

# Unsaturated hydrocarbons

## Chapter 3

# Alkenes

1432-2011

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By the end of this chapter you should be familiar with:


- definition for Alkenes.
- The hybridization of Alkenes.
- IUPAC naming of Alkenes.
- Geometric isomerism among the Alkenes.
- Physical properties of Alkenes.
- General Methods of Preparation of Alkenes.
- Reactions of Alkenes.

## Alkenes:

The second class of simple hydrocarbons the **alkenes**, consists of molecules that contain at least **one double-bonded** carbon pair.

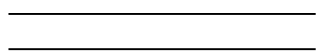
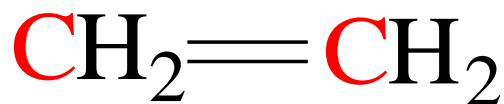
**The chemical formula** for the simple **alkenes** follows the expression:



 Alkenes are also called **OLEFINS** because they form oily liquids on reaction with chlorine gas

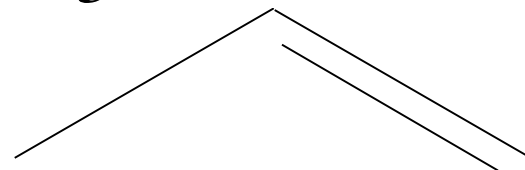
# Nomenclature

The simplest members of the **alkenes** series (**C<sub>2</sub>** and **C<sub>3</sub>**) are usually called by their **common Names**, which are derived from the corresponding **alkanes** by replacing the **(-ane)** ending by **(-ylene)**.



Common Name:

Ethylene



Propylene

IUPAC Name:

Ethene

Propene

The IUPAC rules for naming **alkenes** are similar to those used for naming **alkanes**.

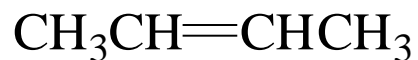
The rules are:

1. The longest continuous carbon chain *containing the double bond* is selected as the parent chain.
2. The name of the parent carbon chain is obtained by replacing the *-ane* ending of the corresponding alkane by *-ene*.
3. The parent carbon chain is numbered in a manner that will give the doubly bonded carbon atoms the *lowest* numbers even if it results in the substituents getting higher numbers.
4. The position of the double bond is indicated by the number of the *lower* numbered doubly bond.
5. In **cycloalkenes**, the double bond is always found between **carbon 1** and **carbon 2**. It is therefore not necessary to specify the position of the double bond with a number. If the substituents are present, the ring must be numbered, starting from the double bond, in the direction that gives the substituents the *lowest* number(s).

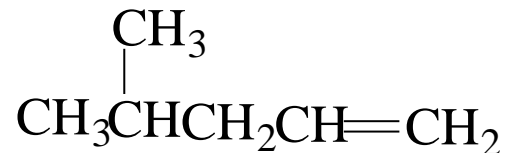
# Examples



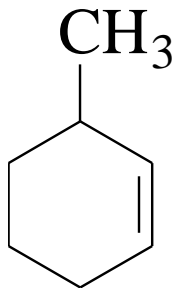
1-Butene  
(*not* 3-Butene)



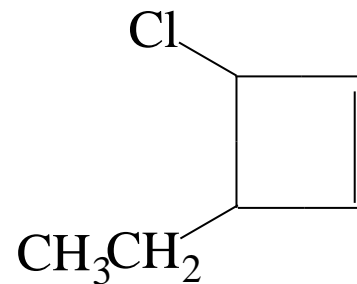
2- Butene



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



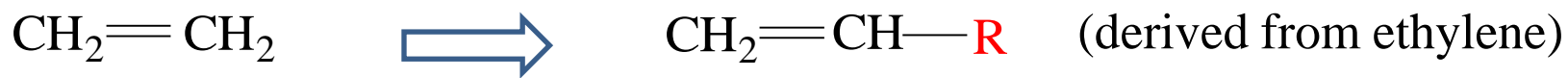
3-Methylcyclohexene  
(*not* 1-Methyl-2-cyclohexene)



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

# Important derivatives from Alkenes:

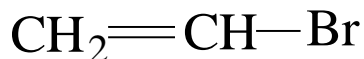
## 1- Vinyl group



## 2- Allyl group



## Examples



Common Name: **Vinyl bromide**

**Allyl chloride**

IUPAC Name: **Bromoethene**

**3-Chloro-1-Propene**

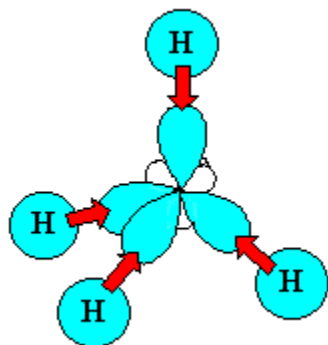




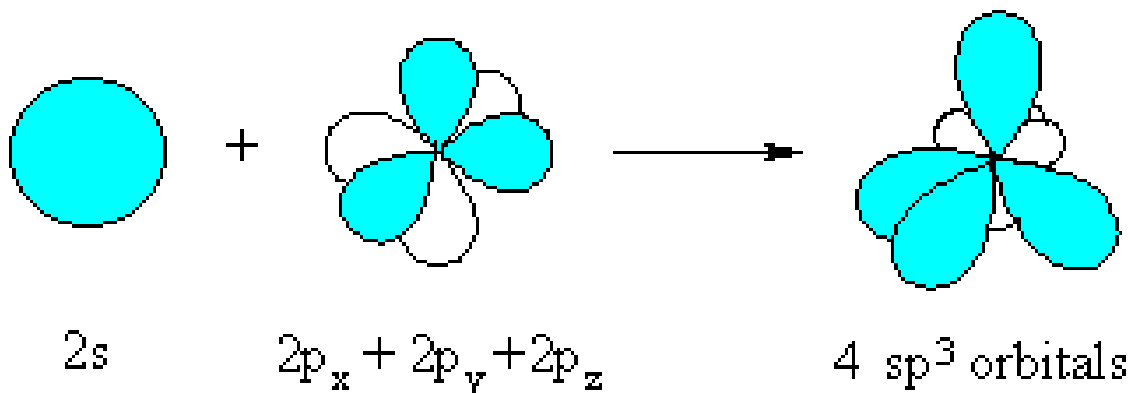
# Rapid Revision

## In Alkanes:

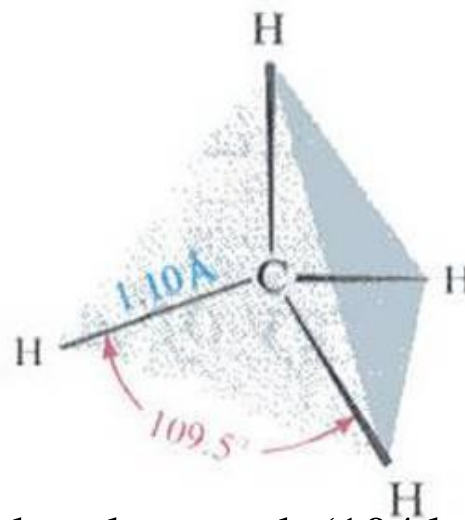
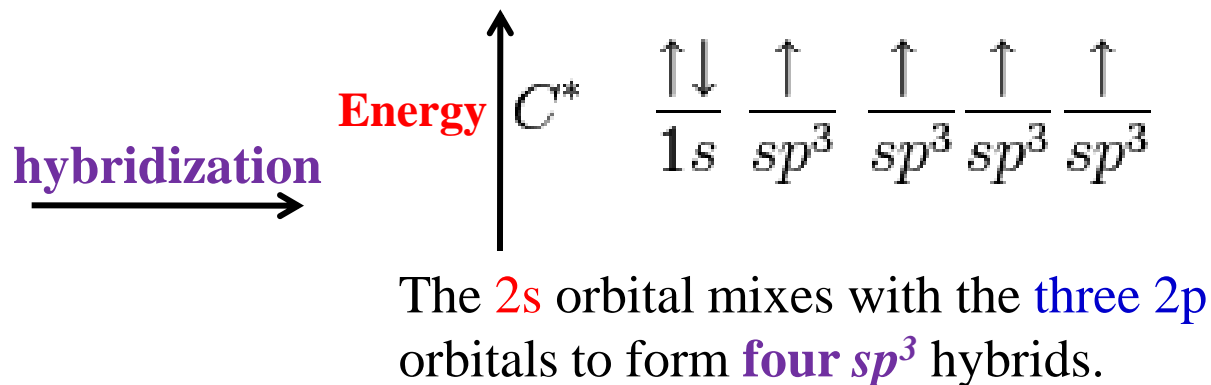
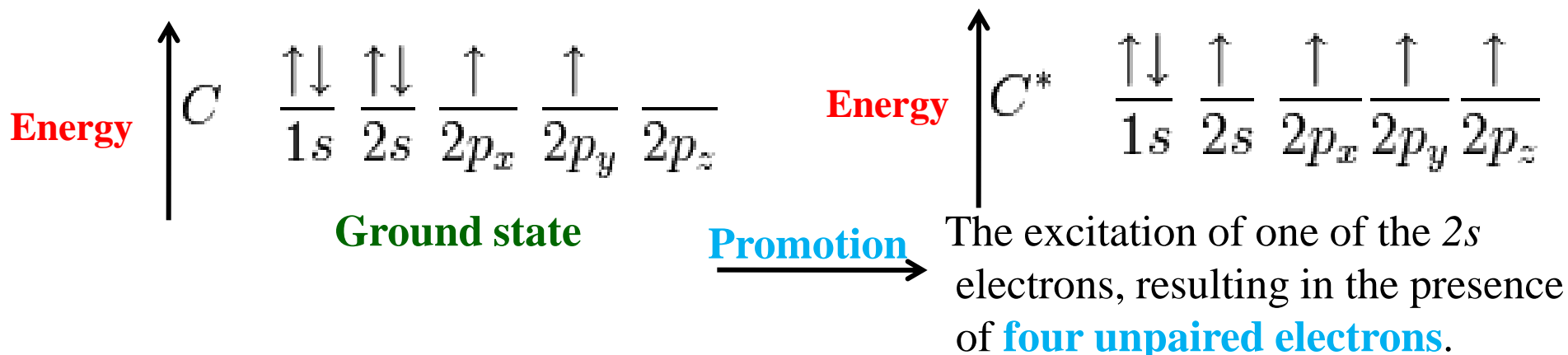
When **C** is bound to four groups, as we saw with *methane*, it is  $sp^3$ -hybridized, 4 equivalent **C-H**  $\sigma$  bonds can be made by the interactions of  $Csp^3$  with a  $H1s$



In order to minimize the forces of electrostatic repulsion, *the electron pairs will arrange themselves in the configuration which allows them to be as far away from each other as possible*. They are directed to the corners of a regular **tetrahedron**.



# Hybridization & Structure

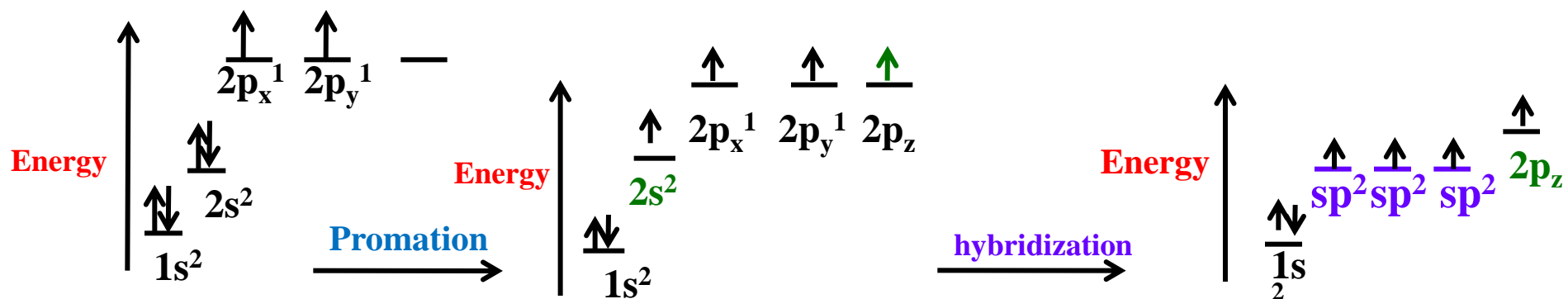


The **four bonds** are of the same **length** (1.10 Angstroms) and bond strength (104 kcal / mol). **The angle** between any two of the orbitals is the tetrahedral angle **109.5** degrees.

# Hybridization in Alkenes:

## Example:

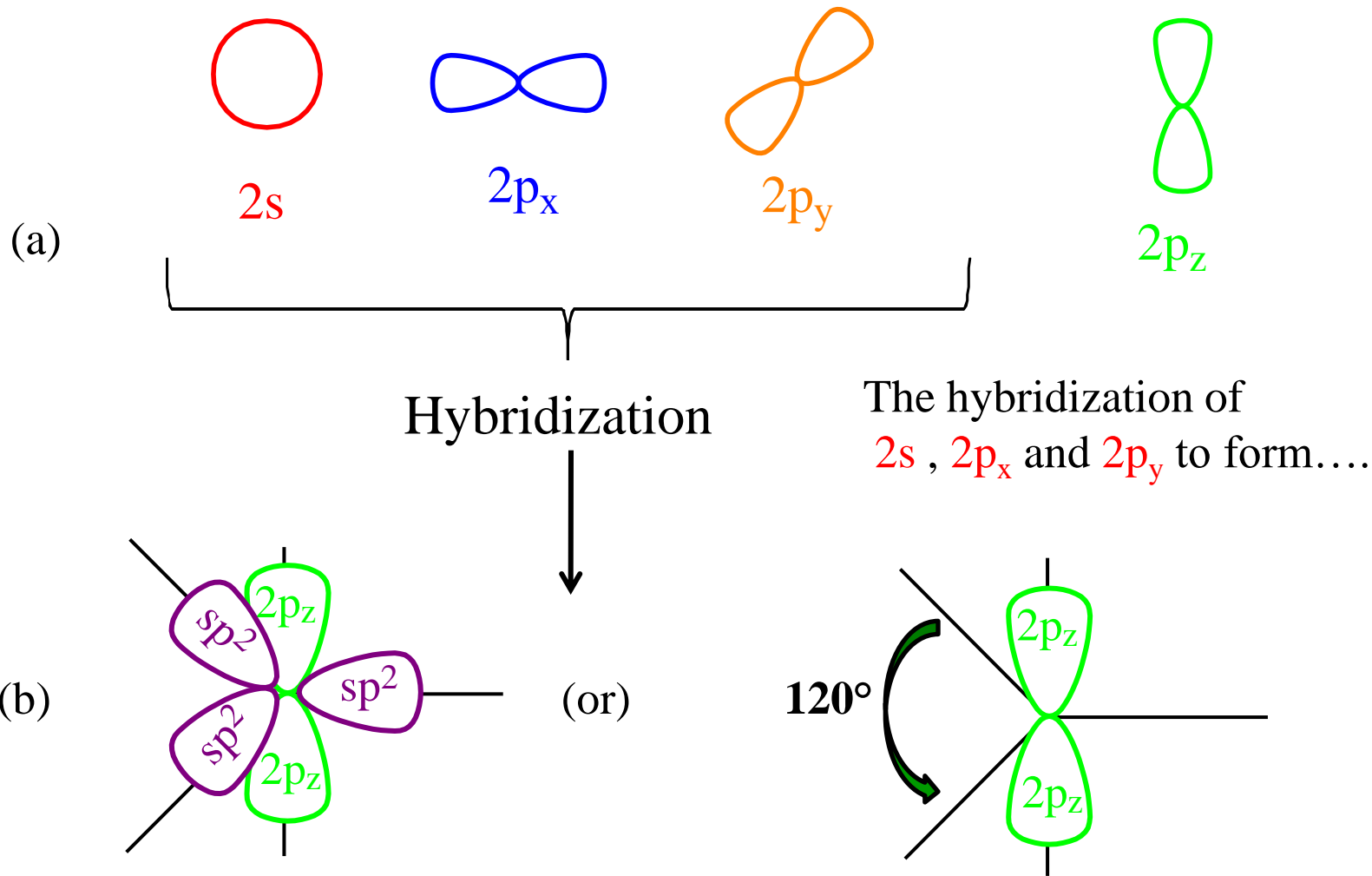
For the simplest alkene, Ethylene,



These orbitals are formed in the following manner:

- $2s$  orbital and *only two* of the three  $2p$  orbitals hybridize, the result is 3 equivalent  $sp^2$  hybrid orbitals and **one unhybridized** orbital  $2p_z$  orbital.

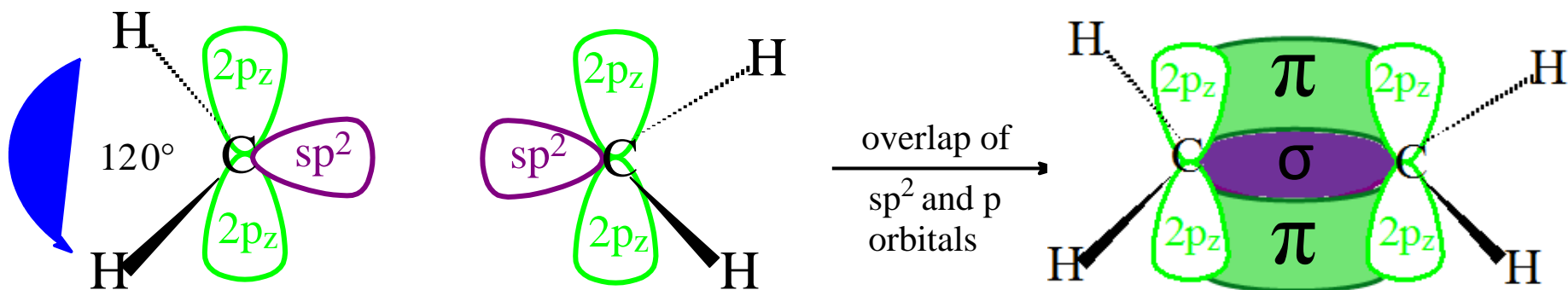
The double bond is always attached to only three other atoms. As a consequence, the doubly bound carbon *must* use a **different kind of hybridization** & *must* assume a **different shape**.



Three planar *sp<sup>2</sup>-hybridized orbitals* with bond angles of **120°** and a **2p<sub>z</sub> orbital Perpendicular to the plane.**

The three sp<sup>2</sup> orbitals get as far away from each other as possible assuming a planer arrangement with an angle of 120° between hybrid orbitals, (trigonal planer).

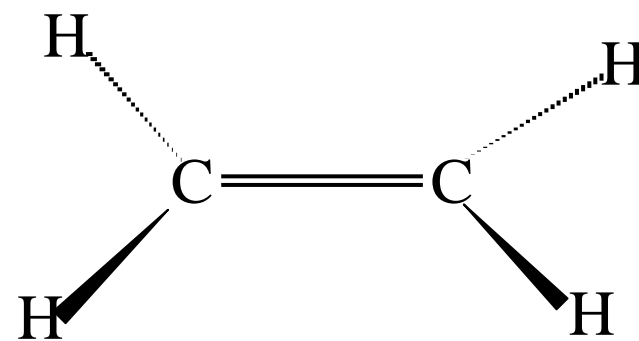
The remaining **unhybridized  $2p_z$**  orbital is perpendicular to the plane of the  $sp^2$  orbitals.



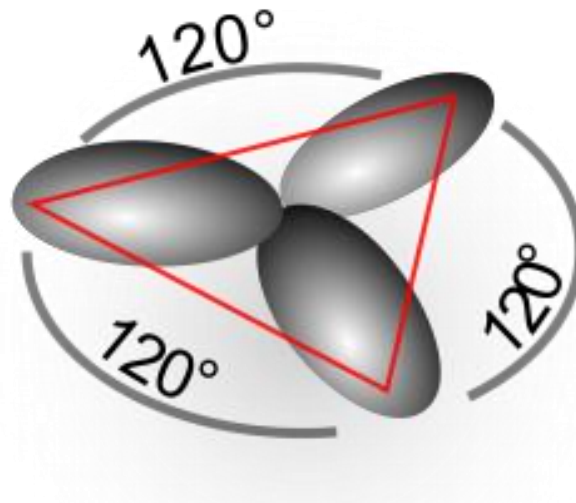
*The two carbons of Ethylene are attached to gather by an  $Sp^2$ ----- $Sp^2 = \sigma$  bond.*

*The  $2p_z - 2p_z$  overlap resulting the carbon---carbon double bond =  $\pi$  bond*

Equivalent to



The Ethylene molecule has trigonal planer geometrical shape, with a bond angle equal to  $120^\circ$ , and bond length  $1.34 \text{ \AA}$



**Note that;** the restricted rotation about the carbon – carbon double bond and the planar geometry give type of geometric isomersim called  
**The E/Z notation**

The pi-bond in an alkene **does not permit rotation**, thus **all of the atoms** attached directly to the alkene **lie in a plane**. The restricted rotation about C=C and the planer geometry give rise to a type of isomerism.

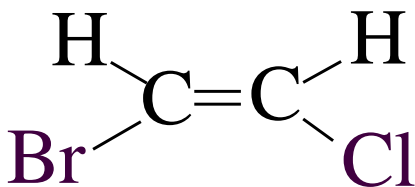
Called... ***Geometric Isomerism***

**Case 1:**

**Two different substituents**

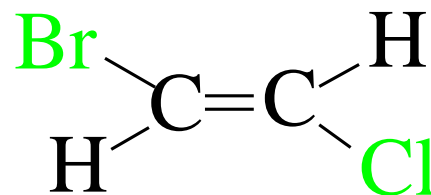
Groups attached to the **alkene** could be positioned...

on the **same side** of the alkene,



**Cis-1- Bromo-2-chloroethene**

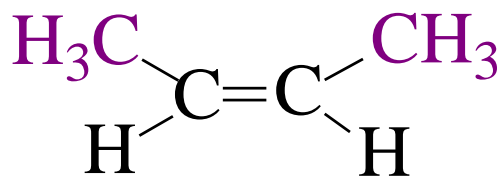
on **opposite sides** of the alkene.



**Trans-1-Bromo-2-chloroethene**

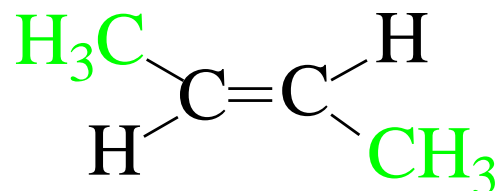
Geometric isomers **differ** from one another **only** in the way in which **the substituents are arranged in space** related to **the plane of the C=C bond**.

**Example:** the isomers of 2-Butene



**Cis**-2-Butene

(mp= -139°C; bp= 3.7°C)



**Trans**-2-Butene

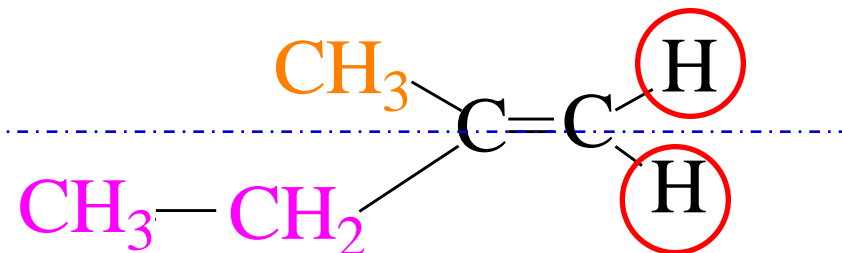
(mp= -106°C; bp= 0.9°C)

**Cis** and **Trans** are stable molecules have **different physical properties** and **same chemical properties**.



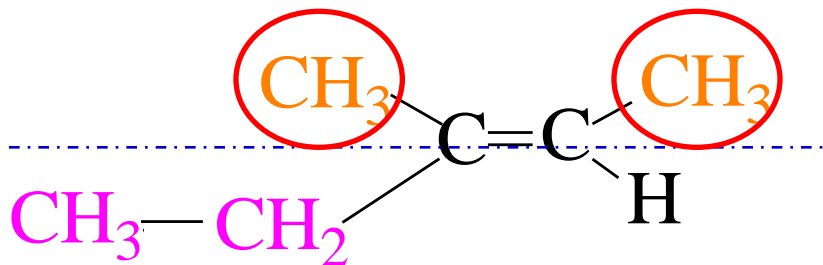
## Does this molecule have geometric isomers?

1. *Must contain a C=C (or another double bond).*
2. *On each C of the C=C, there must be 2 different groups.*

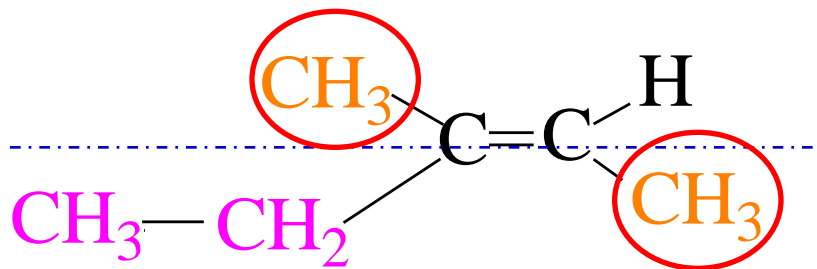


The molecule above *does not have cis or trans isomers*. *On the right C of the C=C, there are 2 H atoms (must have different groups on each C of the C=C.)*

Find the 2 groups *that are the same on the 2 C of the C=C and circle them; if they're on the same side of the line: cis; different sides: trans.*



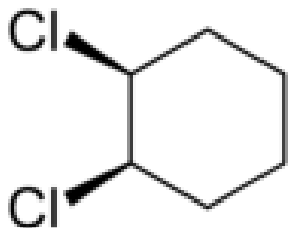
*Cis*



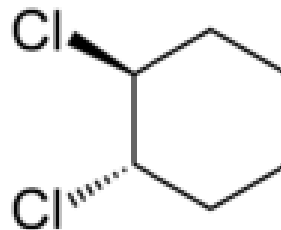
*trans*

## Examples on *Cis* & *Trans* isomers

1-



*cis*-1,2-dichlorocyclohexane

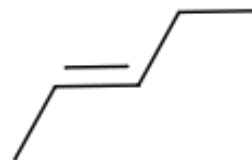


*trans*-1,2-dichlorocyclohexane

2-

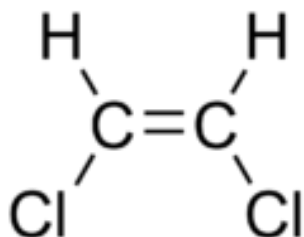


*cis*-2-pentene

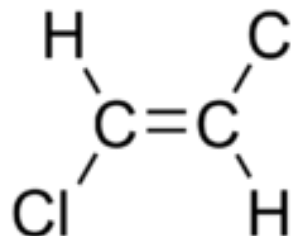


*trans*-2-pentene

3-



*cis*-1,2-dichloroethene

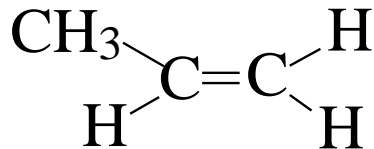


*trans*-1,2-dichloroethene

## Exercise:

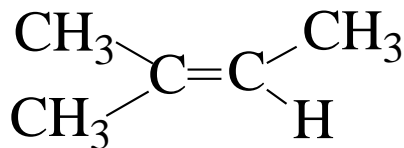
which of the following compound has geometric isomerism? Why?

(a) Propene



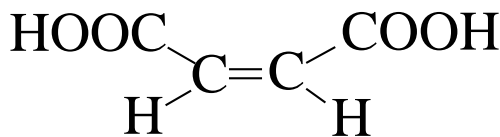
Geometric isomerism is not possible

(b) 2-Methyl-2-butene

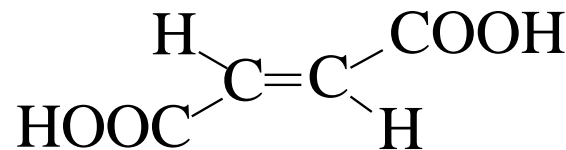


Geometric isomerism is not possible

(c) 2-butenedioic acid

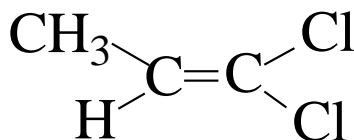


Cis-form (Maleic acid)



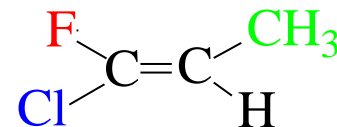
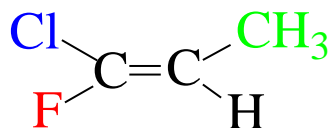
Trans-form (Fumaric acid)

(d) 1,1-Dichloropropene



Geometric isomerism is not possible

(e) 1-chloro-1-fluoropropene



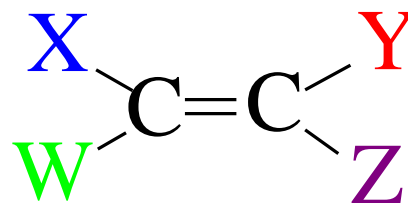
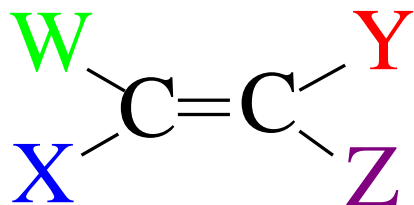
*New type of Isomerism*

**Z- 1-chloro-1-fluoropropene**

**E- 1-chloro-1-fluoropropene**

## Case 2:

For alkenes with *3 to 4 different substituents* such as:



The *cis/trans system* for naming isomers is not effective when there are **more than two different** substituents on a double bond.

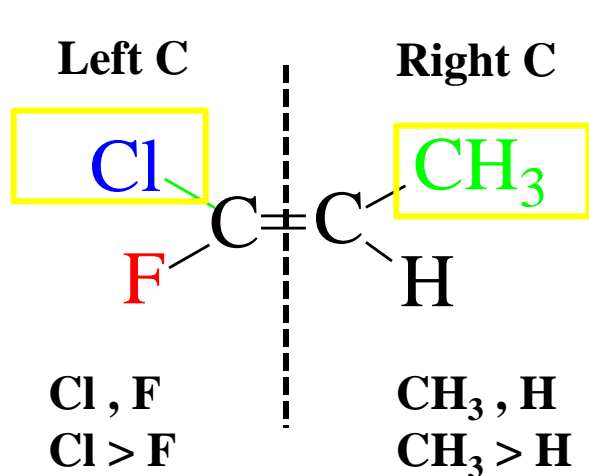
Another system such as; The *E/Z system* should then be used for distinguishing **the two geometric isomers**.

## How can I apply the E-Z system to substituted alkenes?

✓ In the **E-Z** system the geometry is specified by **the relative positions** of **the two highest priority substituents on the two carbons of the double bond**.

✓ **The priorities of the substituents** are determined by **the atomic number** with atoms of higher atomic number having higher priority.

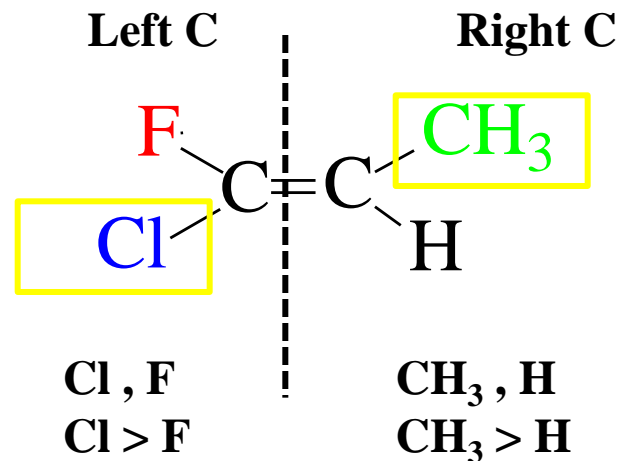
### Example



If the two groups of higher priority are on the same side of the C=C plane, the isomer is labeled **Z**

(from German *zusammen*, **together**)

**Z**-1-Chloro-1-fluoropropene



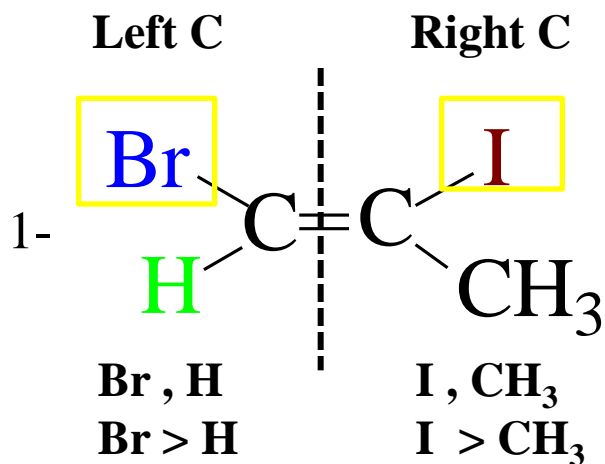
If the two groups of higher priority are in opposite sides of the C=C plane, the isomer is labeled **E**

(from the German *entgegen*; **opposite**)

**E**-1-Chloro-1-fluoropropene

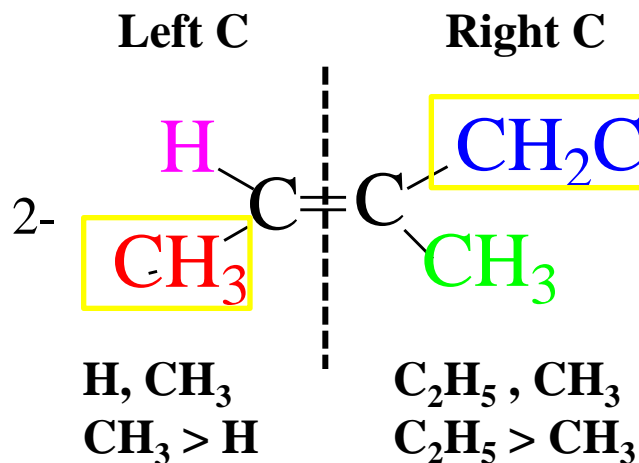
## Exercise

Name the following compounds using the E, Z nomenclature.



As the two atoms of high priority **in the same side**  
The compound is **Z**

**Z**-1-Bromo-2-Iodopropene



As the two atoms of high priority **in the opposite side**  
The compound is **E**

**E**- 3-methyl-2-pentene

H.W

Page: 66, problems 3.4, 3.5

Page: 67, problem 3.6



# □ The Physical Properties of Alkenes

## ▪ *Physical State:*

The first lower member like ethene, propene and butene are colorless gases. Alkenes with five to seventeen carbon atoms are liquids. and higher ones are solids at ordinary temperatures.

## ▪ *Solubility*

Alkenes are insoluble in water and soluble in nonpolar organic solvents such as benzene  $C_6H_6$  or carbontetrachloride  $CCl_4$ .

## ▪ *Boiling point*

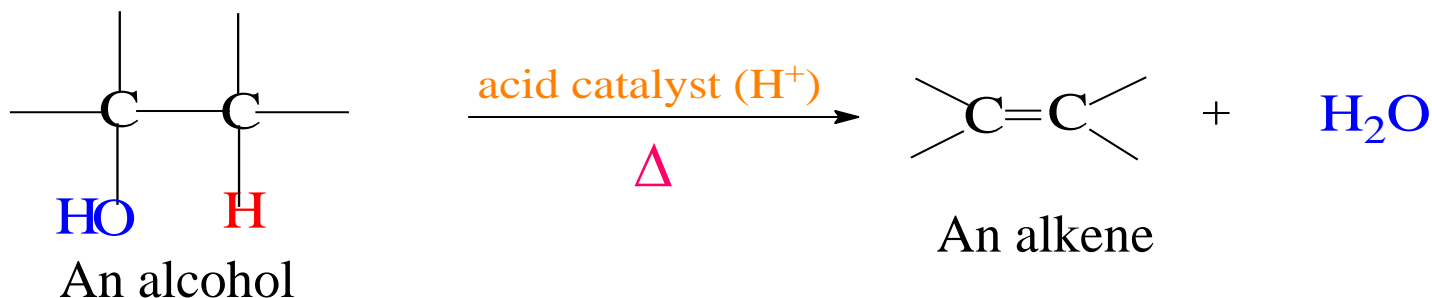
1. The boiling points of alkenes gradually increase with an increase in the molecular mass (or chain length).
2. Branched chain alkenes have lower boiling points than the corresponding straight chain isomers.



## □ General Methods of Preparing Alkenes

Alkenes are prepared in the laboratory by one of two general methods. They can be prepared from *alcohols* or *alkyl halides* by *Elimination reactions*.

### 1. Dehydration of Alcohols



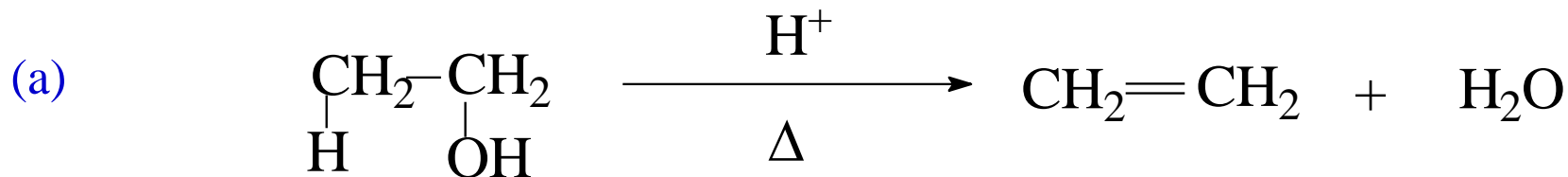
When an *alcohol* is heated in the presence of a mineral acid catalyst, it loses a molecule of water to give an *alkene*.

The acid catalyst  $\text{H}^+$  ex;  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  &  $\Delta$  is *Heat* .



In Latin "De-" means= removal of

## Examples



IUPAC Name:

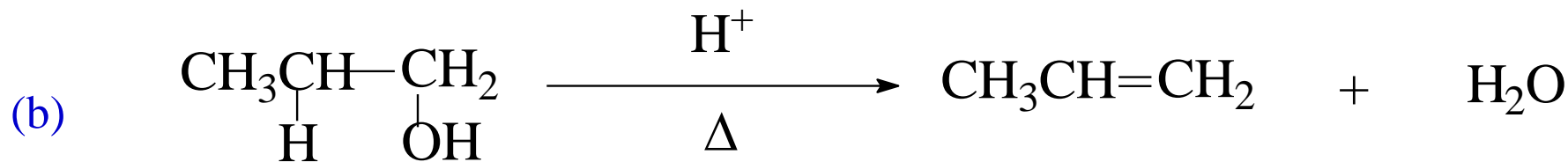
Ethanol

Ethene

Common Name:

Ethyl alcohol

Ethylene



IUPAC Name:

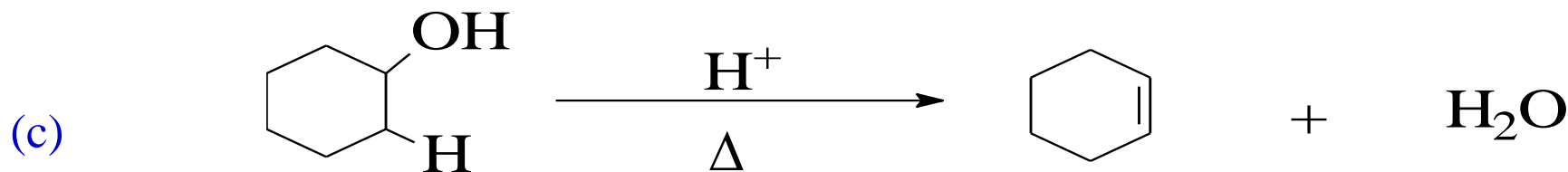
1-Propanol

Propene

Common Name:

*n*-propyl alcohol

Propylene



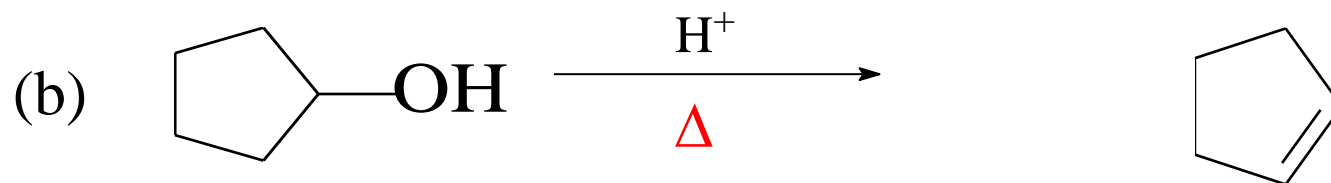
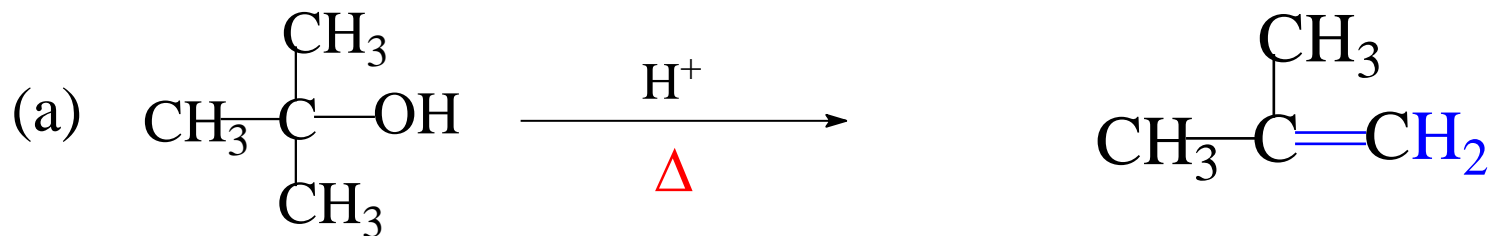
IUPAC Name:

Cyclohexanol

Cyclohexene

Common Name: Cyclohexyl alcohol

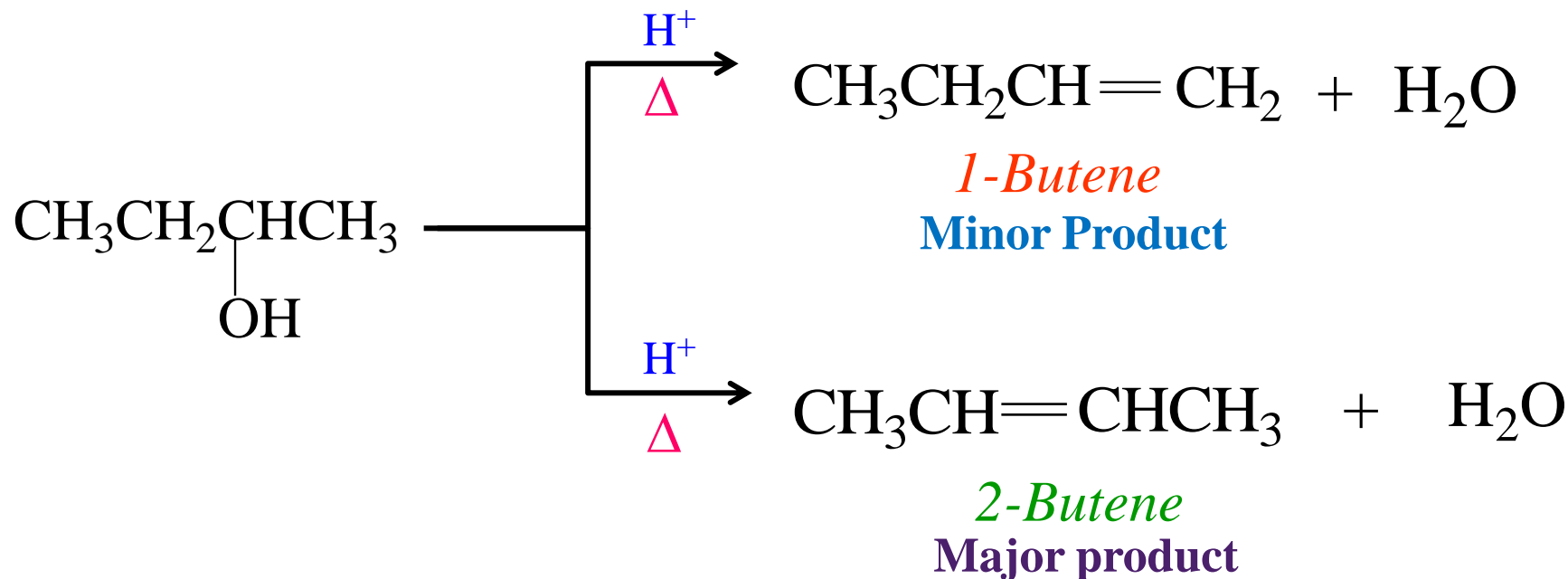
**Problem 3.7** Write the structure of the product of the dehydration of each of the following alcohols.



The previous examples of dehydration of alcohols produced **a single alkenes** as a possible product.

Suppose, that **the loss of water** from adjacent carbon atoms can give rise to **more than one alkene** as in:

The dehydration of **2-Butanol**



Which *alkene* predominates,

**1-Butene**

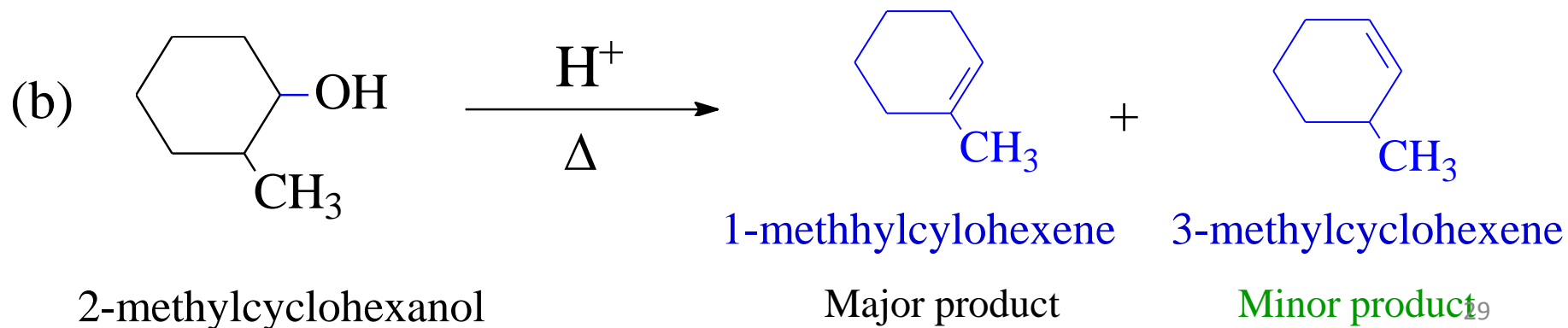
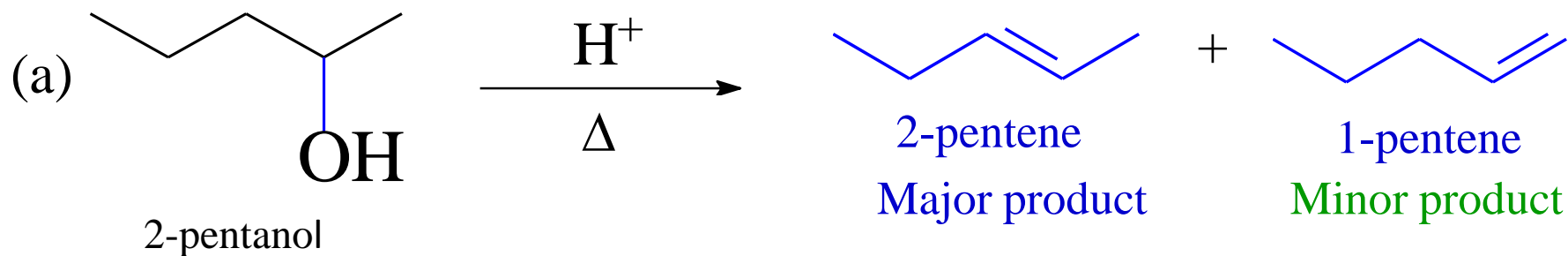
or

**2-Butene**

# Saytzeff's Rule

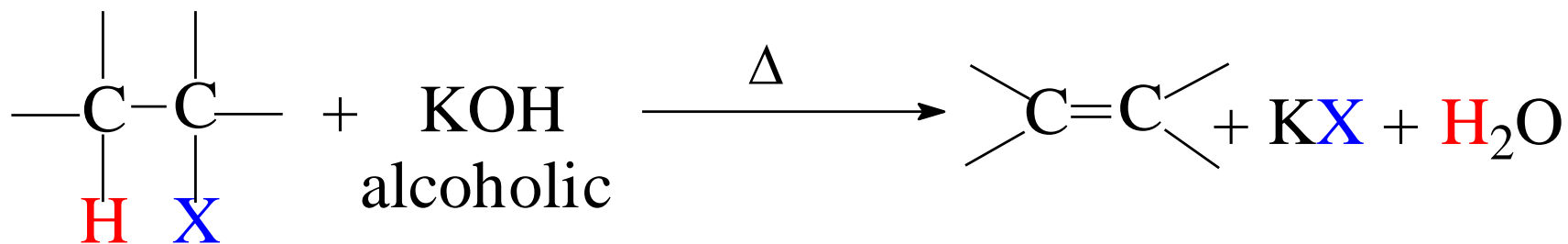
The *major product* is always the alkene with the most substituents attached on the double-bonded carbons.

**Problem 3.8** Give the major and the minor product of the dehydration of



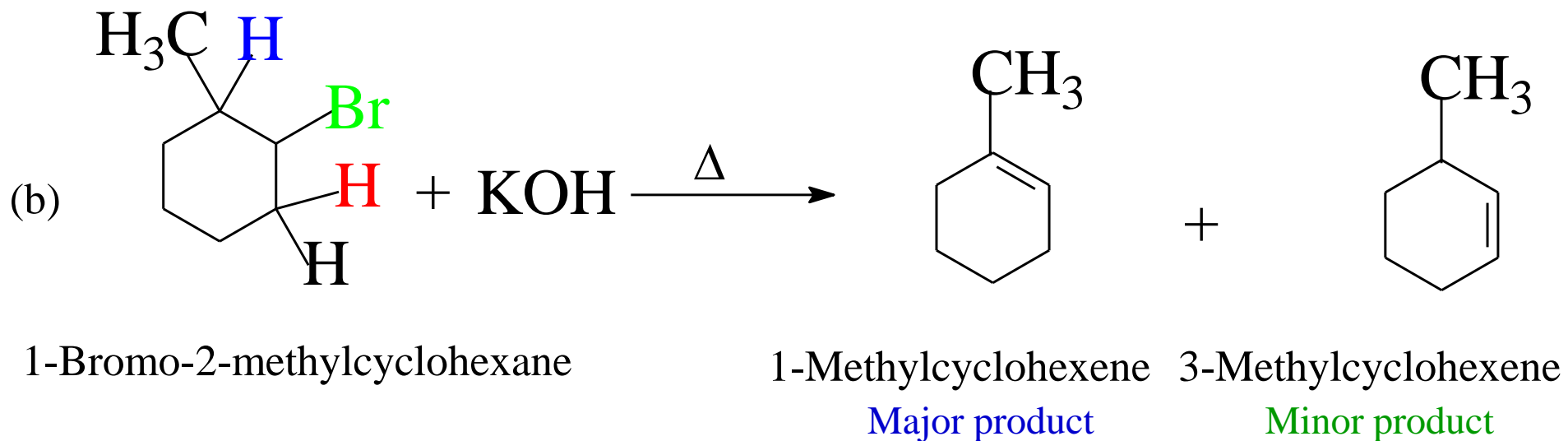
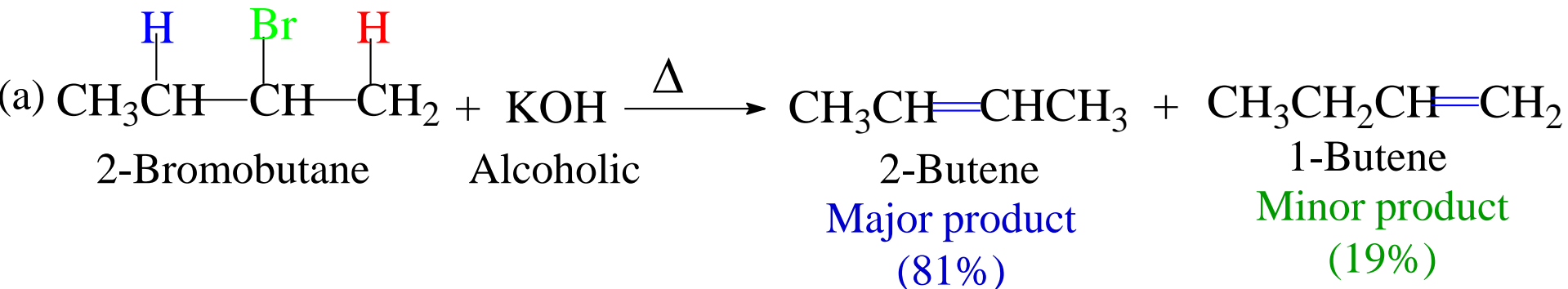
## 2. Dehydrohalogenation of Alkyl halids

The second method for preparing an alkene by using **dehydrohlogenation** reaction, The reaction involves the **elimination** of **H** and of **X** from adjacent carbon.



Heating an **alkyl halide** with a solution of **KOH**, in **alcohol**, yields an **alkenes**.

In similar way to that in the dehydration of an alcohol, **Saytzeff's rule** again applies; that is, *“the alkene with the most alkyl substituents on the double-bonded carbons Predominates”*. For example,

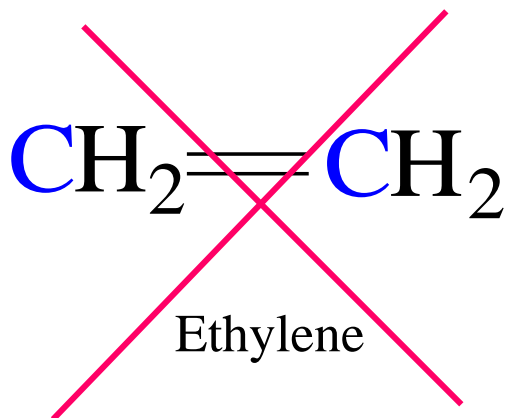






## ☐ Reactions of Alkenes

All alkenes contain ( $\text{C}=\text{C}$  + a saturated alkyl chain) as part of molecule – **except** ethylene – .



Any alkene ex: 1-pentene

As the ethylene has no saturated alkyl chain

I.E. The chemistry of alkenes can therefore be divided into :

# ☐ Reactions of Alkenes

Two types of reactions

*Addition reactions*

On ( C=C )

1. Addition of H<sub>2</sub>
2. Addition of X<sub>2</sub>
3. Addition of HX.
4. Addition of H-OSO<sub>3</sub>H
5. Addition of H<sub>2</sub>O
6. Addition of halohydrin XO<sub>2</sub>H
7. Oxidation (visual test for unsaturation)
8. Ozonolysis
9. Polymerization

*Substitution reactions*

on the saturated alkyl chain

1. Halogenation at High temperature

# Substitution reactions

on the saturated alkyl chain

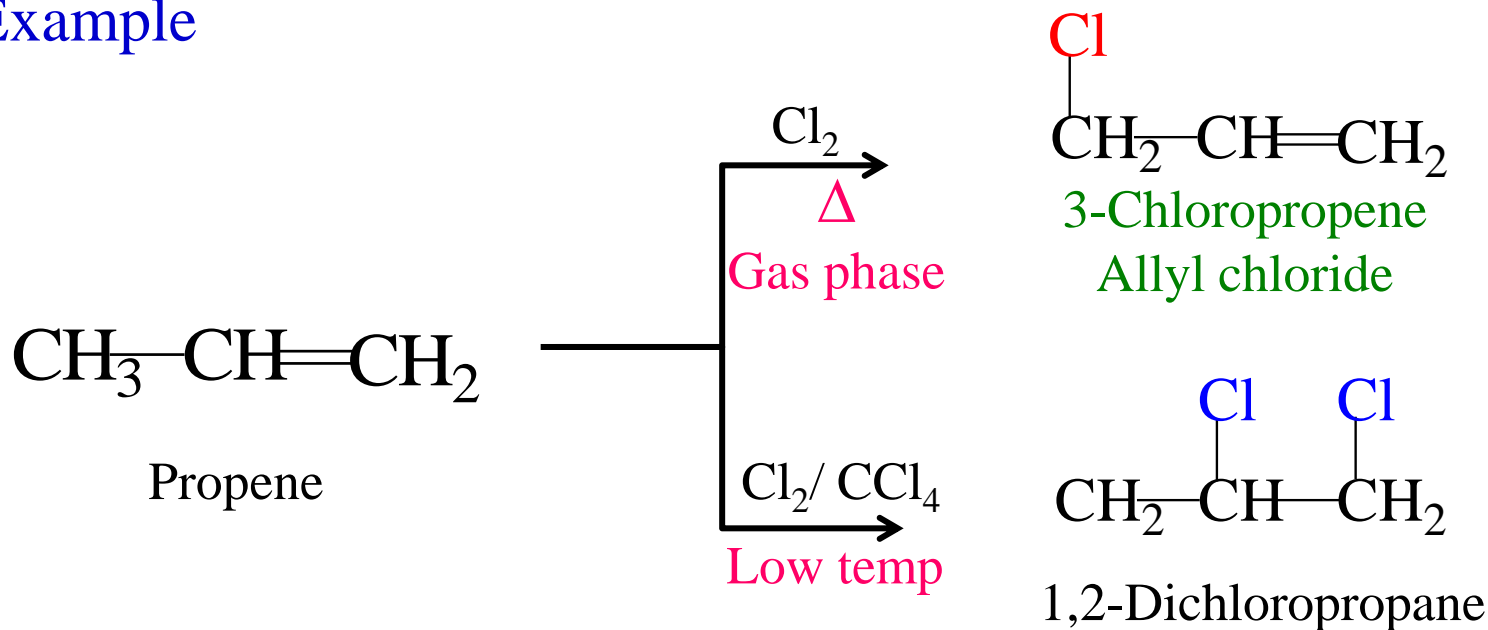
## 1. Halogenation at High temperature

Alkenes are **more reactive** than *alkanes*.

Their reactions therefore take place under milder experimental conditions.

Alkenes undergo *addition of halogen* at **low temperature**, even **in dark**, and generally **in liquid phase**. On the other hand, **alkanes** undergo *substitution by halogen* only at **elevated temperatures** or under **the influence of UV light**, and generally in **the gas phase**.

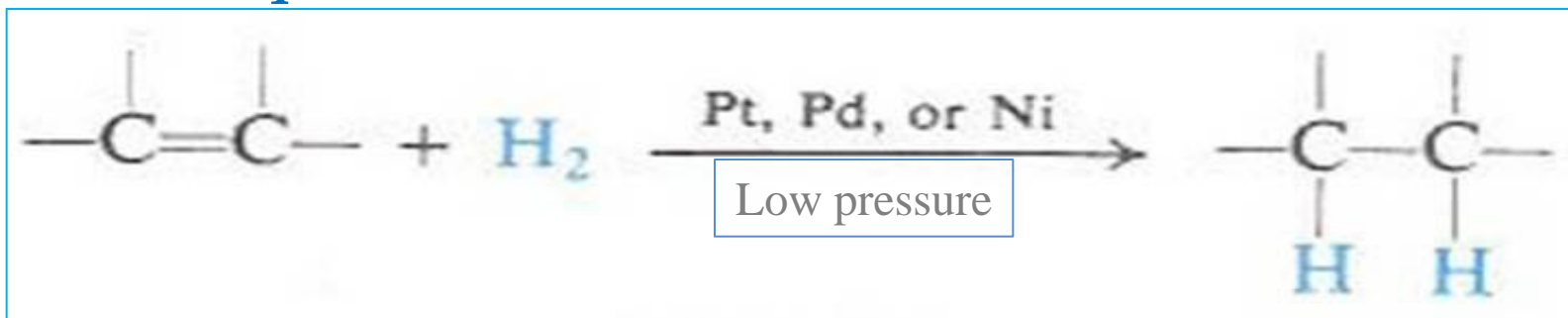
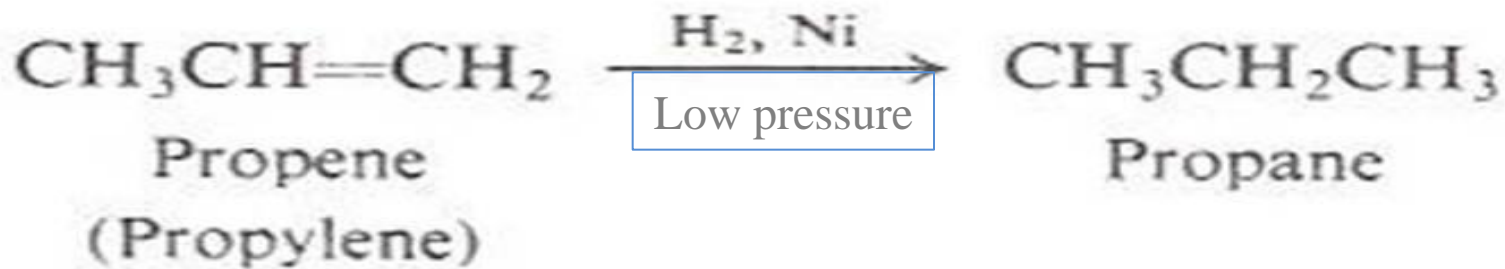
### Example



## Addition Reactions on the C=C

## 1. Addition of Hydrogen: Catalytic Hydrogenation

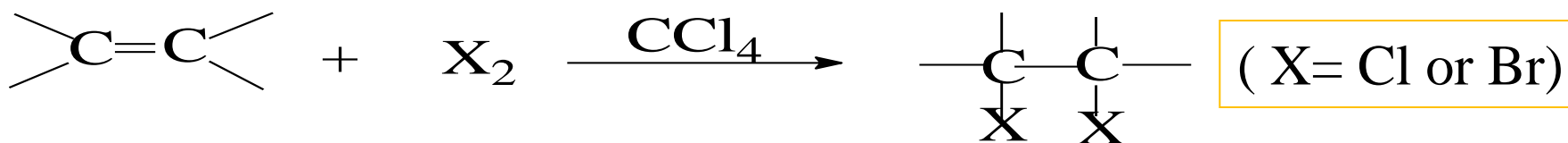
The C=C of alkene can add a mole of Hydrogen in the presence of suitable catalyste such as (Pt, Ni or Pd) at low pressure to give an **alkane**. This method is called **Catalytic Hydrogenation**.

*The General equation**Example:*

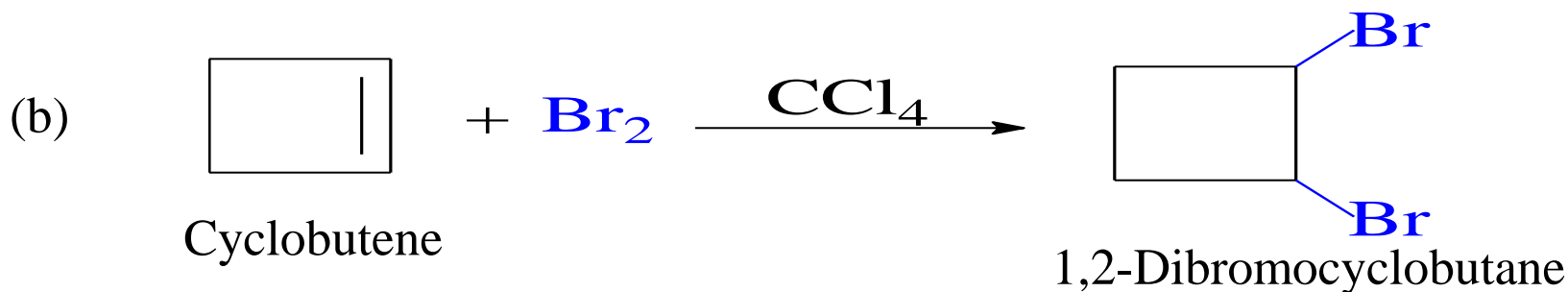
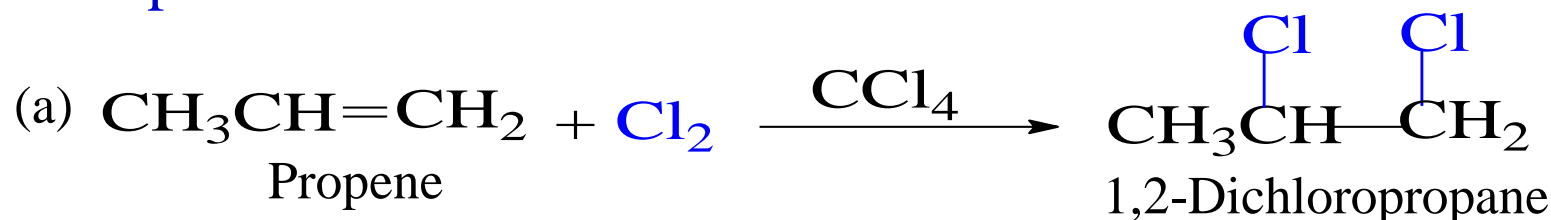
## 2. Addition of Halogens: Halogenation

When an alkene is treated at room temperature with a solution of **bromine Br<sub>2</sub>** or **chlorine Cl<sub>2</sub>** in carbon tetrachloride, the halogen adds rapidly to the double bond of the alkene to give the corresponding **vicinal dihalide**.

### *The General equation*



### Examples

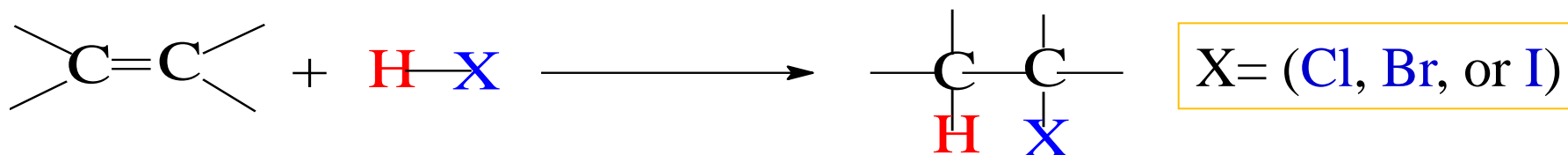


Note that, I “Iodine” is too unreactive and will not add to the C=C of an alkene, F “Fluorine” is too reactive and reacts explosively making the alkene unstable.<sup>37</sup>

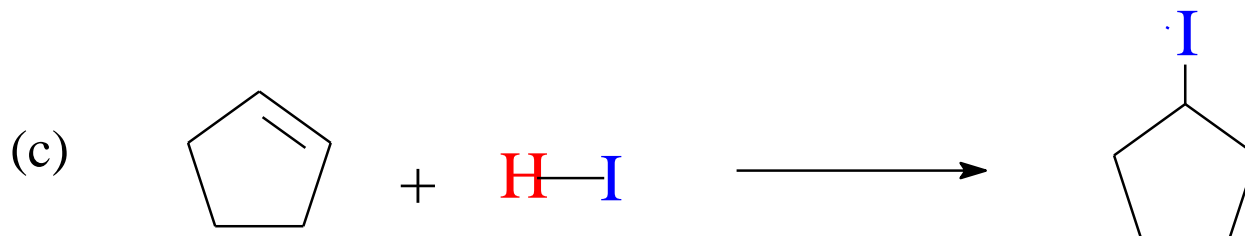
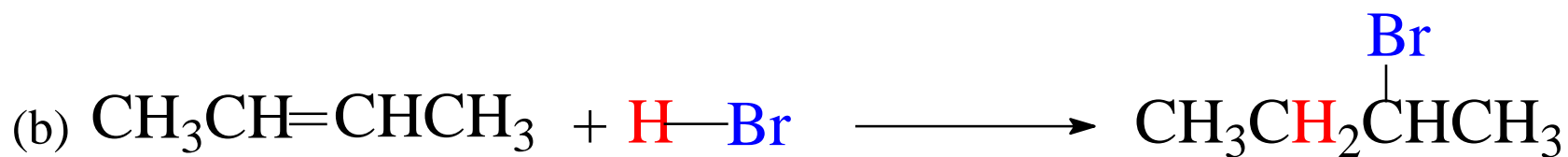
### 3. Addition of Hydrogen Halides: Hydrohalogenation

Alkenes react with hydrogen chloride, **HCl**, hydrogen bromide, **HBr**, and hydrogen iodide, **HI**, to form alkylhalides, **RX**. This reaction is known as *hydrohalogenation*. As **H** and **X** is added to the double-bonded carbons.

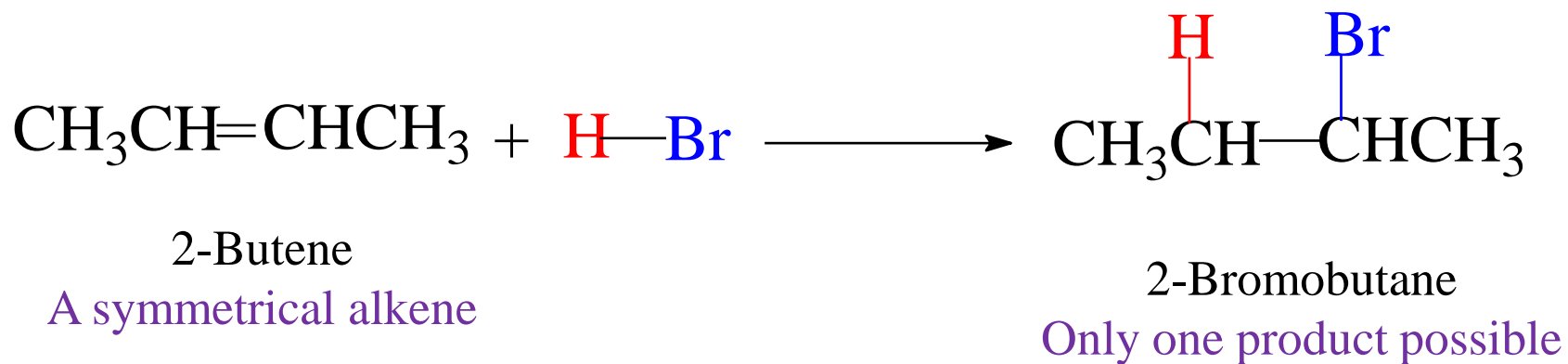
#### *The General equation*



#### Examples



When **hydrogen halide** is added to a *symmetric alkene* such as; 2-Butene [RCH=CHR], there is *only one possible product* because the two double-bonded carbons are equivalent.

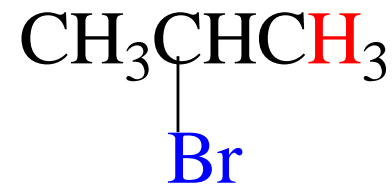
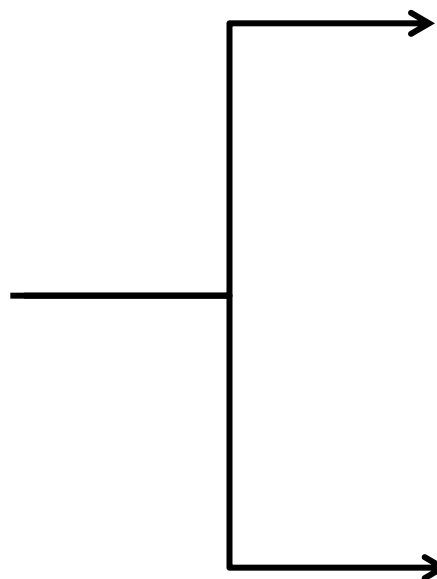


With unsymmetrical alkenes; such as Propene [RCH=CHR'] as (R ≠ R'), the possibility exists for the HX to add in two ways



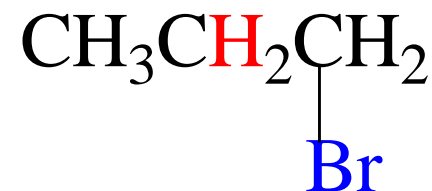
Propene

An Unsymmetrical alkane



2-Bromopropane

(major product)



1-Bromopropane

(minor product)



# Markovnikov's rule

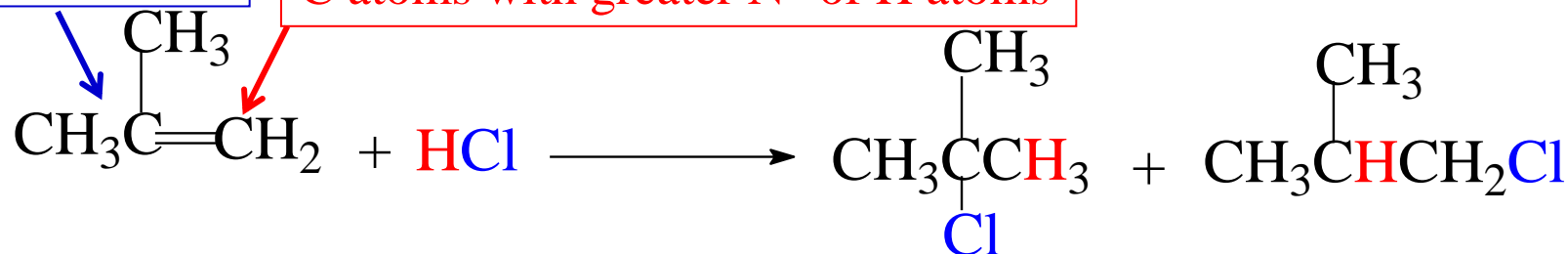
In this type of addition of H---X to unsymmetrical alkenes

The  $\text{H}^+$  of the hydrogen halide adds to the double-bonded carbon that bears the greater number of hydrogen atoms and the  $\text{X}^-$  ion adds to the other double-bonded carbon.

## Examples

The  $\text{X}^-$  part bonds up to the other C, or to the C rich in substituents

C atoms with greater N<sup>o</sup> of H atoms



2-methyl propene

2-Chloro-2-methylpropane

1-Chloro-2-methylpropane

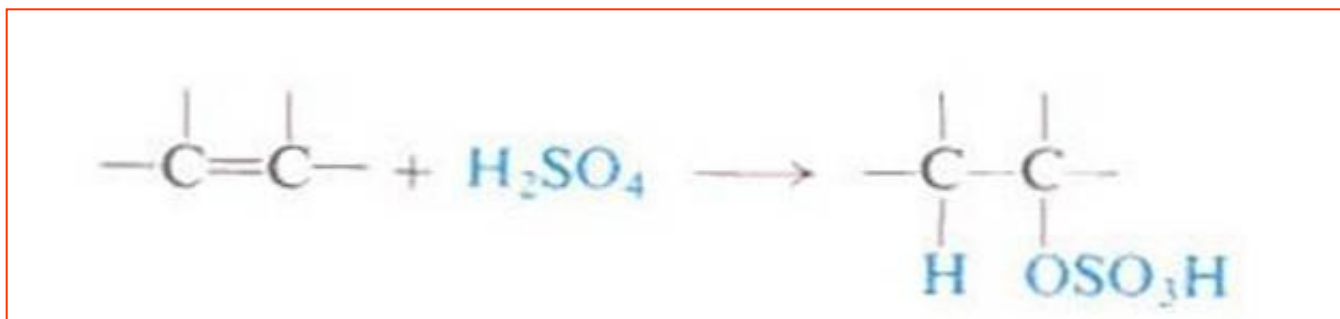
Major product

Minor product

## 4. Addition of Sulfuric Acid

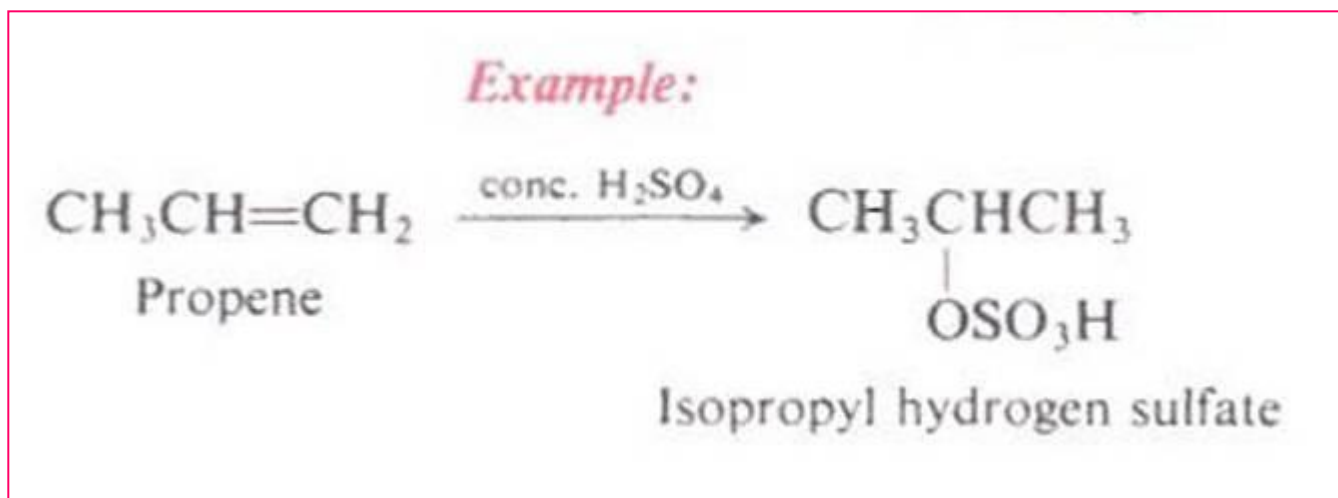
Cold sulfuric acid adds across the double bond of alkene to give alkyl hydrogen sulfate.

### The General equation



An alkyl hydrogen sulfate

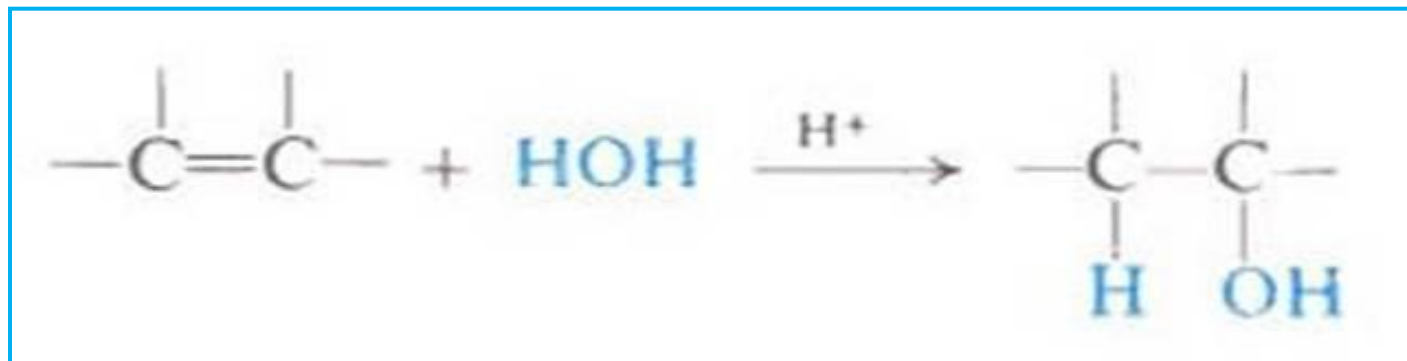
Addition of sulfuric acid to alkenes also follows **Markovnikov's rule**, as the example



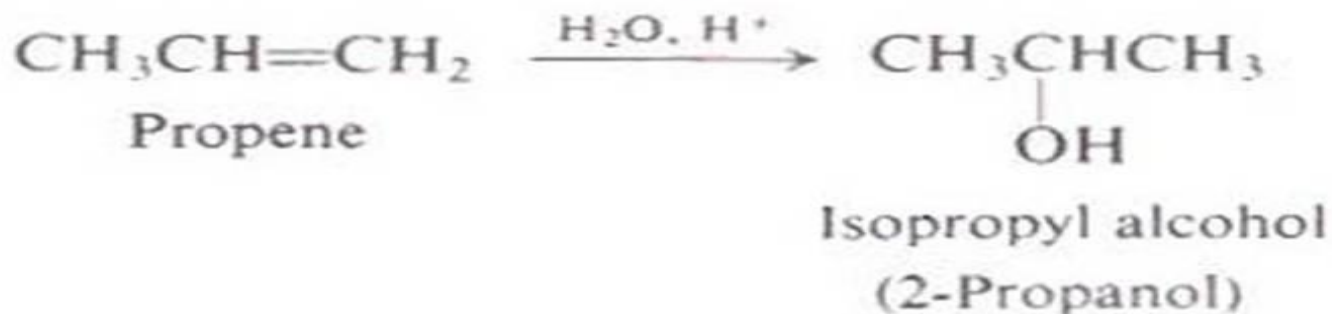
## 5. Addition of Water: Hydration

When heated with water in the presence of an acid catalyst (usually sulfuric acid), alkenes yield alcohols (ROH). The process is called *hydration* of alkenes because it involves the addition of water across the double bond (C=C).

### *The General equation*



### *Example:*



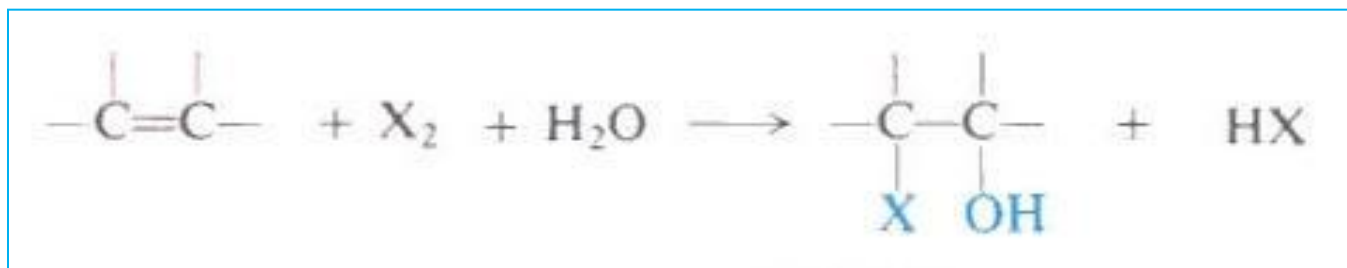
Note that,

The addition of HOH across the double bond is in accordance with *Markovnikov's rule*.

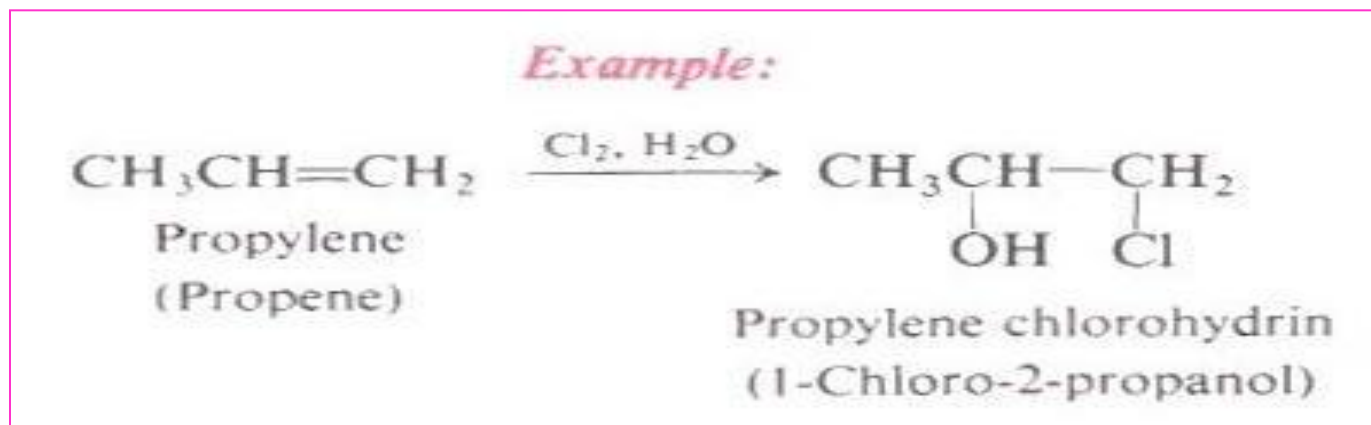
## 6. Addition of HOX: Halohydrin formation

When an alkene is treated with **aqueous chlorine** or **aqueous bromine**, the addition product is a **halohydrin**. (when  $\text{Cl}_2$  is used, the product is **chlorohydrin**; When  $\text{Br}_2$  is used the product is a **bromohydrin**)

### *The General equation*



The addition of the chloronium ion,  $\text{Cl}^+$  or bromonium ion,  $\text{Br}^+$  and the hydroxid ion,  $\text{OH}^-$ , follows the **Markovnikov's rule** as illustrated in the following example.

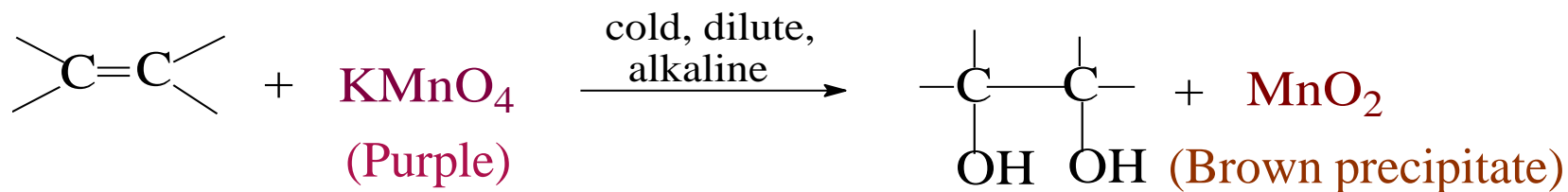


## 7. Oxidation of Alkenes (visual test for unsaturation)

A simple visual test can be used to detect unsaturation:

Alkenes can easily be oxidized by potassium permanganate ( $\text{KMnO}_4$ ) and other oxidizing agents. When alkenes are added to the purple alkaline potassium manganate, there is a color change to brown manganese dioxide ( $\text{MnO}_2$ ) as the alkenes are being oxidized. This reaction is called *Baeyer test* for the unsaturation.

### *The General equation*

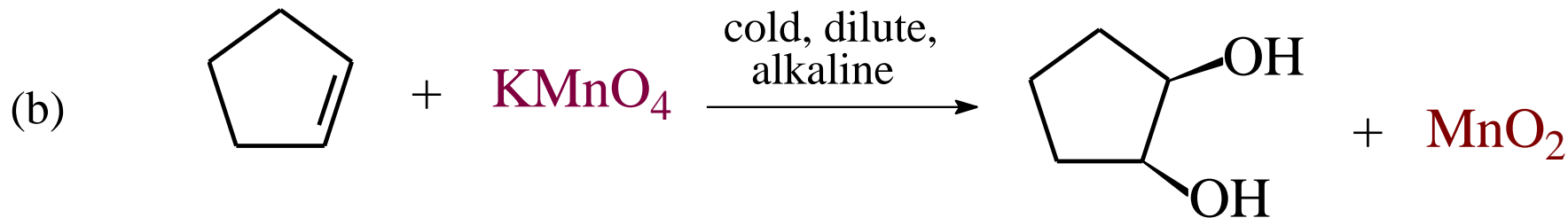
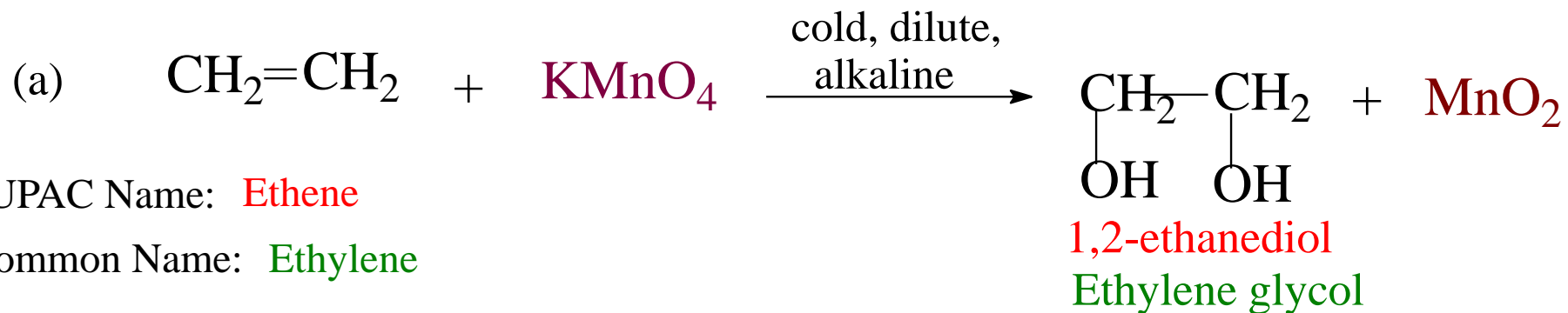


A glycol

**The reaction conditions** can be summarized as follows

At cold temperatures with low concentrations of oxidizing reagents, alkenes tend to form glycols (diol.)

## Examples



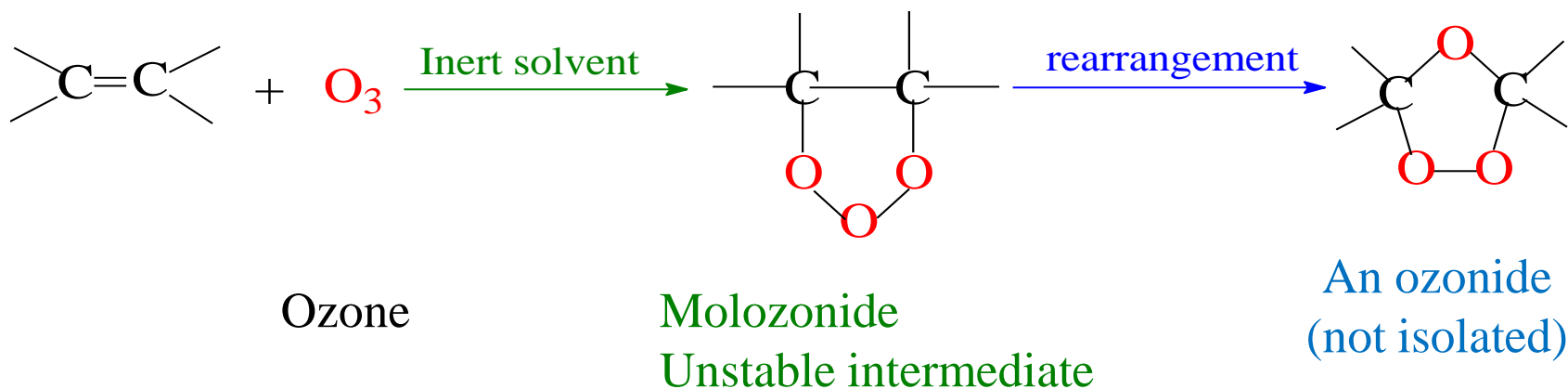
IUPAC Name: cyclopentene

Cis-1,2-cyclopentadiol

## 8. Ozonolysis

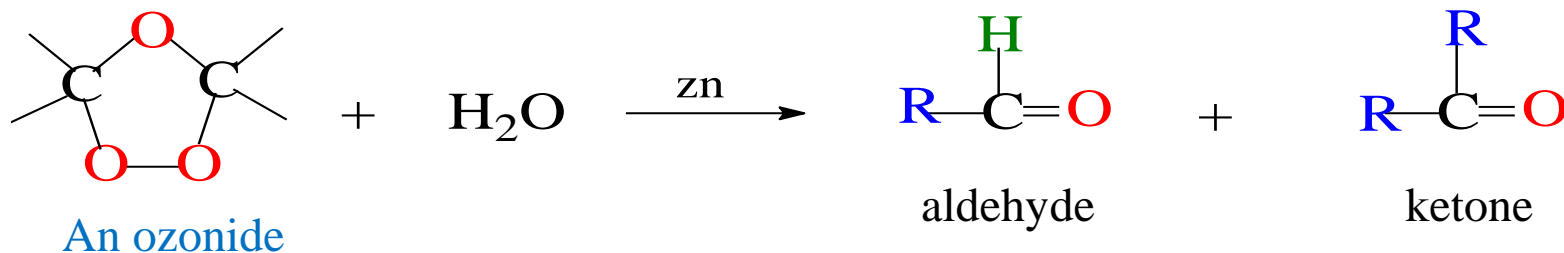
Oxidation of alkenes by **ozone** “O<sub>3</sub>” leads to destruction of both the  $\sigma$  and  $\pi$  bonds of the double-bond system. This cleavage of an alkene double bond, generally accomplished in good yield, is called **ozonolysis**.

### *The General equation*



Further addition of water in the presence of zinc catalyst results in the formation of two carbonyl groups compounds, (at the position of the C=C double bond was.

These products of ozonolysis may be **aldehydes** and **ketones**.

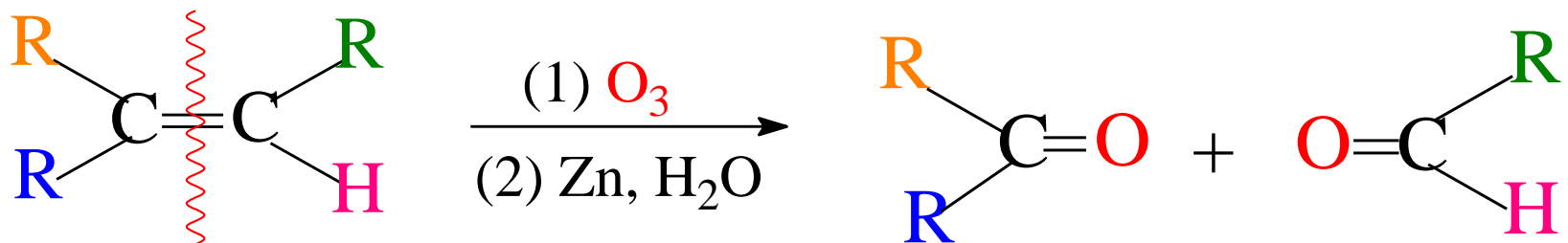


# Examples

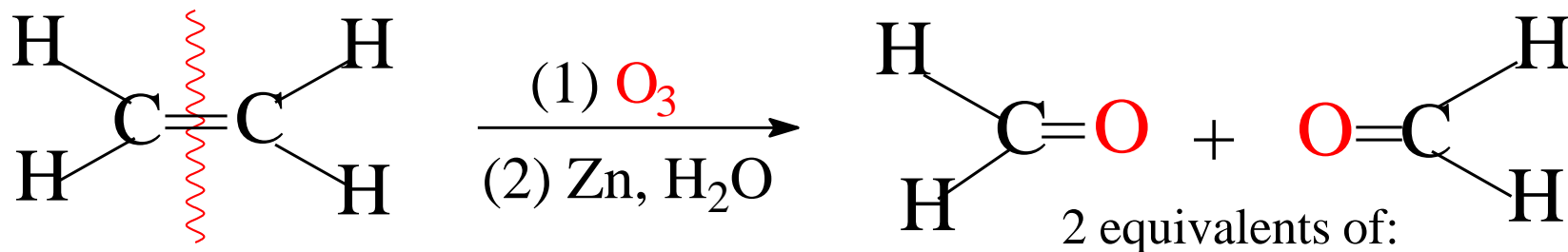
What would be the product of the reaction of each of the following with  $O_3$  followed by  $Zn/H_2O$ ?

- (a) Ethene      (b) 1-Butene      (c) 2-Butene      (d) Isopropylidenecyclohexane

The ozonolysis reaction can be **summarized** by the following equation:



(a) Ethene



IUPAC Name:

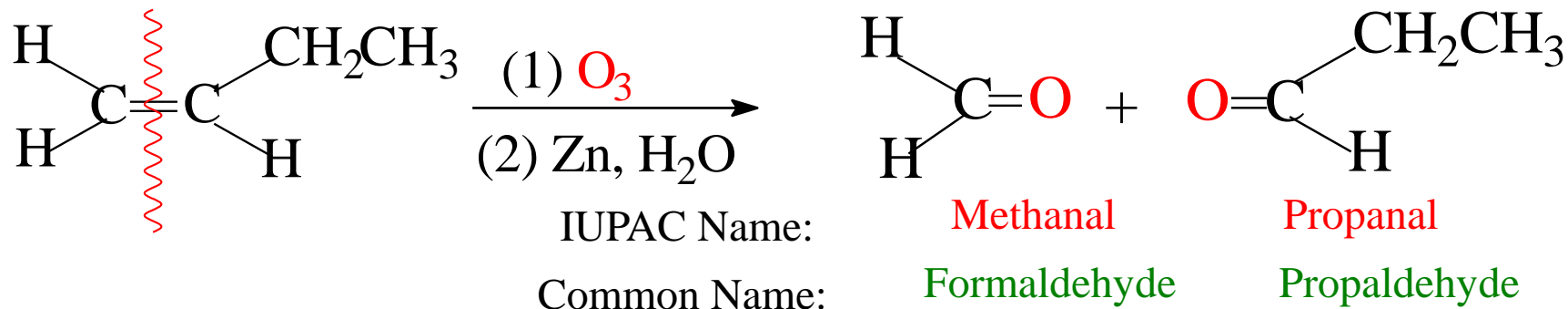
**Methanal**

Common Name:

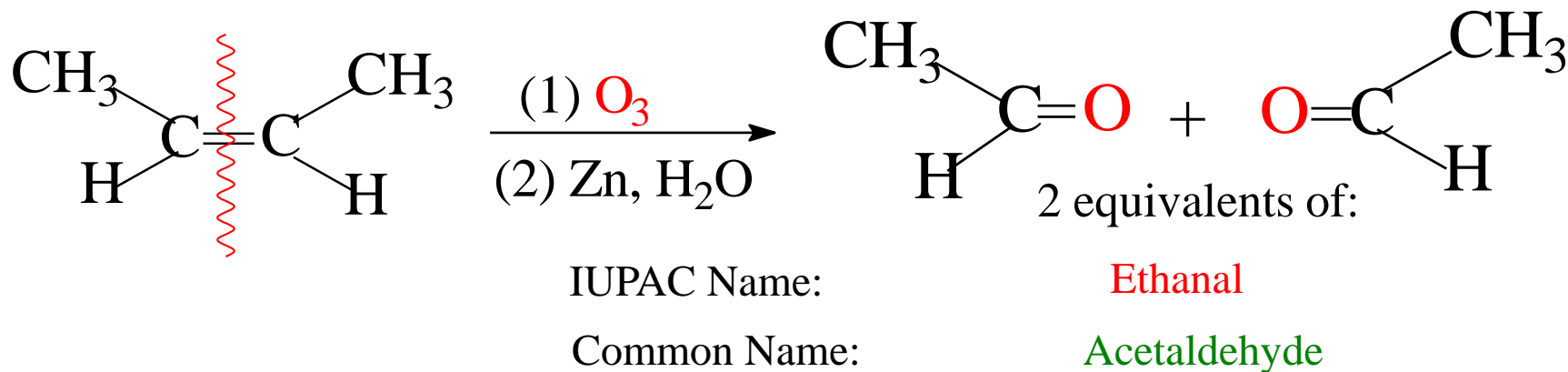
**Formaldehyde**



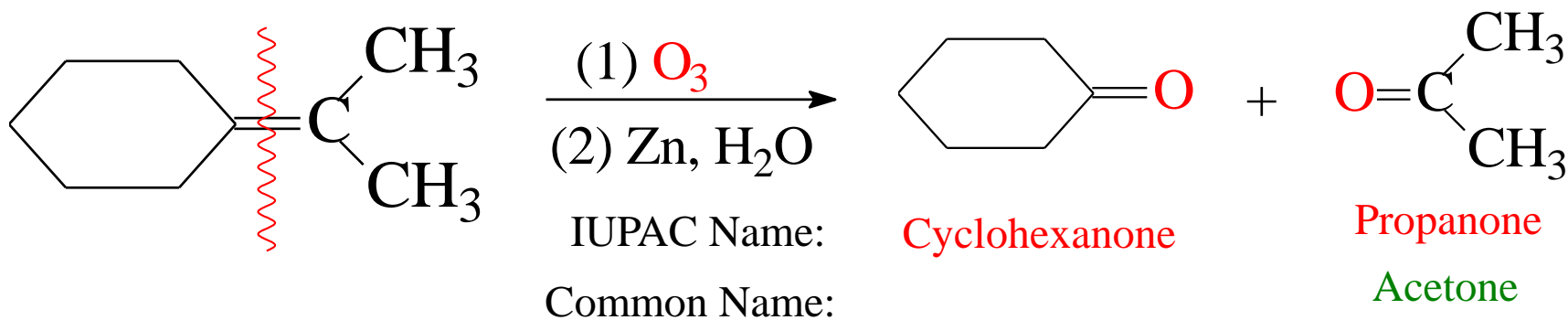
(b) 1-Butene



(c) 2-Butene



(d) Isopropylidenecyclohexane



## 8. Polymerization

can be defined as; the joining together of many small molecules to form very large molecules with repeating identical structural units or "mers". For alkenes; The **polymerization process** can be classified as an **addition reaction**, in which the alkene units **monomer** are join together with themselves to give a single giant molecules called **polymers**.

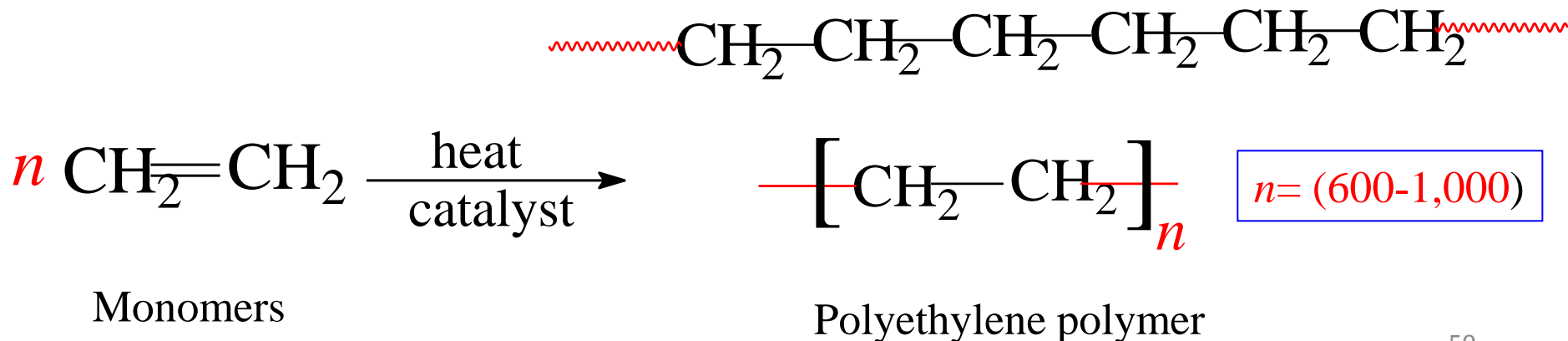
The basic alkene unit is called **monomer**

The Huge molecule formed is called **Polymer**

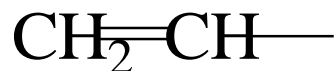
( from the Greek; **poly** = many & **meros** = units)

### Example

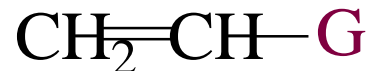
When ethylene is heated in the presence of suitable catalyst, thousands of **ethene** molecules join together to make poly(ethene) - commonly called **polyethylene**.



The substitution of one of the H's of the ethylene by some other group produces a vinyl compound



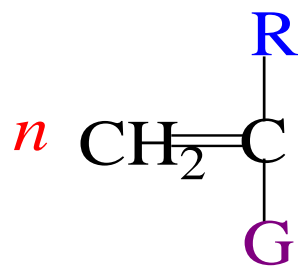
Vinyl group



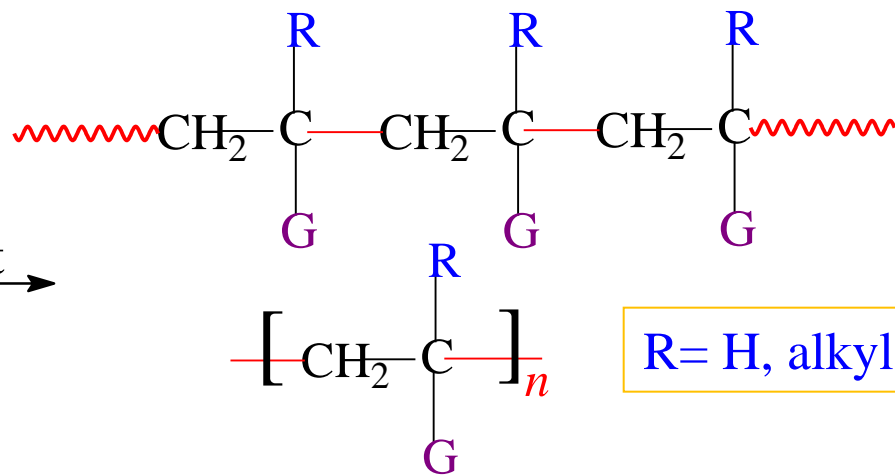
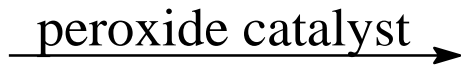
Vinyl compound

Similarly, as **vinyl compound** is used as the *monomer*, therefore; the *vinyl polymerization* can be represented by the following equation

*The general equation*



A vinyl compound



A vinyl polymer

R= H, alkyl or Cl

## H.W

Page: 80, problems 3.17, 3.18

Page: 81, problem 3.20

Page: 83, problem 3.22

Page: 84, problem 3.23

Page: 85, problem 3.25



*Good Luck*