This addition is a useful industrial process because 1,2-dichloroethane can be used as a solvent and can be used to make vinyl chloride which is the starting material for poly(vinyl)chloride [PVC]

Other examples of the addition of halogens to a double bond are as follows:

$$H_3C$$
 CH_3
 CH_3

