Organic Chemistry
CHEM 145

2 Credit hrs

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Unsaturated Hydrocarbons

- **These compounds are deficient in hydrogen**
  - **Carbon-carbon double bond.**
    is called the Alkenes or Olefins
    General formula is C_nH_{2n}
  - **Carbon-carbon triple bond.**
    is called the Alkynes or Acetylenes
    General formula is C_nH_{2n-2}
- **The simplest members of the alkenes series are C_2 & C_3**

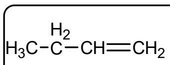
	$CH_2{=}CH_2$	$H_3C{-}CH{=}CH_2$
Common name:	Ethylene	Propylene
IUPAC name:	Ethene	Propene

Nomenclature of Alkenes

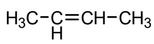
The IUPAC rules for naming alkenes are:

- **The longest continuous carbon chain containing the double bond is selected as the parent chain.**
- **The name of the parent carbon chain is obtained by replacing the –ane by –ene.**
- **The parent carbon chain is numbered to give the doubly bonded carbon atoms the lowest number.**

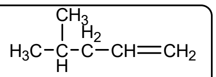
  even if it results in the substituting getting higher numbers.
- **The position of the double bond is indicated by the number of the lower numbered doubly bonded carbon.**
- Examples



1-Butene
(*not* 3-Butene)

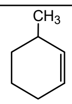


2-Butene

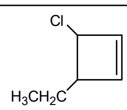


4-Methyl-1-pentene
(*not* 2-Methyl-4-pentene)

- **In cycloalkenes, the double bond is always found between carbon 1 & carbon 2.**

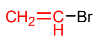
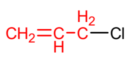
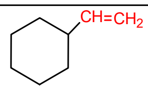


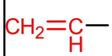
3-Methylcyclohexene
(*not* 1-Methyl-2-cyclohexene)



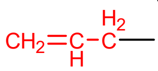
3-Chloro-4-ethylcyclobutene
(*not* 1-Chloro-2-ethyl-3-cyclobutene)

- Examples

			
Common name:	Vinyl bromide	Allyl chloride	Vinyl cyclohexane
IUPAC name:	Bromoethene	3-Chloro-1-propene	Cyclohexylethene



Vinyl

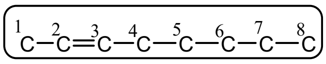


Allyl

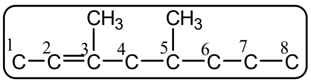
Example: Write the structural formula of 4-Isopropyl-3,5-dimethyl-2-octene.

1) The parent carbon chain is an octene.

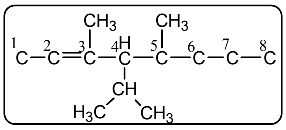
The double bond is located between the 2nd and 3rd carbons.



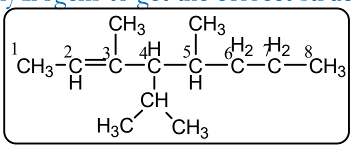
2) Two methyl groups are attached on the parent carbon chain, one on carbon 3 and the other on carbon 5.



3) An isopropyl group is attached on carbon 4.

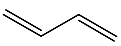


4) Put the missing hydrogens to get the correct structure.

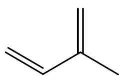


Dienes or diolefins

- **Diene or diolefin is a hydrocarbon that contains two carbon double bonds.**
- **Dienes occur occasionally in nature.**
- **Conjugated dienes are widely used as monomers in the polymer industry**

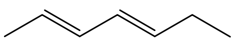


1,3-Butadiene
OR
Buta-1,3-diene

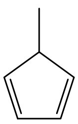


2-Methyl-1,3-butadiene
OR
2-Methyl-buta-1,3-diene

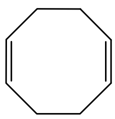
Isoprene



2,4-Heptadiene
OR
Hepta-2,4-diene



5-Methyl-1,3-cyclopentadiene
OR
5-Methyl-cyclopenta-1,3-diene



1,5-Cyclooctadiene
OR
Cycloocta-1,5-diene

Physical Properties of Alkenes

- The physical properties of alkenes are much the same as those of corresponding alkanes

  C_2 to C_4 alkenes are gases

  C_5 to C_{18} alkenes are liquids

  above C_{18} are solids.

- Alkenes are insoluble in water and soluble in nonpolar organic solvents such as benzene or in carbon tetrachloride.

Geometry of Unsaturated Hydrocarbones

- Geometry of the Carbon-Carbon Double Bond: *sp*^{2} Hybridization
  - Ethylene is a trigonal *planar* molecule with a bond angle of 120°.
- Geometry of the Carbon-Carbon Triple Bond: *sp* Hybridization
  - Acetylene is a linear molecule with a bond angle of 180°.

Geometric Isomerism in Alkenes

- Alkenes of the type WXC=CYZ, where W differs from X and Y from Z

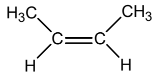
  Alkenes exist as geometric isomers

- In cycloalkanes geometric isomerism is due to restricted rotation about the carbon-carbon single bond in a ring
- In alkenes geometric isomerism is due to rotation about the carbon - carbon double bond.

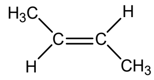
Geometric isomers

- When two similar groups are on
  - The same side of the double bond, the compound is called the *cis* isomer.
  - The opposite sides of the double bond, the compound is called the *trans* isomer.
- They have different physical properties and can be separated by fractional crystallization or distillation.

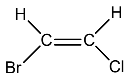
Geometric Isomerism in Alkenes



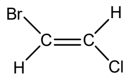
cis-2-Butene
m.p. = -139°C; b.p. = 3.7°C



trans-2-Butene
m.p. = -106°C; b.p. = 0.9°C

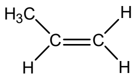


cis-1-Bromo-2-chloroethene

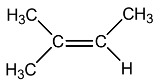


trans-1-Bromo-2-chloroethene

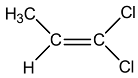
If (W = *X* or *Y* = Z), geometric isomerism is not possible.
The following compounds have no geometric isomers.



Propene



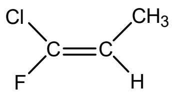
2-Methyl-2-butene



1,1-Dichloropropene

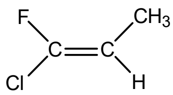
Geometric Isomerism in Alkenes

For alkenes with four different substituent such as



(I)

or



(II)

Another system, the *E, Z* system,

Basically, the E,Z system works as follows;

Arrange the groups on each carbon of the C=C bond in order of priority

The priority depends on atomic number:

The higher the atomic number of the atom directly attached to the double-bonded carbon, the higher the priority.

Thus, in structure (I),

Cl > F, and CH_3 > H.

Geometric Isomerism in Alkenes

- If the two groups of higher priority are on the same side of the C=C plane, The isomer is labeled *Z*; (from the German *zusammen*, together).
- If the two groups of higher priority are on opposite sides of the C=C plane, The isomer is labeled *E*; (from the German *entgegen*, opposite).

Priority: Cl > F, CH_3 > H

Z-1-Chloro-1-fluoropropene (Cl and CH_3 on same side)

E-1-Chloro-1-fluoropropene (Cl and CH_3 on same side)

Priority: Br > H, I > CH_3

Priority: Br > H, Cl > F

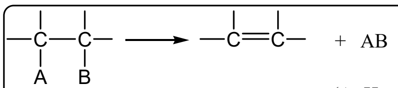
Z-1-Bromo-2-iodopropene

E-1-Brfomo-2-chloro-2-fluoroethene

Preparation of Alkenes

- Alkenes are prepared by

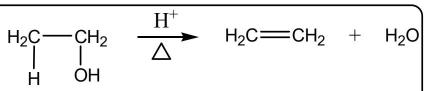
  Elimination of an atom or group of atoms from adjacent carbons formation of a carbon-carbon double bond.



(A=H or halogen; B=OH or halogen)

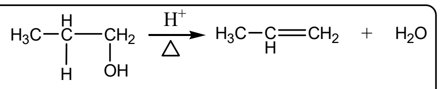
Dehydration of Alcohols

- When an alcohol is heated in the presence of a mineral acid catalyst, it readily loses a molecule of water to give an alkene.

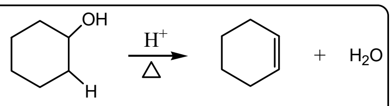


IUPAC name:	Ethanol	Ethene
Common name:	Ethyl alcohol	Ethylene

- The acid catalysts most commonly used are sulfuric acid, H_2S0_4, and phosphoric acid, H_3P0_4.



IUPAC name: 1-Propanol — Propene
Common name: *n*-Propyl alcohol — Propylene

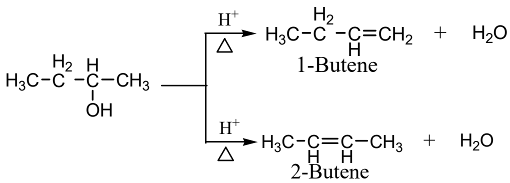


IUPAC name: Cyclohexanol — Cyclohexene
Common name: Cyclohexyl alcohol

Which Alkene Predominates?; Saytzeff's Rule

- **The loss of water from adjacent carbon atoms, can give rise to more than one alkene.**

Example: the dehydration of 2-butanol.



- **Saytzeff's Rule applies:**

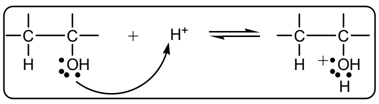
  In every instance in which more than one alkene can be formed
  the major product is always the alkene with the most alkyl substituents attached on the double-bonded carbons.

- **Applying Saytzeff's Rule to dehydration of 2-butanol**

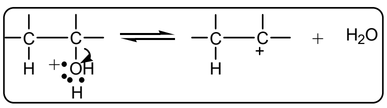
  2-butene is the major *(with two alkyl substituents attached to C=C)*

Mechanism of Dehydration of Alcohols

Step 1. **Protonation of the alcohol.**

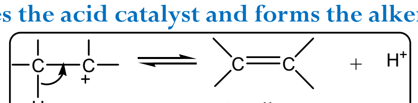


Step 2. **Formation of a carbocation.**



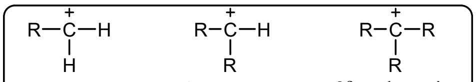
Step 3. **Loss of a proton from the carbocation.**

regenerates the acid catalyst and forms the alkene.



Classes of Carbocations and Ease of Dehydration of Alcohols

- **Carbocations are classified as**



1^o carbocation 2^o carbocation 3^o carbocation

according to the number of carbon atoms attached to the positively charged carbon.

The ease of formation and the stabilities of carbocations follow the order

$3^o > 2^o > 1^o$

← Ease of formation and stabilities of carbocations

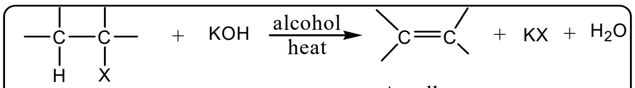
Generally

1. **The dehydration of alcohols requires an acid catalyst.**
2. **The predominant alkene formed follows Saytzeffs rule.**
3. **The reaction proceeds *via* a carbocation intermediate.**
4. **The stabilities of carbocations and the ease of dehydration of alcohols follows the order 3° > 2° > 1°.**

Dehydrohalogenation of Alkyl Halides

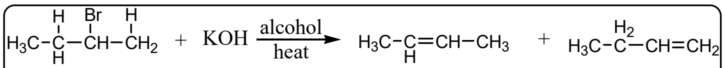
- **Alkenes can also be prepared under alkaline conditions.**

heating an alkyl halide with a solution of potassium hydroxide, KOH, in alcohol, yields an alkene.

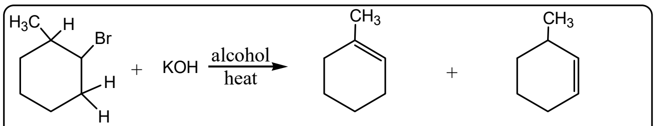


An alkyl halide An alkene

- **Apply Saytzeff's Rule**

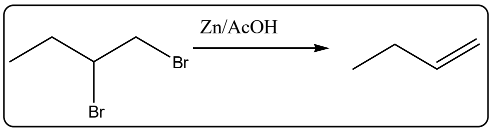


2-Bromobutane 2-Butene (major product) (81%) 1-Butene (minor product) (19%)



1-Methylcyclohexene (major product) 3-Methylcyclohexene (minor product)

3. Dehalogenation of Vicinal Dibromides

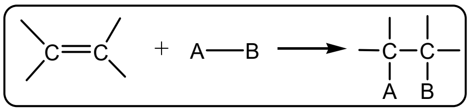


Reactions of Alkenes

- The chemistry of alkenes can therefore be divided into two general types of reactions:
  - (1) **Addition reactions** that involve the carbon—carbon double bond.
  - (2) **Substitution reactions** that usually involve the saturated alkyl chain.

Additions to the Carbon-Carbon Double Bond

- The typical reaction of alkenes is addition to the C=C group.



1. Addition of Hydrogen: Catalytic Hydrogenation

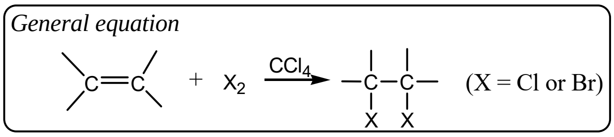
Addition of a mole of hydrogen to carbon-carbon double bond of alkenes in the presence of suitable catalysts to give an alkane.

2. Addition of Halogens: Halogenation

- When an alkene is treated at room temperature with a solution of bromine or chlorine in carbon tetrachloride.

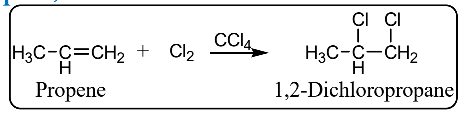
  the halogen adds rapidly to the double bond of the alkene to give the corresponding vicinal dihalide

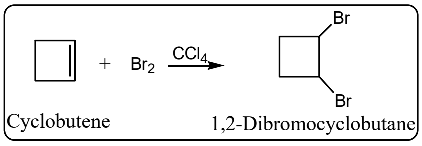
  (two halogens attached to adjacent carbons)



- Iodine is too unreactive and will not add to the double bond.
- Fluorine is too reactive and reacts explosively with an alkene.

Specific examples;





3. Electrophilic Addition to Alkenes: Addition of Acids

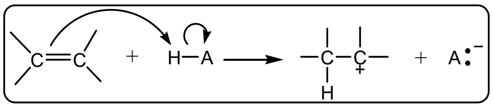
- **General formulas are represented by H—A.**
  These may be hydrogen halides (H—Cl, H—Br, H—I), sulfuric acid (H—OSO_3H), water (H—OH)
- **Hydrogen halides, sulfuric acid, and water contain an ionizable hydrogen.**

$$H{-}A \longrightarrow H^+ + A{:}^-$$

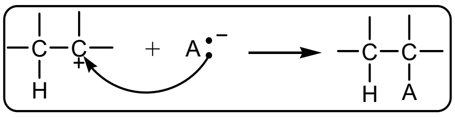
- **Any electron-deficient species is called an electrophile.**
  Any electron-rich species is called a nucleophile.

- **The addition of H—A to an alkene is believed to be a two-step process.**

Step 1. The hydrogen ion (the electrophile) attacks the ∏-electrons of the alkene, forming a C—H bond and a carbocation.



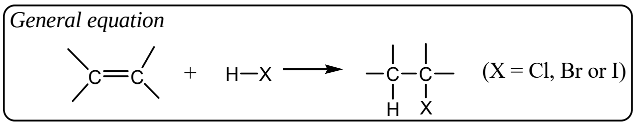
Step 2. The negatively charged species A: - (a nucleophile) attacks the carbocation and forms a new C—A bond.



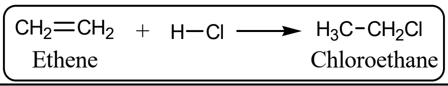
- **The attack by an electrophilic reagent on the ∏-electrons, falls in a general category called electrophilic addition reactions.**

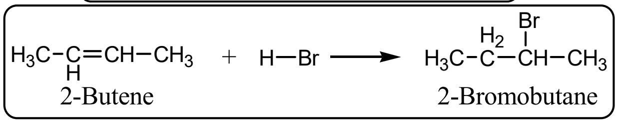
3.1. Addition of Hydrogen Halides

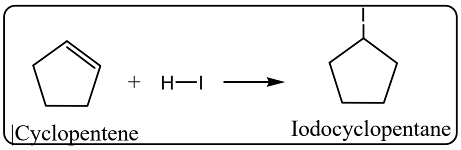
- **Alkenes react with hydrogen chloride, HC1, hydrogen bromide, HBr and hydrogen iodide, HI, to form alkyl halides, RX.**



- **Examples;**

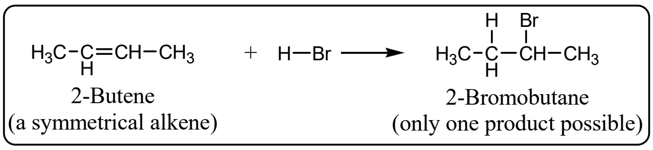




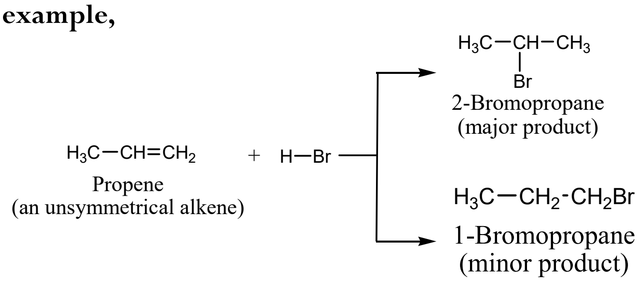


Markovnikov's Rule

- **When hydrogen halide is added to a *Symmetrical Alkene* such as RCH=CHR, there is only one possible product**



- **With *Unsymmetrical Alkenes*, The addition of HBr to propene, for example,**

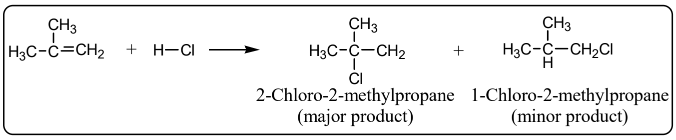


- **In fact, the major product is 2-bromopropane.**

Markovnikov's rule:

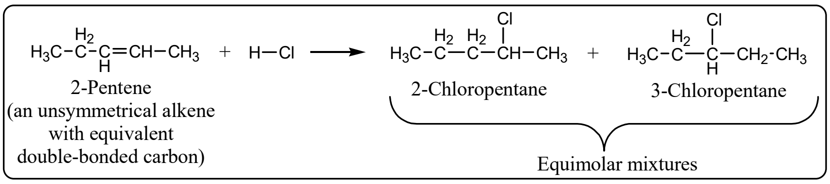
In electrophilic addition of H—X *to Unsymmetrical Alkenes the hydrogen of the hydrogen halide adds to the double-bonded carbon that bears the greater number of hydrogen atoms and the negative halide ion adds to the other double-bonded carbon.*

Addition of HCl to 2-methylpropene



In some *unsymmetrical alkenes* the two double-bonded carbons may be equivalent

Equimolar mixture of the two possible addition products is obtained.



Explanation for Markovnikov's Rule

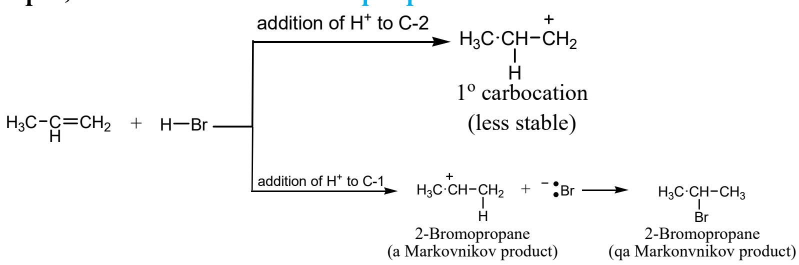
The addition of HX to an alkene

the formation of a carbocation intermediate.

the more stable carbocation to be preferentially formed.

The stability of a carbocation follows the order 3° > 2° > 1°.

Example; the addition of HBr to propene

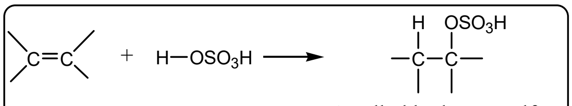


In modern terms Markovnikov's rule can be restated:

The addition of an unsymmetrical reagent **HX** *to an unsymmetrical alkene proceeds in such a direction as to produce the more stable carbocation.*

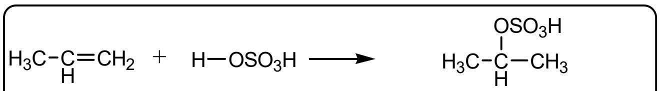
3.2. Addition of Sulfuric Acid

- Cold concentrated sulfuric acid adds across the double bond of alkenes to give alkyl hydrogen sulfate.
- General equation for this reaction is



An alkyl hydrogen sulfate

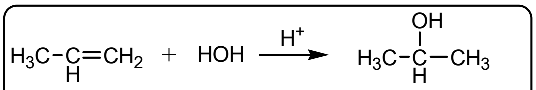
- Addition of sulfuric acid to alkenes also follows Markovnikov's rule.



Propene — Isopropyl hydrogen sulfate

3.3. Addition of Water: Hydration

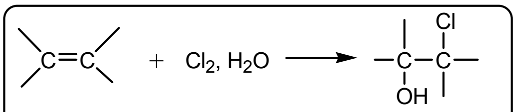
- When heated with water in the presence of an acid catalyst, alkenes yield alcohols (ROH).



Propene — Isopropyl alcohol (rubbing alcohol)

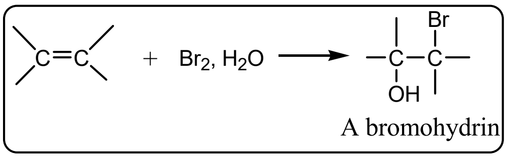
3.4. Addition of HOX: Halohydrin Formation

- When an alkene is treated with aqueous chlorine or aqueous bromine, the addition product is a halohydrin.
  - When Cl_2 is used, the product is a chlorohydrin.



A chlorohydrin

➦ When Br_2 is used, the product is a bromohydrin.

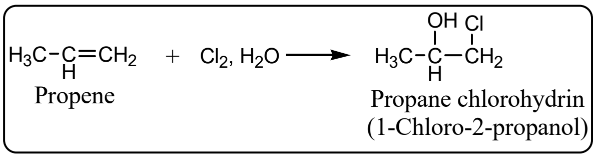


➡ The reaction proceeds as if hypochlorous acid, HO—Cl, or hypobromous acid, HO—Br, were the adding reagent.

➦ The electrophile is
chloronium ion, Cl^+, or bromonium ion, Br^+.

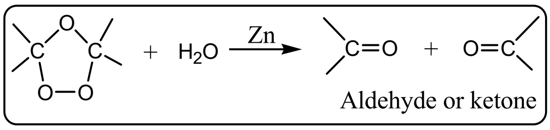
➦ The nucleopbile is
hydroxide ion, OH^-.

➡ Addition of HOX also follows Markovnikov's rule.



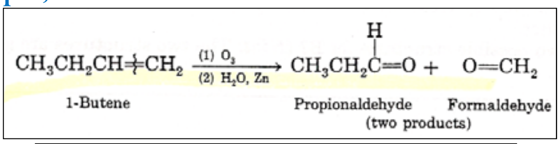
Ozonolysis

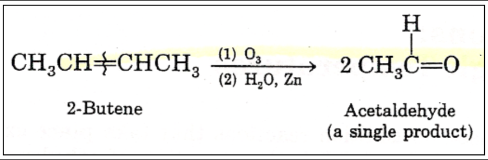
➡ Addition of water in the presence of a zinc catalyst results in the formation of two smaller products;
each of which contains a carbonyl group, C=O



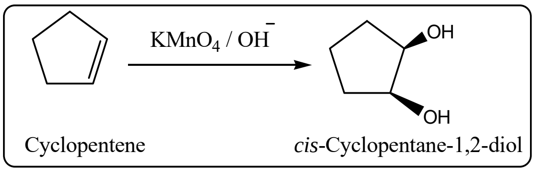
➦ These products may be aldehydes, or ketones, depending on the structure of the starting alkene.

➡ For example;





Oxidation Using $KMnO_4$



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