University of Al-Mustaqbal
College of Engineering and
Engineering Techniques
Engineering Techniques of
Fuel and Energy department

Organic Chemistry

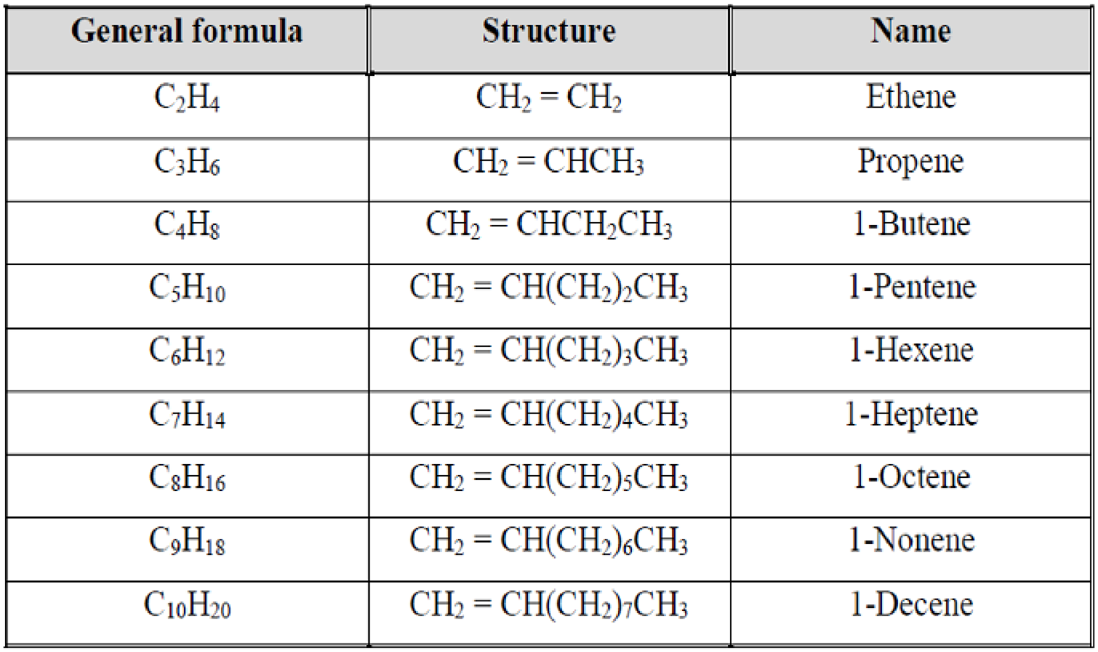
Lecture Four

Alkenes, Alkynes, Alcohols

1. Alkenes

Alkenes are a homologous series of hydrocarbons that contain a carbon carbon double bond. The number of hydrogen atoms in an alkene is double the number of carbon atoms, so they have the general formula C_nH_{2n}.

The carbon-carbon double bond is unsaturated and hence highly reactive toward a wide variety of reagents. The first nine member of the alkenes:



General formula	Structure	Name
C_2H_4	$CH_2 = CH_2$	Ethene
C_3H_6	$CH_2 = CHCH_3$	Propene
C_4H_8	$CH_2 = CHCH_2CH_3$	1-Butene
C_5H_{10}	$CH_2 = CH(CH_2)_2CH_3$	1-Pentene
C_6H_{12}	$CH_2 = CH(CH_2)_3CH_3$	1-Hexene
C_7H_{14}	$CH_2 = CH(CH_2)_4CH_3$	1-Heptene
C_8H_{16}	$CH_2 = CH(CH_2)_5CH_3$	1-Octene
C_9H_{18}	$CH_2 = CH(CH_2)_6CH_3$	1-Nonene
$C_{10}H_{20}$	$CH_2 = CH(CH_2)_7CH_3$	1-Decene

1.2. Naming of alkenes

Common names are seldom used except for three simple alkene; ethylene, propylene, and isobutylene. Most alkene are named by IUPAC system.

1- The longest continuous chain of carbon atoms containing the double bond serves as the parent compound.
2- The ending –ane of the corresponding alkane hydrocarbon name is replaced by the ending –ene.
3- The position of the double bond is indicated by the lower number of the numbers of the carbon atoms to which it is attached. The number that represents this position is placed before the parent compound name. Alkyl groups attached to the parent compound are designated as is done for the alkane.

4- If a geometric isomer is designated, the name begins with cis- or trans-.

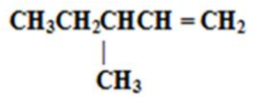
Examples:

$CH_3CH_2CH_2CH_2CH{=}CH_2$

1- Hexene

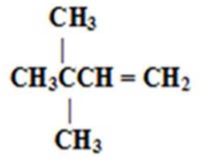
$CH_2{=}CHCH_2CH_3$

1-Butene



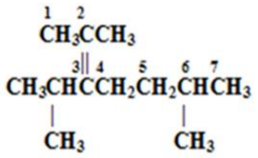
$$CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH=CH_2$$

3-Methyl-1-pentene



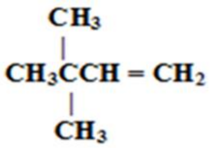
$$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH=CH_2$$

3,3-Dimethyl-1-butene



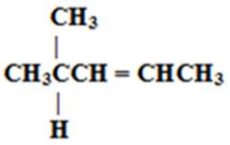
$$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{\overset{1\ \ 2}{CH_3CCH_3}}{3\|}}{C}\overset{4}{C}H_2\overset{5}{C}H_2\underset{\underset{CH_3}{|}}{\overset{6}{C}}H\overset{7}{C}H_3$$

3-Isopropyl-2,6-dimethyl-2-heptene



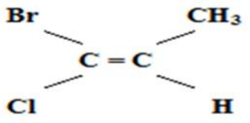
$$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH=CH_2$$

3,3-Dimethyl-1-butene

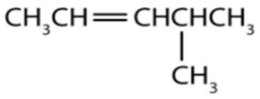


$$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}CH=CHCH_3$$

4-Methyl-2-pentene

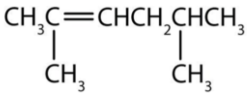


1-Bromo-1-chloropropene



$$CH_3CH=CH\underset{\underset{CH_3}{|}}{C}HCH_3$$

4-methyl-2-pentene



$$CH_3\underset{\underset{CH_3}{|}}{C}=CHCH_2\underset{\underset{CH_3}{|}}{C}HCH_3$$

2,5 di methyl hexene

1.3. Preparation of Alkenes

There are four ways to prepare alkenes: dehydrohalogenation of alkyl halides, dehydration of alcohols, dehalogenation of vicinal dihalides, and Cracking of petroleum hydrocarbons

1.3.1. Dehydrohalogenation of alkyl halides

Dehydrohalogenation involves loss of the halogen atom and of hydrogen atom from a carbon adjacent to the one losing the halogen (1,2 elimination).

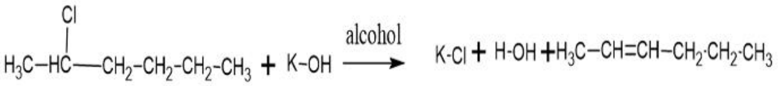
$-\underset{H}{C}-\underset{X}{C}- + KOH \xrightarrow{alcohol} -C=C- + KX + H_2O$

Ease of dehydrohalogenation of alkyl halides 3° > 2° > 1°

$CH_3CH_2CH_2CH_2Cl \xrightarrow{KOH,\ alcohol} CH_3CH_2CH=CH_2 + KCl + H_2O$

n-Butyl chloride 1-Butene

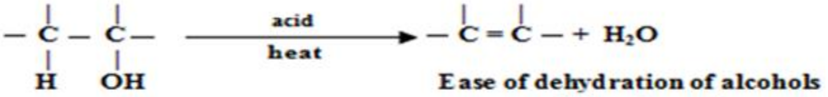
Example : prepare 2-hexene by using KOH ?



$H_3C-\overset{Cl}{HC}-CH_2-CH_2-CH_2-CH_3 + K-OH \xrightarrow{alcohol} K\text{-}Cl + H\text{-}OH + H_3C-CH=CH-CH_2\cdot CH_2\cdot CH_3$

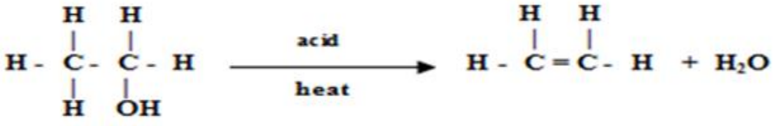
1.3.2. Dehydration of alcohols

In the dehydration of alcohols, the H and OH are lost from adjacent carbons (1,2- elimination). An acid catalyst is necessary and application of heat.



$-\underset{H}{C}-\underset{OH}{C}- \xrightarrow[heat]{acid} -C=C- + H_2O$

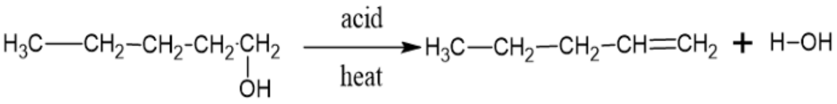
Ease of dehydration of alcohols 3° > 2° > 1°



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-H \xrightarrow[heat]{acid} H-\overset{H}{C}=\overset{H}{C}-H + H_2O$

Ethyl alcohol Ethylene

Example : prepare 1- pentene from alcohol



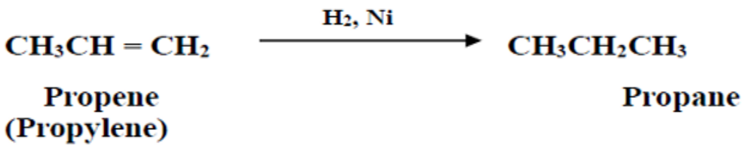
$H_3C-CH_2-CH_2-CH_2\cdot\underset{OH}{CH_2} \xrightarrow[heat]{acid} H_3C-CH_2-CH_2-CH=CH_2 + H-OH$

1.4. Reactions of alkenes

The presence of the carbon-carbon double bond confers very considerable chemical activity on the alkenes and consequently they react with a much wider variety of reagents than do the alkanes. The π-bond component of the double bond is weaker than the σ-bond component and the π-electrons are more easily accessible to attacking reagents. There is about six reactions of alkenes, the most important of which are summarized as follows

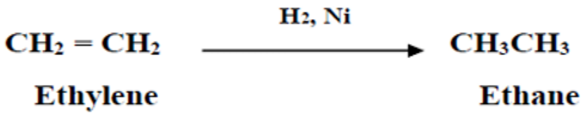
1.4.1. Addition of hydrogen

When an alkene is mixed with hydrogen, there is no appreciable reaction, but in the presence of certain metal catalysts such as nickel, platinum or palladium, a fairly rapid reaction occurs leading to the uptake of hydrogen.



$$CH_3CH = CH_2 \xrightarrow{H_2,\ Ni} CH_3CH_2CH_3$$

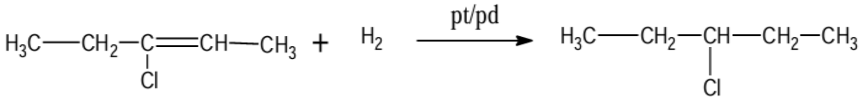
Propene (Propylene) Propane



$$CH_2 = CH_2 \xrightarrow{H_2,\ Ni} CH_3CH_3$$

Ethylene Ethane

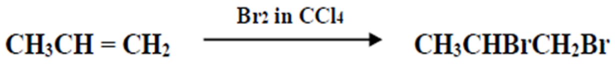
Example : give a productions of 3-chloro-2-pentene hydrogenation?



$$H_3C-CH_2-\underset{Cl}{C}=CH-CH_3 + H_2 \xrightarrow{pt/pd} H_3C-CH_2-\underset{Cl}{CH}-CH_2-CH_3$$

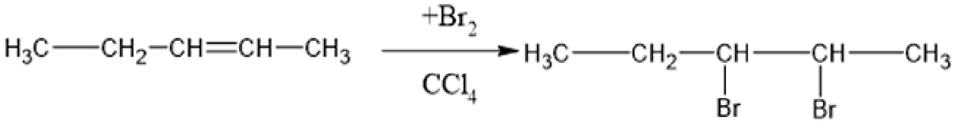
1.4.2 Addition of halogen

Chlorine and bromine react readily with alkenes, in the liquid or vapour states, to form dihalogeno addition products, the two halogen atoms are attached to adjacent carbons. Iodine generally fails to react.



$$CH_3CH = CH_2 \xrightarrow{Br_2\ in\ CCl_4} CH_3CHBrCH_2Br$$

Example : complete this reaction :



$$H_3C-CH_2-CH=CH-CH_3 \xrightarrow[CCl_4]{+Br_2} H_3C-CH_2-\underset{Br}{CH}-\underset{Br}{CH}-CH_3$$

2. Alkynes

Molecules of alkyne series of hydrocarbon are characterized by having two adjacent carbon atoms joined to one another by a triple bond. The carbon-carbon triple bond is unsaturated and highly reactive toward the reagents that double bonds react with.

$HC \equiv CH$	Ethyne (acetylene)
$HC \equiv CCH_3$	Propyne
$HC \equiv CCH_2CH_3$	1-Butyne
$HC \equiv C(CH_2)_2CH_3$	1-Pentyne
$HC \equiv C(CH_2)_3CH_3$	1-Hexyne
$HC \equiv C(CH_2)_4CH_3$	1-Heptyne
$HC \equiv C(CH_2)_5CH_3$	1-Octyne
$HC \equiv C(CH_2)_6CH_3$	1-Nonyne
$HC \equiv C(CH_2)_7CH_3$	1-Decyne

2.1. Naming of alkynes

1- Find the longest carbon chain that includes both carbons of the triple bond.

2- Number the longest chain starting at the end closest to the triple bond.

3- After numbering the longest chain with the lowest number assigned to the alkyne, label each of the substituents at its corresponding carbon. While writing out the name of the molecule, arrange the substituents in alphabetical order. If there are more than one of the same substituent use the prefixes di, tri, and tetra for two, three, and four substituents respectively. These prefixes are not taken into account in the alphabetical order.

4- When there are two triple bonds in the molecule, find the longest carbon chain including both the triple bonds. Number the longest chain starting at the end closest to the triple bond that appears first.

The suffix that would be used to name this molecule would be –diyne.

5- A molecule that contains both double and triple bonds is called an alkenyne. The chain can be numbered starting with the end closest to the functional group that appears first.

Examples:

$HC\equiv CCH_2CH_3$

1-Butyne

$CH_3C\equiv CCH_3$

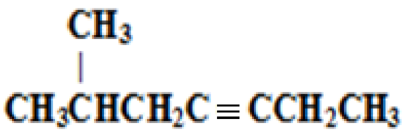
2-Butyne

$CH_3C\equiv CCH_2CH_3$

2-Pentyne

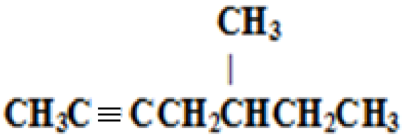
$CH_3CH=CHCH_2C\equiv CH$

4-Hexen-1-yne



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2C\equiv CCH_2CH_3$

6-Methyl-3-heptyne



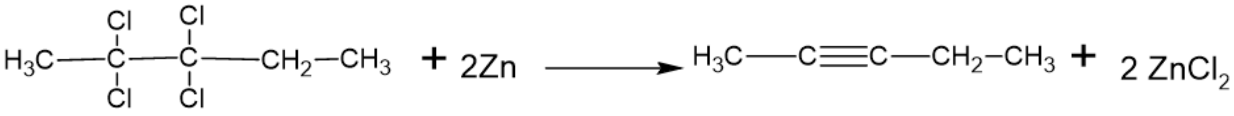
$CH_3C\equiv CCH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$

5-Methyl-2-heptyne

2.2. Preparation of Alkynes

Alkynes can be prepared by three main ways: de hydrogenation of vicinal di halides, reduction of calcium carbid with H_2O, de halogenation of tetra halides, and Reaction of metal acetylides with alkyl halides.

2.2.1. De halogenation of tetra halides



$$H_3C-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-CH_2-CH_3 + 2Zn \longrightarrow H_3C-C\equiv C-CH_2-CH_3 + 2\,ZnCl_2$$

$$H_3C-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-CH_3 + 2Zn \longrightarrow H_3C-C\equiv C-CH_3 + 2ZnBr_2$$

2.3. Reactions of alkynes

The carbon-carbon triple bond –C≡C– consists of one σ-bond , so it is not surprising that addition reactions are a characteristic feature of this functional group. Despite its high formal unsaturation, the triple bond dose not usually react so vigorously as a carbon-carbon double bond, as in alkenes, and it is therefore sometimes possible to stop the addition reaction after the uptake of 1 mol of reactant, rather than 2 mol which would be possible in principle. The most important reactions of alkynes are summarized as follow:

1. Addition of hydrogen
2. Addition halogen acid
3. Addition of halogens
4. Hydration
5. Ozonolysis

3. Alcohols

All alcohols contain the hydroxyl group (-OH) attached to a saturated carbon. These have the general formula R-OH, where R is an alkyl or substituted alkyl group.

The group may be primary, secondary, or tertiary; it may be open chain or cyclic; it may contain a halogen atom, an aromatic ring, or additional hydroxyl group.

The -OH group is the functional group, determines the properties characteristic of this family. Variations in structure of the R group may affect the rate at which the alcohol undergoes certain reactions, and even, in a few cases, may affect the kind of reaction.

Compound in which the hydroxyl group is attached directly to an aromatic ring are not alcohols; they are phenols.

3.1. Classification of alcohols

Alcohols classified in three types:

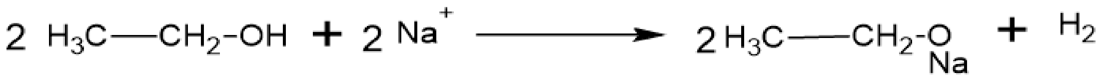
a. Monohydric : which containing one of hydroxyl group (OH)

b. Dihydric : which containing two of hydroxyl group (OH)

c. Trihydric: which containing three of hydroxyl group (OH)

3.2. Reactions of alcohols

3.2.1. Reaction with active metal



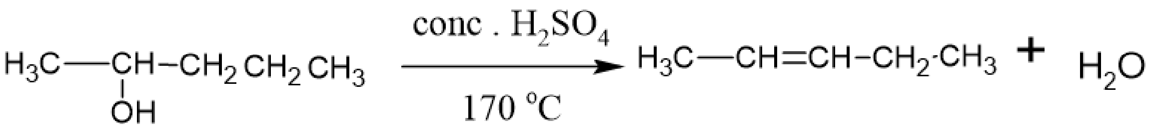
$$2\,H_3C{-}CH_2{-}OH + 2\,Na^+ \longrightarrow 2\,H_3C{-}CH_2{-}\underset{Na}{O} + H_2$$

$$H_3C{-}CH_2{-}CH_2{\cdot}OH + PCl_5 \longrightarrow H_3C{-}CH_2{-}CH_2Cl + POCl_3 + HCl$$

3.2.2. Reaction with hydrogen halides

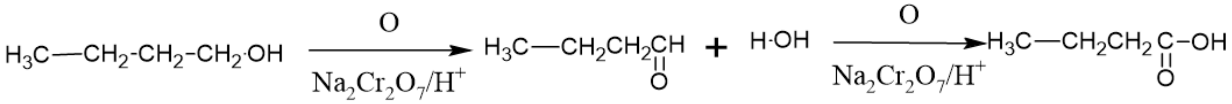
$$H_3C{-}CH_2{-}CH_2{-}CH_2{\cdot}OH + HCl \longrightarrow H_3C{-}CH_2CH_2CH_2Cl + H_2$$

3.2.3. Dehydration of alcohol



$$H_3C{-}\underset{OH}{CH}{-}CH_2\,CH_2\,CH_3 \xrightarrow[170\ ^{o}C]{conc\ .\ H_2SO_4} H_3C{-}CH{=}CH{-}CH_2{\cdot}CH_3 + H_2O$$

3.2.4. Oxidation of alcohols



$$H_3C{-}CH_2{-}CH_2{-}CH_2{\cdot}OH \xrightarrow[Na_2Cr_2O_7/H^+]{O} H_3C{-}CH_2CH_2\underset{\underset{O}{\|}}{CH} + H{\cdot}OH \xrightarrow[Na_2Cr_2O_7/H^+]{O} H_3C{-}CH_2CH_2\,\underset{\underset{O}{\|}}{C}{-}OH$$