



Chem 145

Unsaturated hydrocarbons

Alkenes

Chapter 3

1434-1435

2013-2014

2nd semester

Dr. Seham ALTERARY

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

❑ Definition of Alkenes.

❑ Nomenclature of Alkenes.

➤ Substituted groups from Alkenes; (**Alkenyl**)

❑ The Hybridization of Alkenes.

❑ Geometric isomerism among the Alkenes.

▪ *Cis-Trans* isomerism.

❑ Physical properties of Alkenes.

❑ General Methods of Preparation of Alkenes.

❑ Reactions of Alkenes.

Definition 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:



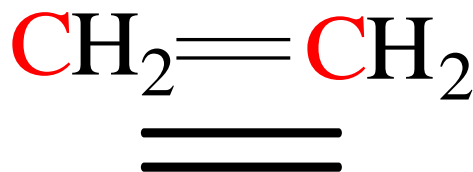
Nomenclature

I. Common or trivial name

- The **common** or **trivial name** may be used, often have their **origin in the history of the science** and **the natural sources** of specific compounds.
- Common names used **in 1800's** are **still in used** for some compounds today. Particularly, those of **low molecular weight**.

Example

The simplest members of the **alkenes** series (**C₂** and **C₃**) are usually called by their **common Names**, which are derived from the corresponding **alkanes** by replacing the (**-ane**) ending by (**-ylene**).

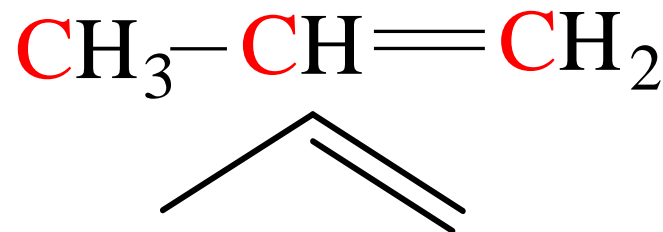


Common Name:

Ethylene

IUPAC Name:

Ethene



Propylene

Propene

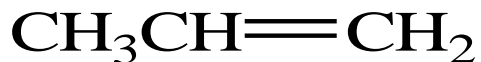
II. IUPAC naming

II-a. Open-chain Nomenclatures

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**.



Propene

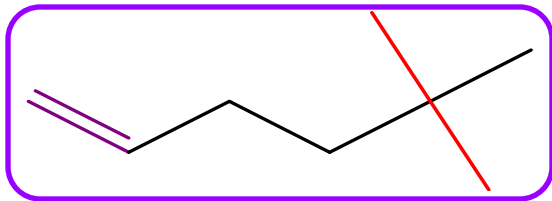
3. The **postion** of **the double bond** is indicated by *the number of the lower* numbered **doubly bond**.



1-Butene

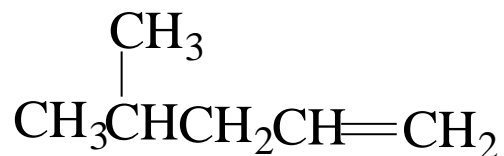
(**not 3-Butene**)

4. The **parent carbon chain** is numbered in a manner than will give the **doubly bonded carbon** atoms the *lowest* numbers even if it results in the **substituents** getting **higher numbers**.

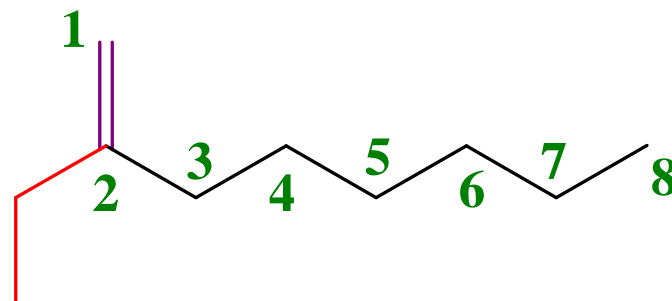


5,5-Dimethyl-1-hexene

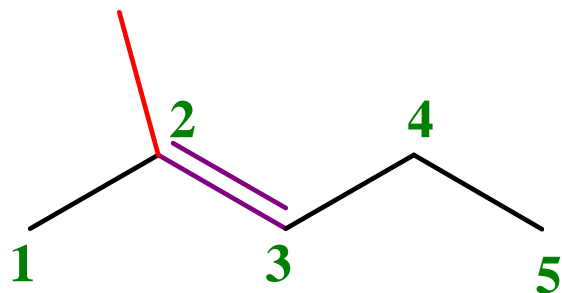
Examples



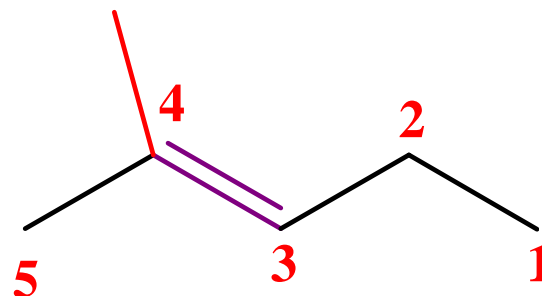
4-Methyl-1-pentene
(*not* 2-Methyl-4-pentene)



2-ethyl-1-octene



Not



4-Methyl-3-pentene

or

2-Methyl-pent-2-ene

2-Methyl-2-pentene

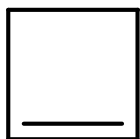
II-b. Cycloalkenes Nomenclature

A **cycloalkene** or **cycloolefin** is a type of **alkene hydrocarbon** which contains **a closed ring** of carbon atoms, but **has no aromatic character**.

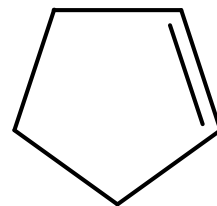
Examples



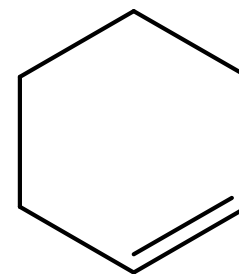
Cyclopropene



Cyclobutene



Cyclopentene



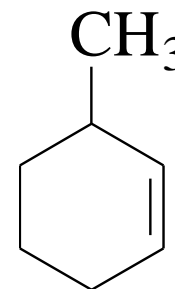
Cyclohexene

In cycloalkene, **the numbering must begin at the double bond** .
i.e, the double bond is always found between **carbon 1** and **carbon 2**.



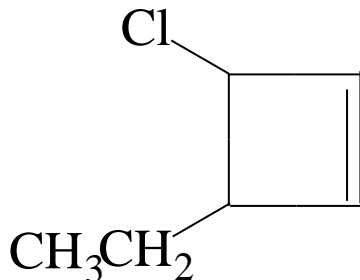
Note that

It is therefore not necessary to specify
the position of **the double bond** with a
number.

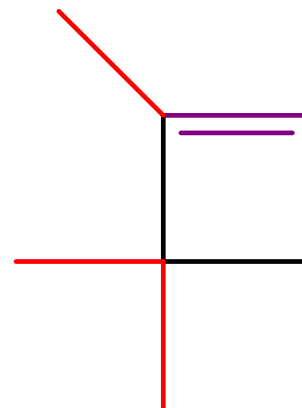


3-Methylcyclohexene
(**not** 1-Methyl-2-cyclohexene)

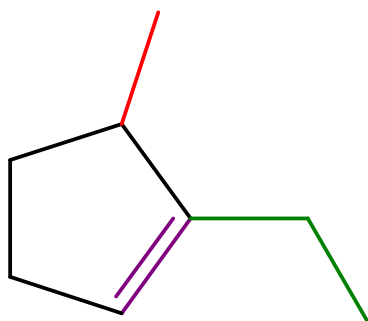
Examples



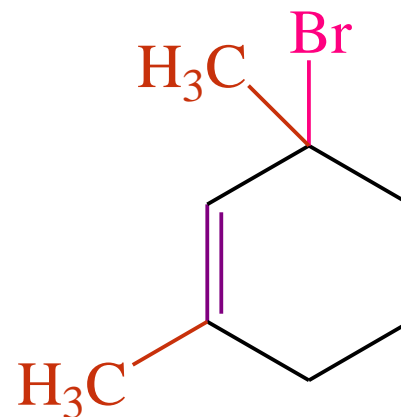
3-Chloro-4-ethylcyclobutene
(*not* 1-Chloro-2-ethylcyclobutene)



1,4,4-trimethylcyclobutene
(*not* 2,3,3-trimethyl cyclobutene)



1-ethyl-5-methylcyclopentene

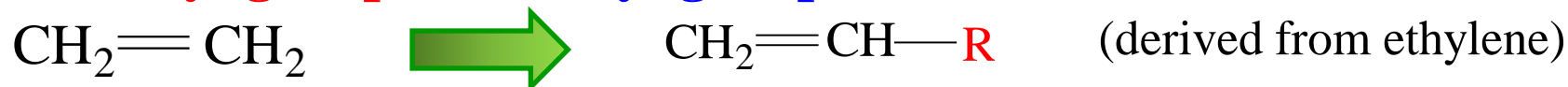


3-Bromo-1,3-dimethyl-cyclohexene

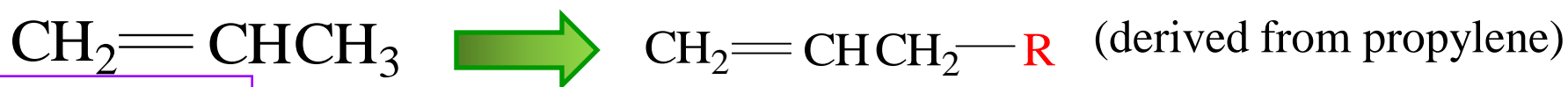
Alkenyl substituted Group

- A hydrocarbon group containing carbon-carbon double bond is to be treated as a substituent.
- In these cases the substituent is named in a similar fashion to simple alkyl substituents.
- The substituent is named in a similar way to the parent alkene. It is named based on the number of carbon atoms in the branch plus the suffix -yl. *i.e.* alkenyl.
- There are **two common names** that are widely used:

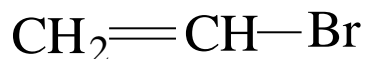
1- Vinyl group (=Ethenyl group)



2- Allyl group (=Propenyl group)



Example



Common Name:

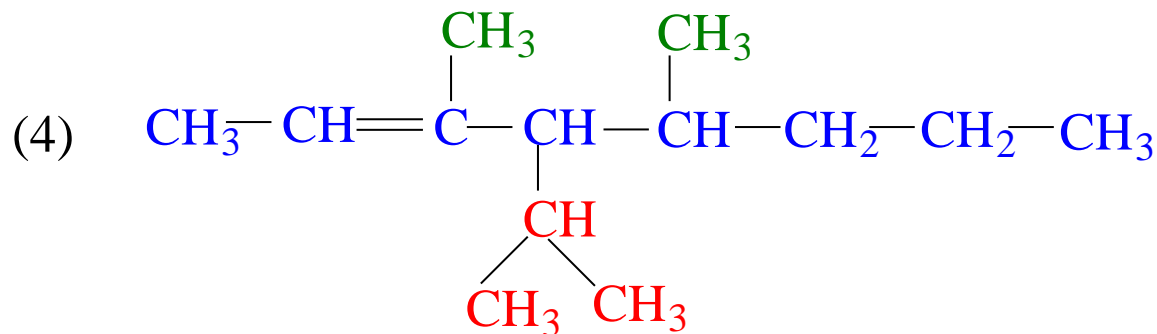
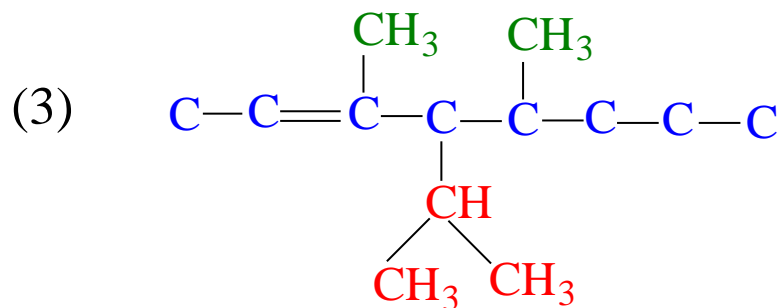
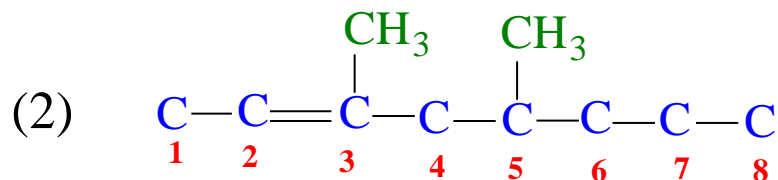
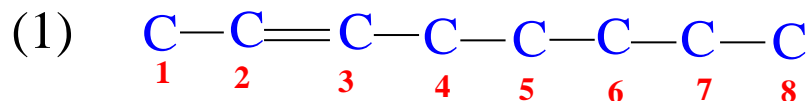
Vinyl bromide



Allyl chloride

Exercise:

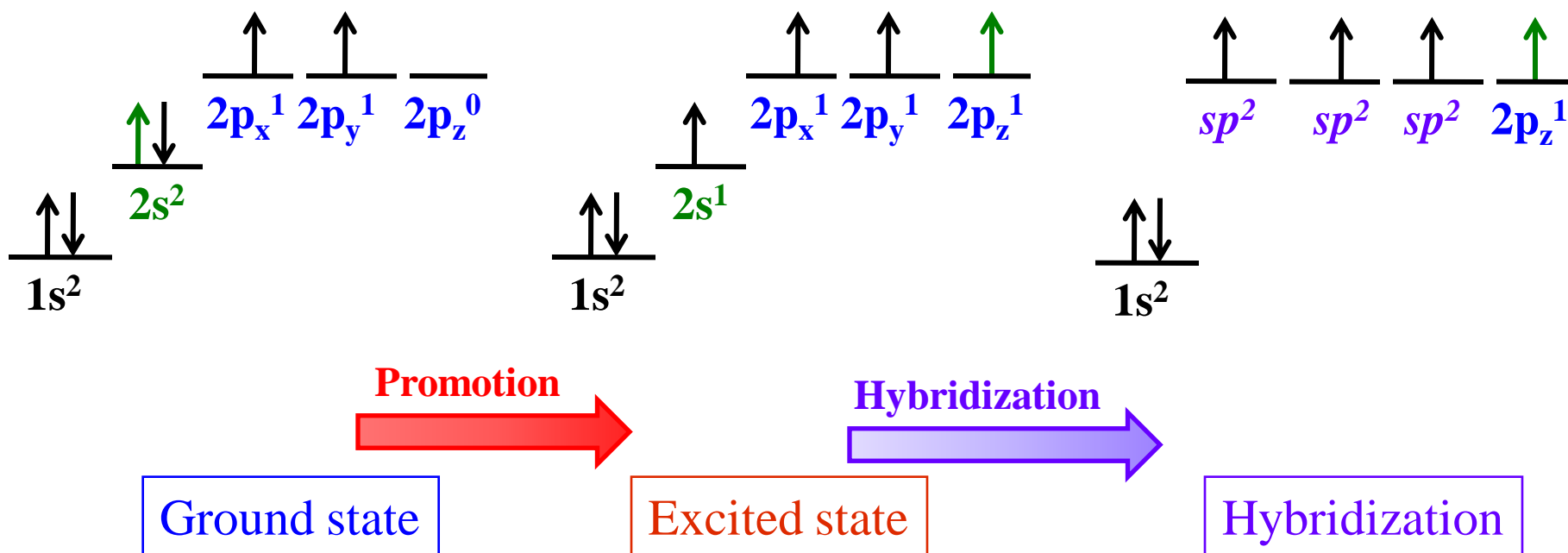
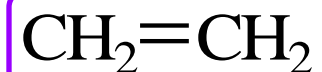
Write the structural formula of 3,5-dimethyl-4-isopropyl-2-octene.



Hybridization in Alkenes

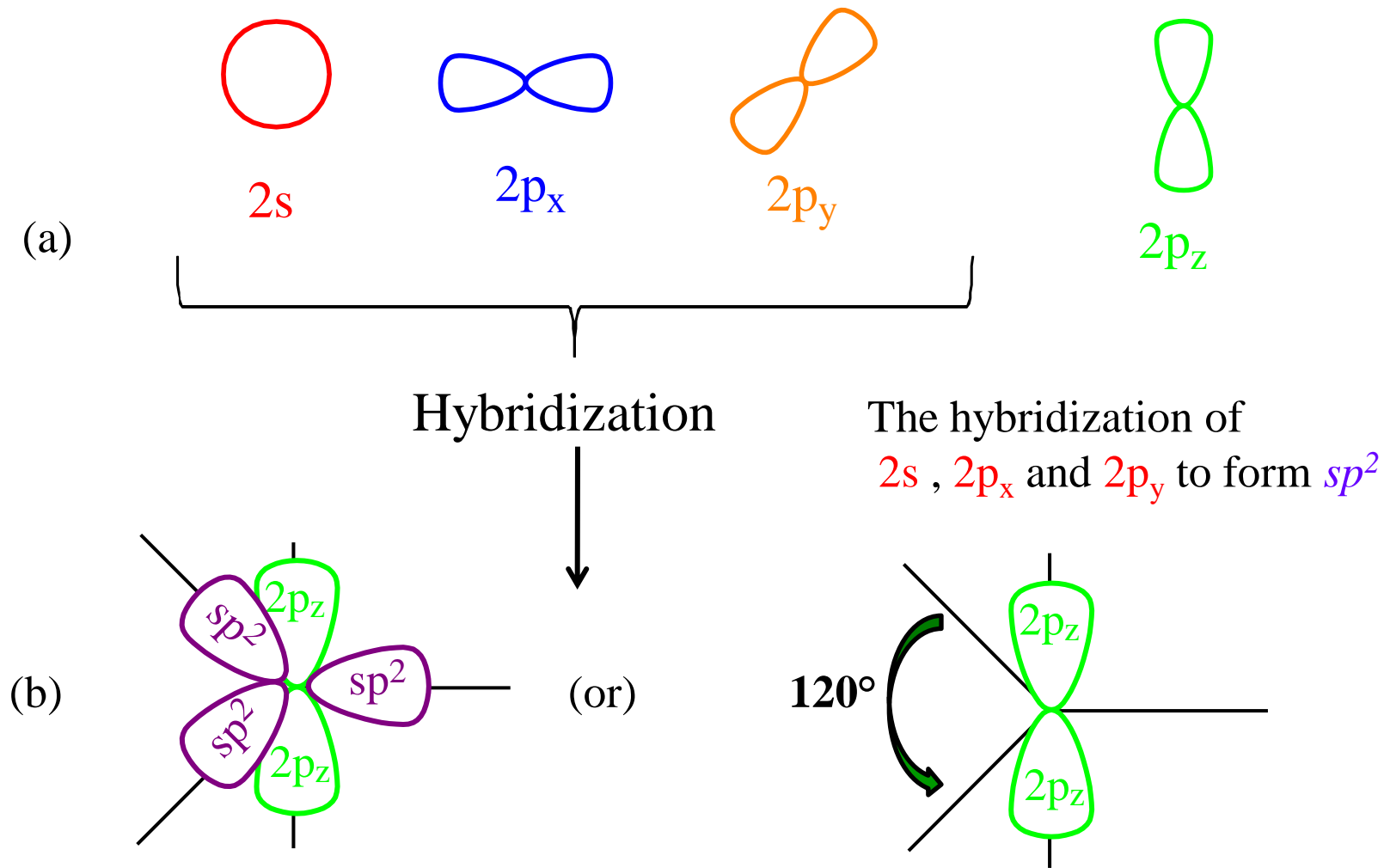
Example:

For the simplest alkene, Ethylene, or Ethene



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.



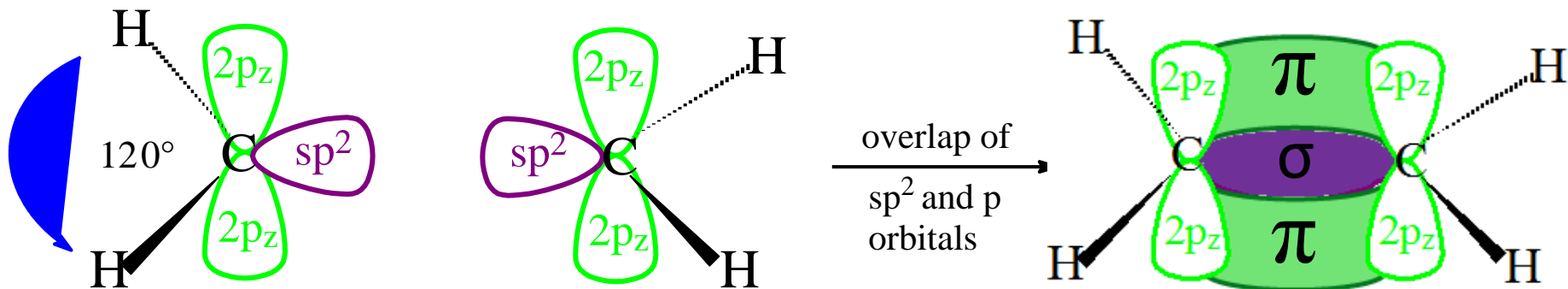
□ The three sp^2 orbitals get as far away from each other as possible assuming a **planer arrangement** with an angle of 120° between hybrid orbitals, (**trigonal planer**).

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

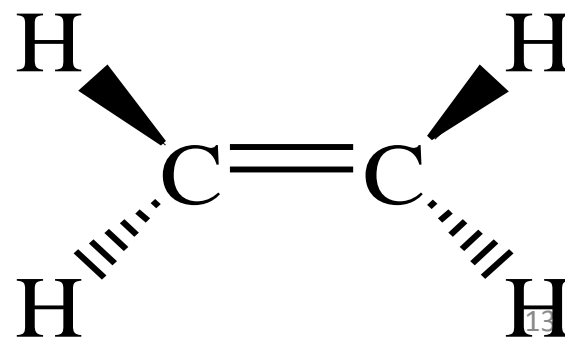
Bond Formation in Ethylene

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

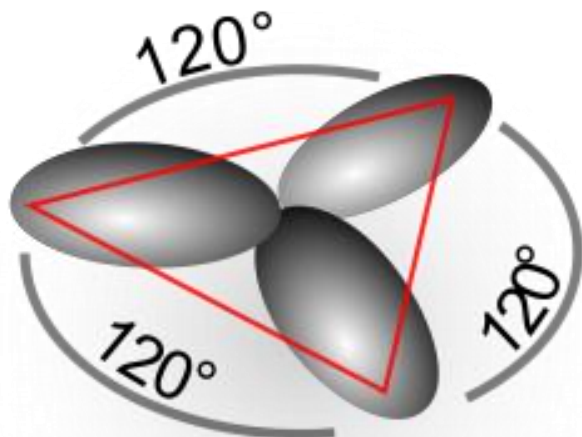
The $2p_z - 2p_z$ overlap resulting the carbon---carbon double bond = π bond.



Equivalent to



The Ethylene molecule has trigonal planer geometrical shape, with a bond angle equal to 120° , and bond length 1.34 \AA



Note that;

the restricted rotation about the carbon – carbon double bond and the planar geometry give type of *geometric isomersim*.

Geometric isomerism among the Alkenes.

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.

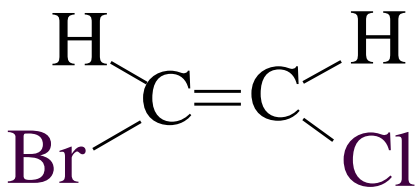
Called... ***Geometric Isomerism***

Cis-Trans isomerism.

Two different substituents

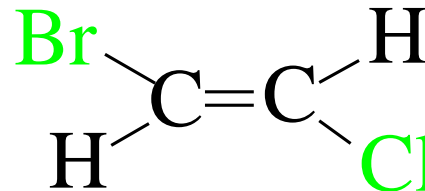
Groups attached to the **alkene** could be positioned...

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



Cis-1- Bromo-2-chloroethene

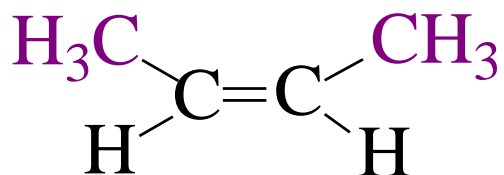
on **opposite sides** of the alkene.



Trans-1-Bromo-2-chloroethene

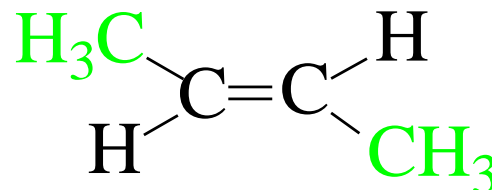
Geometric isomers **differ** from one another **only** in the way in which **the substituents are arranged in space** related to **the plane of the C=C bond**.

Example: the isomers of 2-Butene



Cis-2-Butene

(mp= -139°C; bp= 3.7°C)



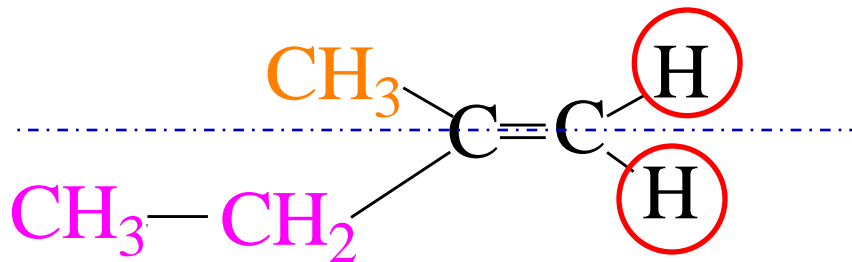
Trans-2-Butene

(mp= -106°C; bp= 0.9°C)

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

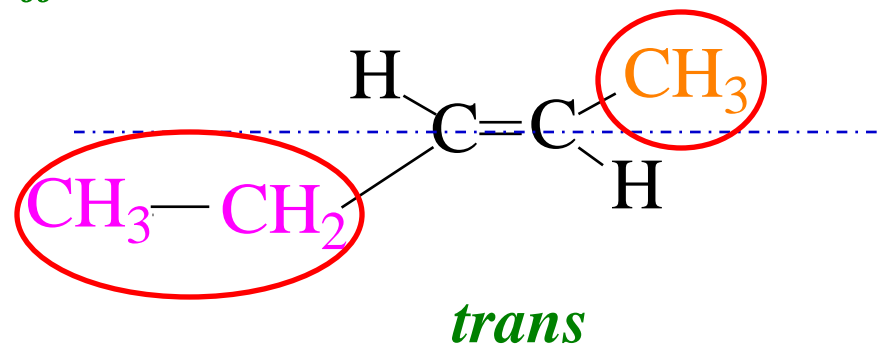
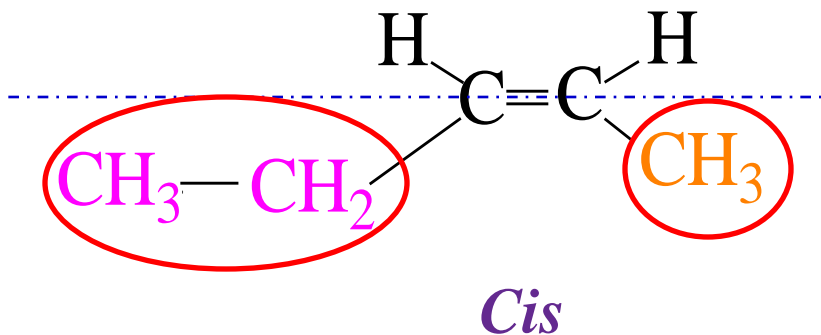
Does this molecule have geometric isomers?

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



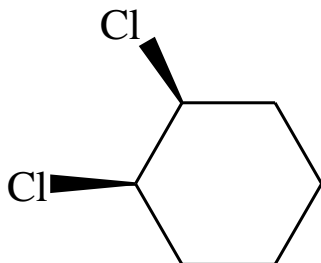
3. The molecule above *does not have cis or trans isomers*. *On the right C of the $C=C$, there are 2 H atoms (must have different groups on each C of the $C=C$.)*

➤ 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*.

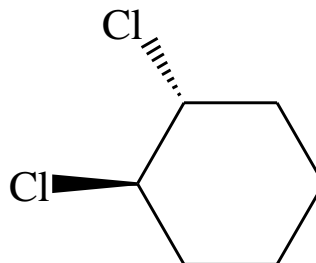


Examples on *cis* & *trans* isomers

1-

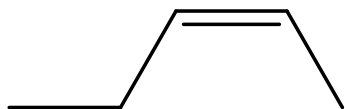


cis-1,2-dichlorocyclohexane

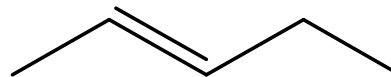


trans-1,2-dichlorocyclohexane

2-

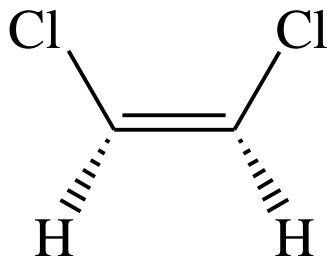


cis-2-pentene

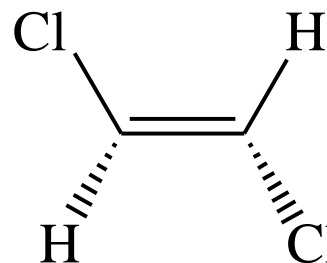


trans-2-pentene

3-



cis-1,2-dichloroethene

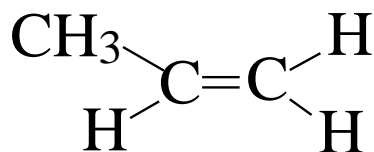


trans-1,2-dichloroethene

Exercise:

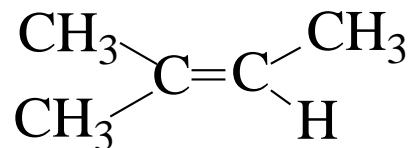
which of the following compound has geometric isomerism? Why?

(a) Propene



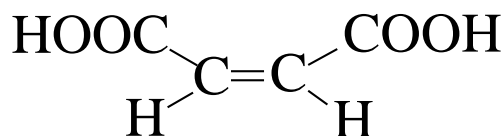
Geometric isomerism is not possible

(b) 2-Methyl-2-butene

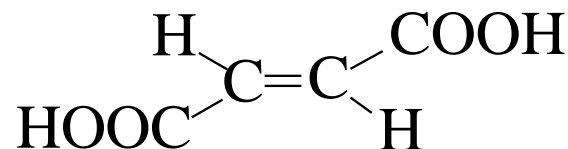


Geometric isomerism is not possible

(c) 2-butenedioic acid

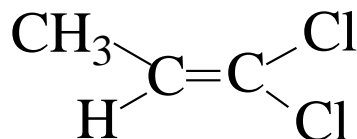


Cis-form (Maleic acid)



Trans-form (Fumaric acid)

(d) 1,1-Dichloropropene



Geometric isomerism is not possible

The Physical Properties of Alkenes

▪ *Physical State:*

The first lower member like ethene, propene and butene are colorless gases. Alkenes with five (C_5) to seventeen (C_{17}) 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).

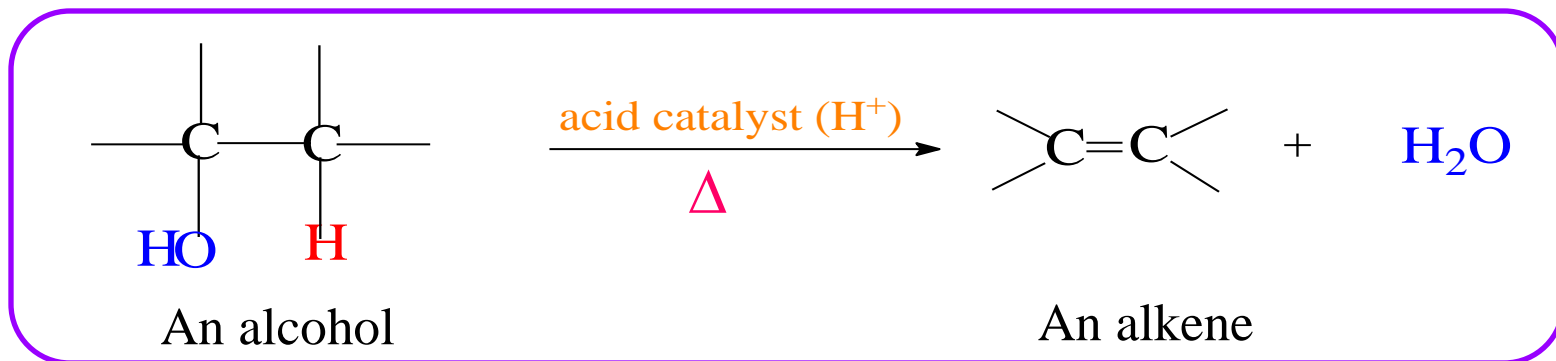
2. Branched chain alkenes have **lower boiling points** than the corresponding straight chain isomers.

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

The General Equation



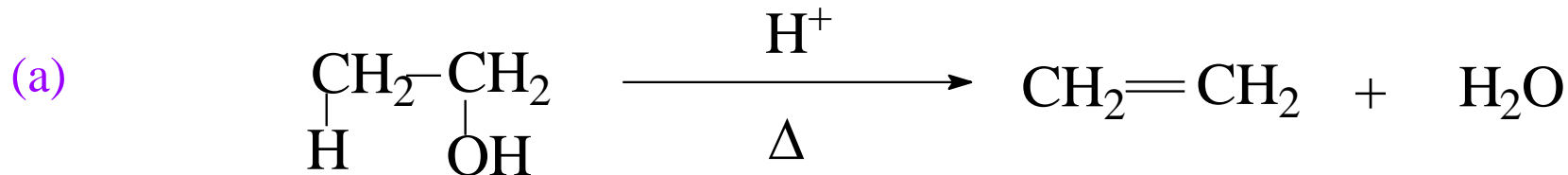
When an *alcohol* is *heated* in the presence of a mineral acid catalyst, it *loses a molecule of water* to give an *alkene*.



In Latin” *De-*” means= *removal of*

The acid catalyst **H⁺** ex; **H₂SO₄** or **H₃PO₄** & **Δ** is *Heat* .

Examples



IUPAC Name:

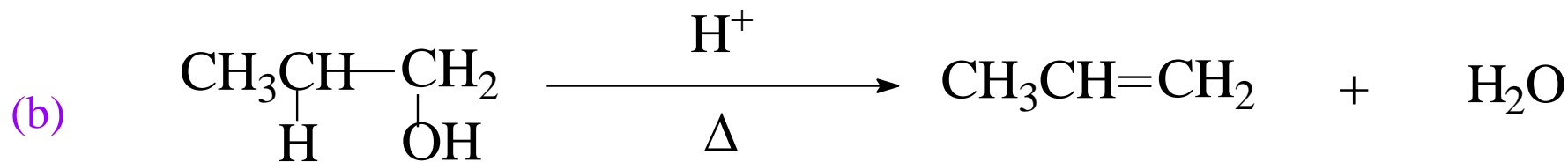
Ethanol

Ethene

Common Name:

Ethyl alcohol

Ethylene



IUPAC Name:

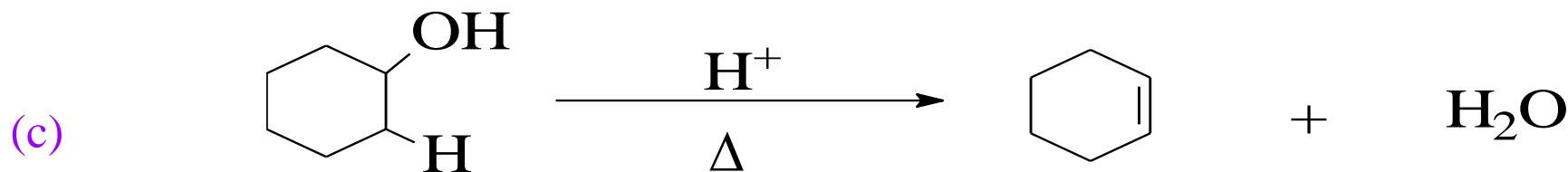
1-Propanol

Propene

Common Name:

n-propyl alcohol

Propylene



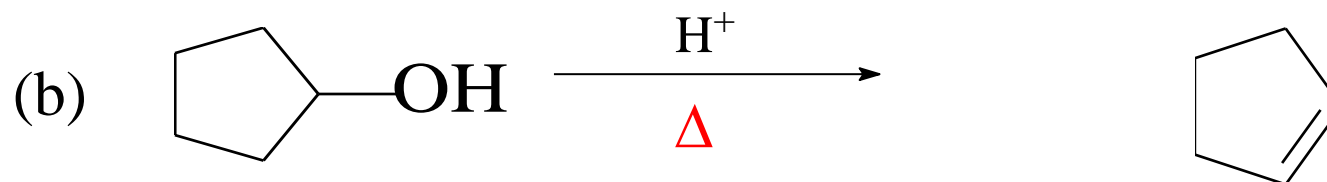
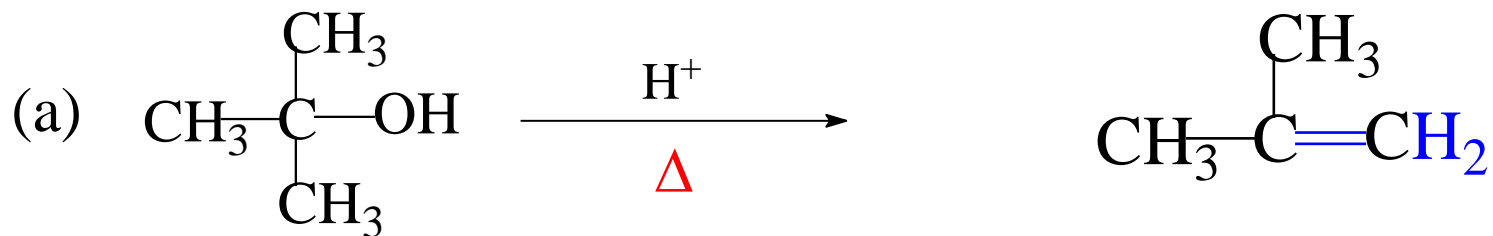
IUPAC Name:

Cyclohexanol

Cyclohexene

Common Name: Cyclohexyl alcohol

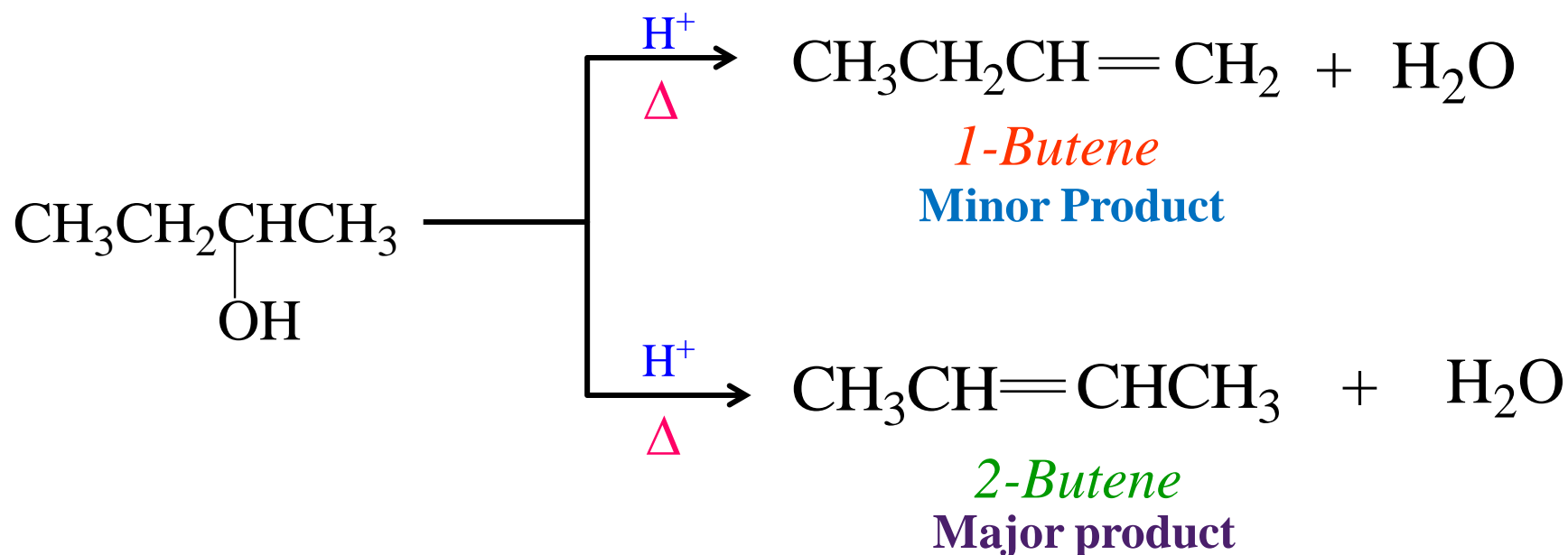
Problem 3.7 Write the structure of the product of the dehydration of each of the following alcohols.



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

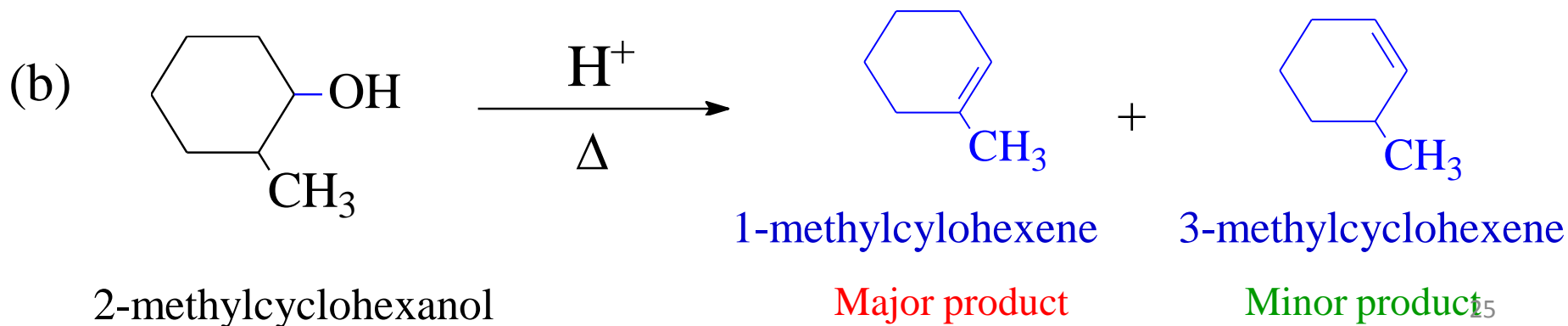
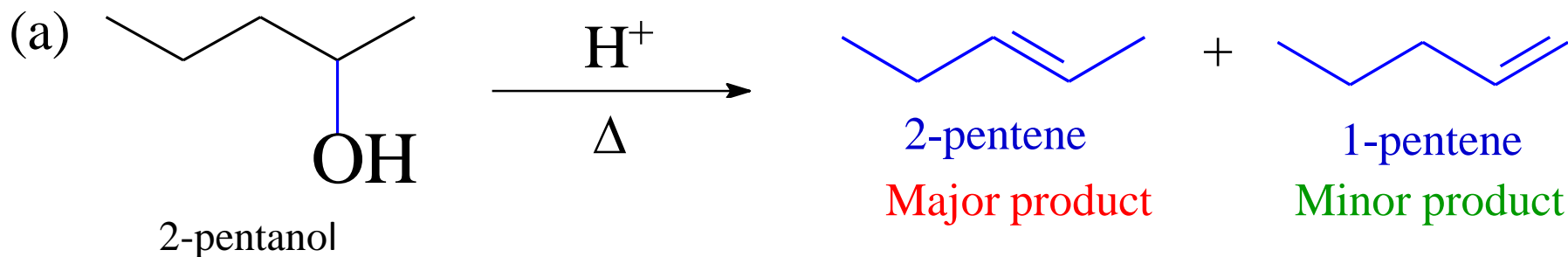
or

2-Butene

Saytzeff's Rule

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

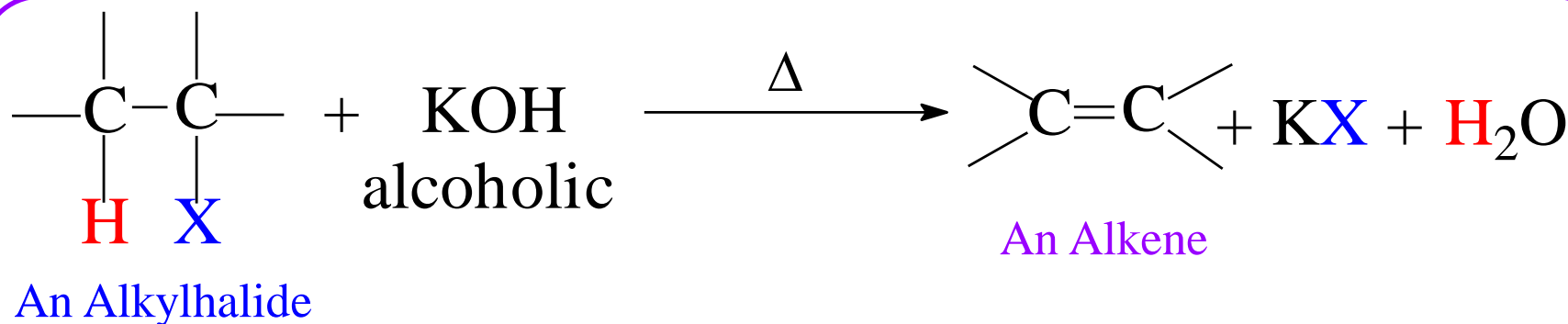
Problem 3.8 Give the major and the minor product of the dehydration of



2. Dehydrohalogenation of Alkyl halids

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

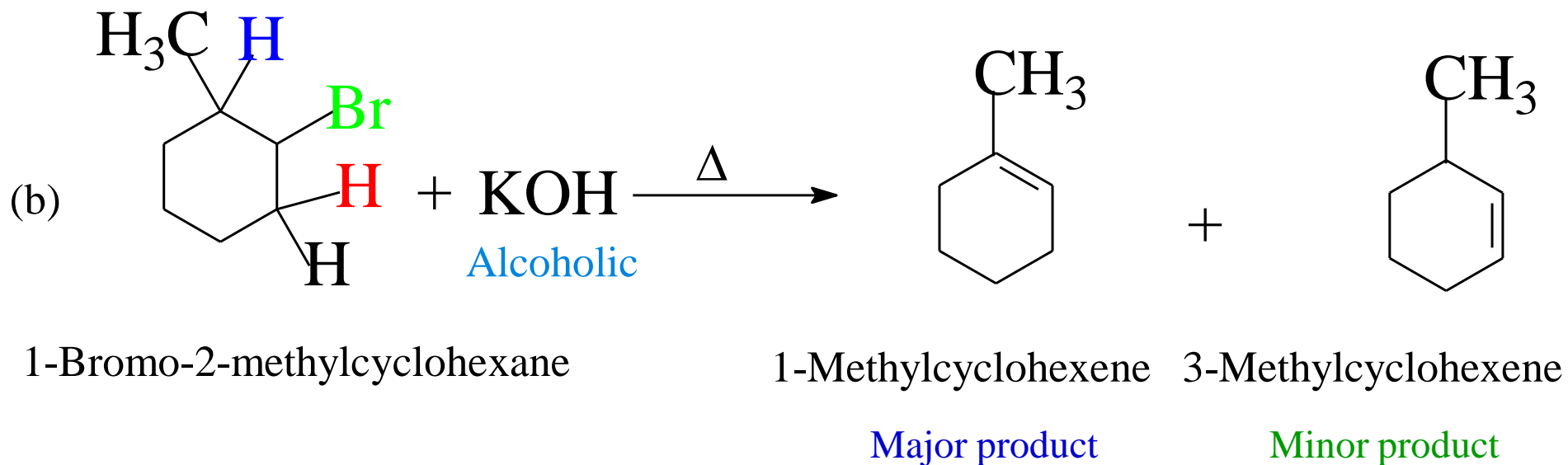
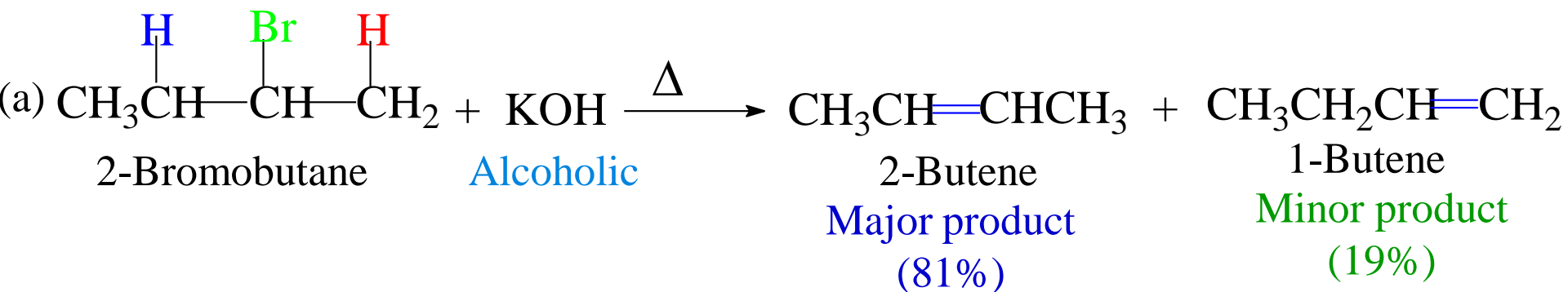
General equation



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

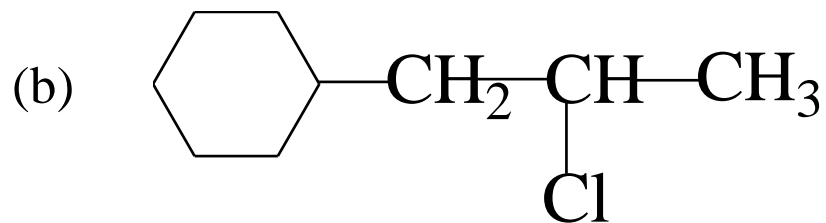
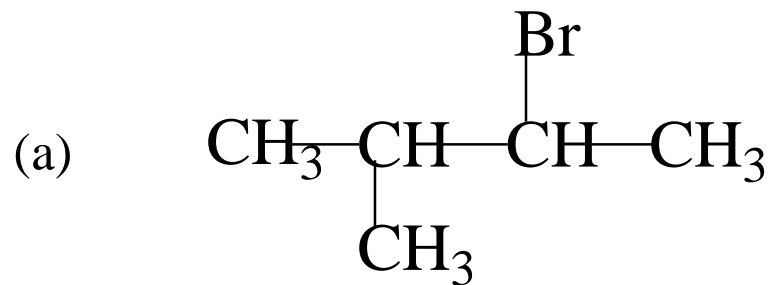
In similar way to that in the dehydration of an alcohol, **Saytzeff's rule** again applies; that is, *“the alkene with the most alkyl substituent on the double-bonded carbons Predominates”*.

Examples



Problem 3.12

Give the structure of the major and minor products of dehydrohalogenation of:



3-Dehalogenation of vicinal dihalides

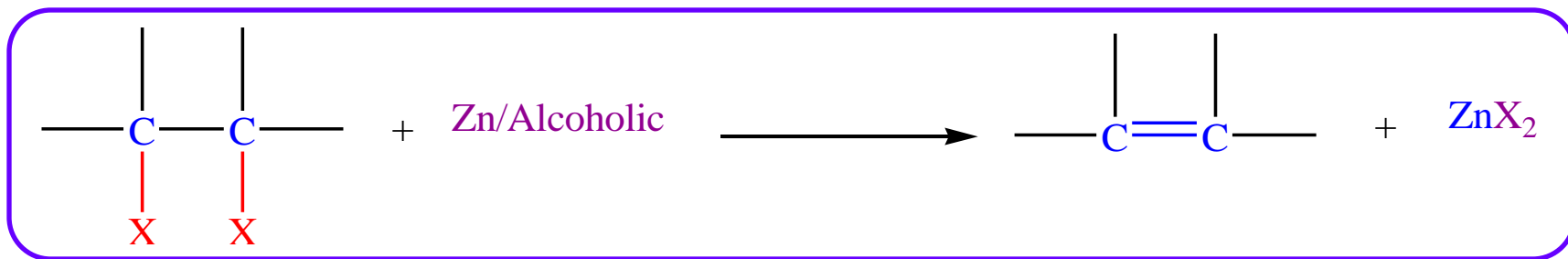
The dehalogenation of vicinal dihalide gives alkene.

The reaction takes place in the presence of alcoholic solution of Zn at high temperature.

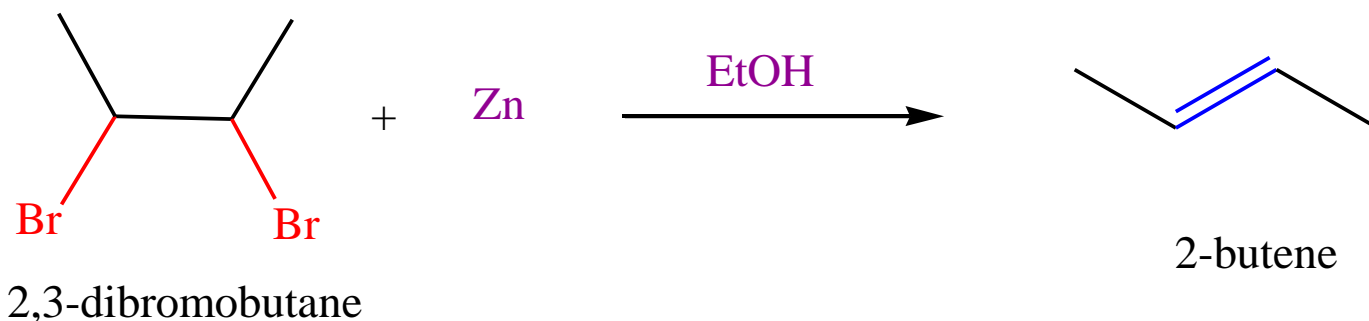
For example:

Dehalogenation of 2,3-Dibromobutane leads to the formation of 2-Butene in the presence of catalyst.

General Equation



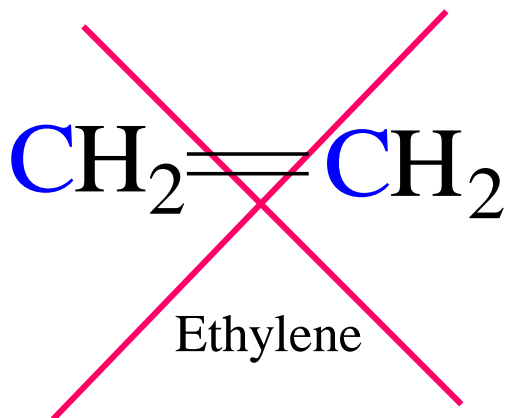
Example



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

Substitution reactions
on the saturated alkyl chain



Halogenation at High temperature

Two types of reactions

Addition reactions

On (C=C)

1. Addition of H_2
2. Addition of X_2
3. Addition of HX .
4. Addition of H_2O
5. Addition of halohydrin XOH

Oxidation reactions

On (C=C)

6. Oxidation (visual test for unsaturation)
7. Ozonolysis

Alkane vs **Alkene**
the way to react

	Alkane	Alkene
Reactivity	Less reactive	More reactive
Reaction condition	Hard condition <ul style="list-style-type: none">-Elevated temperature-Under the influence of UV light-In the gas phas	Mild condition <ul style="list-style-type: none">-Low temperature-Dark-Solvent

Substitution reactions
on the saturated alkyl chain

1. Halogenation

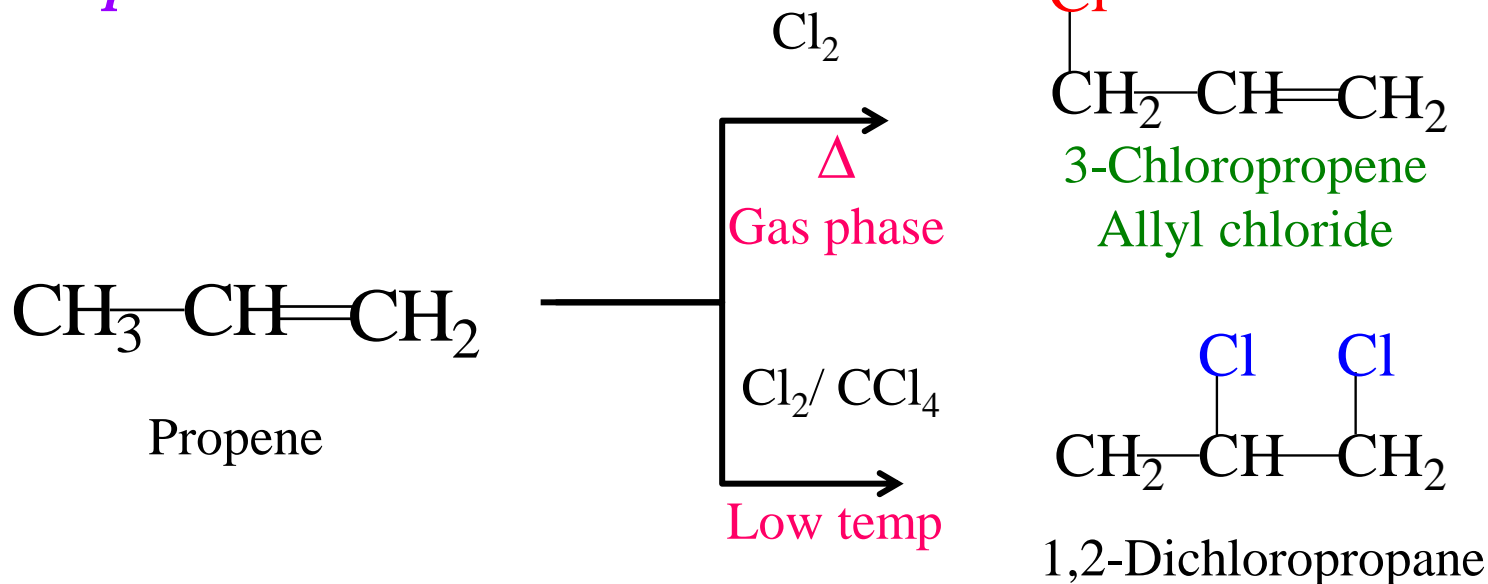
The **product** of any reaction is directly **affected by** factors that known as **reaction condition** such as *temperature, solvent,...*etc

Please see the link below



<http://www.youtube.com/watch?v=PE1CDR1S5pk&feature=related>

Example **substitution vs addition**



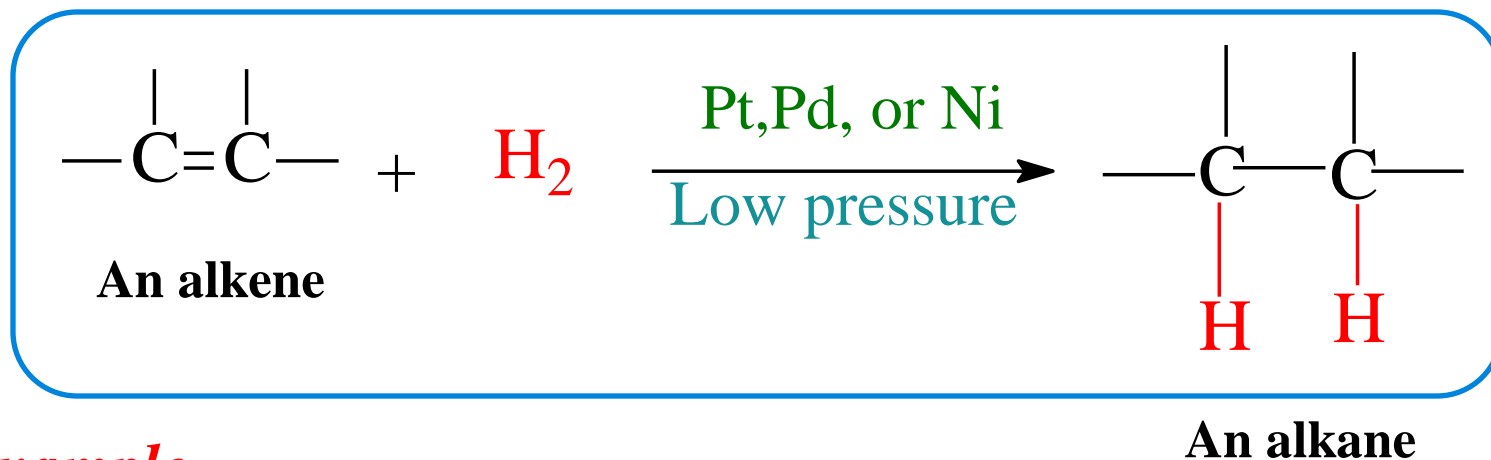
Addition Reactions on the C=C

1. Addition of Hydrogen: Catalytic Hydrogenation

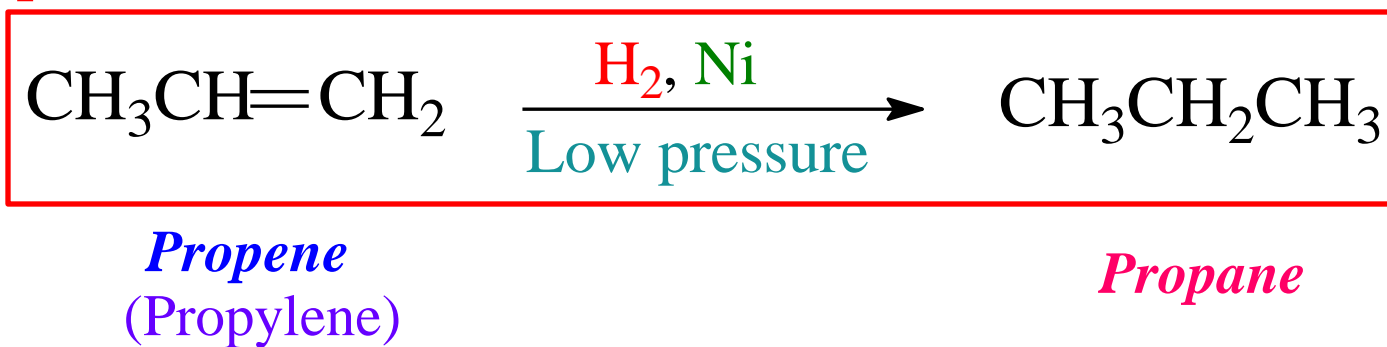
The C=C of alkene can add a mole of Hydrogen in the presence of suitable catalyste such as (Pt, Ni or Pd) at low pressure to give an **alkane**.

This method is called **Catalytic Hydrogenation**.

The General equation



Example



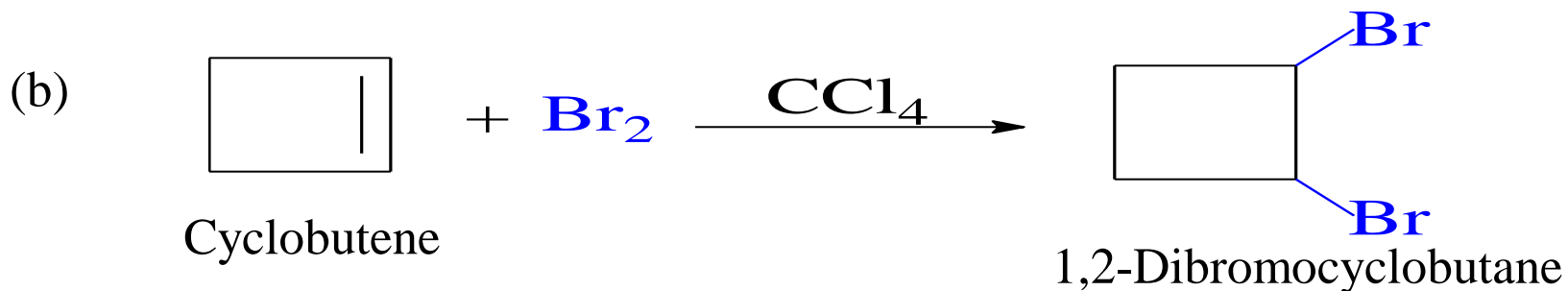
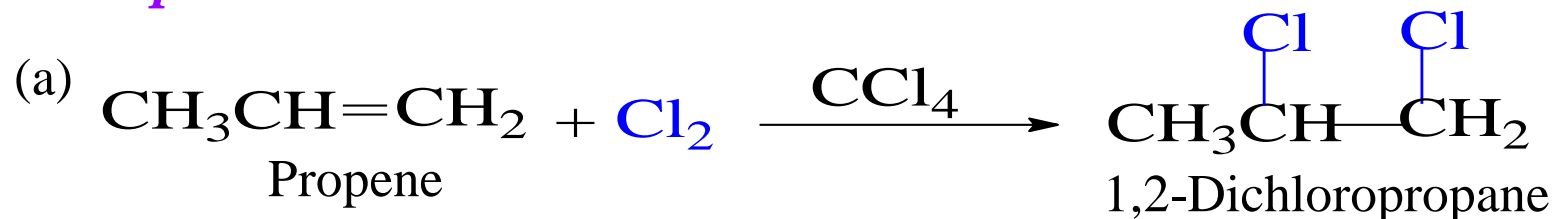
2. Addition of Halogens: Halogenation

When an alkene is treated at room temperature with a solution of **bromine Br₂** or **chlorine Cl₂** in carbon tetrachloride, the halogen adds rapidly to the double bond of the alkene to give the corresponding **vicinal dihalide**.

The General equation



Examples

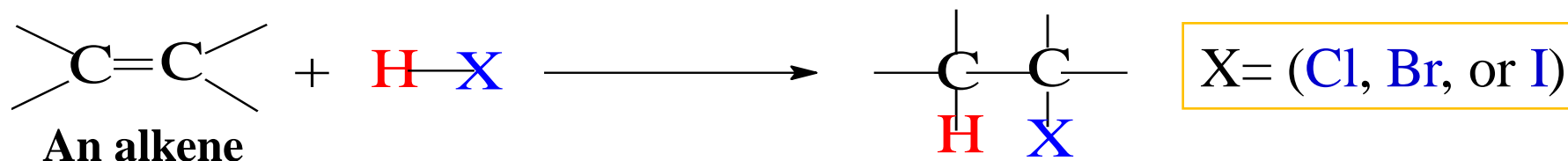


Note that, I “Iodine” is too unreactive and will not add to the C=C of an alkene, F “Fluorine” is too reactive and reacts explosively making the alkene unstable.³⁵

3. Addition of Hydrogen Halides: Hydrohalogenation

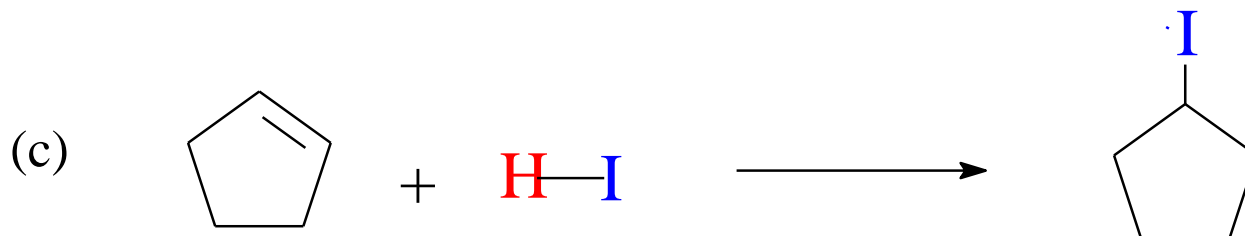
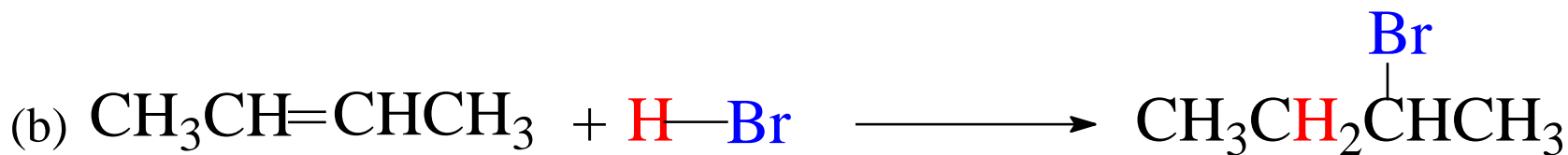
Alkenes react with hydrogen chloride, **HCl**, hydrogen bromide, **HBr**, and Hydrogene Iodide, **HI**, to form alkylhalides, **RX**. This reaction is known as **hydrohalogenation** As **H** and **X** is added to the double-bonded carbons.

The General equation



Examples

An alkylhalide

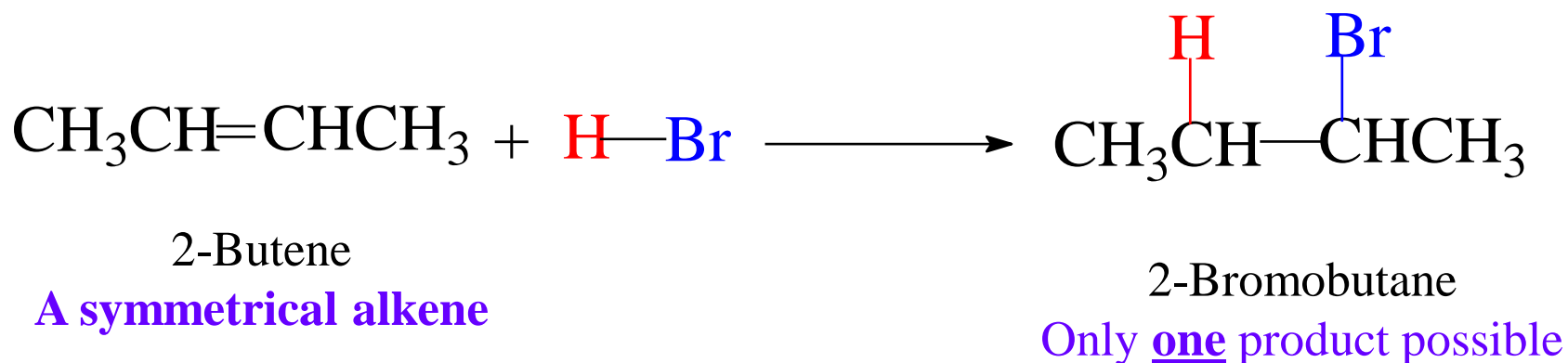


Addition H-X; Case 1:

Addition symmetric alkene

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.

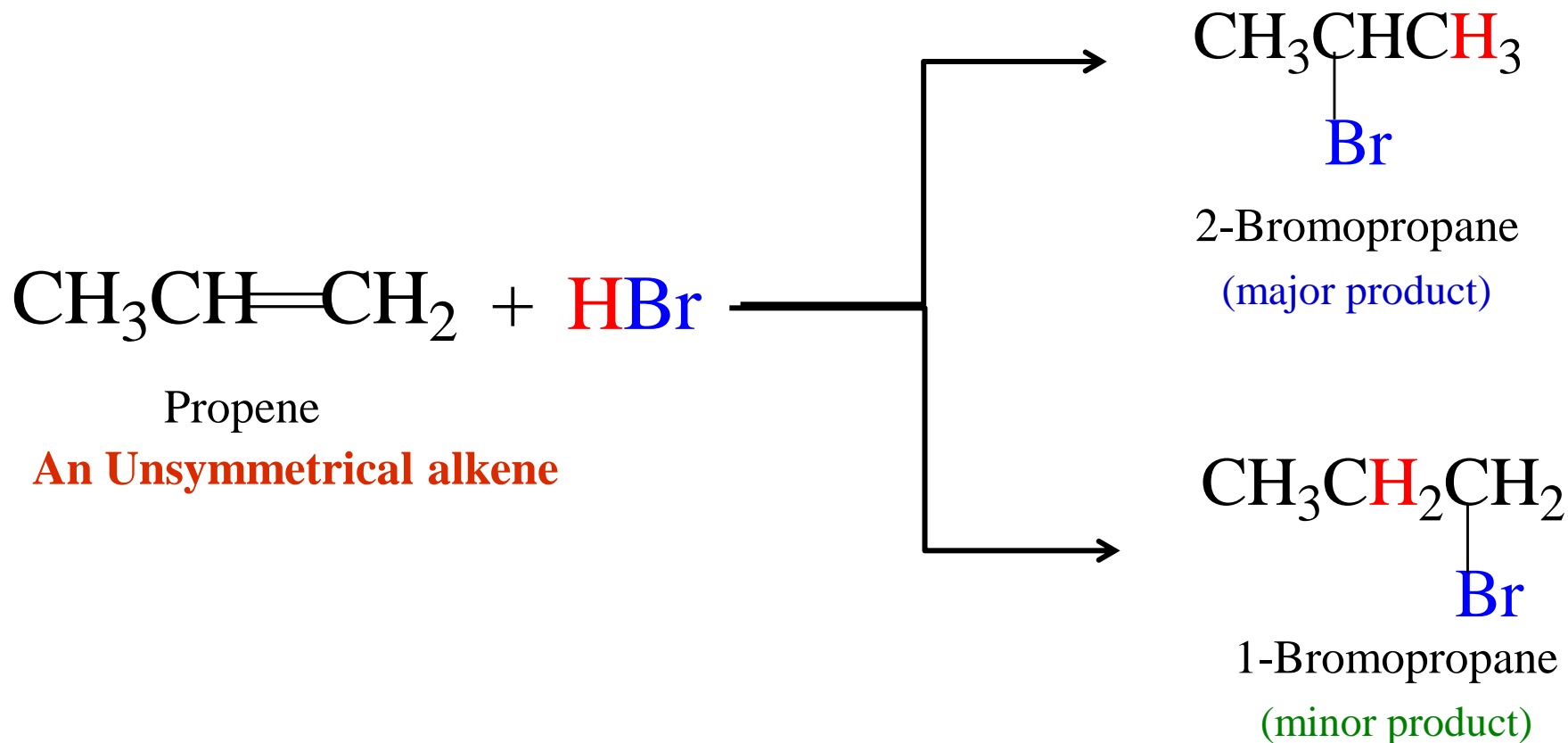
Example



Addition H-X; Case 2:

unsymmetrical alkenes

With **unsymmetrical alkenes**; such as Propene [$\text{RCH}=\text{CHR}'$] as ($\text{R} \neq \text{R}'$), the possibility exists for the **HX** to add in **two ways**.



Markovnikov's rule

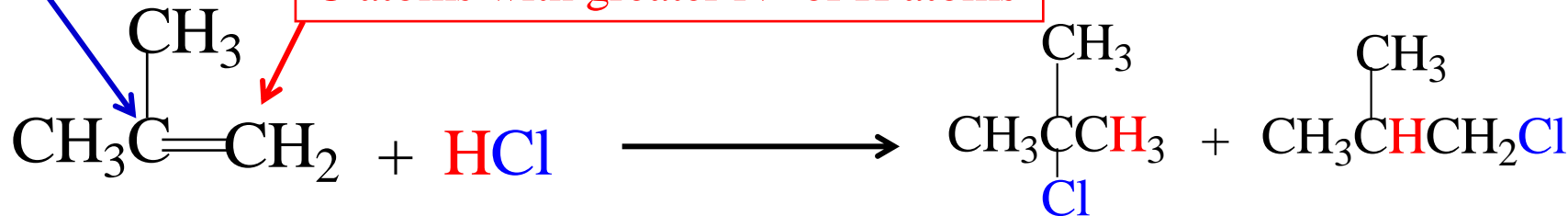
In this type of addition of $\text{H}-\text{X}$ to **unsymmetrical** alkenes

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

Examples

The X^- part
bonds up to the
other C,
or to the C rich
in substituents

C atoms with greater N° of H atoms



2-methyl propene

2-Chloro-2-methylpropane

1-Chloro-2-methylpropane

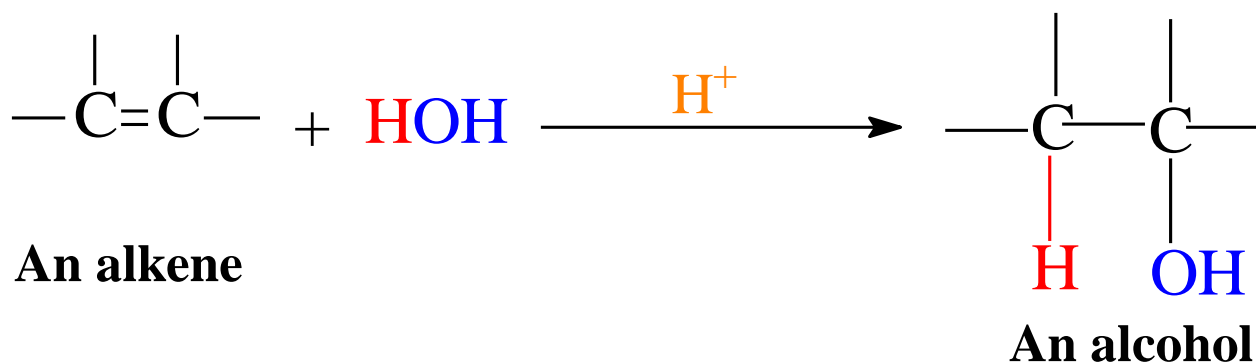
Major product

Minor product

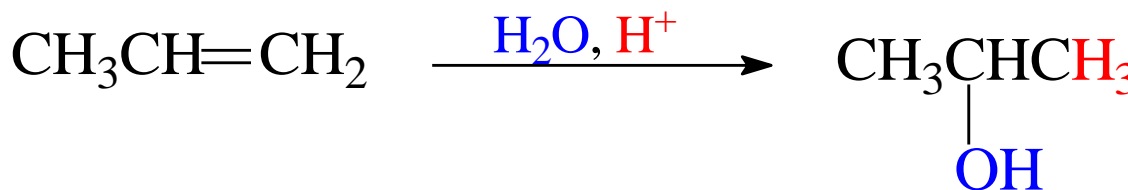
4. Addition of Water:(H₂O) Hydration

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



Propylene
(Propene)

Isopropyl alcohol
2-Propanol

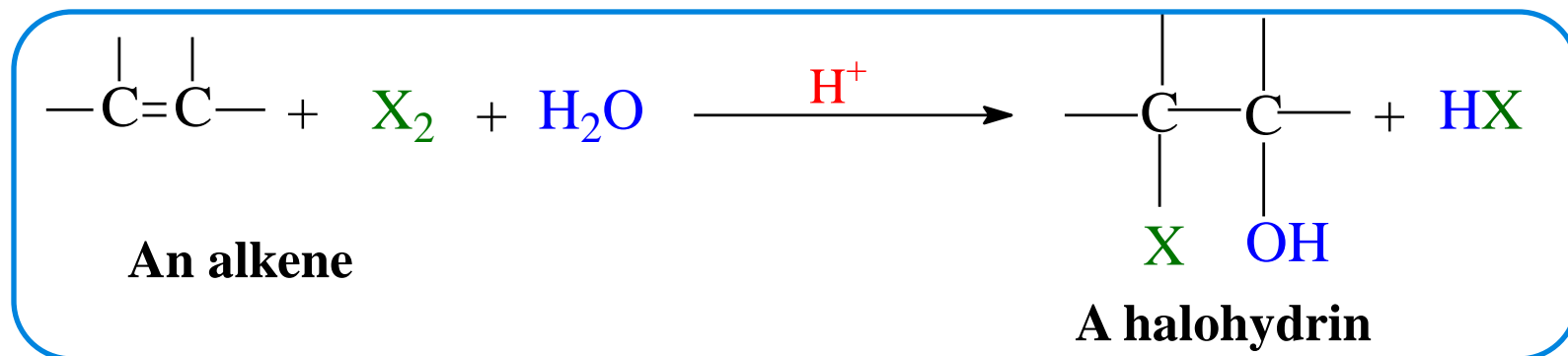
Note that,

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

5. Addition of HOX: Halohydrin formation

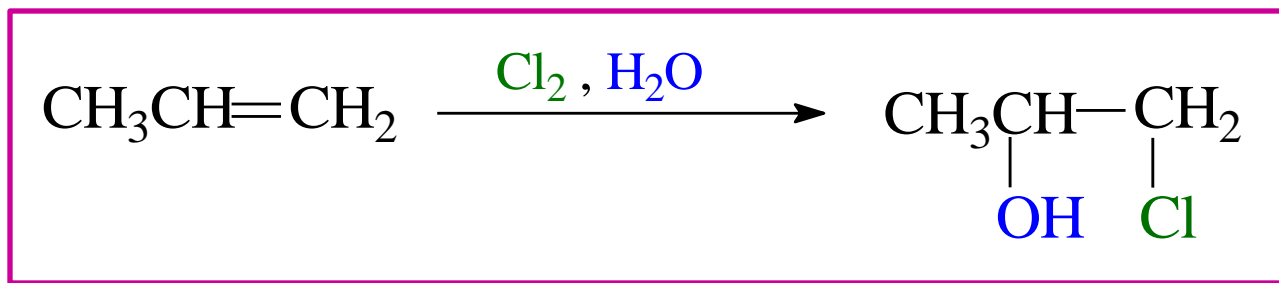
When an alkene is treated with **aqueous chlorine** or **aqueous bromine**, the addition product is a **halohydrin**. (when Cl_2 is used, the product is **chlorohydrin**; When Br_2 is used the product is a **bromohydrin**)

The General equation



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

Example



Propylene
(Propene)

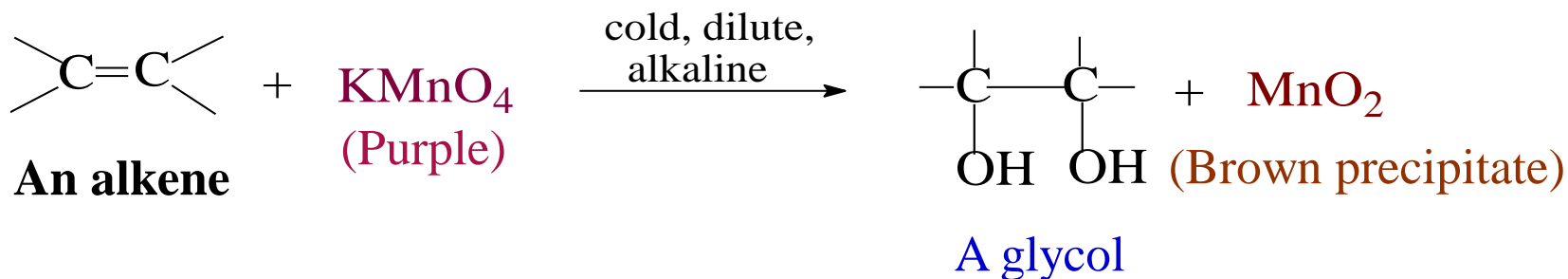
Propylene chlorohydrin
(1-Chloro-2-propanol)

6. 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 (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 (MnO_2) as the alkenes are being oxidized. This reaction is called *Baeyer test* for the unsaturation.

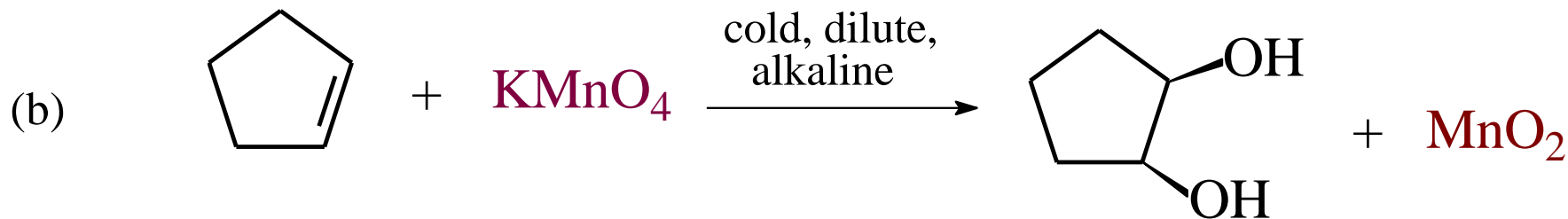
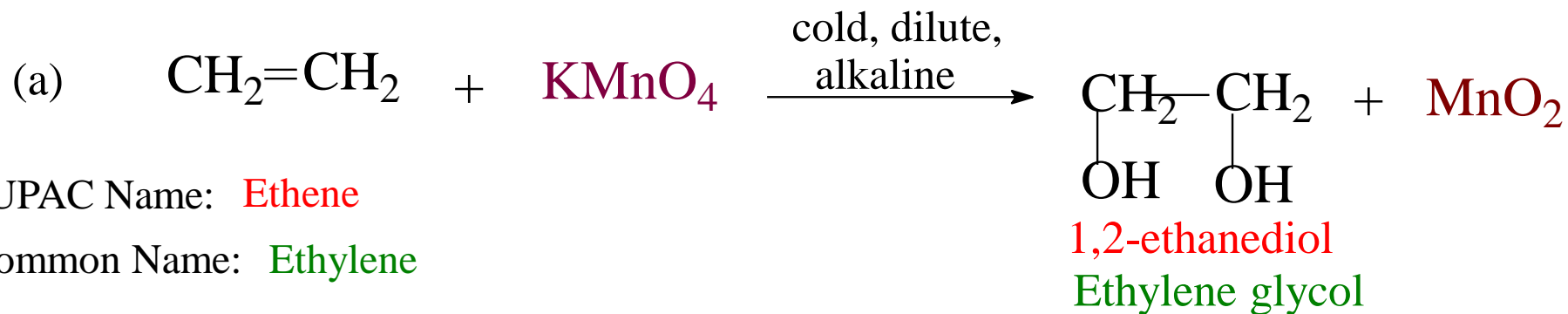
The General equation



The reaction conditions can be summarized as follows

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

Examples



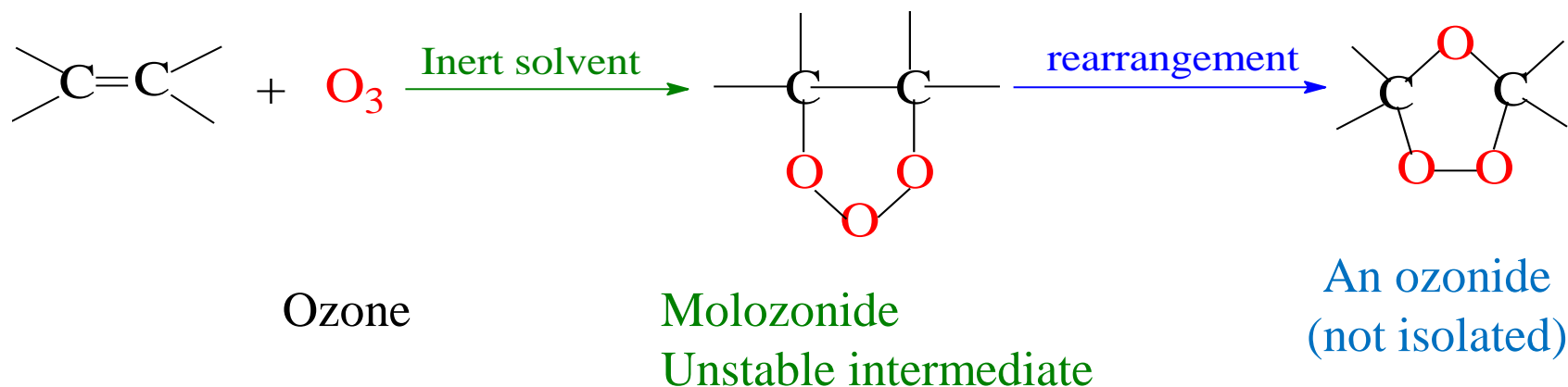
IUPAC Name: cyclopentene

Cis-1,2-cyclopentadiol

7. Ozonolysis (strong oxidation):

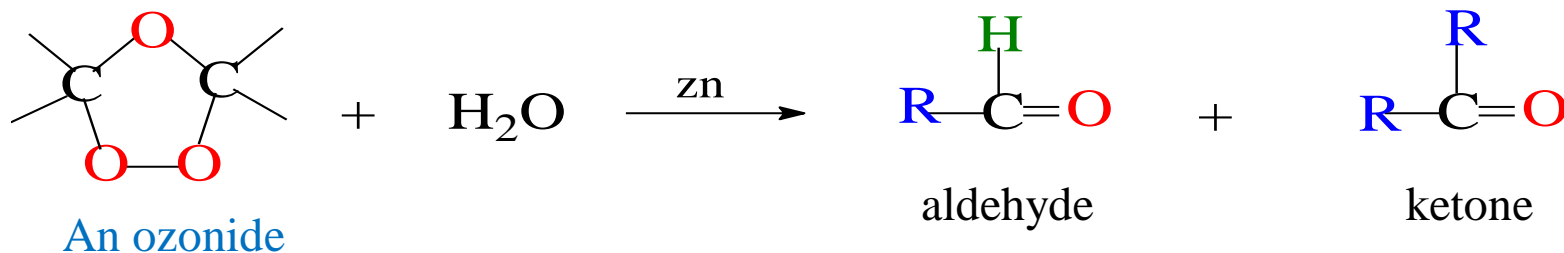
Oxidation of alkenes by **ozone** “O₃” leads to destruction of both the σ and π bonds of the double-bond system. This cleavage of an alkene double bond, generally accomplished in good yield, is called **ozonolysis**.

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**.

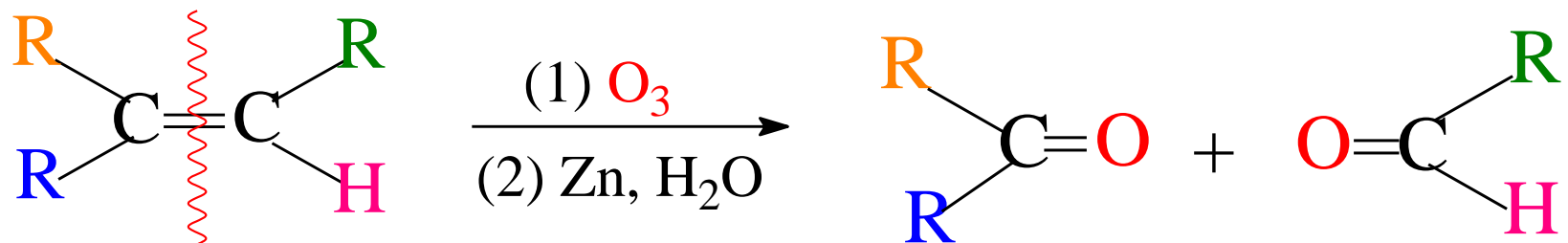


Examples

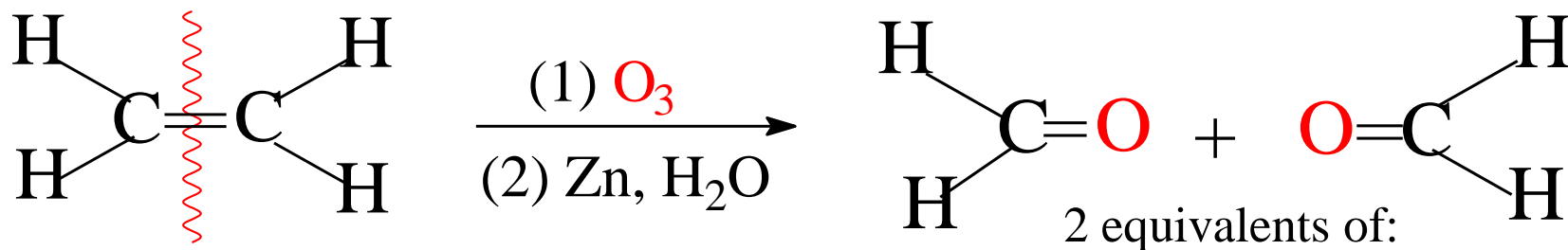
What would be the product of the reaction of each of the following with O_3 followed by $\text{Zn}/\text{H}_2\text{O}$?

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

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



(a) Ethene



IUPAC Name:

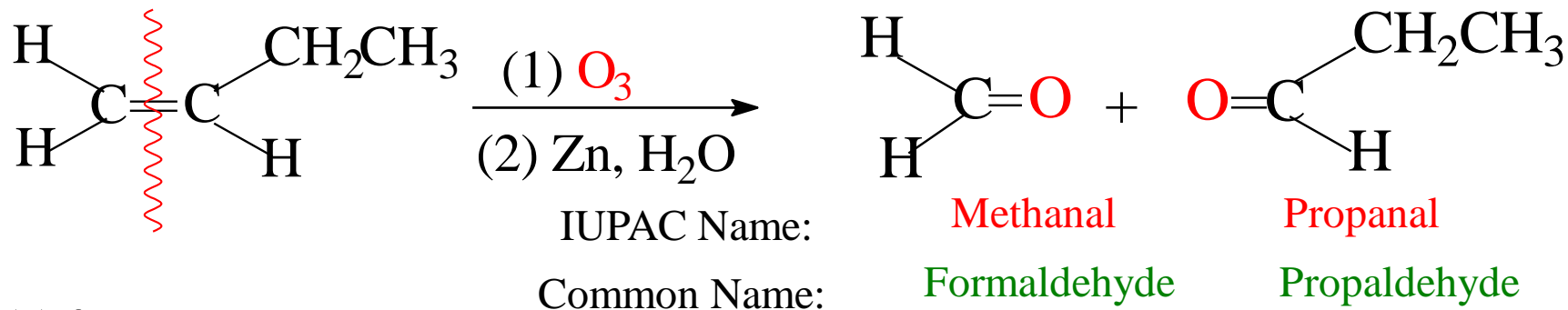
Common Name:

2 equivalents of:

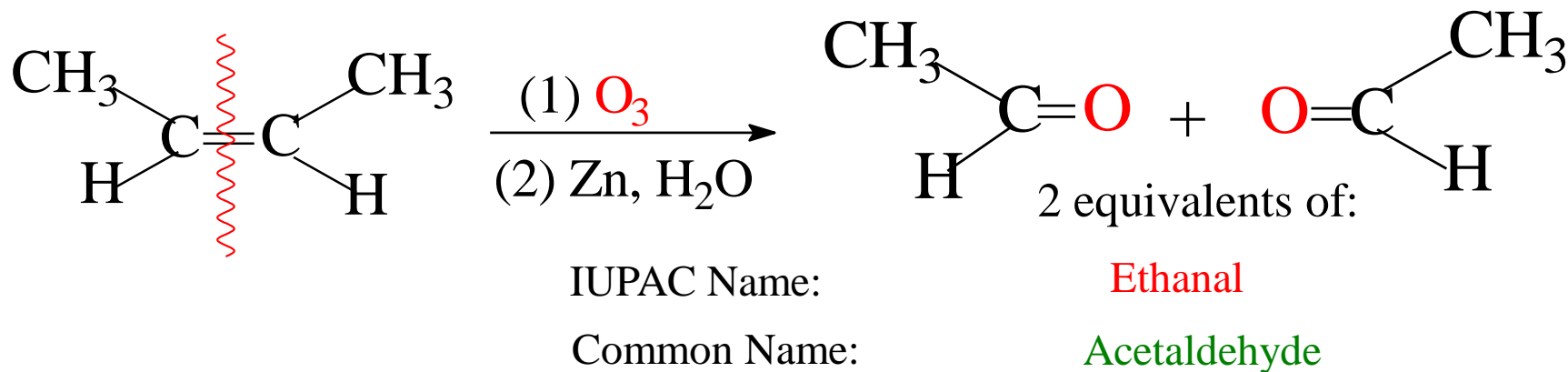
Methanal

Formaldehyde

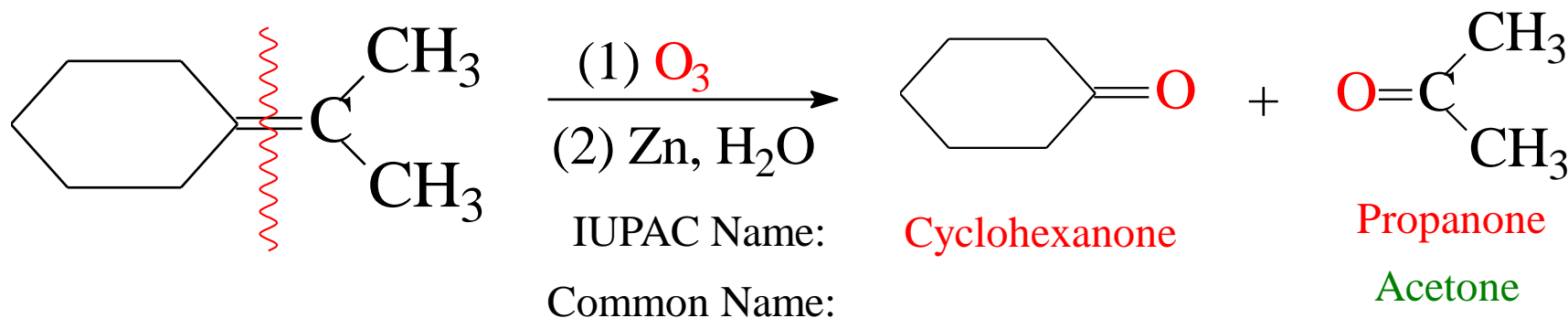
(b) 1-Butene



(c) 2-Butene



(d) Isopropylidenecyclohexane



THANK YOU

