

# *12.2 ALKENES*

# Learning Outcomes

- ❑ Describe alkenes
- ❑ Draw the structure and name the compound according IUPAC nomenclature
  - Straight chain ( $C_2 - C_{10}$ ) and branched alkenes ( $C_4 - C_{10}$ )
  - Cyclic alkenes ( $C_4 - C_6$ )
  - Simple dienes ( $C_4 - C_6$ )

# INTRODUCTION

- General formula :  $C_nH_{2n}$  ,  $n \geq 2$ .
- Functional group : double bond **C=C**
- carbon atom ( C=C ) : sp<sup>2</sup> hybridization
- **Unsaturated** hydrocarbon
- **Restricted rotation** causes cis-trans isomerism

# IUPAC NOMENCLATURE

Branched-chain alkanes are named according to the following rules:

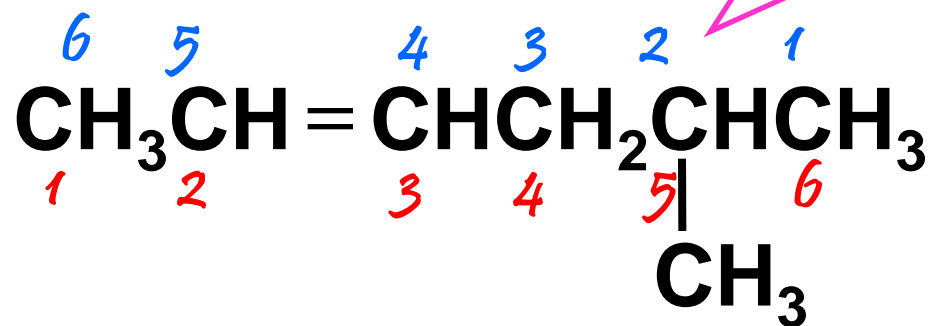
Rule 1: Identify the longest continuous chain (parent's name) that contain double bond, C=C. Change suffix **-ane** to **-ene**.

Rule 2: When the chain contains more than three carbon atoms, a number is need to indicate the location of the double bond. The chain is numbered starting from the end closest to the double bond.

# EXAMPLE:

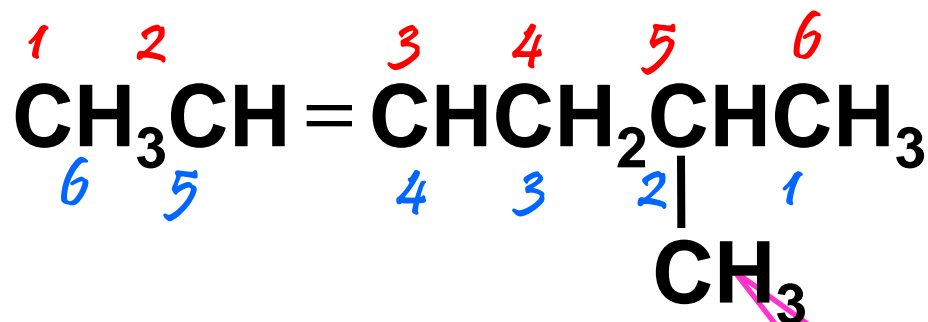
Parent's name:

2-*hexene*



Rule 3: Indicate the location of the substituent groups by the numbers of the carbon atoms to which they are attached.

EXAMPLE:



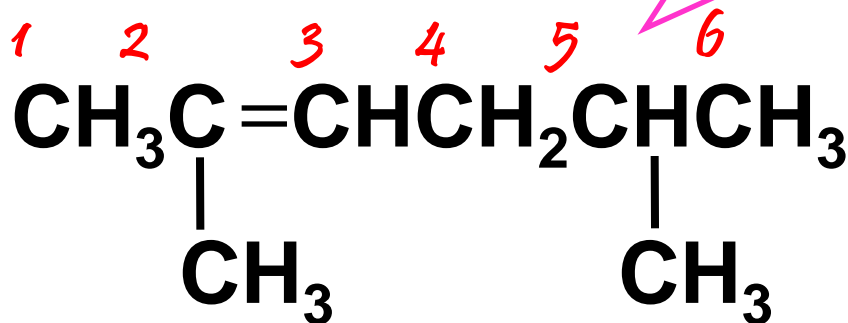
*5-methyl*

Substituent:  
*methyl at C5*  
*not at C2*

# PRACTISE 1:

Parent's name:

2-*hexene*



Substituent:

*methyl at C2*

Substituent:

*methyl at C5*

*2,5-dimethyl-2-hexene*

## Rule 4:

The ending of the alkenes with more than one double bond

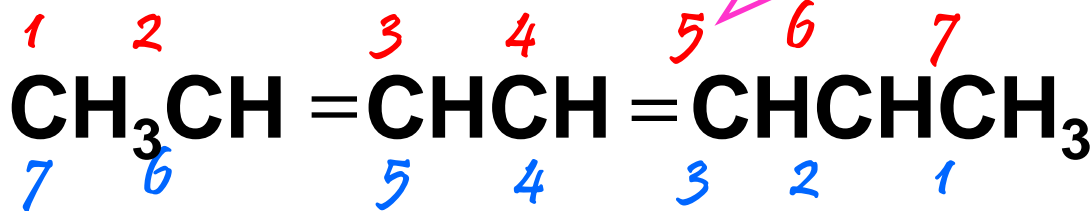
should be change from **ene** to

- **diene** (2 double bonds)
- **triene** (3 double bonds)

## EXAMPLE:

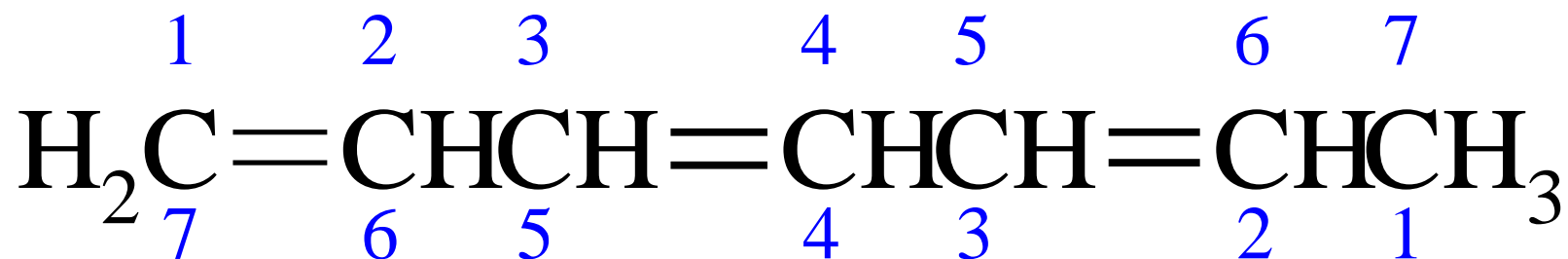
Parent's name:

2,4-*heptadiene*





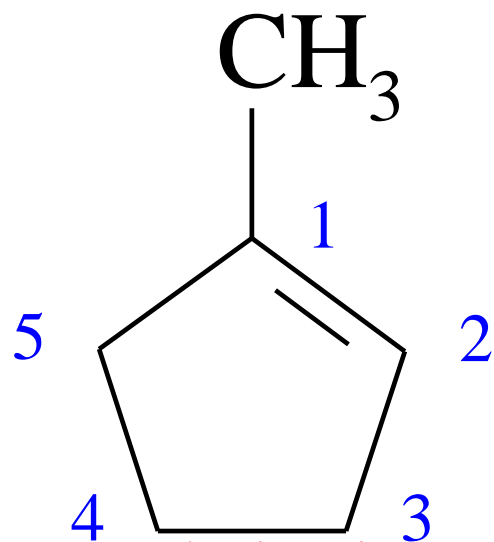
## EXAMPLE:



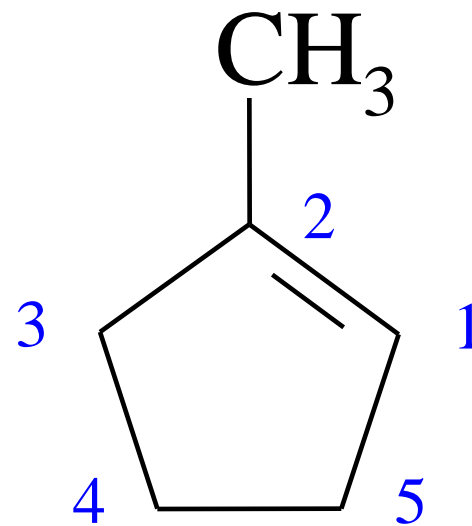
*1,3,5-heptatriene*  
*(not 2,4,6-heptatriene)*

Rule 5: In cycloalkenes; number the carbon atoms with a double bond as 1 and 2, in the direction that gives the substituent encountered first with a small number.

**EXAMPLE:**



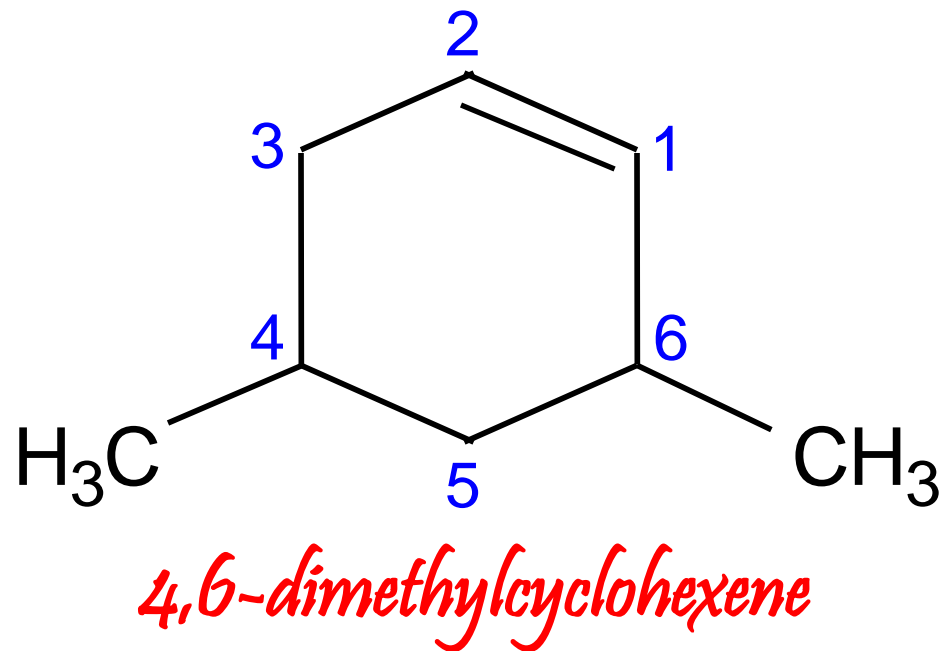
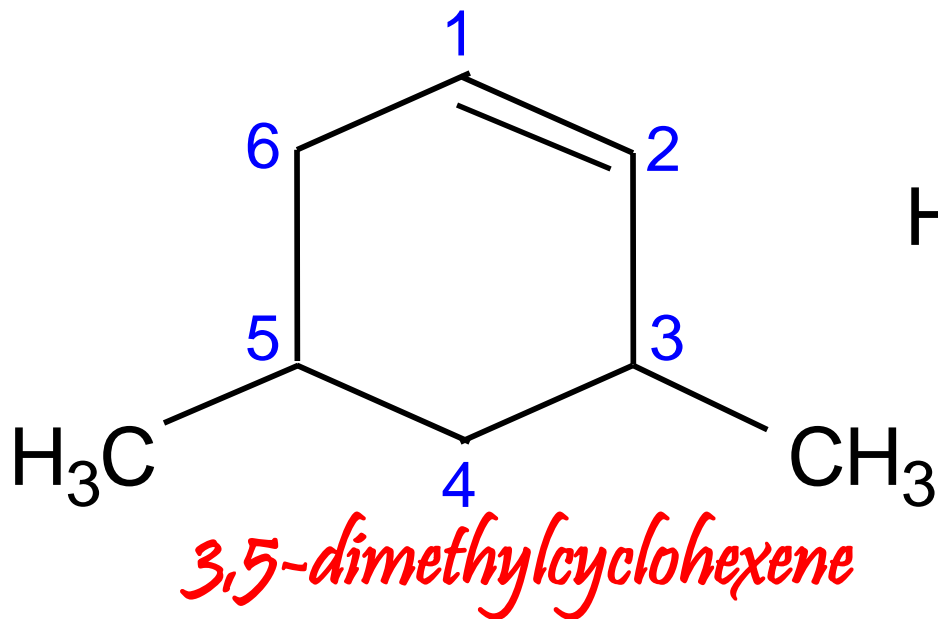
*1-methylcyclopentene*



*2-methylcyclopentene*

*1-methylcyclopentene*  
*(not 2-methylcyclopentene)*

# EXAMPLE:

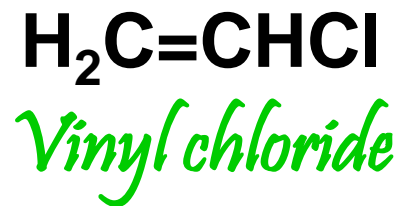


*3,5-dimethylcyclohexene*  
*(not 3,5-dimethylcyclohexene)*

Rule 6: Three frequently encountered **alkenyl** groups are **vinyl** group and **allyl** group.



as in

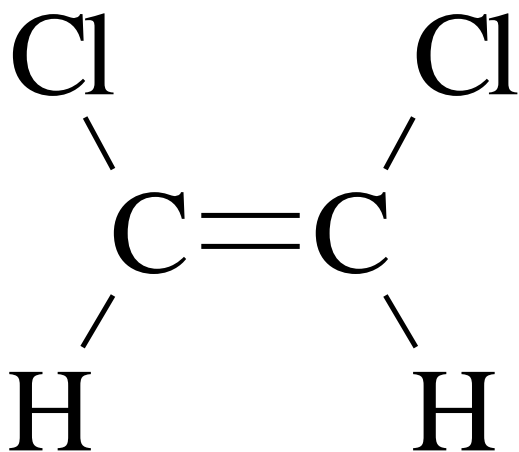


as in

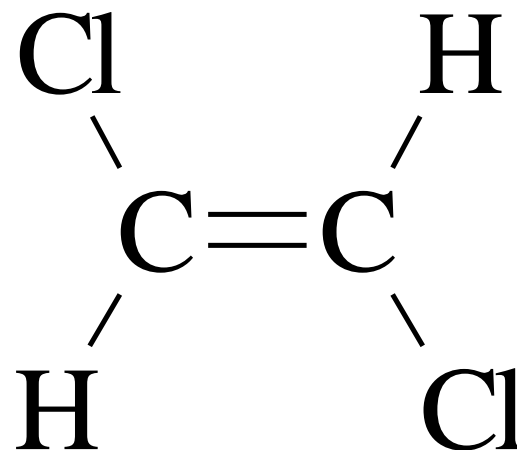


Rule 7: When two identical groups are attached:  
a) on the same side of the double bond, it is cis  
b) on the opposite sides of double bond, it is trans.

**EXAMPLE:**



*cis-1,2-dichloroethene*

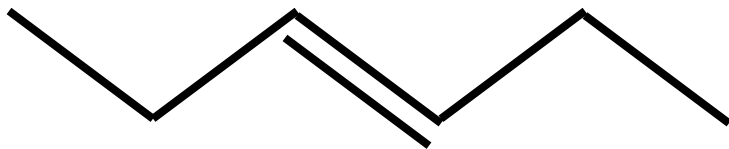


*trans-1,2-dichloroethene*

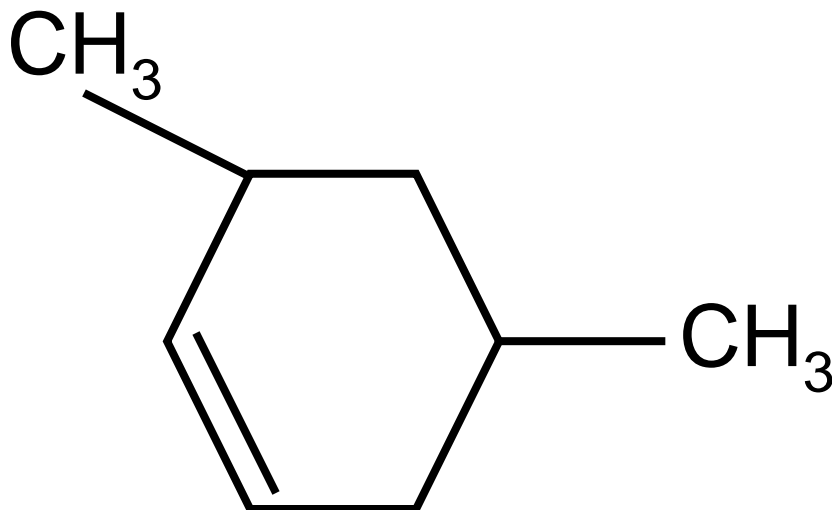
Exercise:

Give IUPAC names for the following alkenes

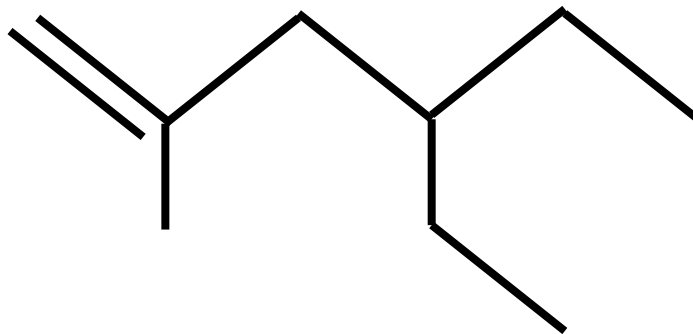
1)



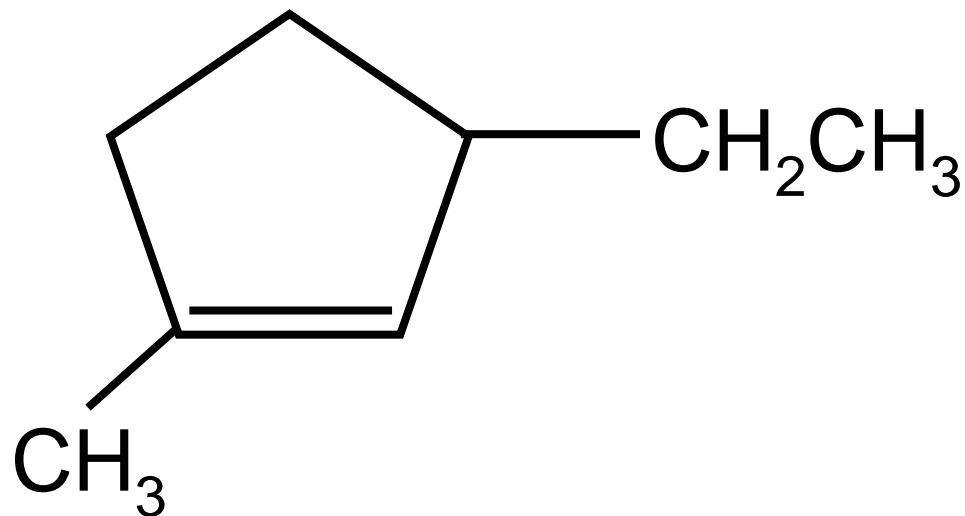
2)



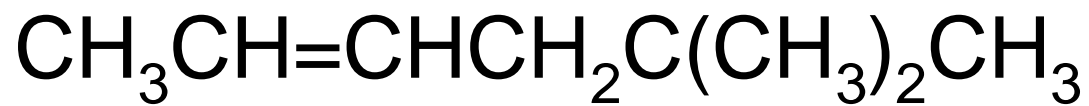
3)



4)



5)



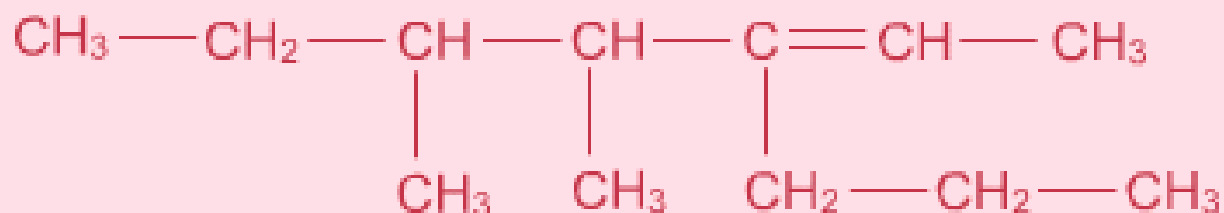
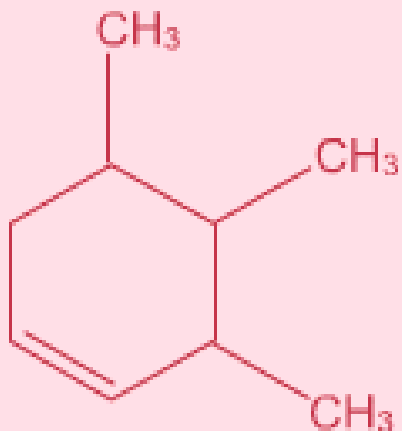
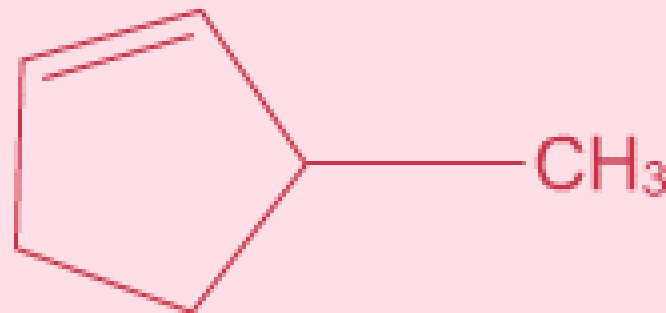
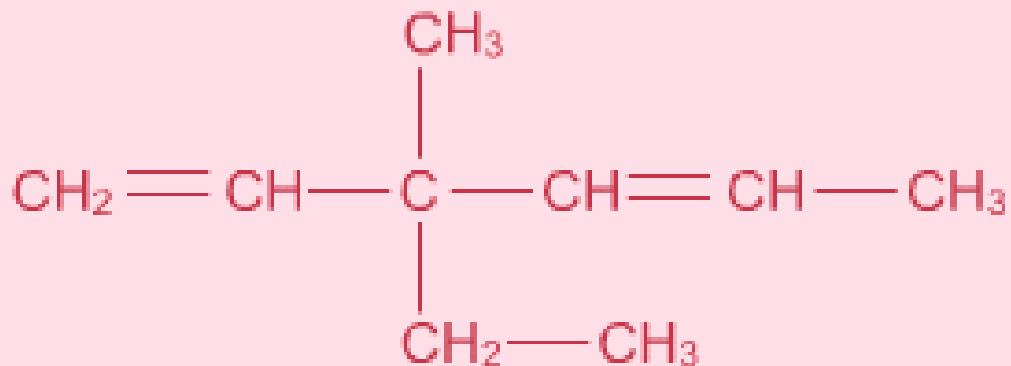
Answer:

1. 3-hexene
2. 3,5-dimethylcyclohexene
3. 4-ethyl-2-methylcyclohexene
4. 3-ethyl-1-methylcyclopentene
5. 5,5-dimethyl-2-hexene



## Exercise:

Give the IUPAC names of the following compounds



# Learning Outcomes

- ❑ Show the preparation of alkenes through:
  - Dehydration of alcohols
  - Dehydrohalogenation of haloalkanes
  
- ❑ Explain the reactivity of alkenes

# SYNTHESIS OF ALKENES

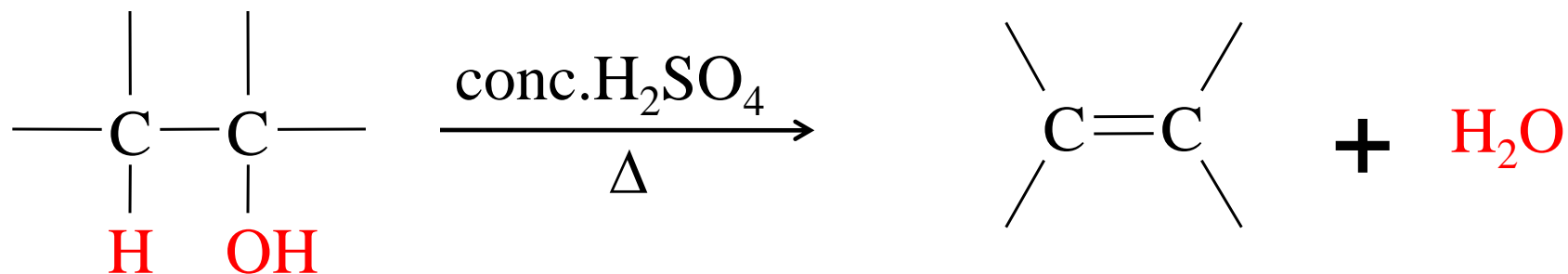
**Dehydration of  
alcohols**

**Dehydrohalogenation of  
haloalkanes**

# DEHYDRATION OF ALCOHOLS

- Alcohols react with strong acids in the presence of heat to form alkenes and water.

General reaction:

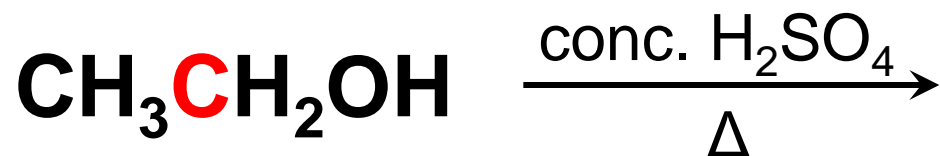


- ❑ Concentrated  $\text{H}_2\text{SO}_4$  / phosphoric acid ( $\text{H}_3\text{PO}_4$ ): act both as acidic catalysts and as dehydrating agents.

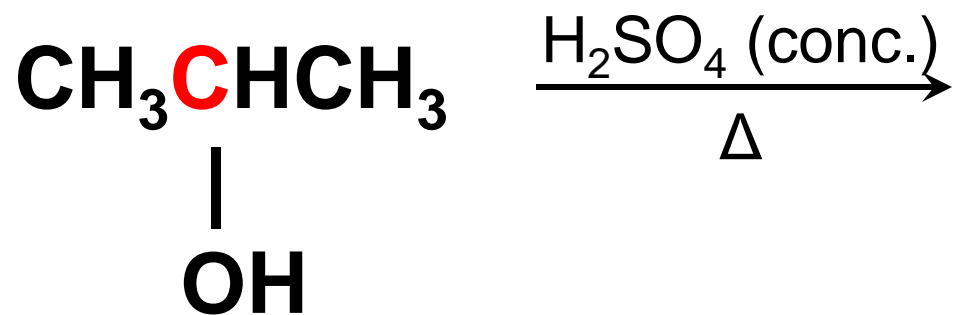
### Saytzeff's Rule:

- ❑ The *major product* is *the most stable alkenes*.
- ❑ The most stable is the alkene that has *greater number of alkyl group*.

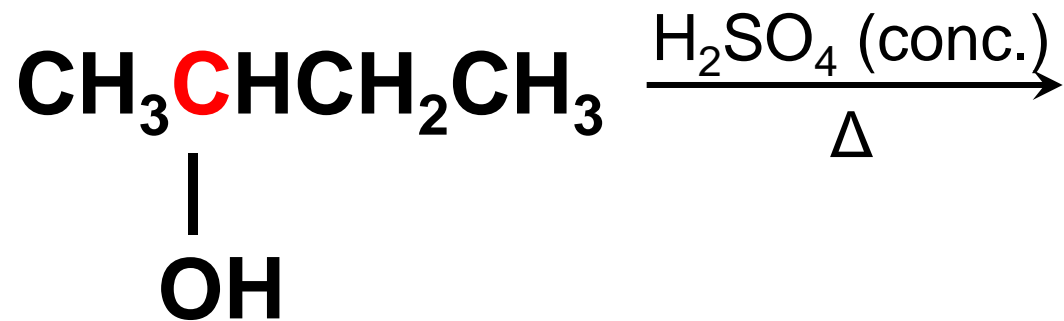
## EXAMPLE 1:



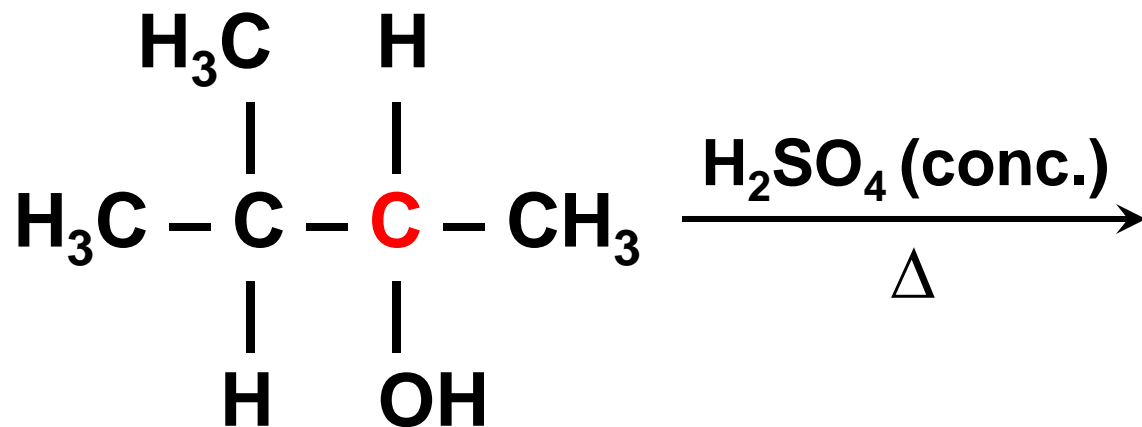
## EXAMPLE 2:



## EXAMPLE 3:

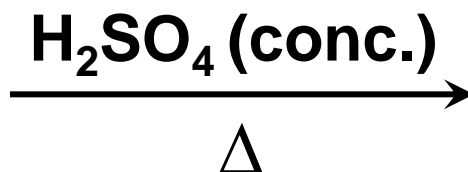
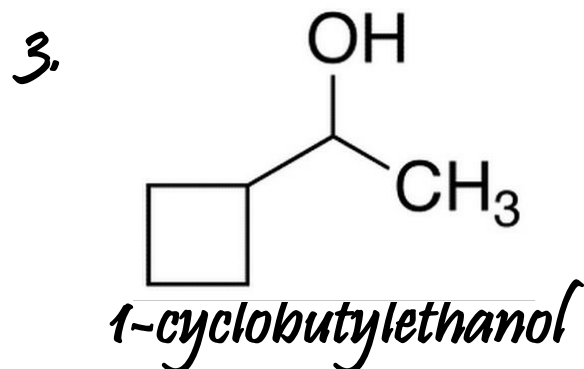
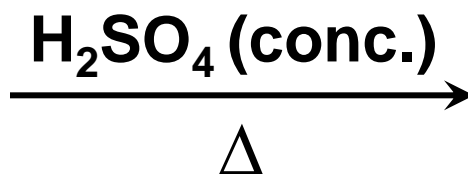
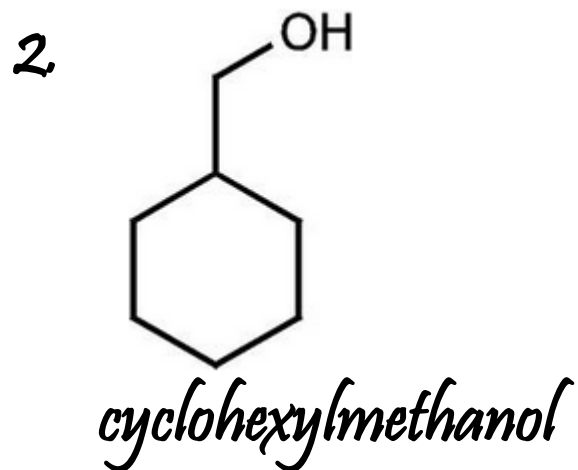
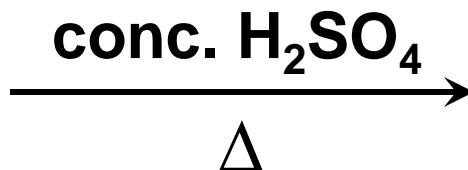
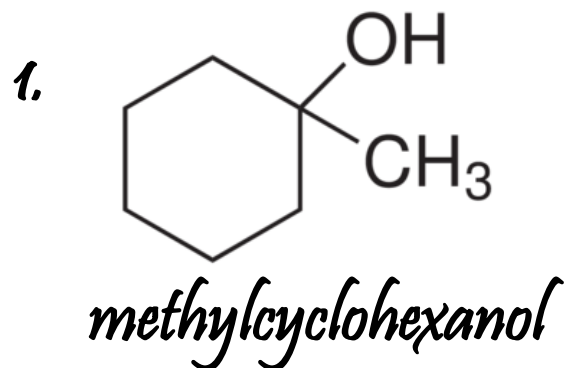


# PRACTISE 1:





# PRACTISE 2: Complete the reaction below.

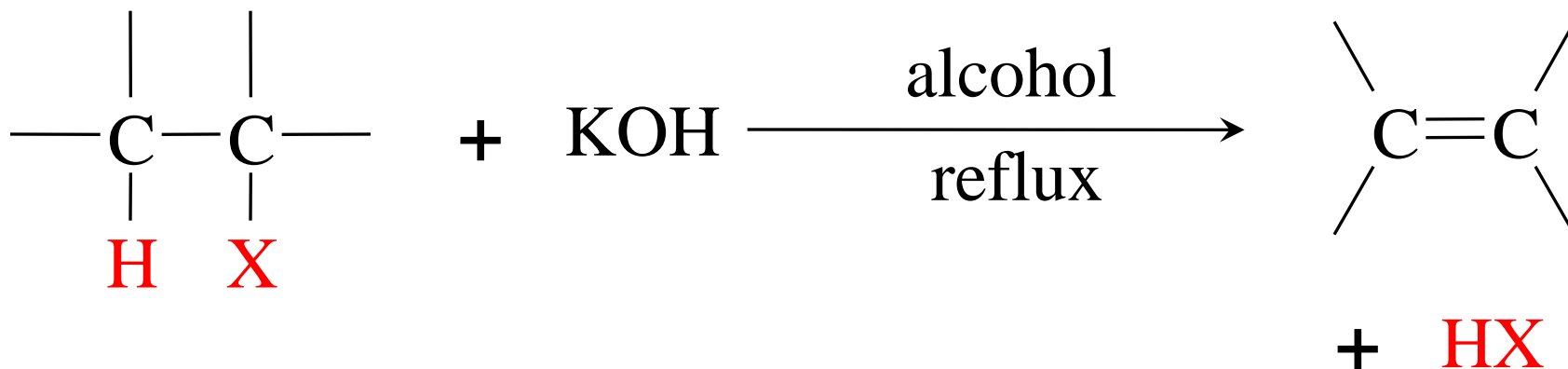


# DEHYDROHALOGENATION OF HALOALKANES

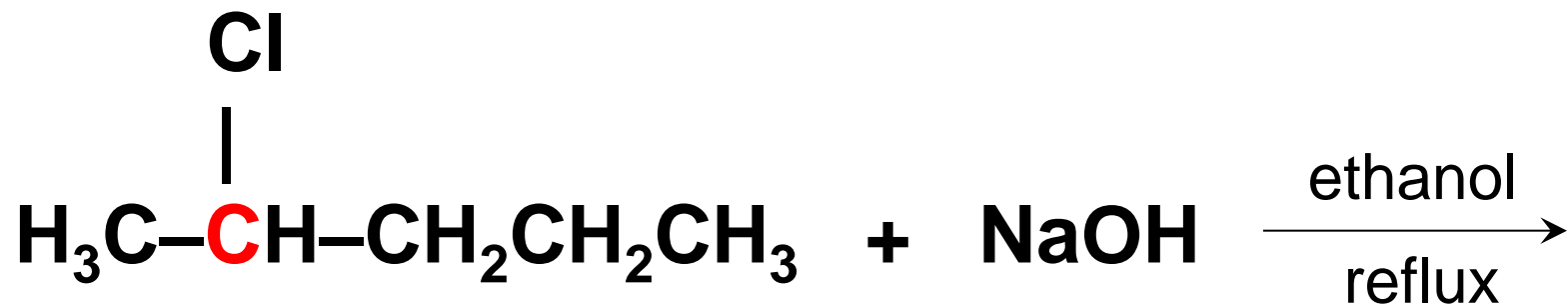
- **Elimination** of a hydrogen and a halogen from an alkyl halide to form an alkene.

**Saytzeff's rule** is used to determine the **major product**.

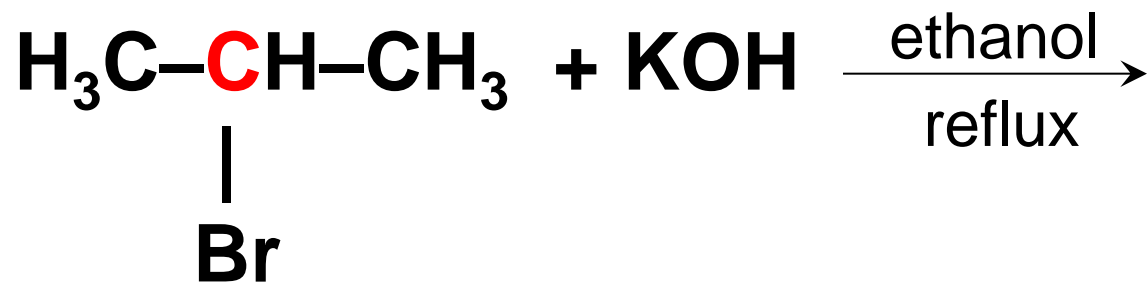
**General reaction:**



## EXAMPLE 4:

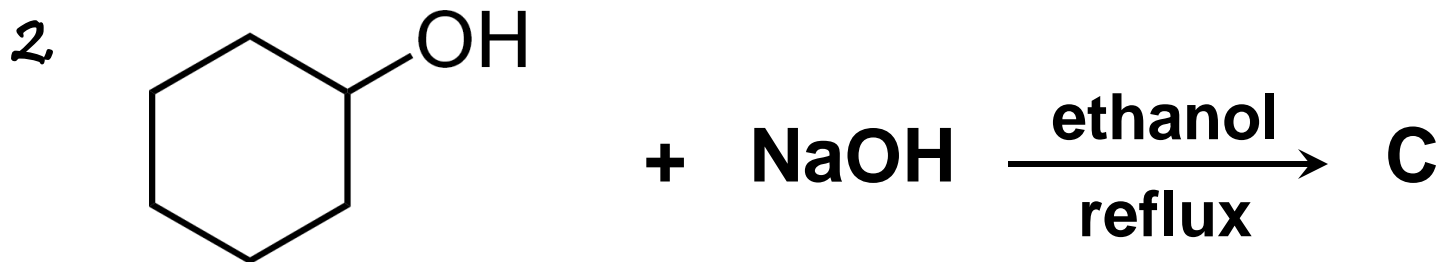
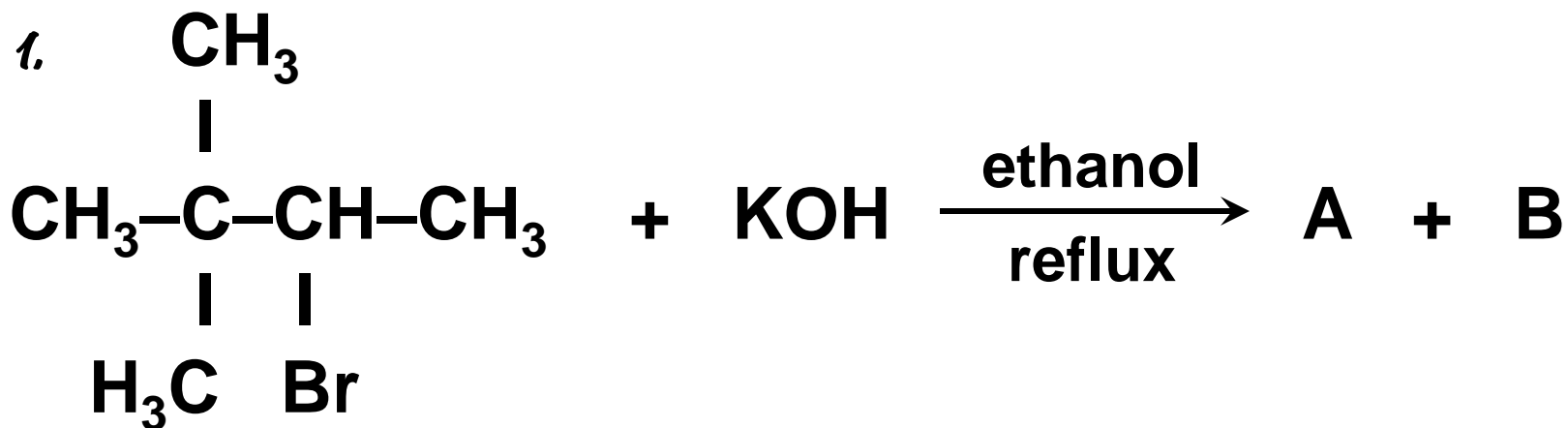


## EXAMPLE 5:



# PRACTISE 3:

Draw the structures of compound A ,B and C.



# COMPARISON OF THE REACTIVITY BETWEEN ALKANES & ALKENES

- ❑ Alkenes are more reactive compared to alkanes.
- ❑ Alkanes have carbon-carbon single bonds ( $\sigma$  bonds) while alkenes have carbon-carbon double bonds ( $\pi$  bonds).
- ❑ The double bond is a site of high electron density (nucleophilic).
- ❑ Therefore most alkenes reactions are electrophilic additions.

# CHEMICAL REACTION OF ALKENES

## Reaction of Alkenes

```
graph TD; A[Reaction of Alkenes] --> B[Electrophilic Addition]; A --> C[Oxidation Reaction]
```

### Electrophilic Addition

- Hydrogenation
- Halogenation
  - In inert solvent ( $\text{CH}_2\text{Cl}_2$ )
  - In aqueous solution ( $\text{H}_2\text{O}$ )
- Hydrohalogenation
  - Markovnikov's Rule
- Hydration
- Addition of  $\text{H}_2\text{SO}_4$

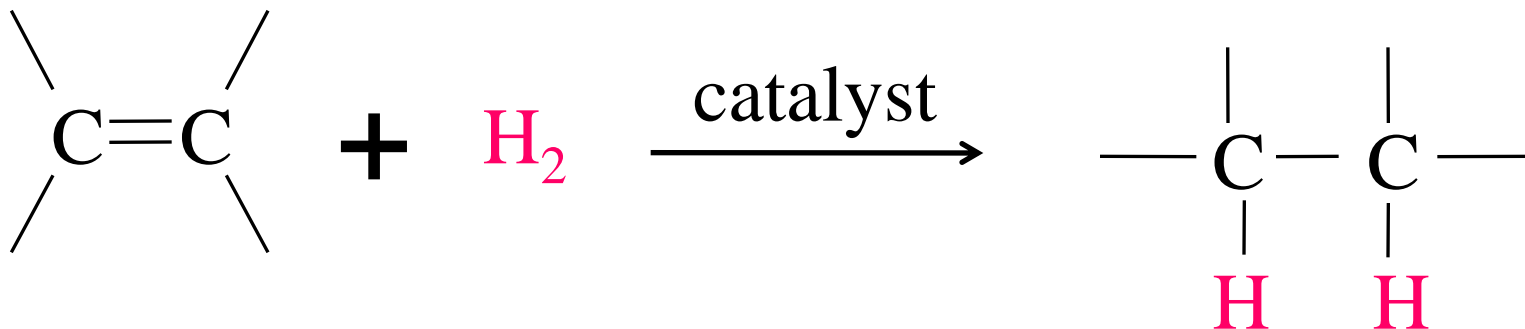
### Oxidation Reaction

- With cold & dilute  $\text{KMnO}_4$

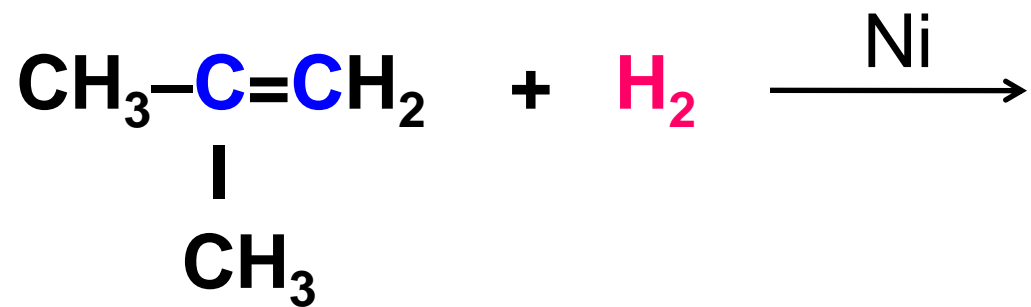
# HYDROGENATION

- Reaction of an **alkene** with **hydrogen** in the presence of **catalyst** (platinum, nickel or palladium) to form alkane.

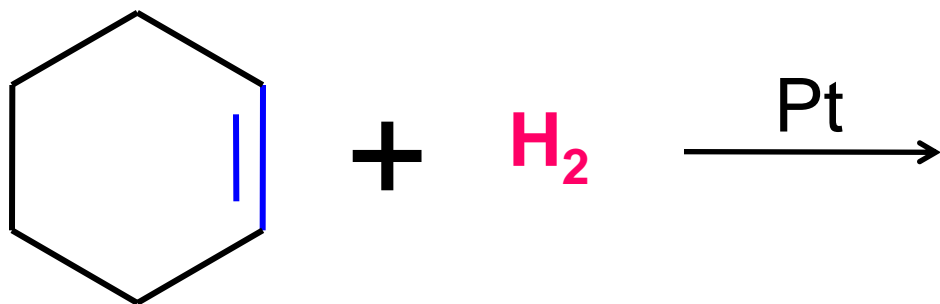
General reaction:



## EXAMPLE 6:



## EXAMPLE 7:

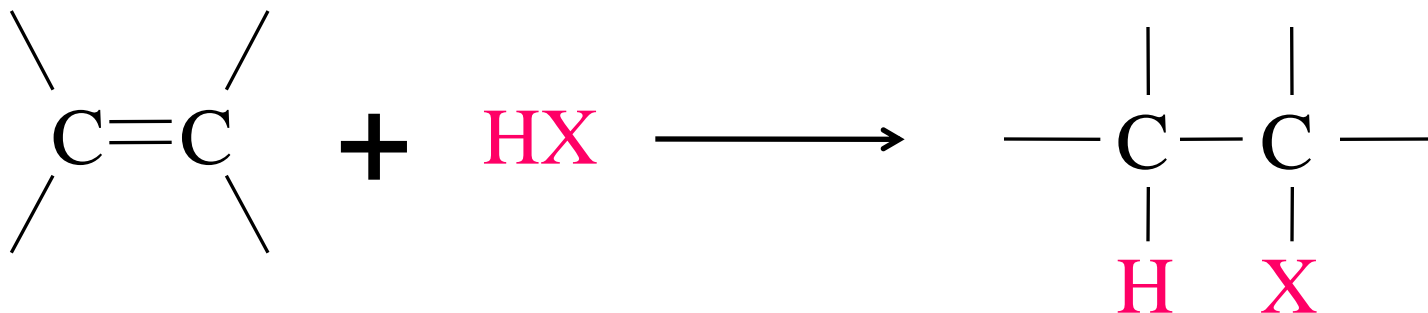




# HYDROHALOGENATION: Markovnikov's Rule

- ❑ Hydrogen halides (HF, HCl, HBr and HI) add to the double bond of alkenes to form haloalkanes.
- ❑ The addition of **HX** to an **unsymmetrical alkenes**, follows **Markovnikov's rule**.

General reaction:



# MARKOVNIKOV'S RULE

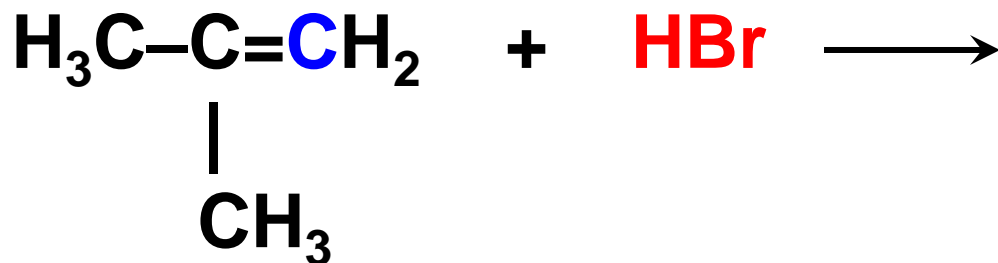
In the addition of HX to an alkenes, the **hydrogen atom** adds to the carbon atom of the double bond that **already has the greater number of hydrogen atoms.**

The addition of **HBr** to **propene**, could conceivably lead to either **1-bromopropane** or **2-bromopropane**.



The **main product**, however, is **2-bromopropane**

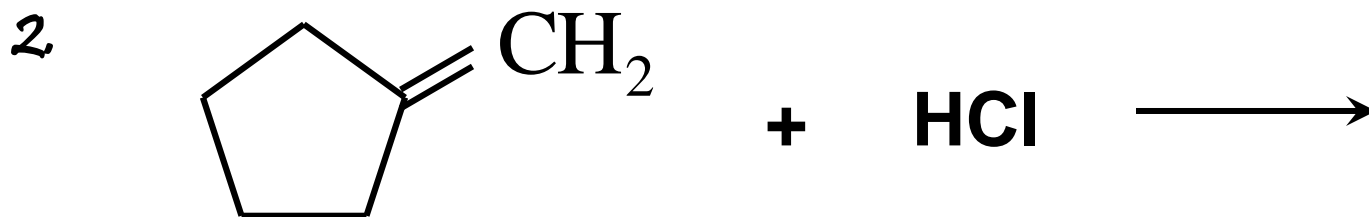
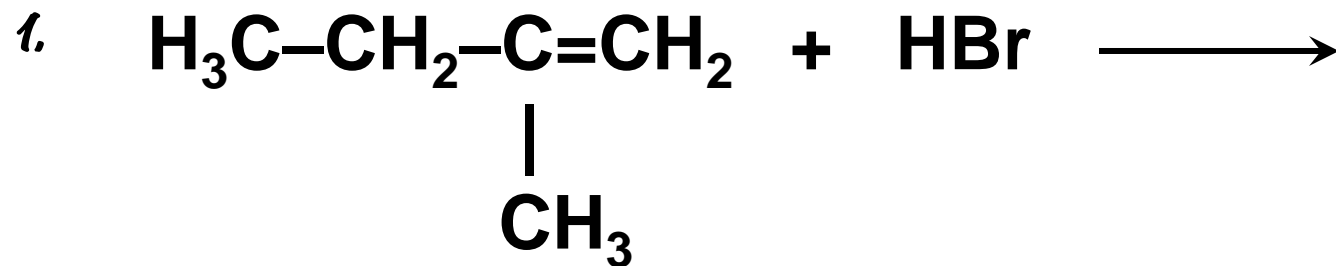
When **2-methylpropene** reacts with HBr, the main product is 2-bromo-2-methylpropane, not 1-bromo-2-methylpropane.



The addition of **HX** to an **unsymmetrical alkenes**, yield the main product according to the **Markovnikov's rule**.

# PRACTISE 4:

Complete the following reactions:

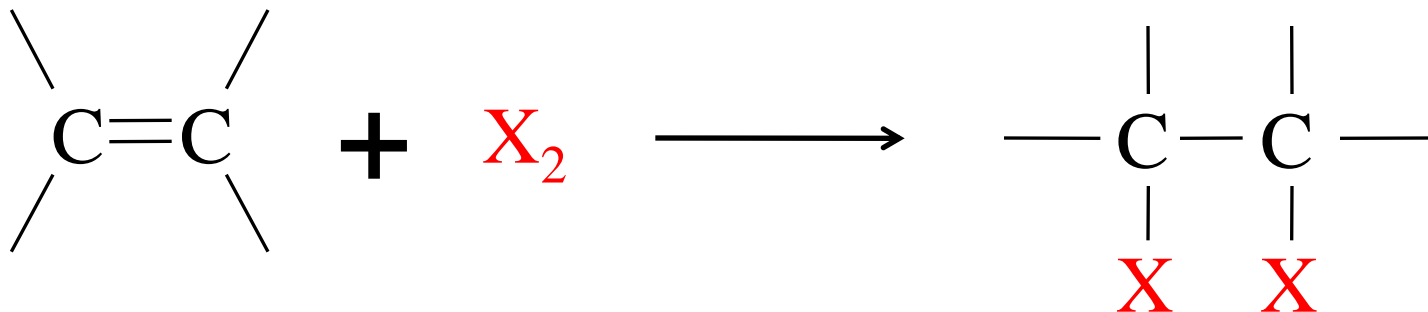


# HALOGENATION OF ALKENES

## i. In inert solvent ( $\text{CH}_2\text{Cl}_2$ )

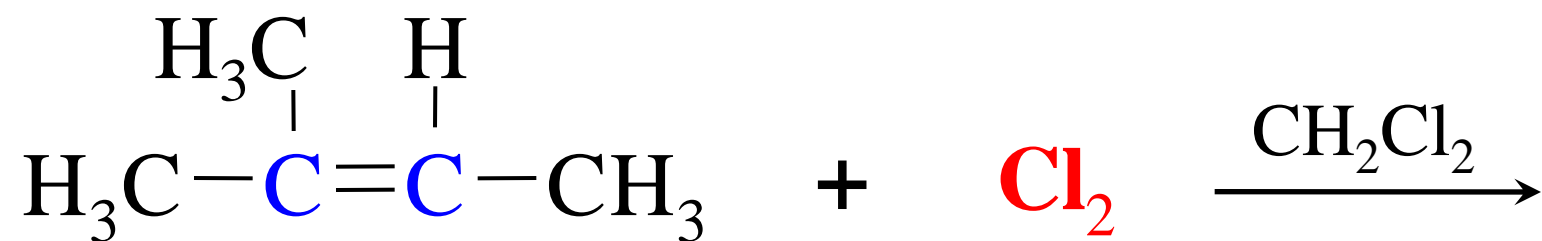
- Alkenes react rapidly with chlorine or bromine in  $\text{CH}_2\text{Cl}_2$  at room temperature to form **visinal dihalides**.

General reaction:



**Visinal dihalide**

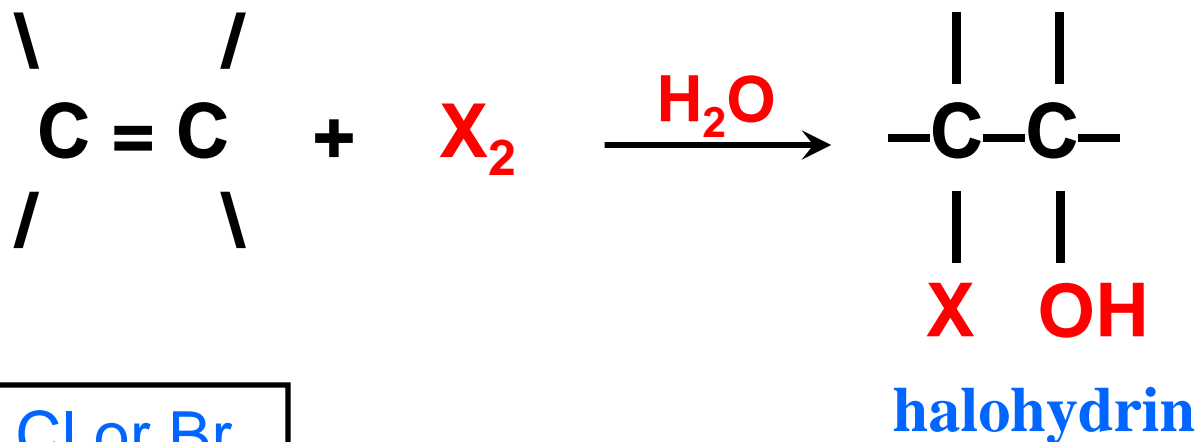
## EXAMPLE 8:



## ii. In aqueous/water (Halohydrin Formation)

- If the halogenation of an alkene is carried out in aqueous solution, the **major product** of the overall reaction is a haloalcohol called a **halohydrin**.
- For **unsymmetrical**, the halogen ends up on the carbon atom with the **greater number of hydrogen atoms**.

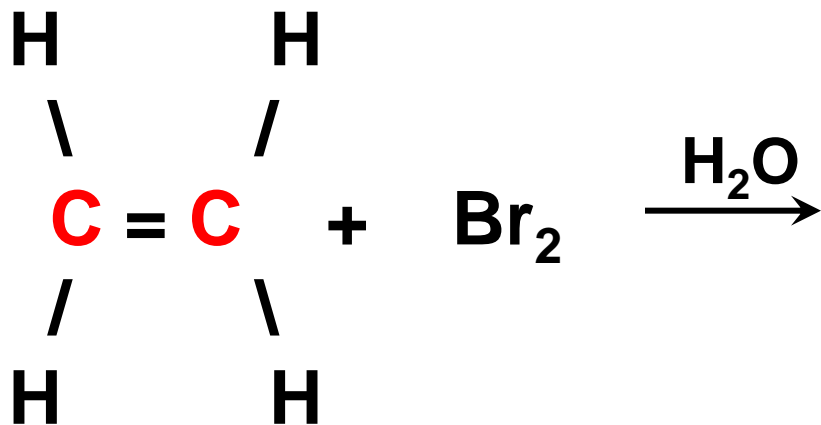
General reaction:



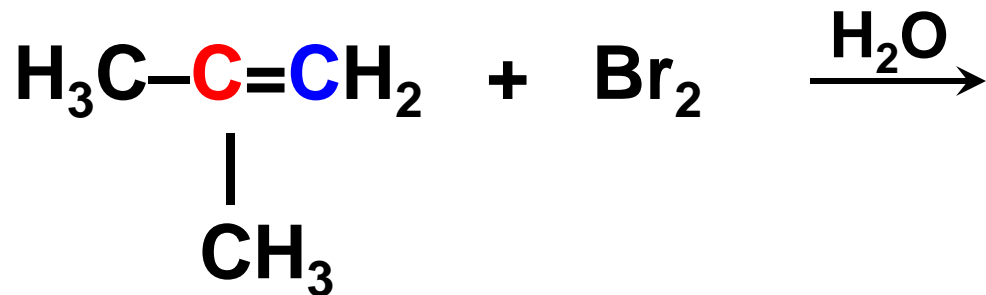
$\text{X}_2 = \text{Cl or Br}$



## EXAMPLE 9:

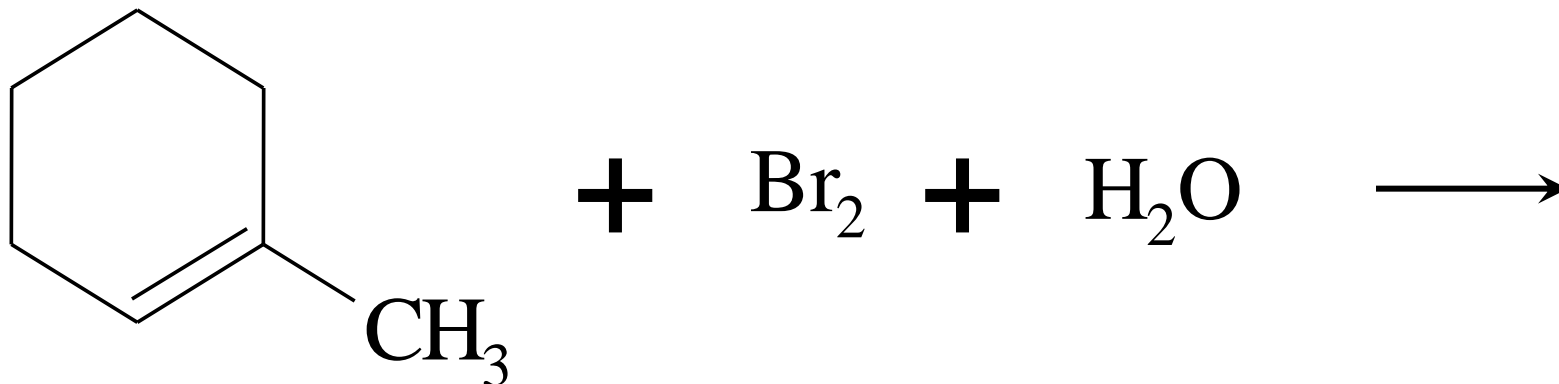


## EXAMPLE 10:



# PRACTISE 1:

Complete the following reaction and name the organic product formed.

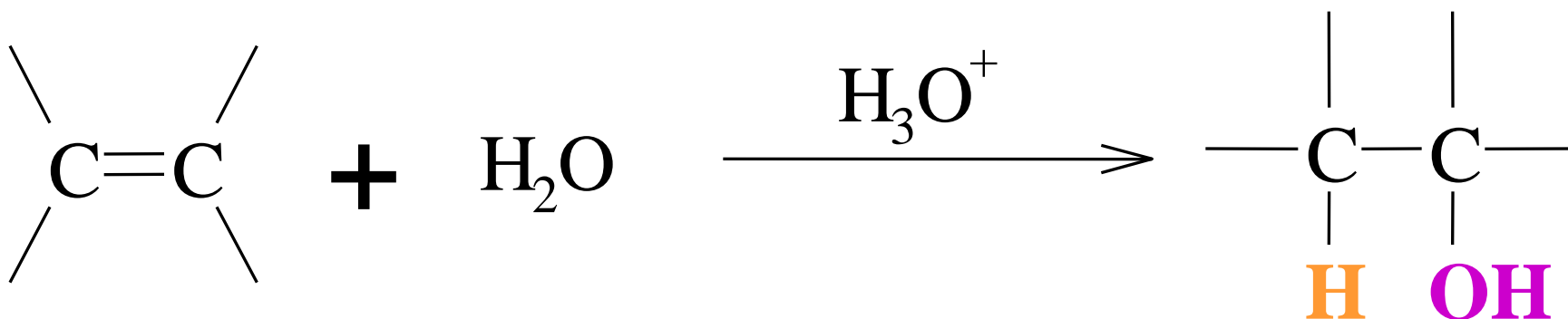


# HYDRATION OF ALKENES

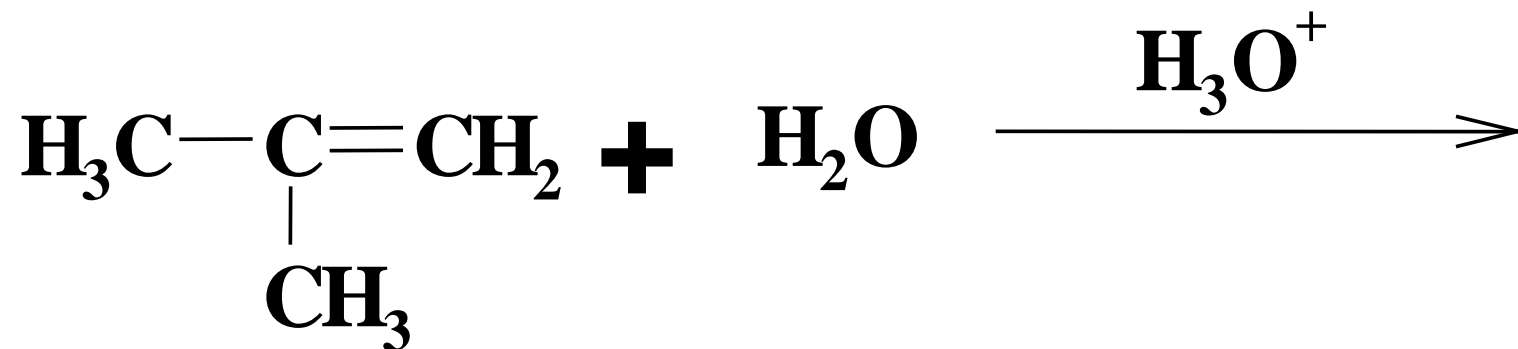
- ❑ The acid-catalyzed addition of water to the double bond of an alkene (hydration of an alkene) is a method for the preparation of low molecular weight alcohols.
- ❑ The most commonly acid used to catalyze the hydration of alkenes are dilute solution of  $\text{H}_2\text{SO}_4$  &  $\text{H}_3\text{PO}_4$ .

- The addition of water to the double bond follows **Markovnikov's rule**.

**General reaction:**



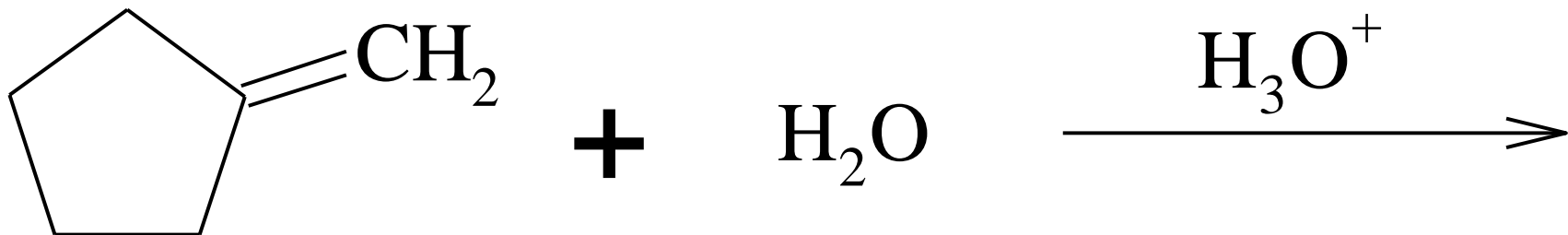
# EXAMPLE 11:



# PRACTISE 5:

Complete the following reactions:

1.



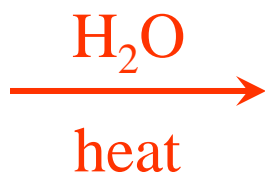
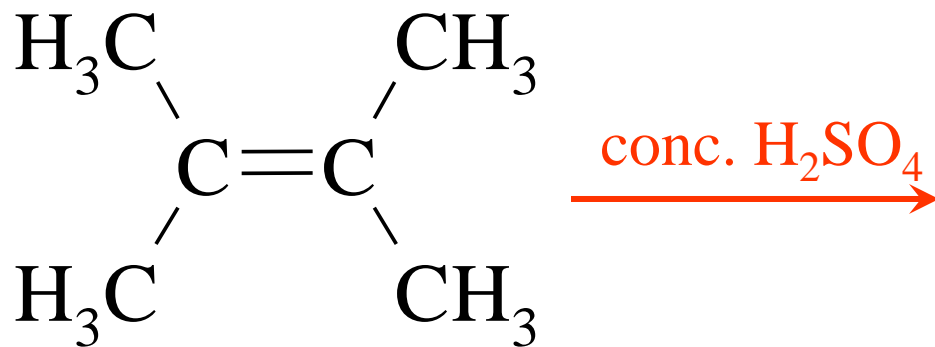
2.



# ADDITION OF SULPHURIC ACID TO ALKENES

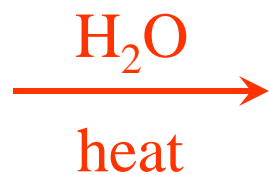
- Alkenes dissolve in concentrated sulphuric acid to form **alkyl hydrogen sulphates**.
- Alkyl hydrogen sulfates can be easily **hydrolyzed to alcohols** by heating them with water.
- The overall result of the addition of sulphuric acid to alkenes followed by hydrolysis is the **Markovnikov addition of -H and -OH**.

# EXAMPLE 12:

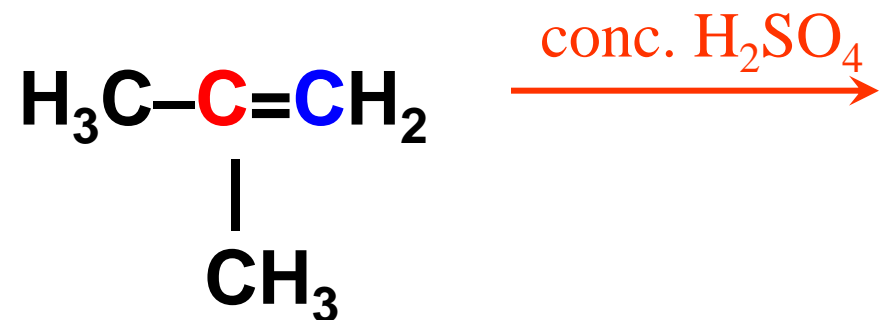




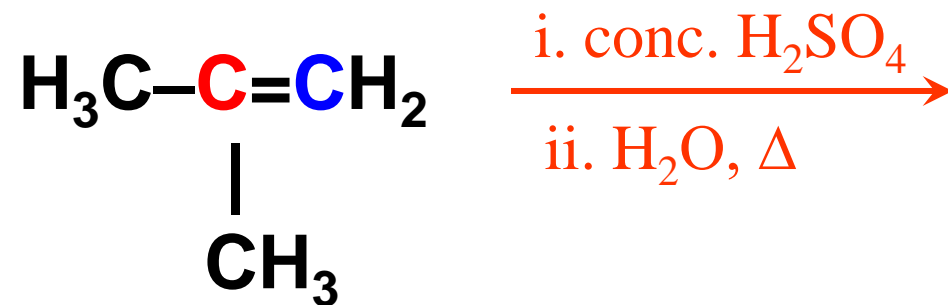
# EXAMPLE 13:



## EXAMPLE 14:



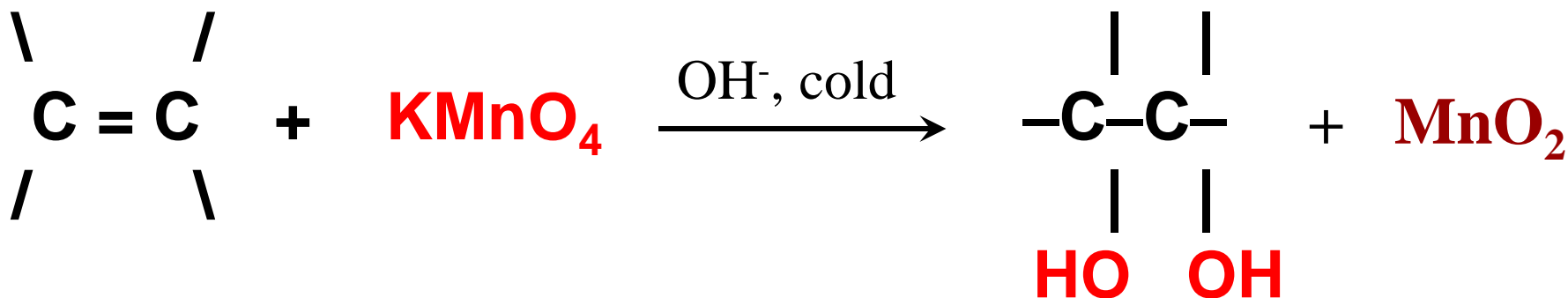
## EXAMPLE 15:



# OXIDATION OF ALKENES

- With cold and dilute potassium permanganate,  $\text{KMnO}_4$
- Potassium permanganate in base can be used to oxidize alkenes to **1,2-diols (glycols)**.

General reaction:



## EXAMPLE 16:

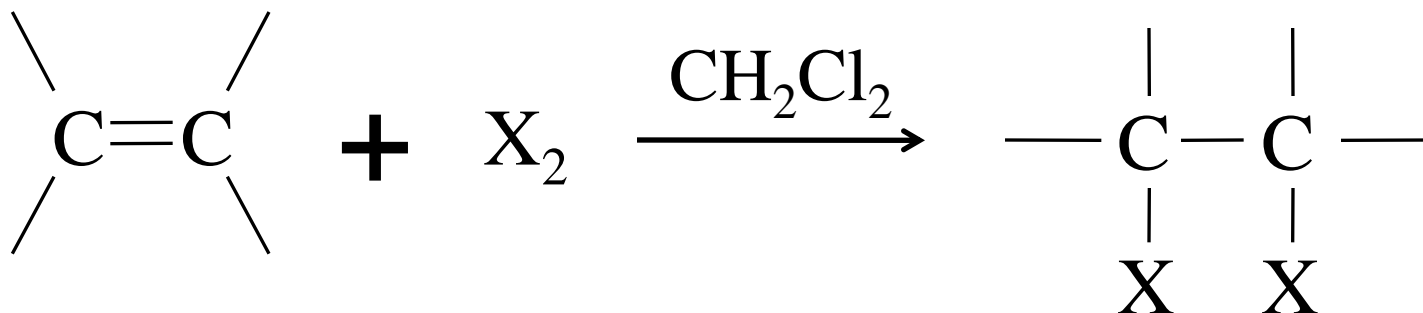


# UNSATURATION TEST FOR ALKENE

- A test for the presence of carbon-carbon double bonds.
- Used to differentiate between alkene and another compound.
- Experiment used to distinguish between 2 compound:
  - Baeyer's Test using cold and dilute alkaline (refer oxidation reaction)
  - Reaction with bromine in  $\text{CH}_2\text{Cl}_2$  (refer halogenation in inert solvent)
  - Reaction with bromine water (refer halogenation in aqueous/water)

# Reaction with bromine in $\text{CH}_2\text{Cl}_2$

*Unsaturation Test: Bromine Test*

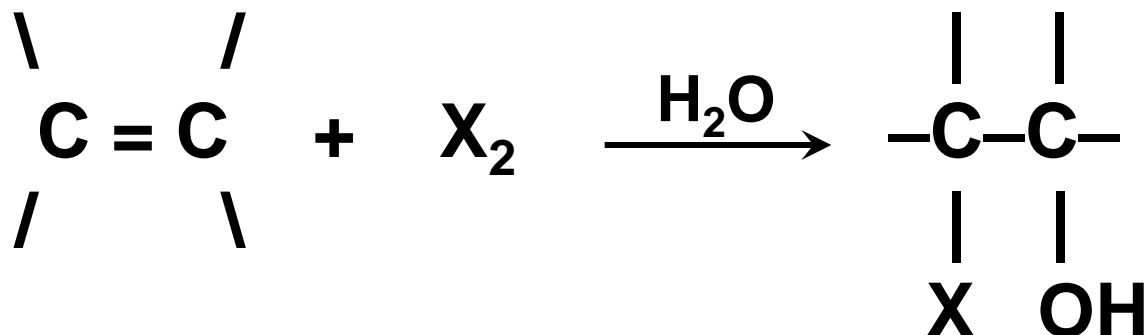


**Visinal dihalide**

- Observation: **Reddish brown colour** of bromine decolourised.

# Reaction with bromine in aqueous

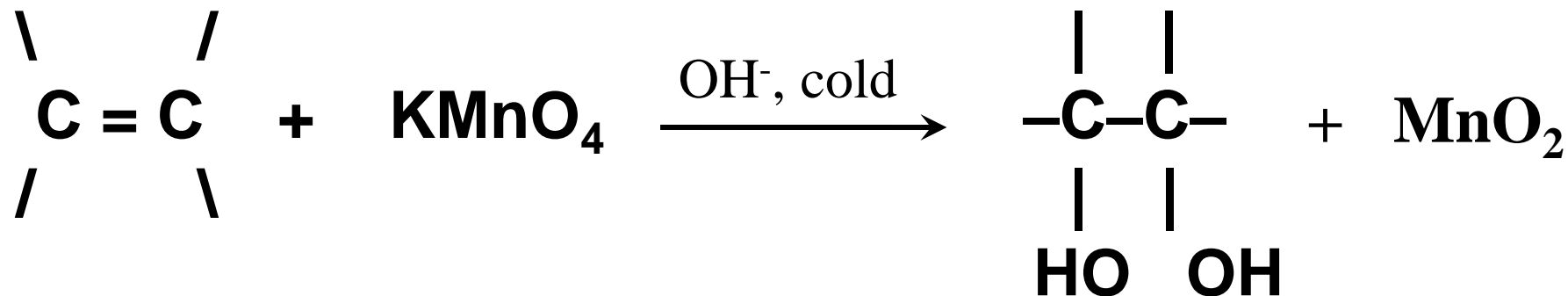
*Unsaturation Test:*



- Observation: **Reddish brown colour** of bromine decolourised.

# Oxidation Reaction

*Unsaturation Test: Baeyer's Test*

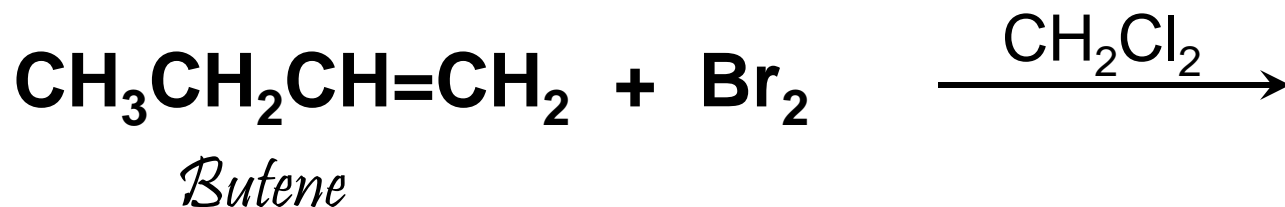
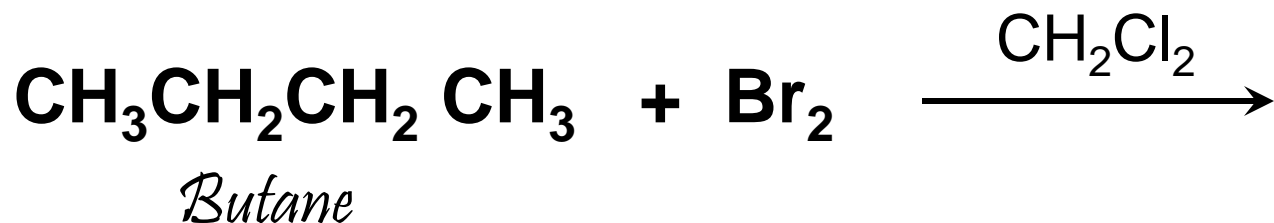


- Observation: **Purple color of  $\text{KMnO}_4$**  decolorised and **brown precipitate,  $\text{MnO}_2$**  formed



## Example: Butane vs Butene

*Unsaturation Test:*



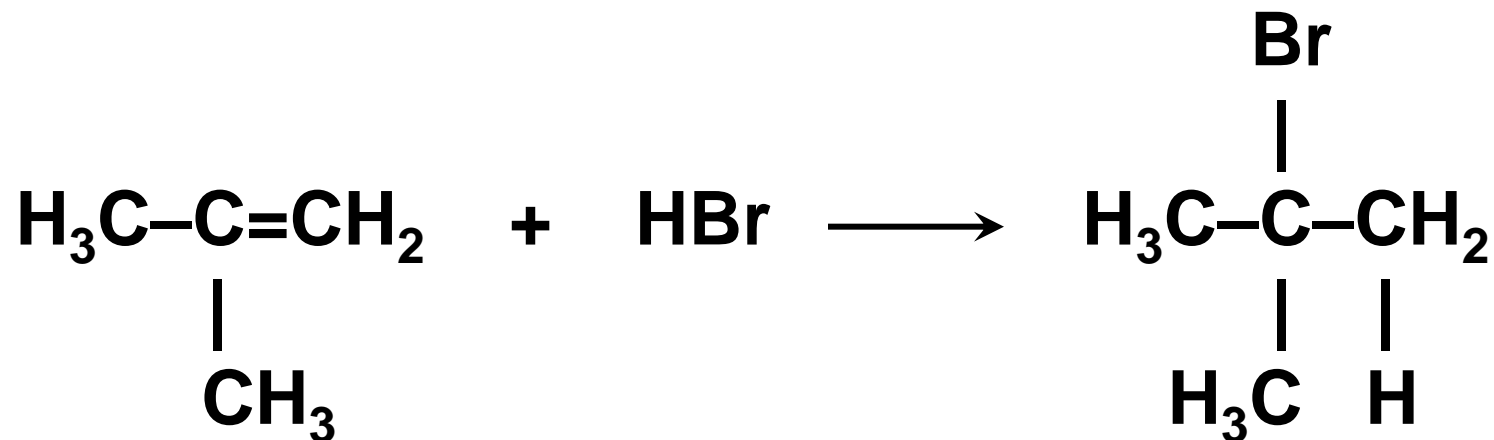
Observation: Reddish brown colour of bromine  
decolourised.

# MECHANISM OF ELECTROPHILIC ADDITION REACTION

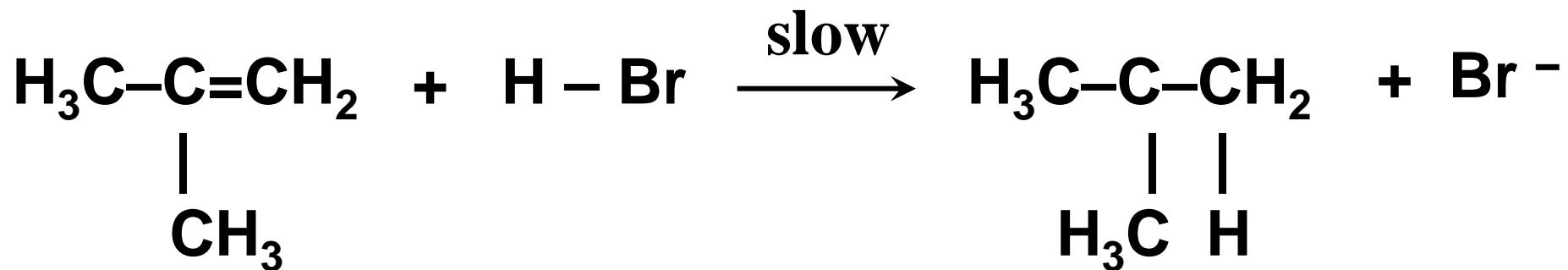
1. Hydrohalogenation of alkene
  2. Hydration of alkene
- Carbon-carbon double bond
    - Electron rich part @ Nucleophilic site @ high electron density
  - Electrophile reagent
    - Electron seeking
    - Attack region of high electron density

# MECHANISM OF HYDROHALOGENATION OF ALKENE

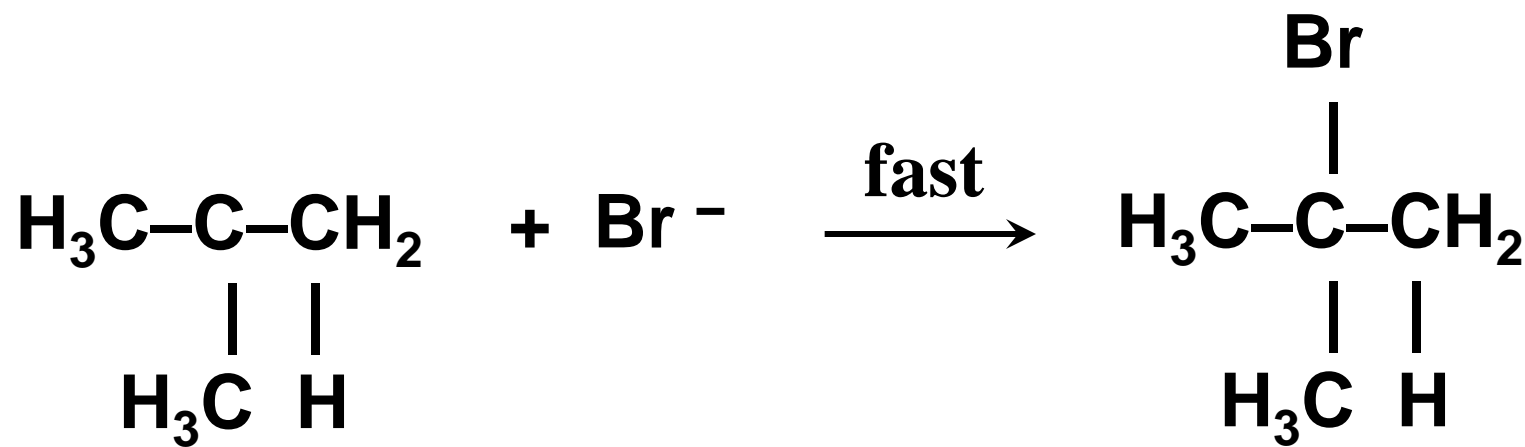
*Example 1: Hydrohalogenation of 2-methylpropene*



*Step 1: Formation of carbocation.*

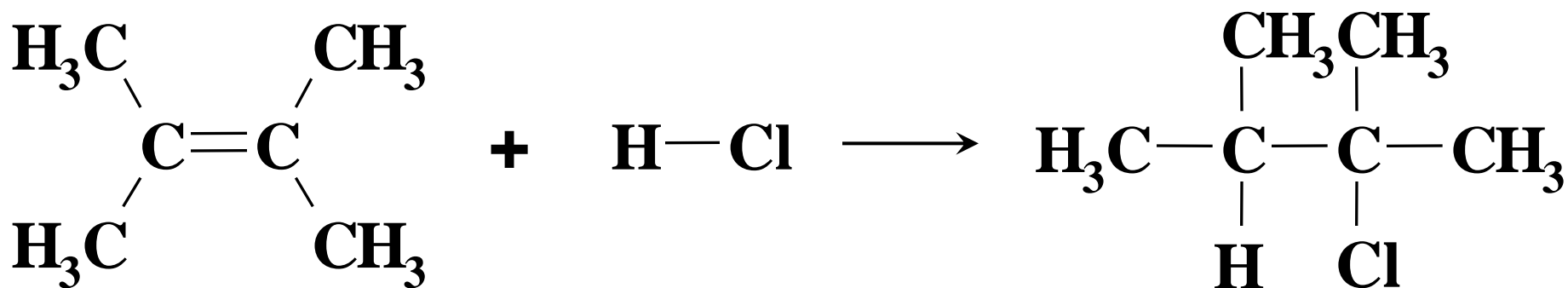


*Step 2: Reaction with a negative ion.*

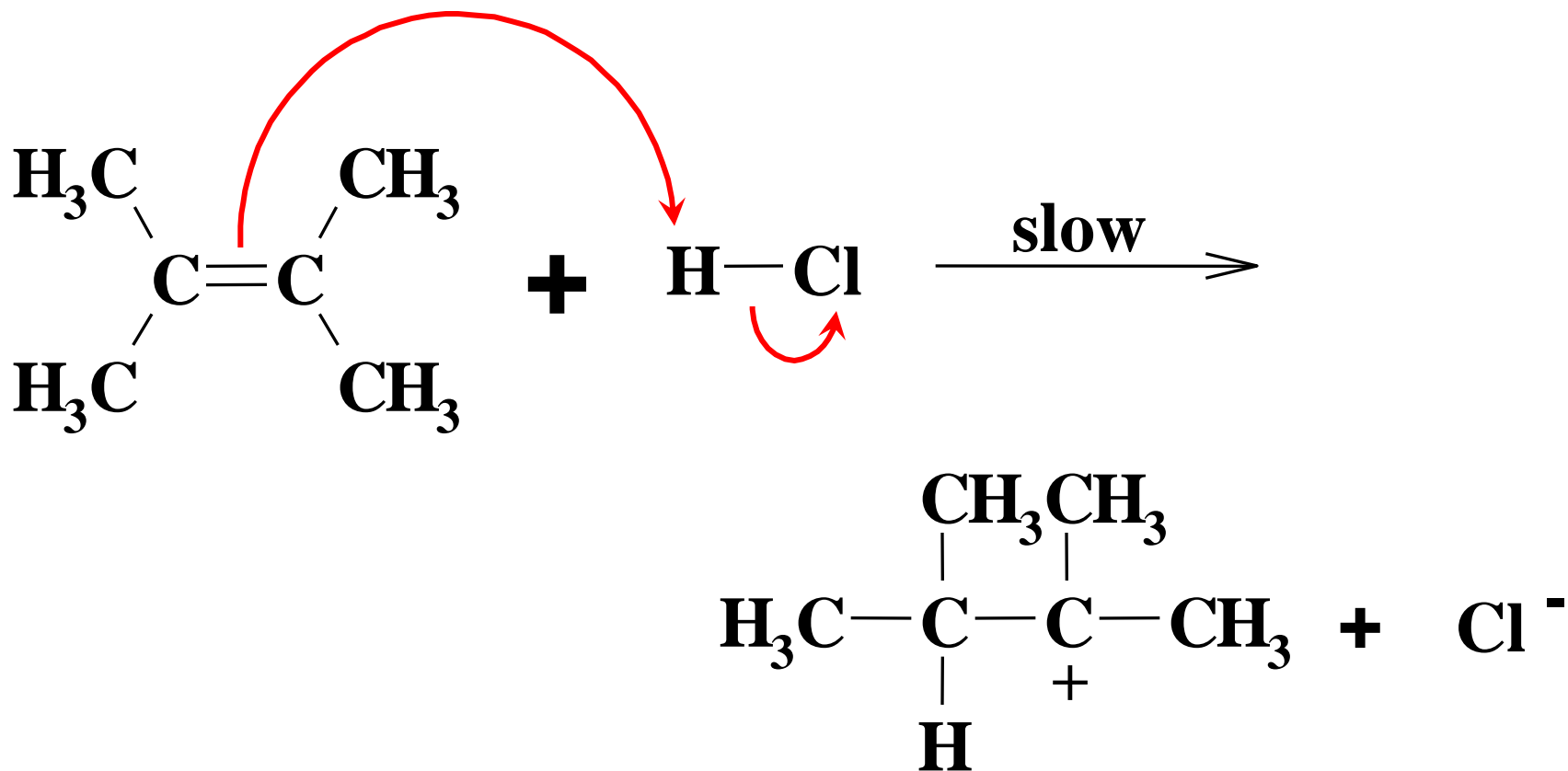


# MECHANISM OF HYDROHALOGENATION OF ALKENE

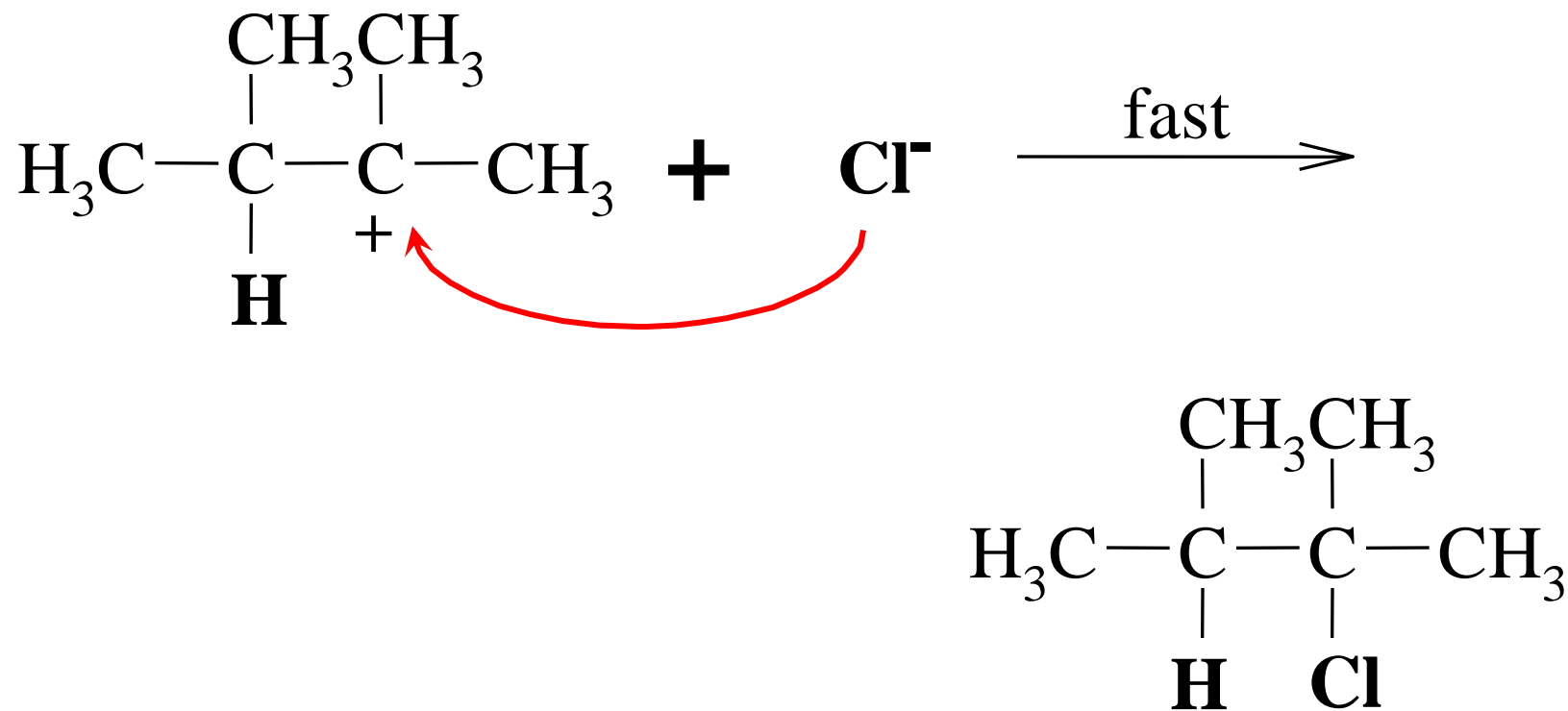
*Example 2: Hydrohalogenation of 2,3-dimethylbutene*



*Step 1: Formation of carbocation.*

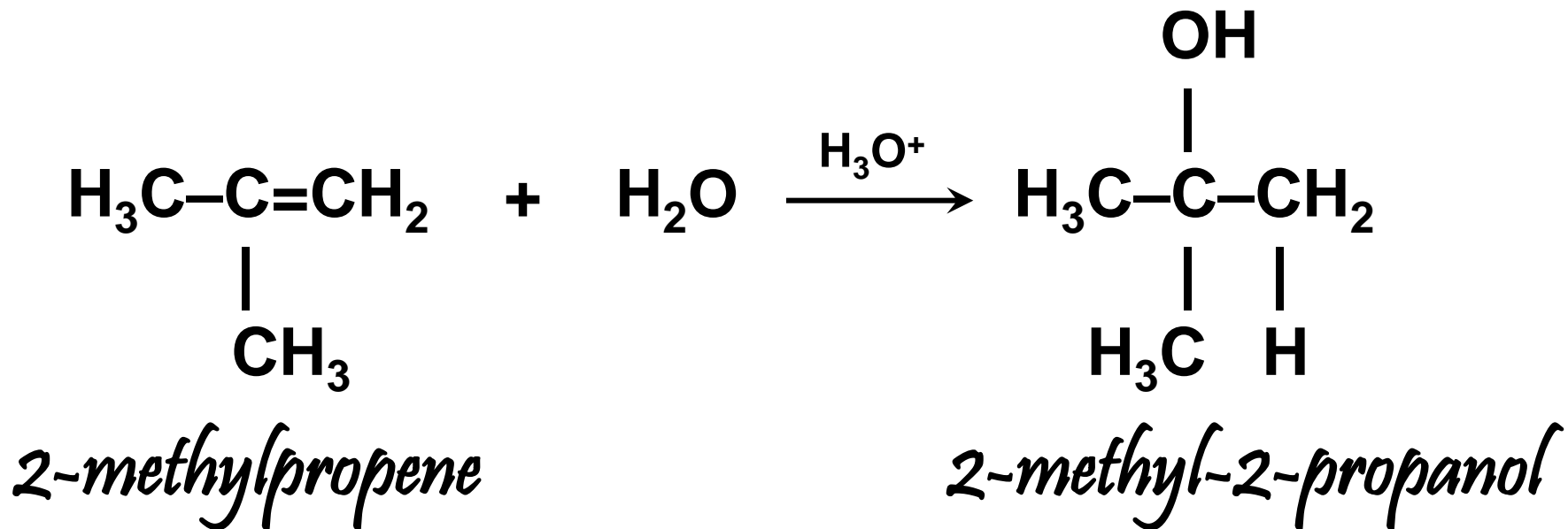


*Step 2: Reaction with a negative ion.*



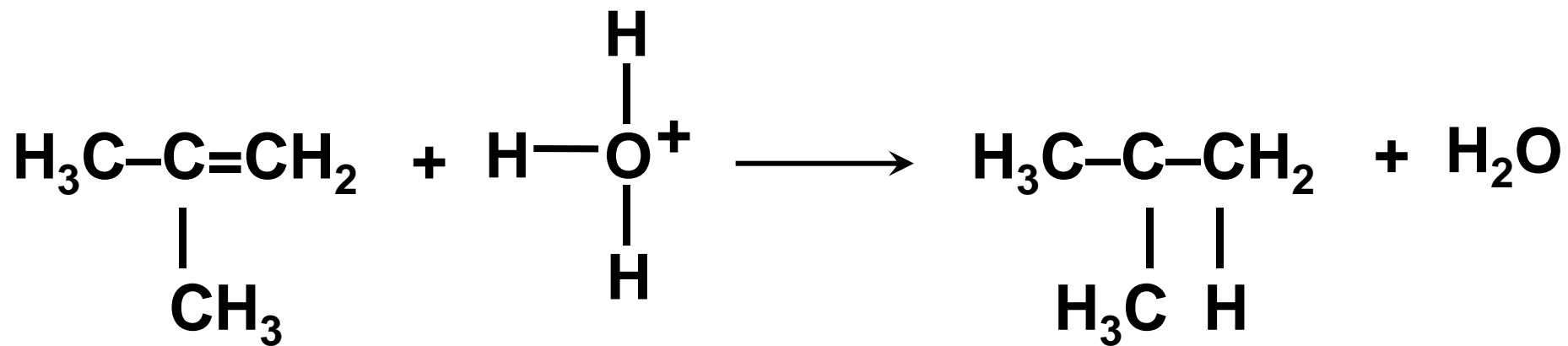
# MECHANISM OF HYDRATION OF ALKENE

*Example 1: Hydration of 2-methylpropene*

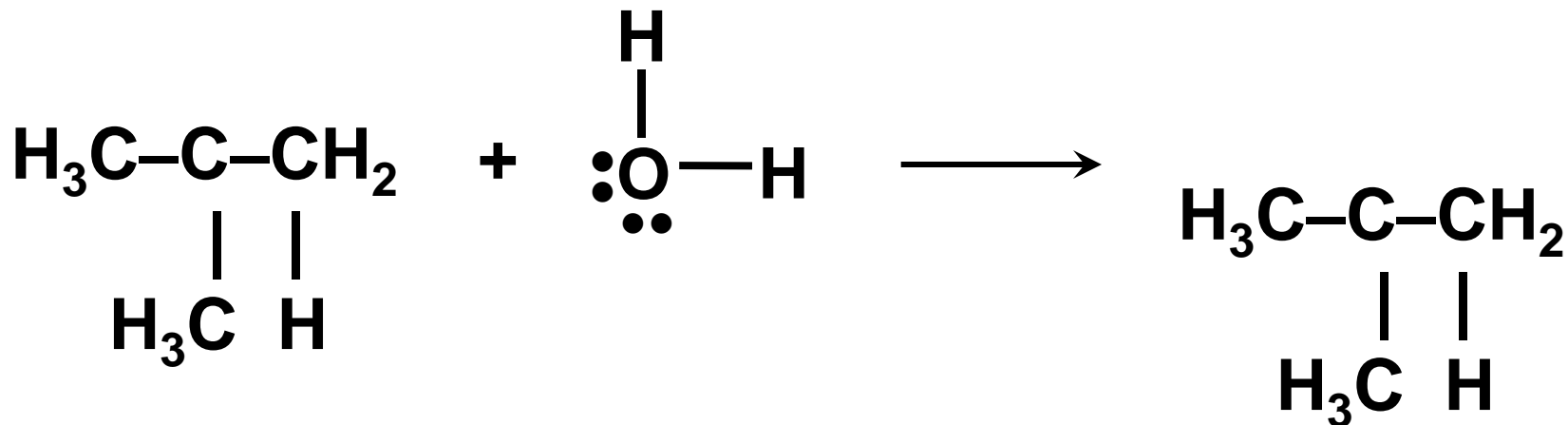




*Step 1: Protonation to form a carbocation.*



*Step 2: Addition of  $\text{H}_2\text{O}$  to form a protonated alcohol.*



*Step 3: Loss of proton (deprotonation) to form alcohol.*

