Thi-Qar University

College of science

Chemistry Department

# Organic Chemistry

# Second stage

# lectures 4 & 5 & 6 & 7

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# THE CHEMISTRY OF ALKENES

- Structure of alkenes
- Nomenclature
- Isomerism
- Physical properties of alkenes
- Preparation of alkene
- Electrophilic addition reactions of alkenes
- Addition to unsymmetrical alkenes
- Other reactions
- Polymerisation
- Preparation of alkenes

Alkenes: are also called olefins unsaturated hydrocarbons with general formula CnH2n.

- Unsaturated = contain a double C=C bond
- Hydrocarbon = contains C and H <u>only</u>



Functional group = carbon-carbon double bond ,  $sp^2$  hybridization => Structure spatial arrangement around the C=C is **planar or trigonal**, **flat**, **120° bond angles**.  $\sigma$  bond &  $\pi$  bond => H<sub>2</sub>C=CH<sub>2</sub> , No rotation about double bond!



#### (The systematic rules for naming alkenes IUPC Name)

- Find the longest chain of carbon atoms that includes the double bond then name as for the corresponding saturated hydrocarbon (alkane) (use the meth, eth, prop... root word) but use the termination -ene rather than -ane
- 2. to determine which carbon is the first carbon, make the double bond the lowest number possible.

3. The number of the carbon where the double bond is located is written before the root word.



4. side chains and substitutions are written in alphabetical order and Indicate the position of any groups (substituents) attached to the parent alkene chain by the appropriate number:





5. if there are more than one double bond each bond position is noted with a number preceding the root name and a prefix; di, tri... is inserted before the ene suffix, -diene or -triene are examples



H<sub>3</sub>C 4 2 CH<sub>3</sub>

1,4-Hexadiene

**Examples:** Give IUPC names of the following structure.



Some non-systematic names still in common name use:

C <sub>3</sub> H <sub>6</sub> propylene	CH <sub>3</sub> CH=CH <sub>2</sub>
C <sub>4</sub> H <sub>8</sub> butylenes	CH <sub>3</sub> CH <sub>2</sub> CH=CH <sub>2</sub>
	α-butylene
	$CH_3$
CH <sub>3</sub> CH=CHCH <sub>3</sub>	$CH_3C = CH_2$
β-butylene	isobutylene
2-butene	2-methylpropene

#### Isomerism in alkenes

#### Three types of isomerism found in alkenes

1- **Structural Isomers :** Different structures are possible due to Different positions for the double bond. Or straight chain and branching chain with the same positions for the double bond.

2-position isomer.



#### **3- Geometric Isomers**



cis-2-butene

trans-2-butene



### **Physical Properties**

**Boiling point** :are similar to those shown in alkanes in increases as they get more carbon atoms in their formula more atoms = greater intermolecular Van der Waals' forces. greater intermolecular force = more energy to separate molecules greater energy required = higher boiling point, cyclohexene  $C_6H_{10}$  is a liquid , for isomers, greater branching = lower boiling point , **Melting point** :general increase with molecular mass increase

**Solubility**: alkenes are non-polar so are immiscible (don't mix with) with water miscible with most organic solvents .

**Notice** / The C—C single bond between an alkyl group and one of the double bond carbons of an alkene is slightly polar because the  $sp^3$  hybridized alkyl carbon donates electron density to the  $sp^2$  hybridized alkenyl carbon.



This C accepts electron density.

Alkenes react with many electrophiles to give useful products by addition (often through special reagents.

# **Preparation of Alkenes:**

# **1-Industrial Preparation of Alkenes:**

Thermal 'cracking' of high molecular weight alkanes:

$$C_{n}H_{2n+2} \xrightarrow{ca. 900 \circ C} H_{2} + CH_{4} + H_{2}C=CH_{2} + CH_{3}CH=CH_{2}$$
$$n = 2-8 + CH_{3}CH_{2}CH=CH_{2}$$

# 2- Laboratory Preparation of Alkenes

- There are four standard laboratory methods for preparing alkenes from nonalkene starting materials:
- (1) From alcohols (dehydration, 1,2- or **\beta-Elimination** of H<sub>2</sub>O).
- (2) From alkyl halides and related compounds of the type RX (1,2- or **ß**-**Elimination** of HX).
  - (3) From aldehydes or ketones *via* the Wittig Reaction . (4) From alkynes .
  - (1) Alkenes from alcohols (dehydration, 1,2- or **B-Elimination** of H2O)

$$\begin{array}{c|c} & | & | \\ -C & -C \\ | & | \\ H & OH \end{array} \quad \text{acid, heat} \quad \Rightarrow \quad -C = C \\ - C = C \\ + H \\ + H \\ - C \\ + H \\ - C \\ + H \\ - C \\ - C \\ + H \\ - C \\ - C \\ - C \\ - H \\ - H \\ - H \\ - C \\ - C \\ - H \\ - H$$

- **1-** Reactivity of ROH:  $3^{\circ} > 2^{\circ} > 1^{\circ}$
- 2- Acid is a catalyst
- **3-** Rearrangements are possible
- 4- Mixtures are possible

## 5- Saytzeffe rule

The E1 and E2 Mechanisms of Alcohol Dehydration, **E1 mechanisms** - The acid-catalyzed dehydration of 3° and 2° alcohols proceeds through a carbocation intermediate . The ease of formation of Carbocation is **Tertiary>Secondary>Primary**.



Unsymmetrical alcohols may yield more than one product.



Zaitsev (or Saytzeff) rule: the most substituted (*i.e.* most stable) alkene is favoured.

Ease of formation of alkenes:

 $R_2C=CR_2 > R_2C=CHR > R_2C=CH_2, RCH=CHR > RCH=CH_2 > CH_2=CH_2$ 

### $R_2C=CR_2 > R_2C=CHR > R_2C=CH_2$ , $RCH=CHR > RCH=CH_2 > CH_2=CH_2$



### E2 Mechanisms - dehydration of $1^{\circ}$ alcohols .



#### **Carbocation Rearrangement During an E1 Mechanism**

The E1 mechanism involves formation of a carbocation intermediate. that carbocations are susceptible to rearrangement via either a **hydride shift** or a **methyl shift**. Here is an example of an E1 mechanism that contains a carbocation rearrangement.

• In hydride shifts, a secondary or tertiary hydrogen from a carbon next to the original carbocation takes both of its electrons to the cation site,

swapping place with the carbocation and renders it a more stable secondary or tertiary cation.



Similarly, when there is no hydride available for hydride shifting, an alkyl group can take its bonding electrons and swap place with an adjacent cation, a process known as **alkyl shift.** 



(2) Alkenes from alkyl halides and related compounds of the type RX (1,2- or β-Elimination of HX). (Dehydrohalogenation )



In the reaction illustrated above an alkene is formed by removal of H and X are from an alkyl halide, *i.e.* a small molecule, HX.

# Some important points:

This reaction illustrated above is called a 1,2- or **β-Elimination** to indicate that the groups being eliminated are located on adjacent atoms in the starting material

Notice that the requirements for a **ß-Elimination** reaction are:

(i) A base

(ii) A leaving group in the substrate such as halide . Alkyl halide relative reactivity order : I > Br > Cl > F

(iii) A C-H bond **adjacent atoms** to the leaving group.

Alkene formation via elimination of HX from alkyl halides can follow two different mechanistic pathways identified as **E2** and **E1**.



Here is the **E2** mechanism



**E2** because the reaction is bimolecular, *i.e.* two species - the base and the organic halide come together to form the transition state.

Here is the **E1** mechanism









# 3- dehalogenation of vicinal dihalide

# Reactions of alkenes, Reactivity of C=C

Alkenes react with many electrophiles to give useful products by addition (often through special reagents.



- 1-Electrons in pi bond are loosely held.
- 2- Electrophiles are attracted to the pi electrons.
- 3- Carbocation intermediate forms.
- 4- Nucleophile adds to the carbocation.
- 5- Net result is addition to the double bond. .





# 1-Addition of Halogens to Alkenes

1-Bromine and chlorine add to alkenes to give 1,2-dihaldes, an industrially important process ,

- 2-F<sub>2</sub> is too reactive and I<sub>2</sub> does not add
- 3-Cl<sub>2</sub> reacts as  $Cl^+ Cl^-$
- 4-Br<sub>2</sub> is similar



Mechanism for Halogenation

- 1-Pi electrons attack the bromine molecule.
- 2- A bromide ion splits off
- 3- Intermediate is a cyclic bromonium ion.





## **Test for Unsaturation:**

Add Br<sub>2</sub> in CCl<sub>4</sub> (dark, red-brown color) to an alkene in the presence of light.

The color quickly disappears as the bromine adds to the double bond. "Decolorizing bromine" is the chemical test for the presence of a double bond.



Carbocations are unstable because they have only six electrons around carbon. Halonium ions are unstable because of ring strain.



# 2- Addition of hydrogen (reduction)



# **3-Addition of Hypohalous Acids to Alkenes: Halohydrin Formation:**

This is formally the addition of HO-X to an alkene to give a **1,2-halo alcohol**, called a halohydrin  $\cdot$ . The actual reagent is the dihalogen (Br<sub>2</sub> or Cl<sub>2</sub> in water in an organic solvent)  $\cdot$ .



Mechanism of Formation of a Bromohydrin.









#### 4-Hydration of an alkene is the addition of H-OH to to give an alcohol

#### • Markovnikov's rule holds

Markovnikov's Rule: The addition of a proton acid to the double bond of an alkene results in a product with the acid hydrogen bound to the carbon atom that already has the greater number of hydrogens attached..

- Addition of H and OH occurs in both syn and anti.
- Carbocation rearrangements can occur





The first step is the protonation of the double bond to generate a carbocation, which in turn is attacked by water (a nucleophile).

## The final step is quick proton removal to generate the product.





#### **5- Oxymercuration - Demercuration**

This is another alternative for converting alkenes to alcohols with Markovnikov orientation. This method has the advantage of not involving free carbocationic species, and thus removes the possibility of rearrangement.



The reagent is called mercuric acetate, and is usually abbreviated to Hg(OAc) In solution it ionizes into acetate ion and a positively charged mercury species which is very electrophilic







#### **Alkoxymercuration - Demercuration**

This is an extension of the previous reaction, where the reaction is performed in the presence of an alcohol rather than water.





### 6- Hydroboration of Alkenes.

We have studied three ways of hydrating alkenes to give Markovnikov orientated alcohols. There is also a way to obtain anti – Markovnikov oriented alcohols: hydroboration.



Borane adds to alkenes with anti – Markovnikov orientation, and these alkylboranes can then be oxidized to alcohols.



#### Mechanism of Hydroboration.

Borane has only six valence electrons and is very electron deficient . Borane is an electrophilic molecule, and reacts with double bonds in a one step process to generate an alkylborane.



#### 7- Addition of Carbenes

Carbenes are neutral, reactive intermediates with a divalent carbon and a lone pair



Carbenes are potent electrophiles and react with double bonds to form 3 membered rings (cyclopropanes).

There are 3 classical ways to generate carbenes:

- (1) diazomethane
- (2) Simmons Smith Reaction
- (3) Alpha Elimination from Haloforms

#### **1-Diazomethane**

The heating or photolysis of diazomethane generates a carbene and nitrogen gas



However, diazomethane is toxic and explosivee, and it often forms carbenes that are so reactive than numerous side products are formed.

#### 2-Simmons -Smith Reaction

The reaction of diiodomethane with zinc metal in the presence of Cu(I) salts generates a Carbenoid species

$$CH_2I_2 + Zn(Cu) \rightarrow ICH_2ZnI$$

3- Alpha Elimination from Haloforms

In the presence of a strong enough base, Bromoform can have its proton removed, and the tribromomethyl anion will eliminate a bromide ion to generate dibromocarbe

This type of carbene reacts with retention of stereochemistry of the reactants.



## 8- Addition of a Hydrogen Halide to an Alkene.

If the electrophilic reagent that adds to an alkene is a hydrogen halide (HF, HCl, HBr, or HI), the product of the reaction will be an alkyl halide.









#### 9- Free Radical addition to Alkenes

It is possible to obtain *anti-Markovnikov* products when HBr is added to alkenes in the presence of free radical initiators.

The free radical initiators change the mechanism of addition from *electrophilic addition* to *free radical addition*.



This change of mechanism gives rise to the opposite regiochemistry.

Free-Radical Addition of H-Br To Alkenes



addition can occur from either face This accounts for mixture of "syn" and "anti" products
Bromine radical is regenerated and can then react with another equivalent of alkene

This change of mechanism gives rise to the opposite regiochemistry.



#### (Radical additions do not proceed with HCl or HI, only HBr).

#### **Oxidation of Alkenes.**

(Addition of hydrogen is termed a chemical reduction.

Addition of oxygen across a double bond is called a chemical oxidation).

Oxidation is normally the formation of C-O bonds .There are three common methods for the introduction of oxygen containing functional groups into molecules via alkenes (epoxidation, hydroxylation and oxidative cleavage).

#### **Epoxidation of Alkenes**

An epoxide (oxirane) is a three membered ring containing an oxygen. (Heterocyclic version of a cyclopropane).



# Mechanism

The epoxidation takes place in a concerted one step electrophilic process.



Syn hydroxylation of alkenes gives syn 1,2 –diols



The two most common methods use osmium tetroxide with hydrogen peroxide, or potassium permanganate and hydroxide ion.

# Osmium Tetroxide Hydroxylation.



### **Permanganate Hydroxylation**

An alkaline, cold solution of potassium permanganate will do exactly the same transformation as osmium tetroxide.



# **Oxidative Cleavage.**

If either acid or heat is used with permanganate, cleavage and further oxidation can occur producing ketones and/or aldehydes. The aldehydes further oxidize to carboxylic acid.



# Ozonolysis.

Ozone (O 3) also cleaves double bonds, but this milder reagent gives aldehyde and ketones as the products.



The intermediate ozonide reacts with reducing agents like dimethyl sulfide to produce DMSO and the carbonyl product. (mechanism)



Dimerization and Polymerization of Alkenes.

Alkenes in the presence of strong acids can be made to polymerize. An electrophile (H  $^+$ ) adds electrophilically to the double bond, and the carbocation is attacked by another alkene double bond.

