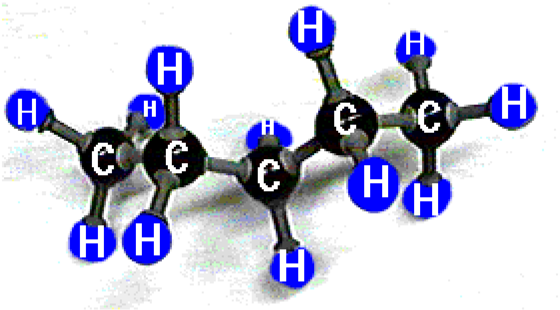
CHAPTER 5 HYDROCARBONS

5.1 Alkanes

5.2 Alkenes



5.1 ALKANES

Learning Outcomes

a) Classify hydrocarbons into:

i) aliphatic and aromatic

ii) saturated and unsaturated

b) Give the name of alkanes according to the IUPAC nomenclature

c) Give the structure formulae of the following alkanes:

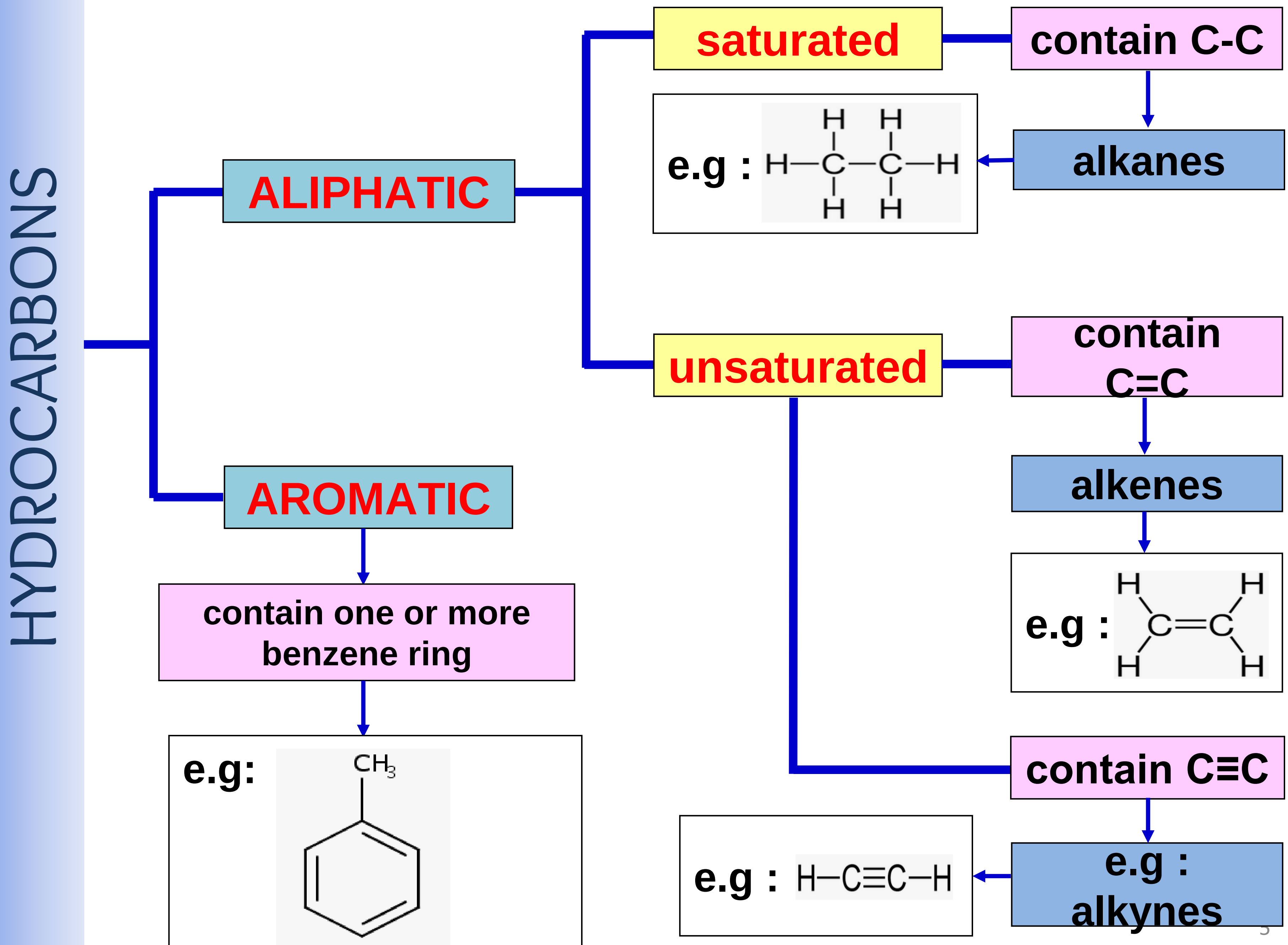
i) straight chain and branched alkanes (parent chain $\leq C_{10}$)

ii) cyclic alkanes (C_3-C_6)

iii) alkyl groups

HYDROCARBON

compounds which contain only carbon and hydrogen atoms.


HYDROCARBONS
ALIPHATIC
saturated
contain C-C
alkanes
e.g :
H—C—C—H
unsaturated
contain C=C
alkenes
e.g :
C=C
contain C≡C
e.g : alkynes
e.g : H—C≡C—H
AROMATIC
contain one or more benzene ring
e.g:
CH3

DRAW & NAME IUPAC NOMENCLATURE OF ALKANES

straight chain & branch alkanes (parent chain ≤ C_{10})

alkyl groups

cyclic alkanes (C_3-C_6)

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ALKANES

- IUPAC names have the **–ane** suffix.

- General formula for **straight chain of alkanes** is $\mathbf{C_nH_{2n+2}}$ where $\mathbf{n \geq 1}$

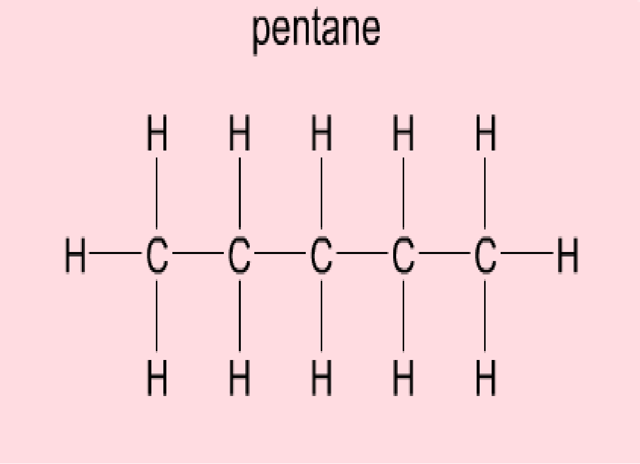
- General formula for **cycloalkanes** is $\mathbf{C_nH_{2n}}$ where $\mathbf{n \geq 3}$

- Starting from $\mathbf{C_4H_{10}}$ **onwards**, the alkanes show the phenomenon of **chain isomerism**.

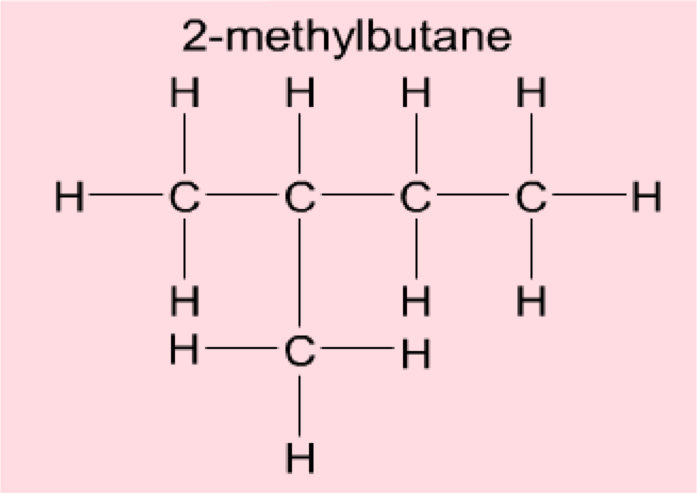
- They can exist as **linear or branched alkanes.**

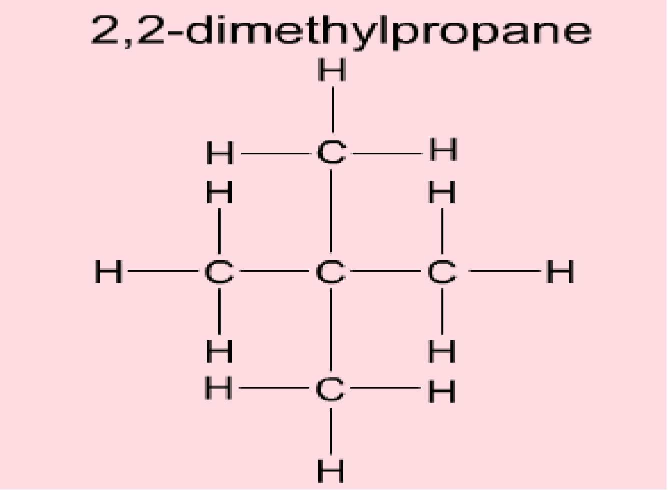
Example : C_5H_{12}

Linear alkane:



Branched alkanes:





Nomenclature of Alkanes

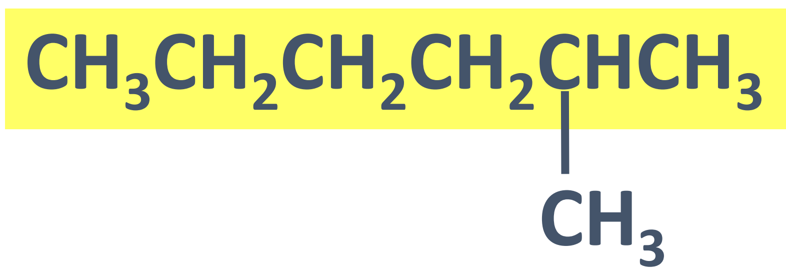
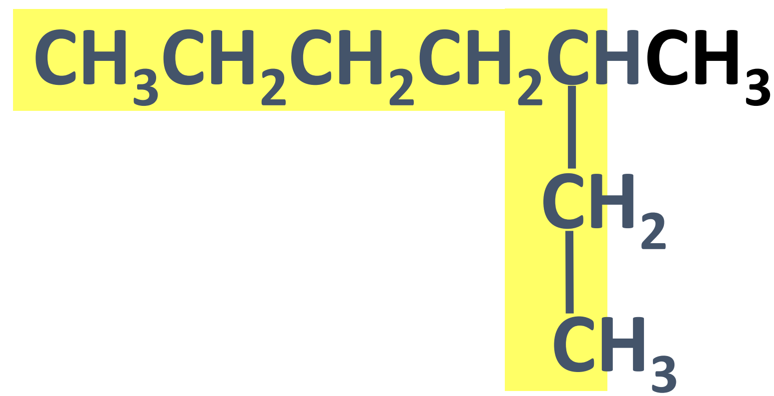
Alkane	Molecular formula	Structural formula	No. of carbon
Methane	CH_4	CH_4	1
Ethane	C_2H_6	CH_3CH_3	2
Propane	C_3H_8	$CH_3CH_2CH_3$	3
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	4
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	5
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	6
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	7
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	8
Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	9
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	10

Rules in Naming Branched Alkanes

- Naming branched alkanes is slightly more complicated than naming the straight chain ones.
- So you need to follow a simple set of steps to arrive at a proper name.

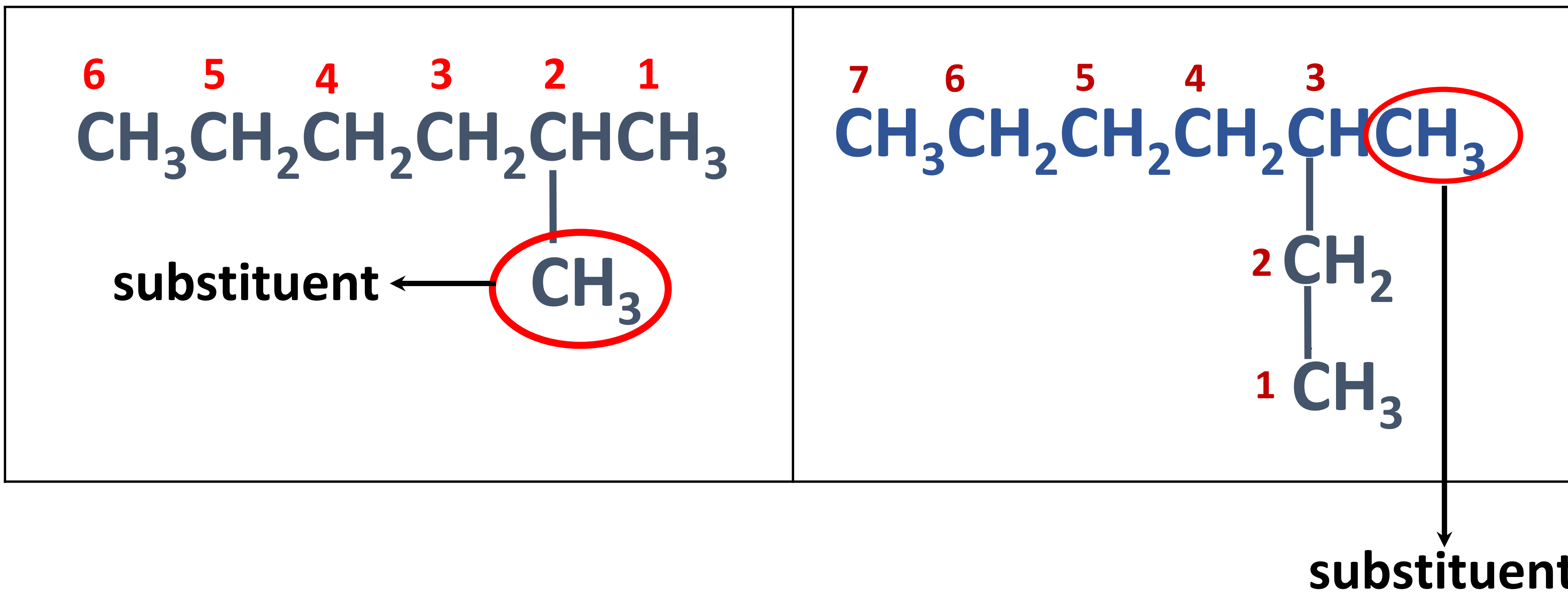
STEP 1: Choose the longest continuous chain of carbon atoms; this chain determines the parent name for alkanes.

Example:

	
Parent name: hexane	**Parent name: heptane**

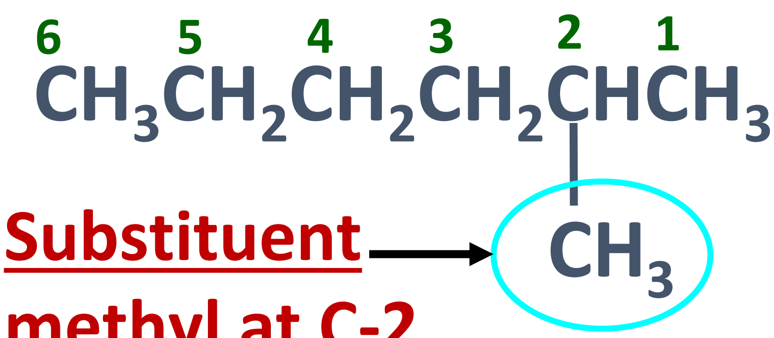
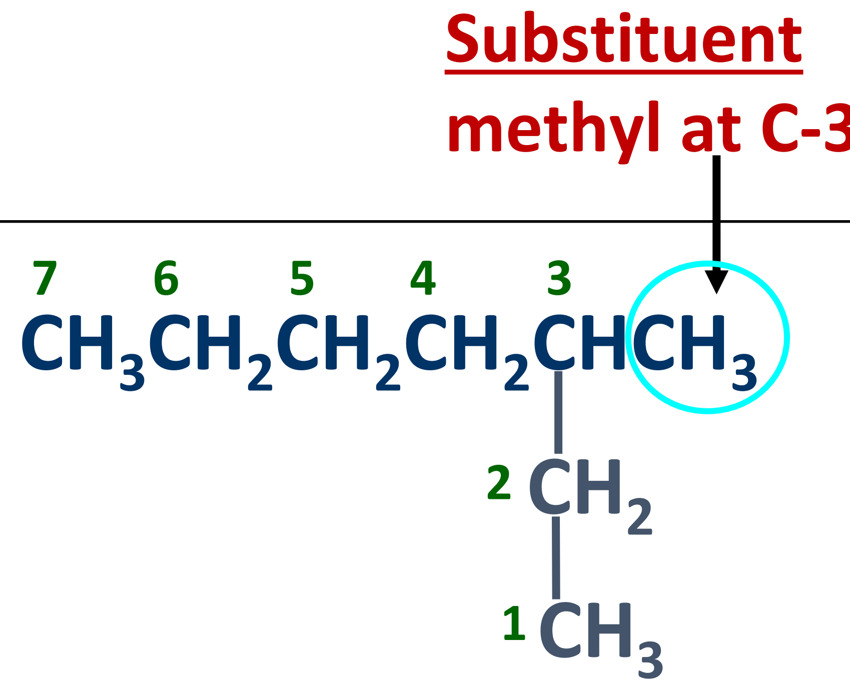
STEP 2: **Number the longest chain beginning with the end of the chain nearer the substituent.**

Example:

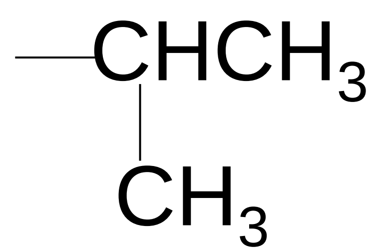


STEP 3: The position and the name of the **substituent** must be written **in front** of the parent chain.

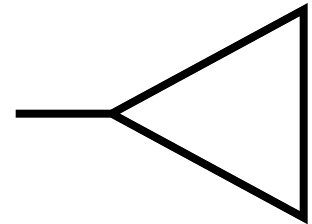
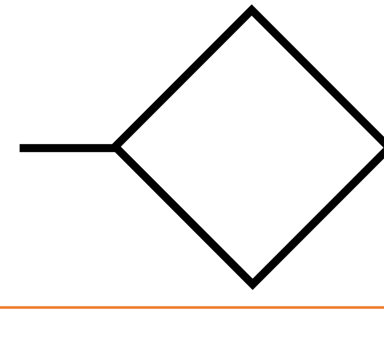
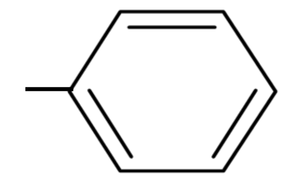
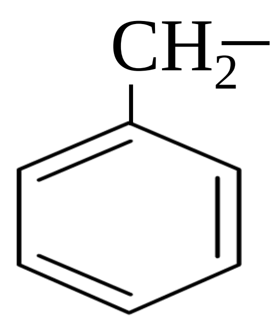
Example:

	
2-methylhexane	**3-methylheptane**

Some Common Substituent Groups

Alkane	Name	Substituent
methane	methyl	$-CH_3$
ethane	ethyl	$-CH_2CH_3$
propane	propyl	$-CH_2CH_2CH_3$
	isopropyl	
butane	butyl	$-CH_2CH_2CH_2CH_3$

isobutyl	$-CH_2CH(CH_3)CH_3$
sec-butyl	$-CH(CH_3)CH_2CH_3$
tert-butyl	$-C(CH_3)_2CH_3$
neopentyl	$-CH_2C(CH_3)_2CH_3$

cyclopropyl	
cyclobutyl	
phenyl	$-C_6H_5$ or 
benzyl	

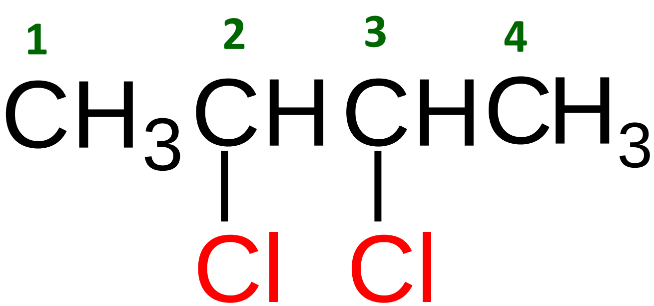
Name	Substituent
bromo	-Br
chloro	-Cl
fluoro	-F
iodo	-I
hydroxyl	-OH
amino	$-NH_2$
cyano	-CN
nitro	$-NO_2$

STEP 4: If the compound contains **more than one identical substituents**, use prefixes:

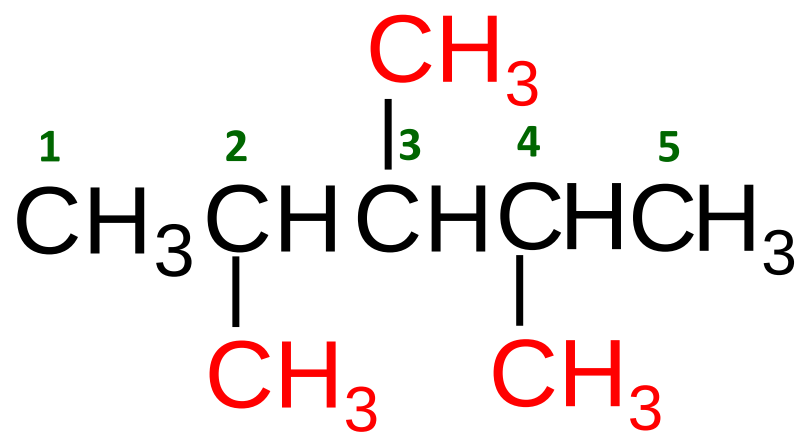
- di- : (2 identical substituents)
- tri- : (3 identical substituents)
- tetra- : (4 identical substituents)

☞ **Commas** are used to separate numbers from each other.

Example :



2,3-dichlorobutane

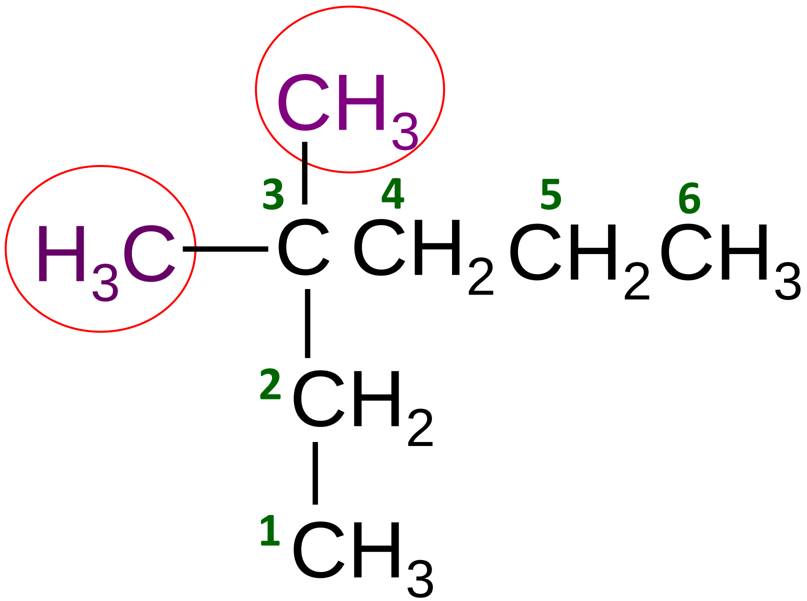


2,3,4-trimethylpentane

STEP 5:

If **two substituents** are present on the same carbon atom, **use that number twice.**

Example :



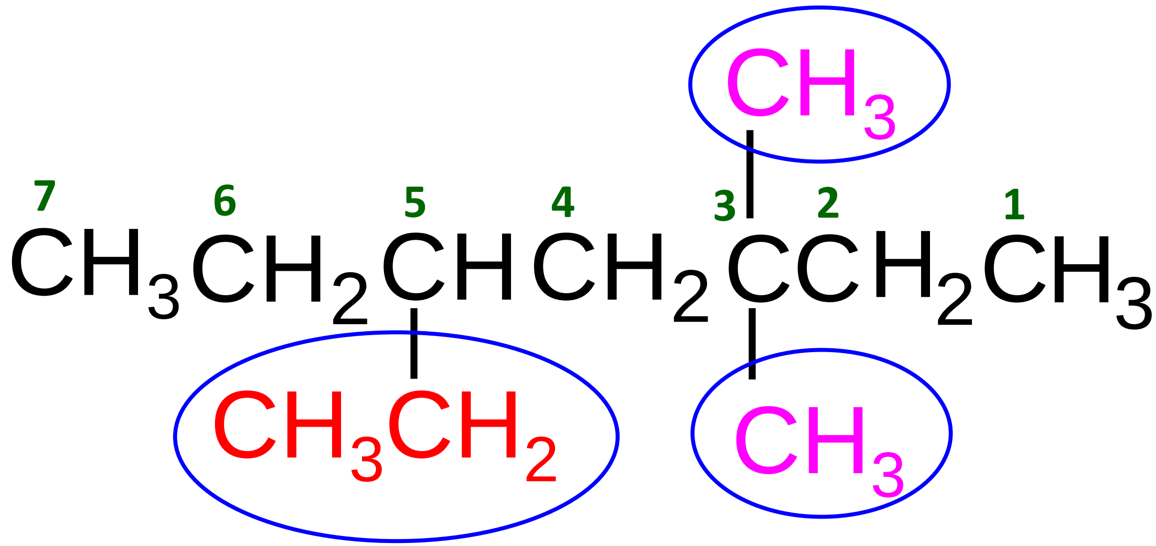
3,3-dimethylhexane

STEP 6: **If two or more substituents are present, give each substituent a number corresponding to its location on the longest chain.**

- ❑ **the substituent should be listed alphabetically.**

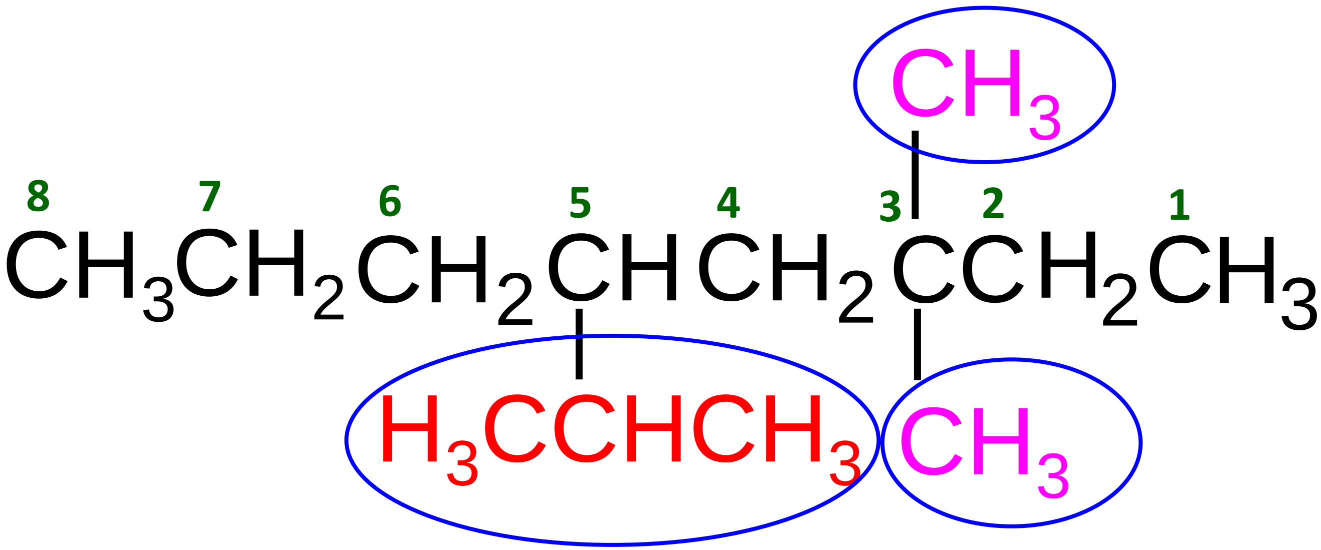
- ❑ **In alphabetizing, the prefixes di, tri, tetra, sec-, tert- are ignored except iso and neo.**

Example 1:



5-ethyl-3,3-dimethylheptane

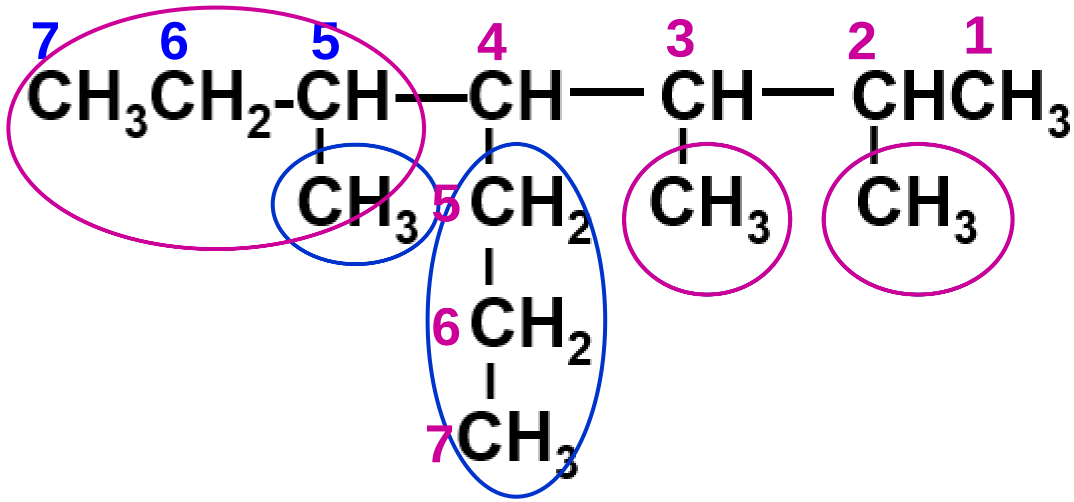
Example 2 :



5-isopropyl-3,3-dimethyloctane

STEP 7: If there are **two chains of equal length** as the **parent chain**, choose the **chain with the <u>greater number</u> of substituents**.

Example :

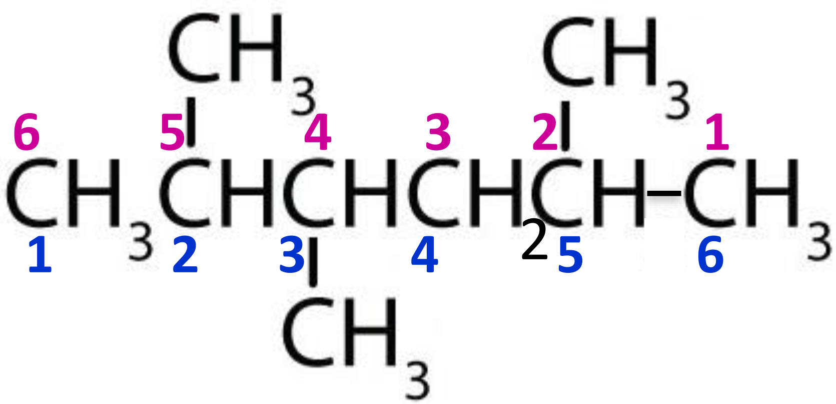


2,3,5-trimethyl-4-propylheptane
(4 substituents)

4-*sec*-butyl-2,3-dimethylheptane
(3 substituents)

STEP 8: **If branching occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.**

Example :



2,3,5-trimethylhexane

2,4,5-trimethylhexane

RULES IN NAMING CYCLIC COMPOUNDS

- **Cycloalkanes:** **alkanes which carbon atoms are joined in rings.**

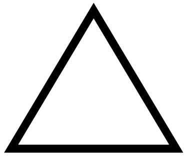
- **Cycloalkanes are known as saturated hydrocarbon, because it has the maximum number of bonded hydrogen (only has single bonds).**

- **General formula:**

  C_nH_{2n} where $n = 3, 4, 5, \ldots\ldots$

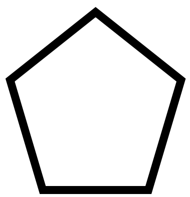
STEP 1: **Prefix cyclo-** **is used to name cyclic compound with a single ring system.**

Example :

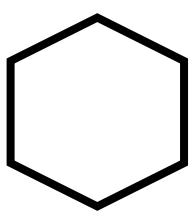


C_3H_6 cyclopropane

C_4H_8 cyclobutane



C_5H_{10} cyclopentane

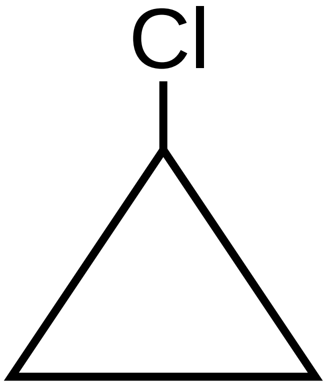


C_6H_{12} cyclohexane

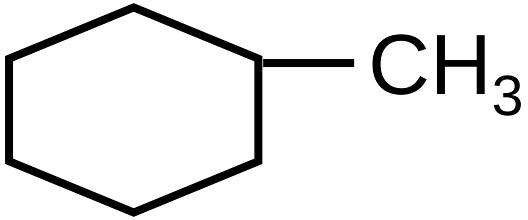
STEP 2:

If only one substituent is present, it is not necessary to designate its position.

Example :



chlorocyclopropane



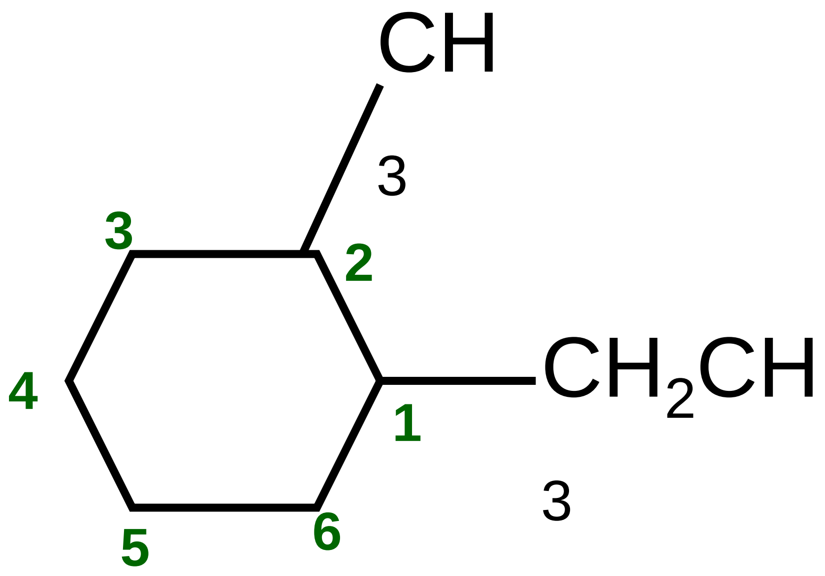
methylcyclohexane

STEP 3:

- If two substituents are present, number carbon in the ring beginning with the substituent according to the alphabetical order.

- Number in the direction that gives the next substituent the lowest number possible.

Example 1:

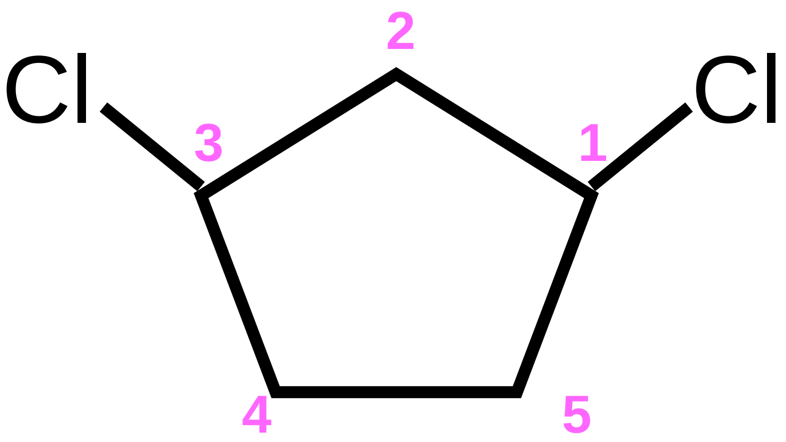


1-ethyl-2-methylcyclohexane

NOT

1-ethyl-6-methylcyclohexane

Example 2:



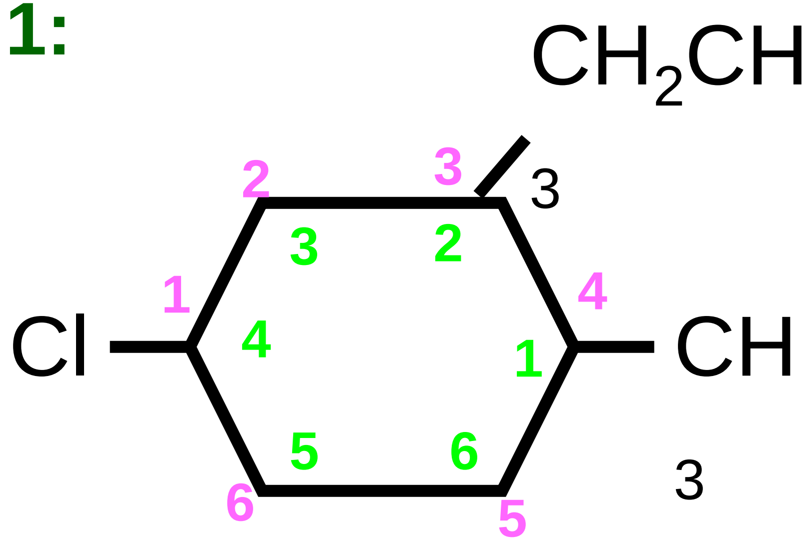
1,3-dichlorocyclopentane

NOT

1,4-dichlorocyclopentane

STEP 4: When three or more substituents are present, begin at the carbon with substituent that leads to the lowest set of locants.

Example 1:

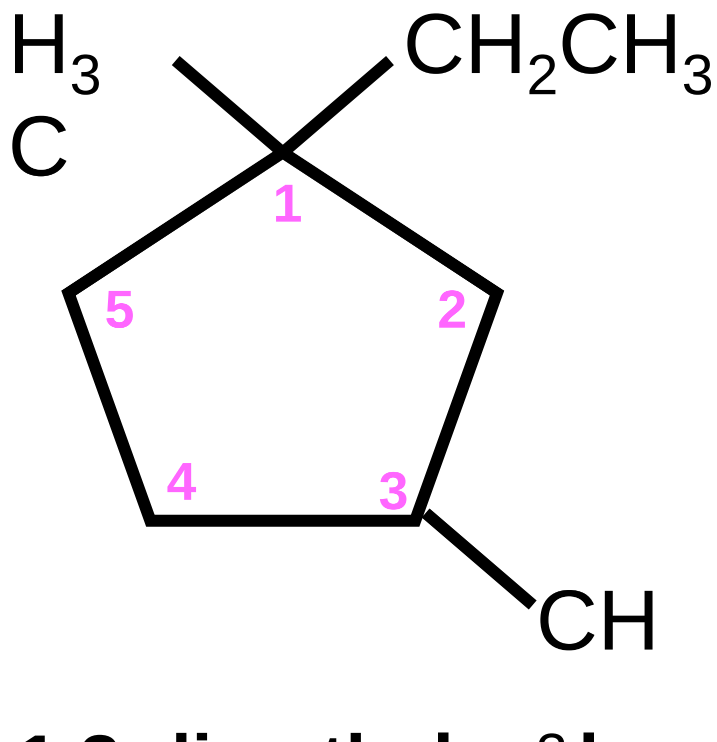


Locants:		
chloro	1	4
ethyl	3	2
methyl	4	1

1-chloro-3-ethyl-4-methylcyclohexane ✗

4- chloro-2-ethyl-1-methylcyclohexane ✓

Example 2:



1-ethyl-1,3-dimethylcyclopentane

NOT

3-ethyl-1,3-dimethylcyclopentane

STEP 5:

If……

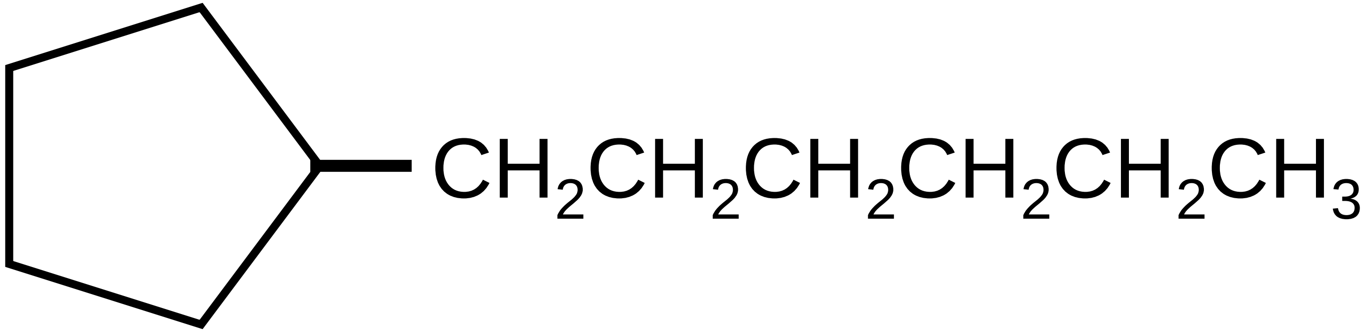
i) **a single ring** system is attached to a single chain with a **greater** number of carbon atoms,

@

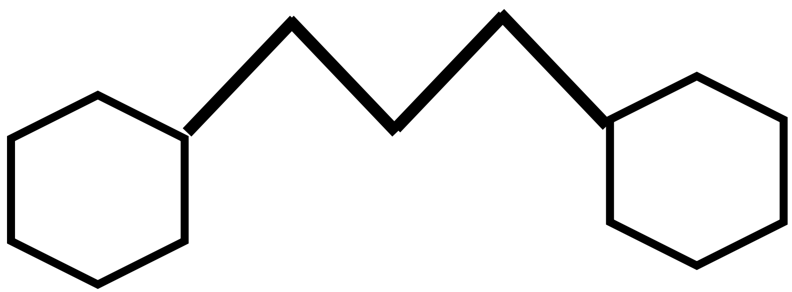
ii) **more** than one ring systems are attached to a **single** chain,

☞ Then it is appropriate to name the compound as **cycloalkylalkane.**

Example:



cyclopentylhexane



1,3-dicyclohexylpropane

Physical Properties of Alkanes

Learning Outcomes

d) Explain the following physical properties:

i) boiling point of:

- alkanes based on molecular weight/size;
- isomeric alkanes
- alkanes and cycloalkanes

ii) solubility in water and organic solvents

PHYSICAL PROPERTIES

- **BOILING POINT**
  - alkanes based on molecular weight, M_r
  - isomeric alkanes
  - alkanes & cycloalkanes
- **SOLUBILITY**
  - in water
  - in organic solvents

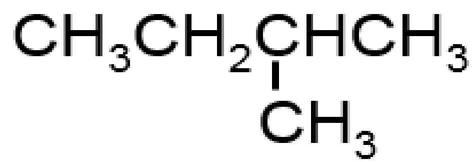
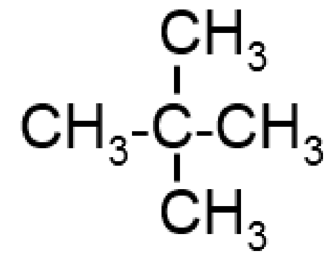
Boiling point of alkanes increase smoothly with increasing number of C atoms (molecular weight / molar mass)

Alkane	Molecular formula	Structural formula	Boiling point (^oC)
Methane	CH_4	CH_4	- 162
Ethane	C_2H_6	CH_3CH_3	- 89
Propane	C_3H_8	$CH_3CH_2CH_3$	- 42
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	- 0.5
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	36
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	69
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	98
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	126
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	174

Effect of increasing number of C atoms on boiling point…

- The boiling points of alkanes show a regular increase with increasing molecular weight because the number of carbon increase.
- the molecule has bigger surface area in contact.
- the stronger Van der Waals attractive forces.
- more energy required to overcome the attractive forces.
- the higher the boiling point.

Effect of branching on boiling point for isomeric alkanes ...

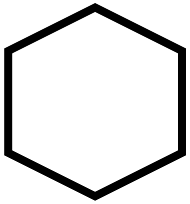
Alkane	$CH_3CH_2CH_2CH_2CH_3$		
Boiling point	35 ^oC	28 ^oC	9.5 ^oC

Effect of branching on boiling point ...

- more branches, molecule become more compact.
- surface area in contact are reduced.
- this causes the branched alkanes to have a weaker Van der Waals attractive forces.
- less energy required to overcome the attractive forces.
- the lower the boiling point.

No. of branches ↑, Surface area ↓, Van der Waals forces ↓, boiling point ↓

Cyclic alkanes have higher boiling point than the corresponding straight chain.

Alkane	$CH_2CH_2CH_2CH_2CH_2CH_3$ hexane	 cyclohexane
Boiling point	69 ^{o}C	81 ^{o}C

Why cyclic alkanes have higher boiling point ??

- cyclic alkanes has larger surface area in contact than the corresponding straight chain alkane.
- the stronger Van der Waals attractive forces.
- more energy required to overcome the attractive forces.
- the higher the boiling point.

Solubility in Water and Organic Solvents..

- Alkanes and cycloalkanes are almost totally insoluble in water because they are:

  (i) non-polar molecules

  (ii) unable to form hydrogen bond with H_2O.

- Alkanes and cycloalkanes are generally dissolve in non-polar solvents.

- Examples of non-polar solvent: benzene, chloroform, carbon tetrachloride, etc.

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Chemical Properties of Alkanes

Learning Outcomes

e) Write a balance chemical equation for the combustion of alkane in:

i) excess oxygen   ii) limited oxygen

f) Explain the halogenation reaction of alkanes

include bromination and chlorination

g) Explain the monosubstitution of alkane containing equivalent and non-equivalent type of hydrogen atoms

h) Illustrate the free radical monosubstitution mechanism of alkanes

CHEMICAL PROPERTIES OF ALKANES

- **COMBUSTION**
  - **in excess O_2**
  - **in limited O_2**
- **HALOGENATION**

  Type of reaction : free radical substitution

  - **reagent : Br_2 @ Cl_2**
  - **condition : under *uv* light @ *hv***
  - **product: haloalkane**

Combustion – in excess oxygen

- Reactant : alkane and excess O_2
- Product: CO_2 and H_2O

Example: $C_3H_8 + 5\ O_2 \longrightarrow 3\ CO_2 + 4\ H_2O$

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Combustion – in limited oxygen

- Reactant : alkane and limited O_2
- Product: CO and H_2O

Example: $$C_3H_8 + \frac{7}{2} O_2 \longrightarrow 3CO + 4H_2O$$

Combustion – in very limited oxygen

- Reactant : alkane and limited O_2
- Product: C (soot) and H_2O

Example: $$C_3H_8 + 2\,O_2 \longrightarrow 3C + 4H_2O$$

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Type of reaction : Free radical substitution

Reagent : X_2 (X= Br_2 @ Cl_2)

Condition : under *uv* light @ *hv*

Product : haloalkane

General equation:

$$\underset{\text{alkane}}{\mathbf{R{-}H}} + \mathbf{X_2} \xrightarrow{uv} \underset{\text{haloalkane}}{\mathbf{R{-}X}} + \mathbf{HX}$$

Example:

i. $CH_4 + Cl_2 \xrightarrow{uv} CH_3Cl + HCl$

ii. $CH_3CH_3 + Br_2 \xrightarrow{uv} CH_3CH_2Br + HBr$

Example (i) and (ii) have **one haloalkane** product only since the reactants (alkane) contain **identical hydrogen atoms (same types of H)**.

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Example:

iii $CH_3CH_2CH_3 \;+\; Cl_2 \xrightarrow{uv} CH_3CH_2CH_2Cl \;+$

(minor product)

$CH_3CH(Cl)CH_3 \;+\; HCl$

(major product)

Example (iii) has **two haloalkane** products because the reactant (alkane) contains **non-identical hydrogen atoms (different types of H)**.

$CH_3CH(Cl)CH_3$ is the **major** product due to the **stability of free radical.**

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iv.

$$CH_3CH_2CH_3 + Cl_2 \xrightarrow{uv} CH_3CH_2CH_2Cl$$ (45%)

propane

1–chloropropane (minor)

fast and unselective!

+

$$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$$ (55%)

2–chloropropane (major)

$$CH_3CH_2CH_3 + Br_2 \xrightarrow{uv} CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$$ (99%)

propane

2–bromopropane

Slow and selective

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Reaction Mechanism of Alkanes

Example 1 :

$$CH_4 + Cl_2 \xrightarrow{uv} CH_3Cl + HCl$$

Steps are …

1. **Initiation**
2. **Propagation** **Most important !**
3. **Termination**

Step 1 – Initiation

-*uv* light or heat provides the energy needed for homolytic bond cleavage.

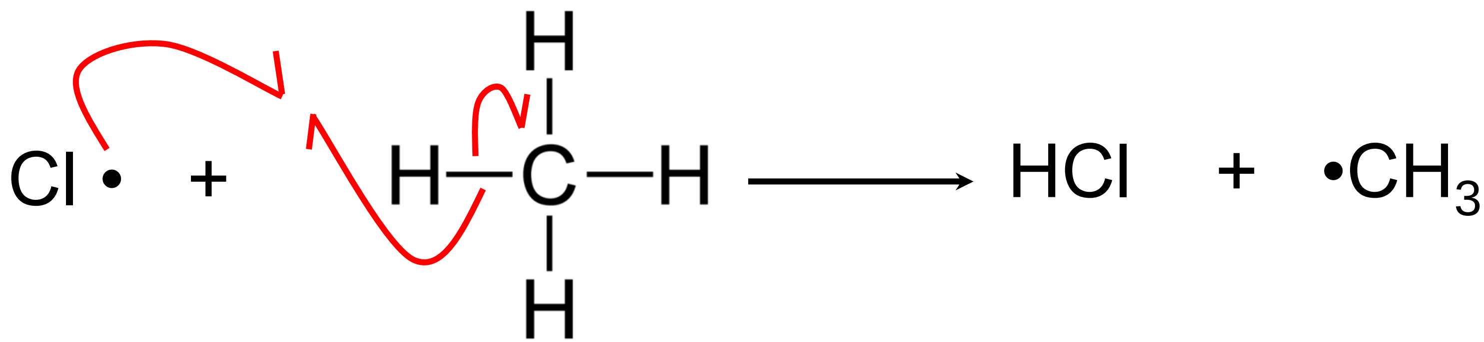
-Free radicals are formed.

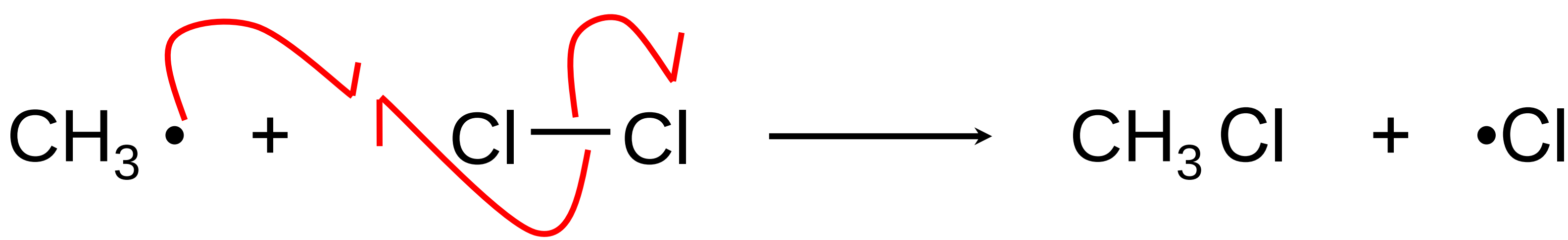
-Reaction begins !

$$Cl{-}Cl \xrightarrow{uv} Cl\bullet \quad + \quad \bullet Cl$$

Step 2 - Propagation

One radical generates formation of another.

(i) 

(ii) 

Step 3 - Termination

Recombination of two free radicals:

(i) $CH_3\bullet + Cl\bullet \longrightarrow CH_3Cl$

(ii) $CH_3\bullet + \bullet CH_3 \longrightarrow CH_3\text{-}CH_3$

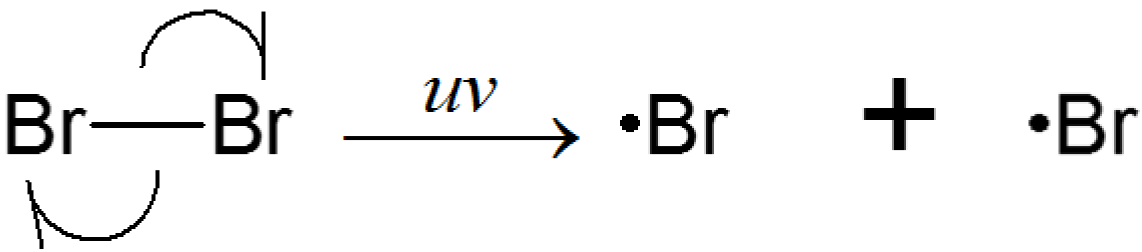
(iii) $Cl\bullet + \bullet Cl \longrightarrow Cl\text{-}Cl$

Example 2 :

Write a complete mechanism for the halogenation reaction of 2-methylpropane with bromine.

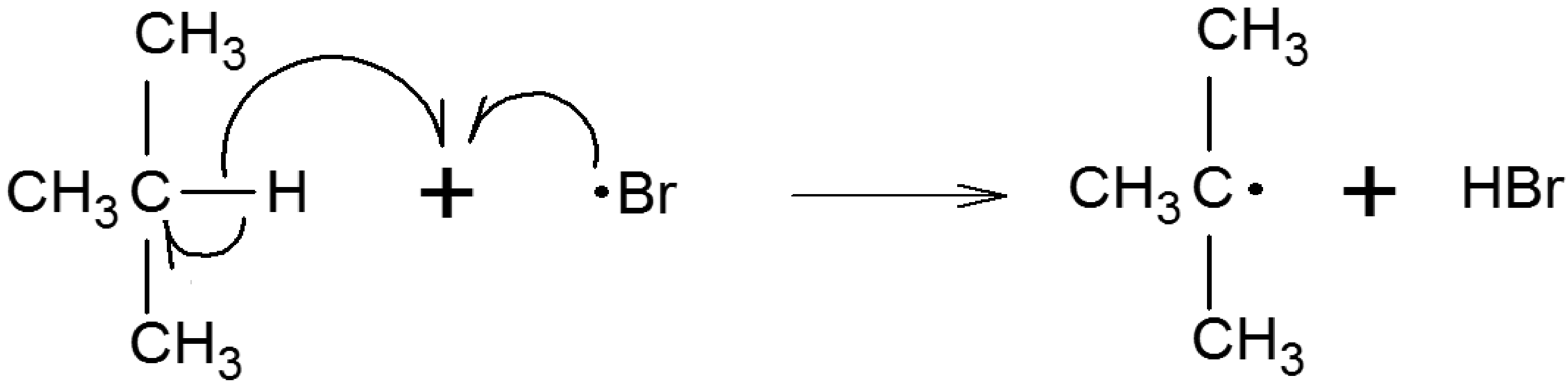
Answer :

Step 1 - Initiation

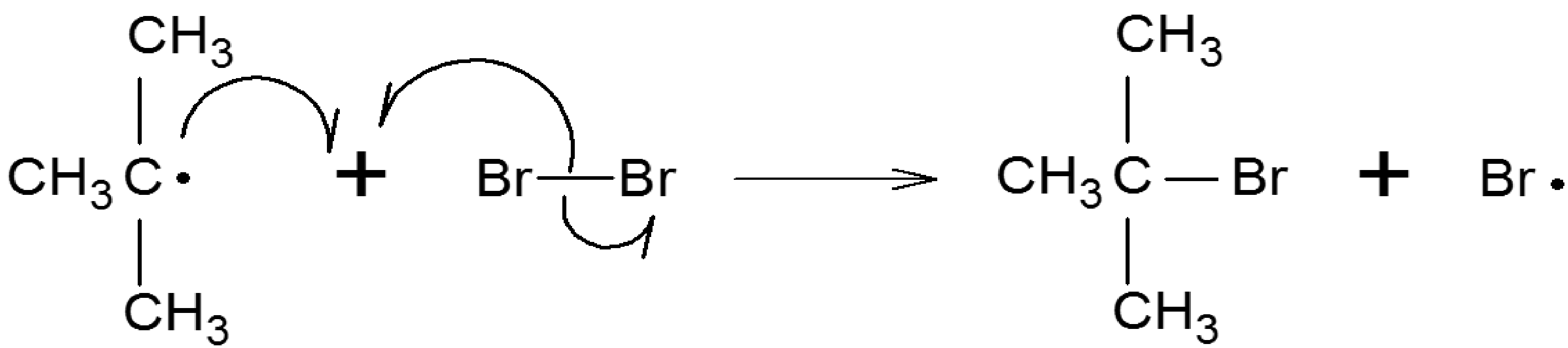


Step 2 - Propagation

(i)



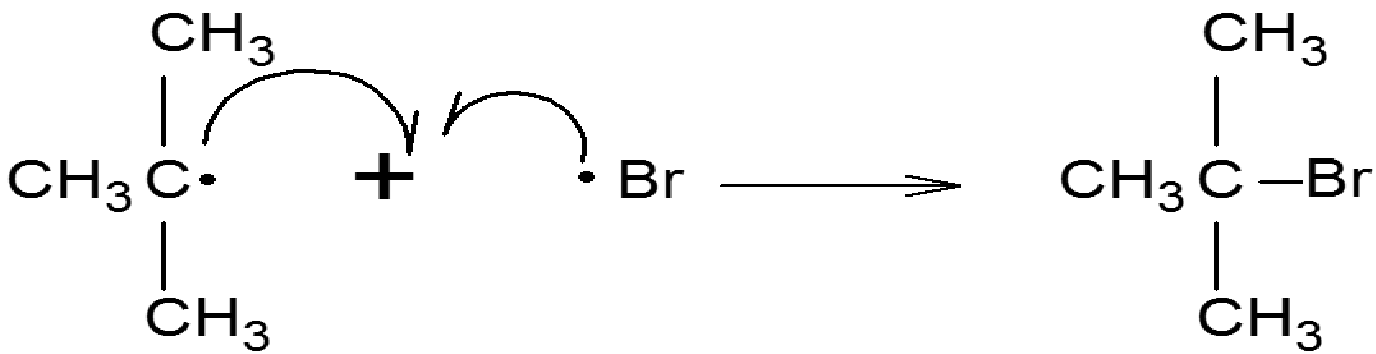
(ii)



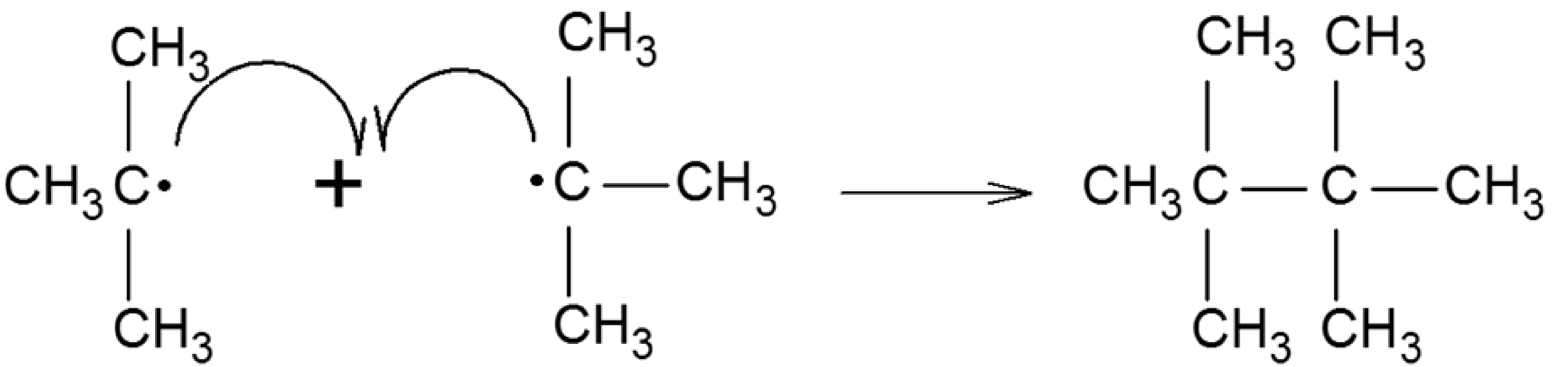
Step 3 - Termination

(i)

(ii)



(iii)



Example 2 :

Bromination reaction of certain alkanes can be used for laboratory preparations, for example in the preparation of bromocyclopentane from cyclopentane.

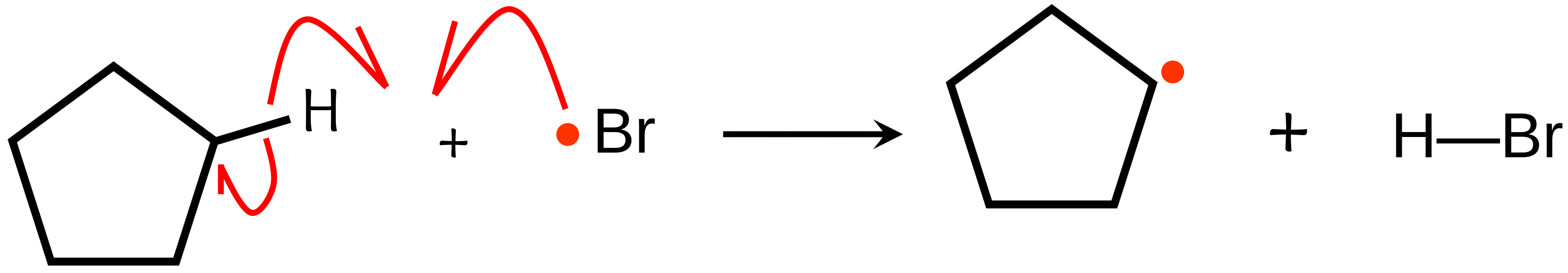
Give the mechanism for the reaction.

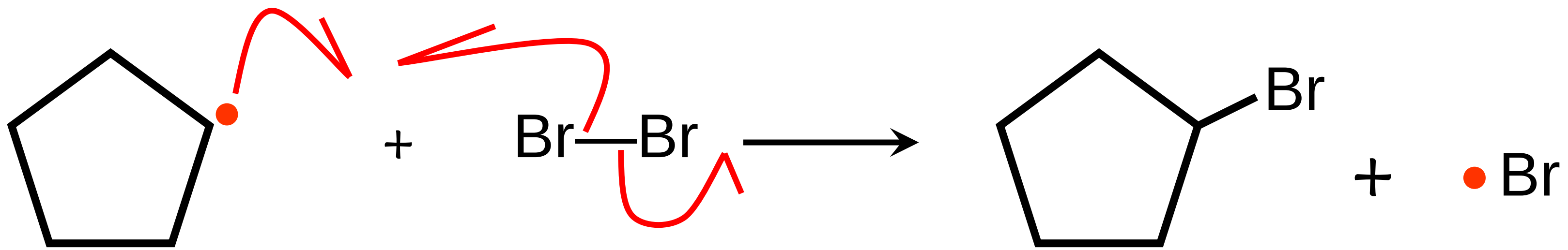
Answer :

<u>Step 1 : Initiation</u>

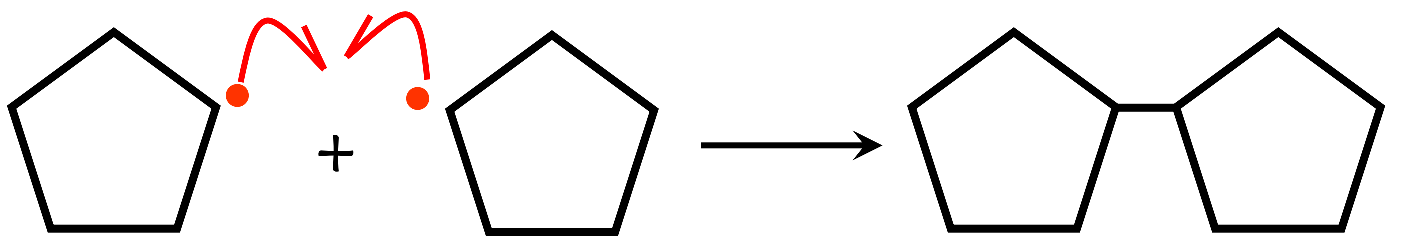
$$Br-Br \xrightarrow{uv} Br\bullet \quad + \quad \bullet Br$$

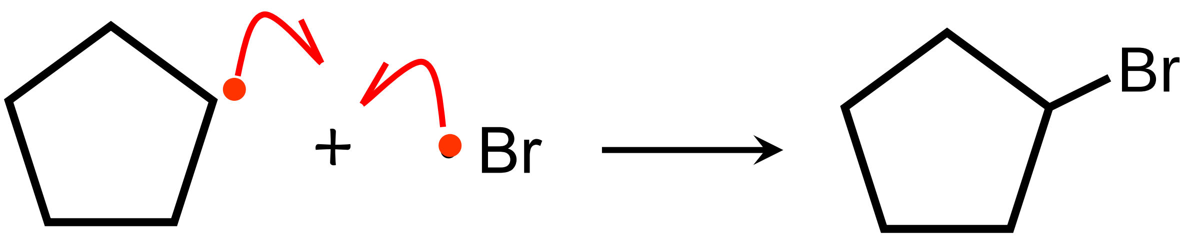
Step 2 : Propagation





Step 3 : Termination





5.2 ALKENES

5.2 : ALKENES

IUPAC Nomenclature

Physical Properties

Preparation

1. Dehydration of alcohols – include *Mechanism*
2. Dehydrohalogenation of haloalkanes

Chemical Test

1. Baeyer's test
2. Bromine in CH_2Cl_2
3. Bromine water

Chemical Reaction

A. Addition reaction of alkenes

1. Hydrogenation
2. Halogenation – In inert solvent(CH_2Cl_2)
3. Halogenation – In water (halohydrin formation)
4. (a) hydrogen halides (Markovnikov's Rule)- *Mechanisme*

(b) Addition of HBr to alkenes in the presence of peroxide (Anti-Markovnikov)

5. Acidified water– *Mechanisme*

B. Oxidation of alkenes

Learning Outcomes

(a) Give the name of alkenes according to the IUPAC nomenclature

(b) Give the structural formulae of the following alkenes

i) straight chain and branched alkenes (parent chain ≤ C_{10})

ii) Cyclic alkenes ($C_3 – C_6$)

iii) Simple dienes ($C_4 – C_6$)

(c) Explain boiling point of isomeric alkenes.

limit to cis-trans isomers only

Alkenes

- General formula C_nH_{2n} **,** n ≥ 2.
- Functional group : **C=C double bond**
- C=C ☞ 1 **σ** bond and 1 **π** bond
- Restricted rotation of carbon-carbon double bond causes cis-trans isomerism

Cycloalkenes

- General formula C_nH_{2n-2}
- Isomeric to alkynes C_nH_{2n-2}

IUPAC Nomenclature

STEP 1:

Determine the **parent name** by selecting the longest chain that **contains the double bond** and change the ending '-ane' in alkane to **'-ene'.**

STEP 2:

When the chain contains more than three carbon atoms, **numbering** is needed to **indicate** the **location of the double bond**.

Make sure position of double bond is the lowest number.

$$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H{=}\overset{4}{C}H\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H_3$$

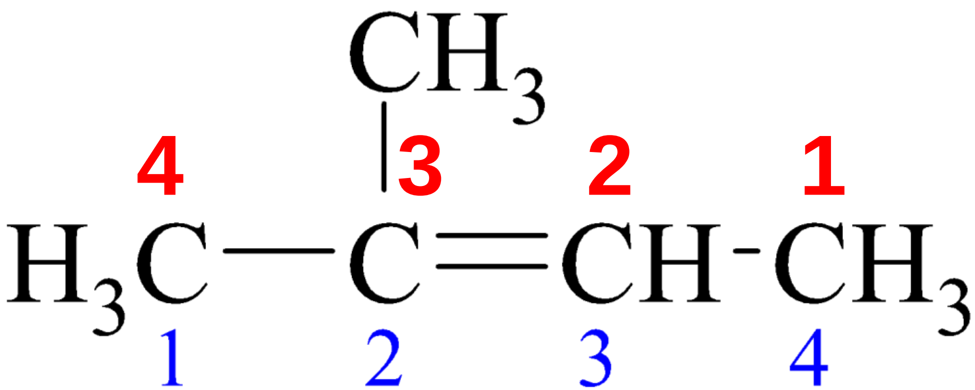
$$\underset{8}{C}H_3\underset{7}{C}H_2\underset{6}{C}H{=}\underset{5}{C}H\underset{4}{C}H_2\underset{3}{C}H_2\underset{2}{C}H_2\underset{1}{C}H_3$$

3-octene

5-octene

STEP 3:

If substituent are present, indicate the **position** of the **substituent** by the number of the carbon atoms to which they are attached.



2-methyl-2-butene

3-methyl-2-butene

STEP 4:

If the alkene contains **more than one double bond,** change the ending '-ene' to:

☞ diene – if there are two double bonds.

☞ triene – if there are three double bonds.

$$\overset{1}{\mathrm{H_2C}}{=}\overset{2}{\mathrm{CH}}\overset{3}{\mathrm{CH}}{=}\overset{4}{\mathrm{CH_2}}$$

1,3-butadiene

1,3-dibutene

$$\overset{1}{\mathrm{H_2C}}{=}\overset{2}{\mathrm{CH}}\overset{3}{\mathrm{CH}}{=}\overset{4}{\mathrm{CH}}\overset{5}{\mathrm{CH}}{=}\overset{6}{\mathrm{CH}}\overset{7}{\mathrm{CH_3}}$$

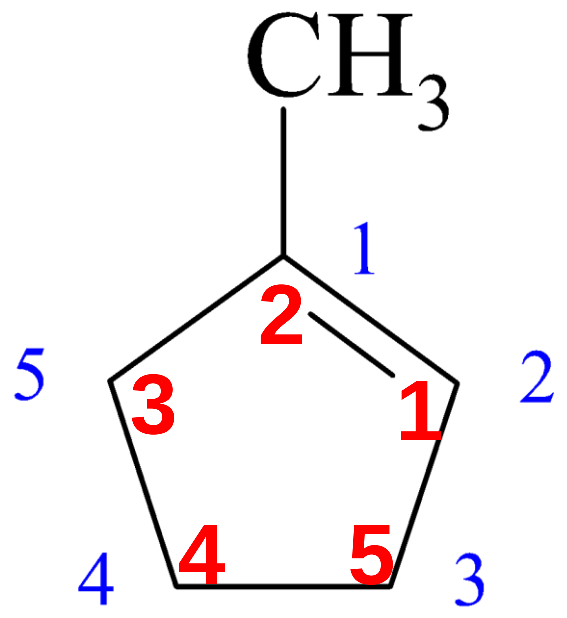
1,3,5-heptatriene

1,3,5-triheptene

STEP 5:

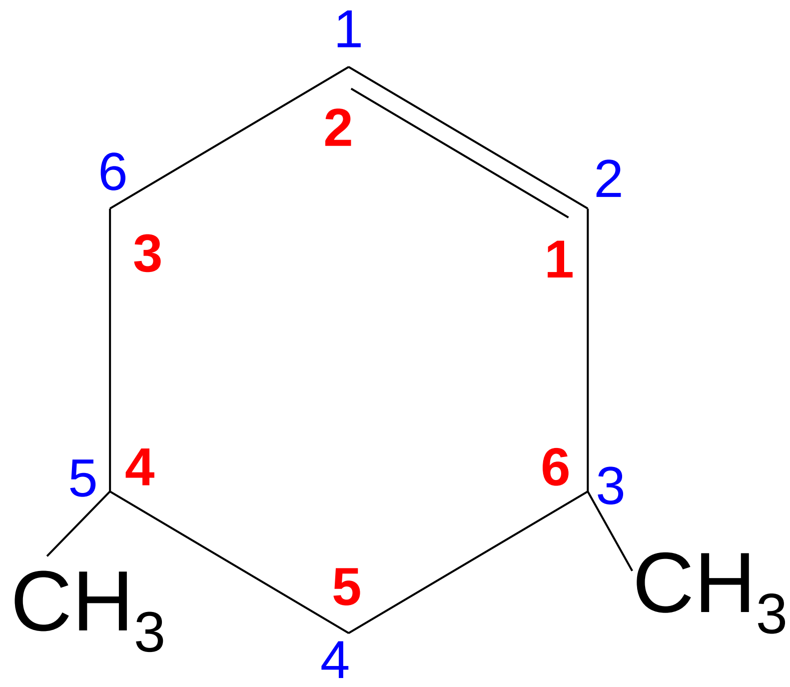
In Cycloalkenes

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.



1-methylcyclopentene

2-methylcyclopentene



3,5-dimethylcyclohexene

4,6-dimethylcyclohexene

STEP 6:

When **alkenyl groups** are perform as a **substituent** it is known as:

$$RCH{=}CHR \xrightarrow{-H} RCH{=}CH-$$

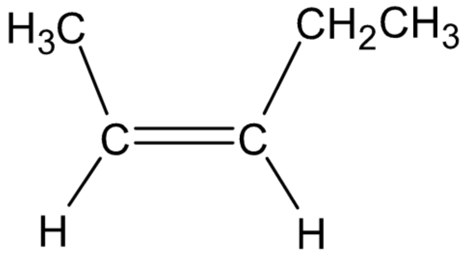
alkene → alkenyl

$CH_2{=}CH-$
vinyl group

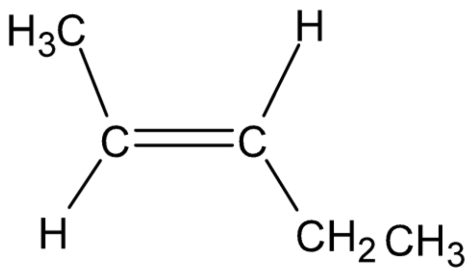
$CH_2{=}CHCH_2-$
allyl group

STEP 7:

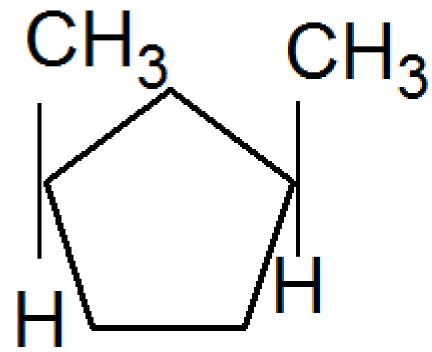
Prefixes **cis-** and **trans-** are used if the alkene shows geometrical isomerism.



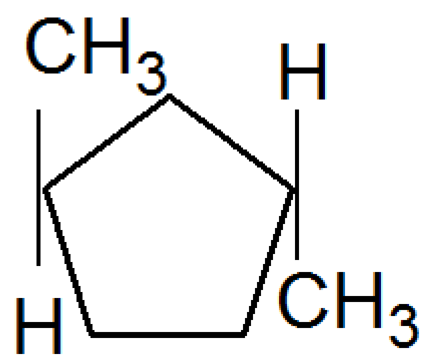
cis-2-pentene



trans-2-pentene



cis-1,3-dimethylcyclopentane



trans-1,3-dimethylcyclopentane

Boiling point of Alkenes

Boiling Point of Isomeric Alkenes:

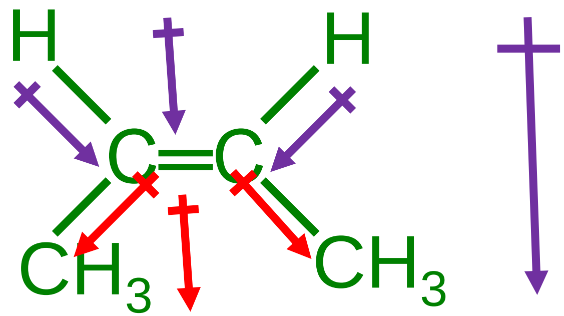
- Cis and trans alkenes have different physical properties.
- For example, *cis*-2-butene has a higher boiling point (4 ^{0}C) than *trans*-2-butene (1 ^{0}C).

- This differences arises because the C-C single bond between an alkyl group and one of the double bond carbons of an alkene is slightly polar.

- In cis isomer, the two C-C bond dipoles reinforce each other, yielding a small net molecular dipoles.

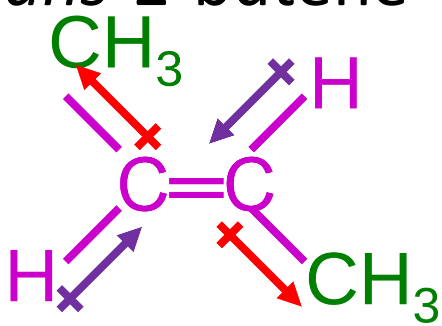
Example :

cis-2-butene



A small net dipole
Higher boiling point (3.7 ^{0}C)

trans-2-butene



No net dipole
Lower boiling point (0.9 ^{0}C)

cis-molecule has higher boiling point because the molecule is polar, therefore the intermolecular forces (van der Waals forces) are relatively stronger.

In a trans isomer, the two bond dipoles cancel each other.

* Boiling point:

cis-isomer > *trans*- isomer

Table show the boiling point for a few stucture of alkene

Alkene	**Structure**	**Boiling point (°C)**
Ethene	$CH_2=CH_2$	-104.0
Propene	$CH_3-CH=CH_2$	-47.0
1-Butene	$CH_2=CH-CH_2-CH_3$	-6.5
Isobutene	$CH_2=CH(CH_3)_2$	-7.0
Trans-2-Butene	$CH_3-CH=CH-CH_3$	0.9
Cis-2-Butene	$CH_3-CH=CH-CH_3$	3.7
1-Pentene	$CH_2=CH-CH_2-CH_2-CH_3$	30.0
Trans-2-Pentene	$CH_3-CH=CH-CH_2-CH_3$	36.0
Cis-2-Pentene	$CH_3-CH=CH-CH_2-CH_3$	37.0
1-Hexene	$CH_2=CH-CH_2-CH_2-CH_2-CH_3$	63.5
1-Heptene	$CH_2=CH-CH_2-CH_2-CH_2-CH_2-CH_3$	115.0

Preparation of Alkenes

Learning Outcomes

(d) Describe the preparation of alkenes through :

i) Dehydration of alcohols;

ii) Dehydrohalogenation of haloalkanes.

(e) Illustrate the mechanism of (d) I

(f) State the Saytzeff's rule.

(g) Explain major product formed using Saytzeff's rule

PREPARATION OF ALKENES

TYPE OF REACTION

- **Elimination**

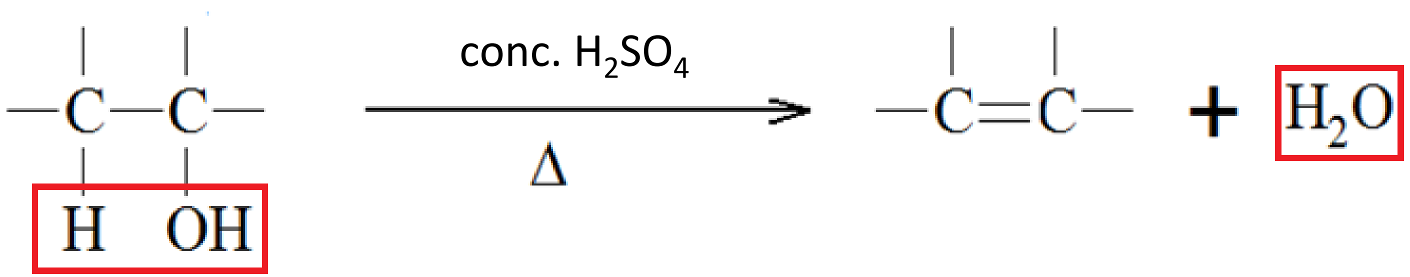
NAME OF REACTIONS

- **1. Dehydration of alcohols**
  - ☞ loss of H_2O from alcohol
- **2. Dehydrohalogenation of haloalkanes**
  - ☞ loss of HX from haloalkane

NAME OF RULE THAT BEING FOLLOWED

- **Saytzeff's rule**

1. Dehydration of alcohols

reagent	conc. H_2SO_4 or conc. H_3PO_4
condition	heat
general equation	

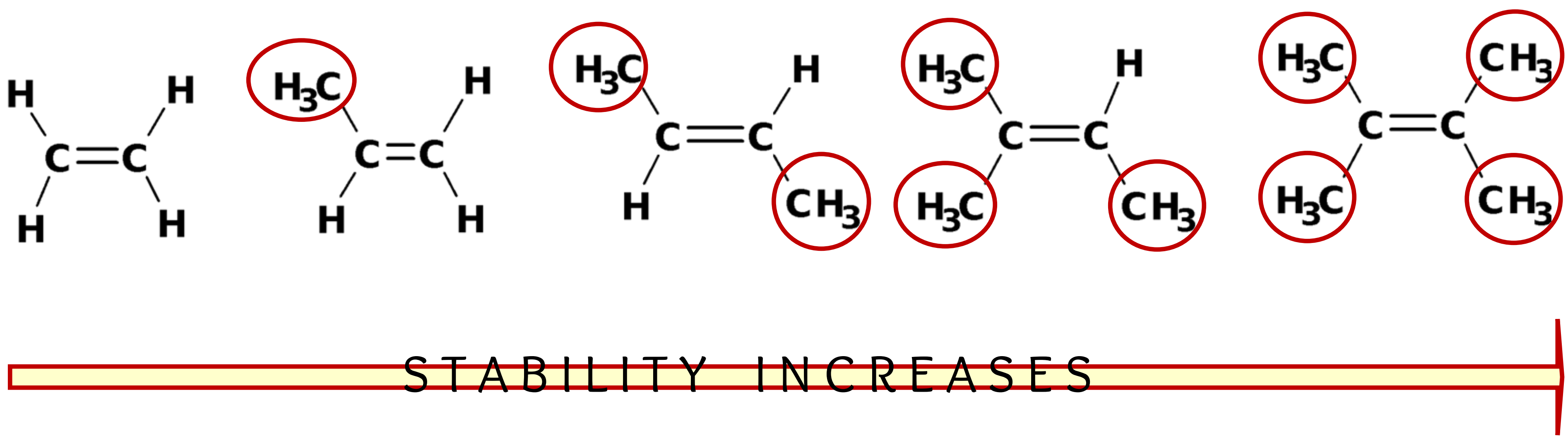
☞ The reaction produces a mixture of product.

☞ The **major product** obtained can be predicted by using **Saytzeff's rule**.

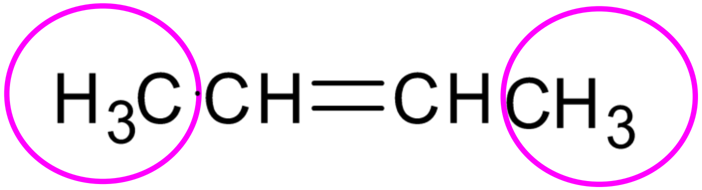
Saytzeff's Rule

The **major product in elimination reaction** is the **most stable** alkenes which **has the most highly substituted double bond.**

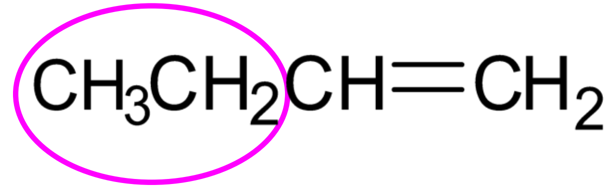
(**greater** number of **alkyl groups** attached to the C=C)



Example 1: Determine the major and minor product

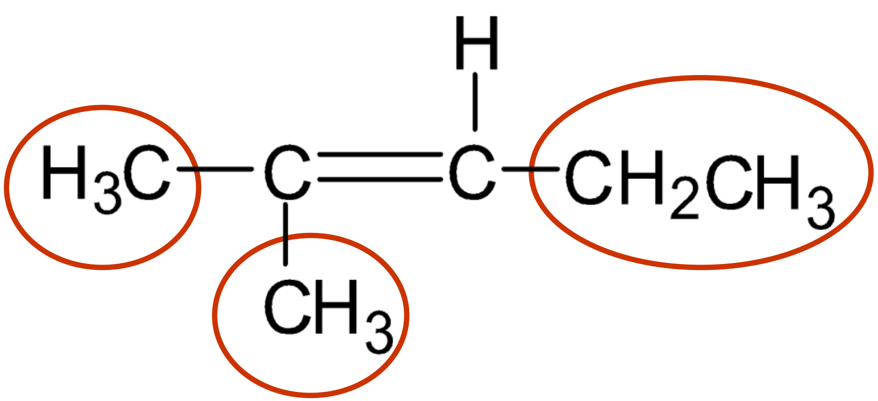


2 alkyl groups
(major product)

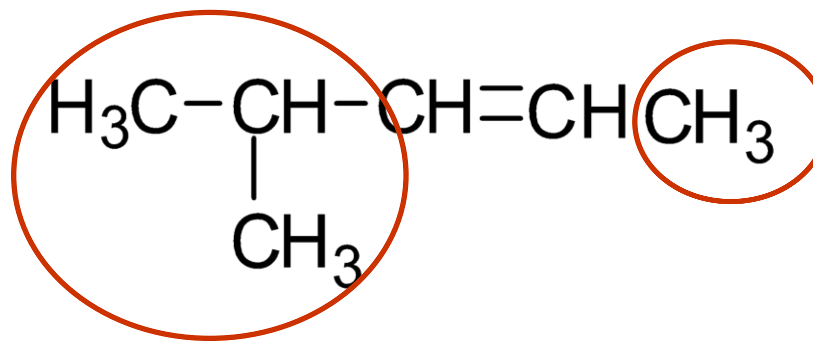


1 alkyl group
(minor product)

Example 2: Determine the major and minor product



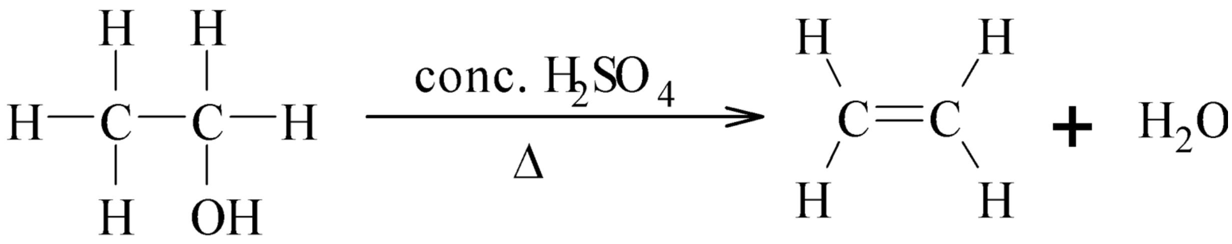
3 alkyl groups
(major product)



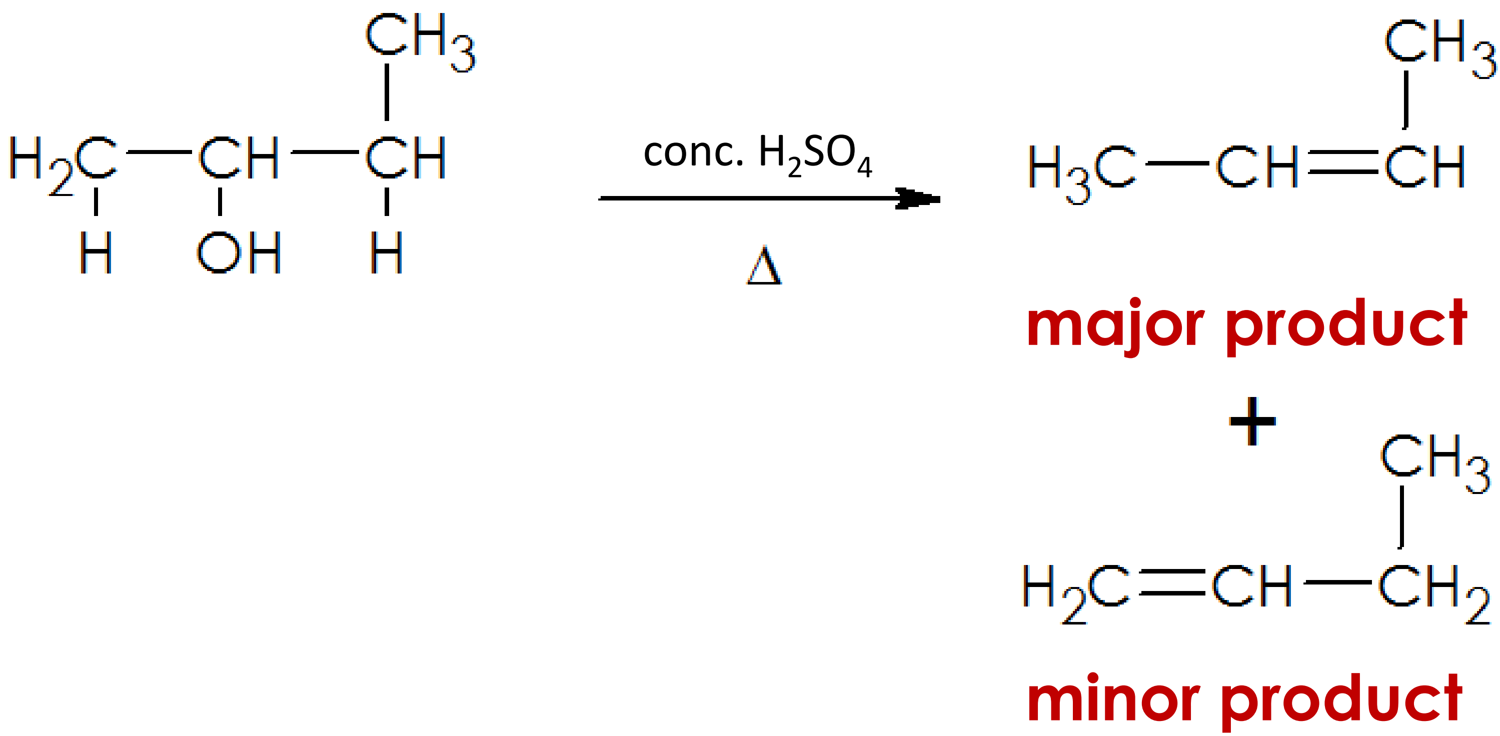
2 alkyl groups
(minor product)

Examples :

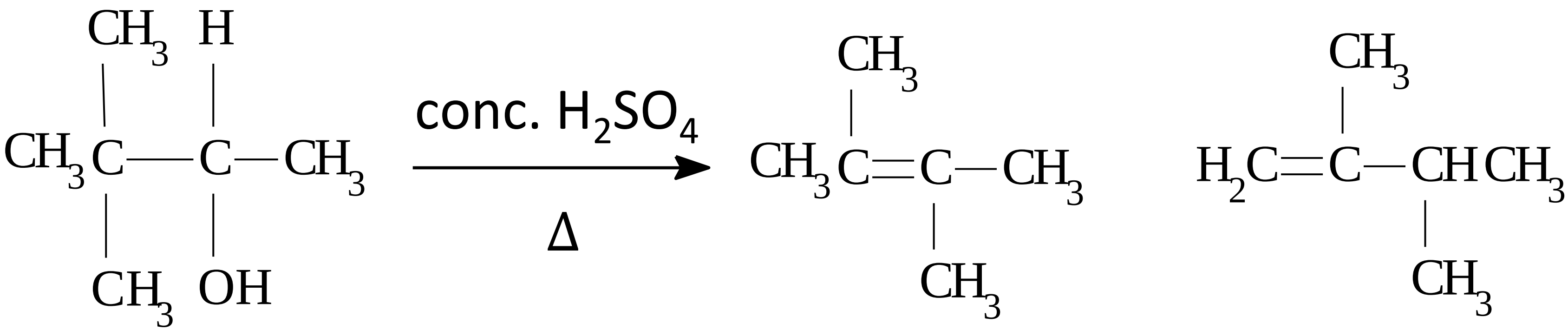
(i)



(ii)



(iii)



(major product)

(minor product)

REARRANGEMENT

1,2-methanide shift

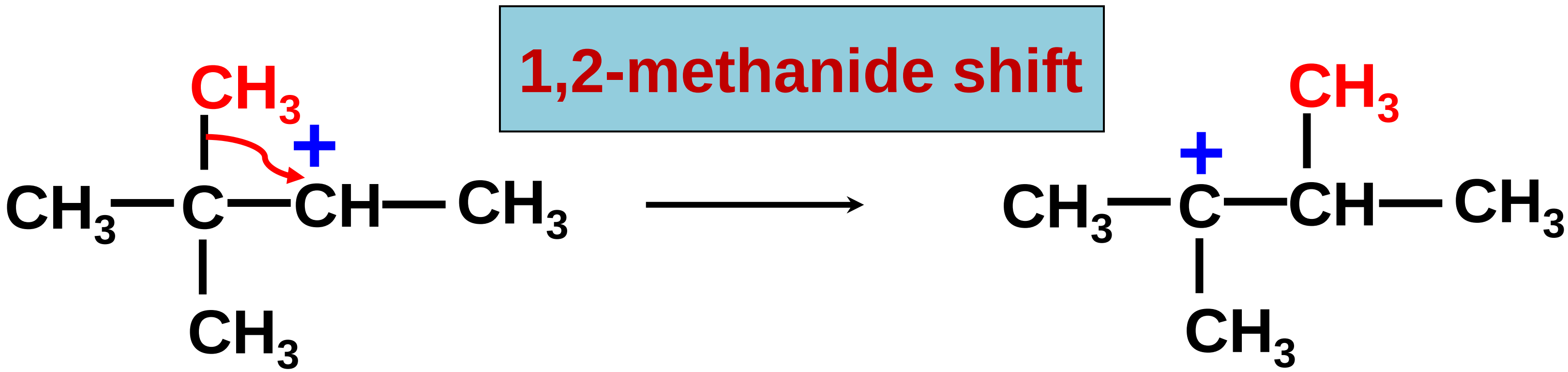
the migration of **$-CH_3$** (methanide ion) from the **C** atom that **adjacent** to the **carbocation**.

1,2-hydride shift

the migration of **-H** (hydride ion) from the **C** atom that **adjacent** to the **carbocation.**

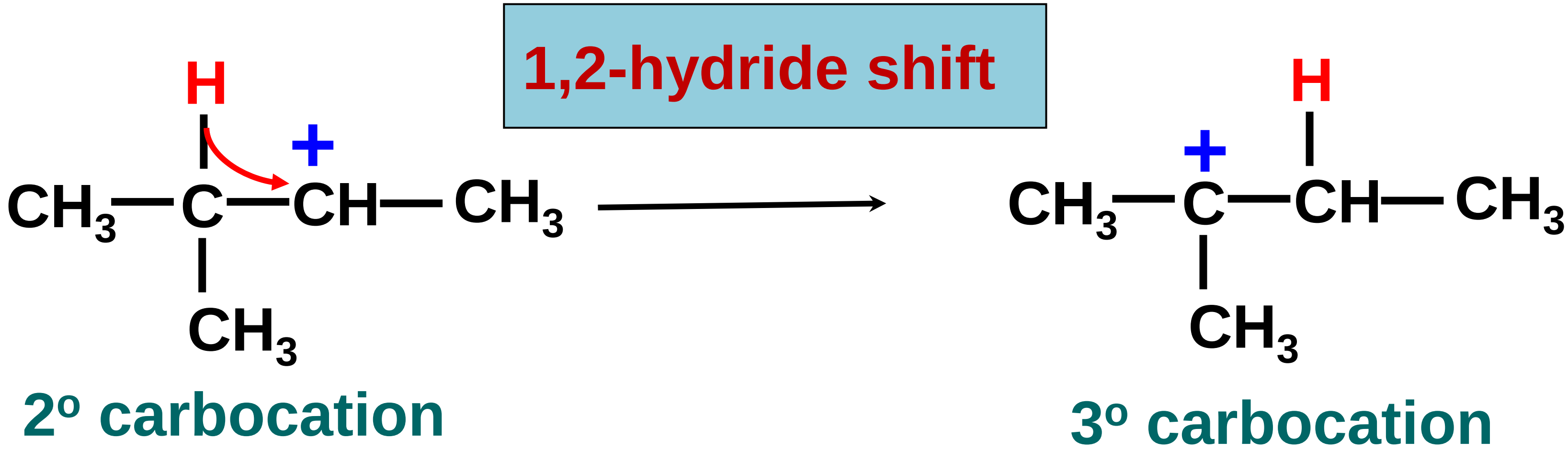
***Rearrangement step occur to form **more stable carbocation**

Example :



2° carbocation 3° carbocation

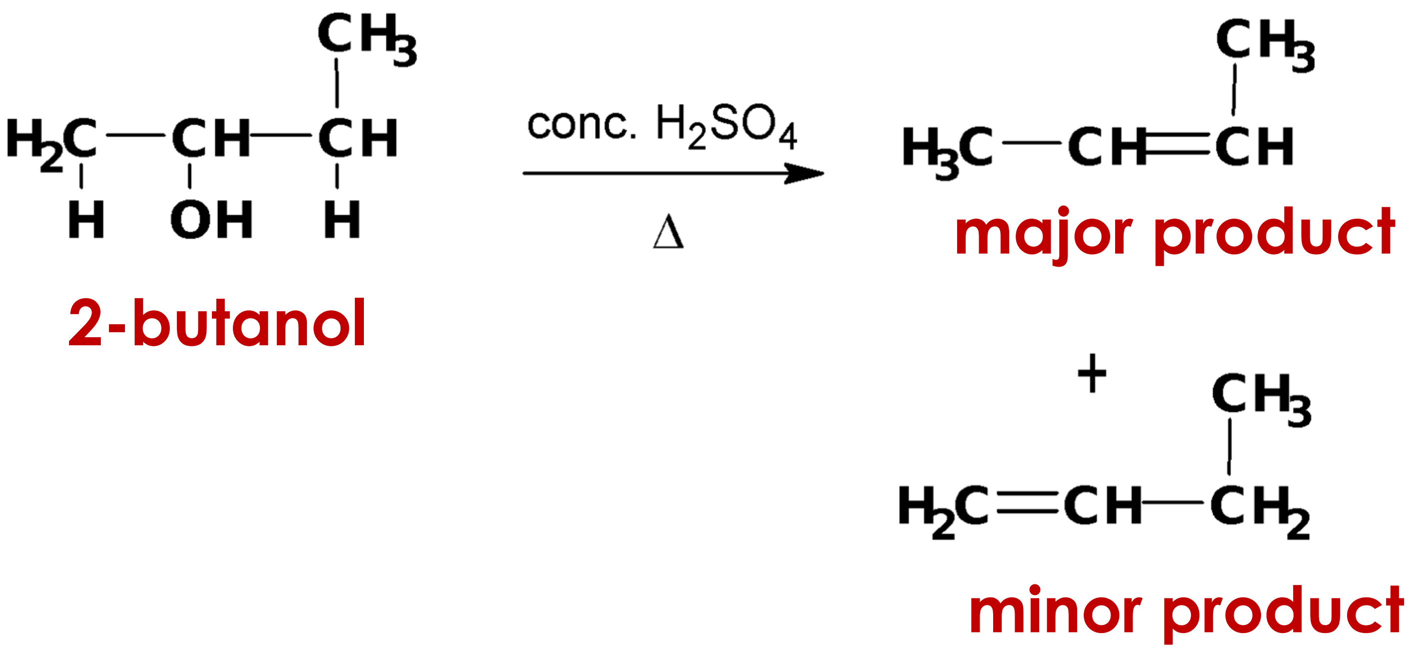
Example :



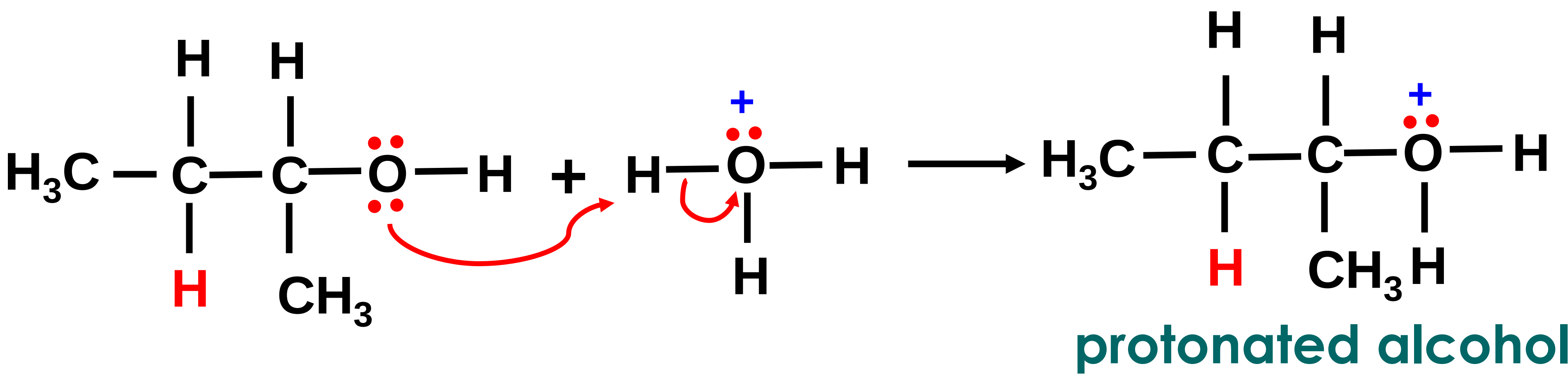
1,2-hydride shift
H
+
CH3
C
CH
CH3
CH3
2o carbocation
3o carbocation

Example 1:

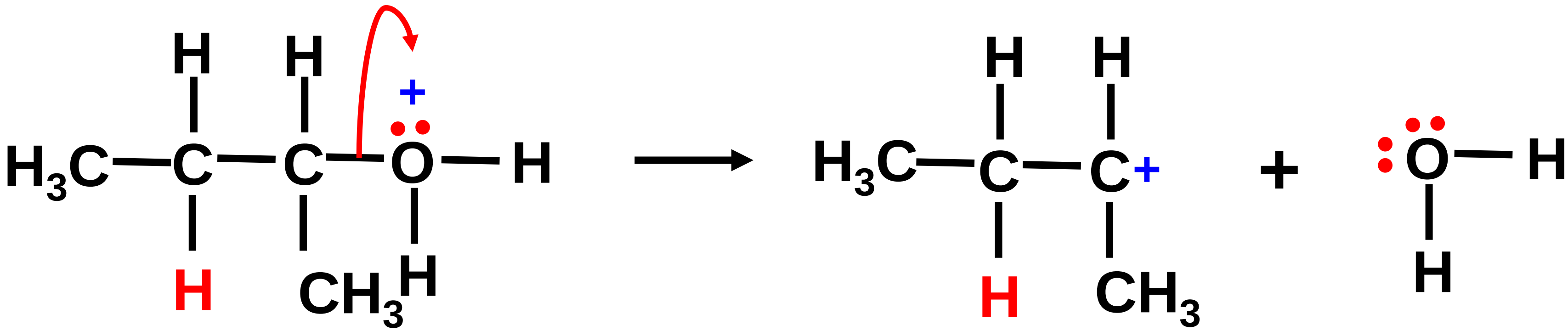
Dehydration of 2–butanol gives a mixture of two alkenes. Propose mechanisms to account the formation of major alkene (major product).



Step 1: Protonation of –OH group



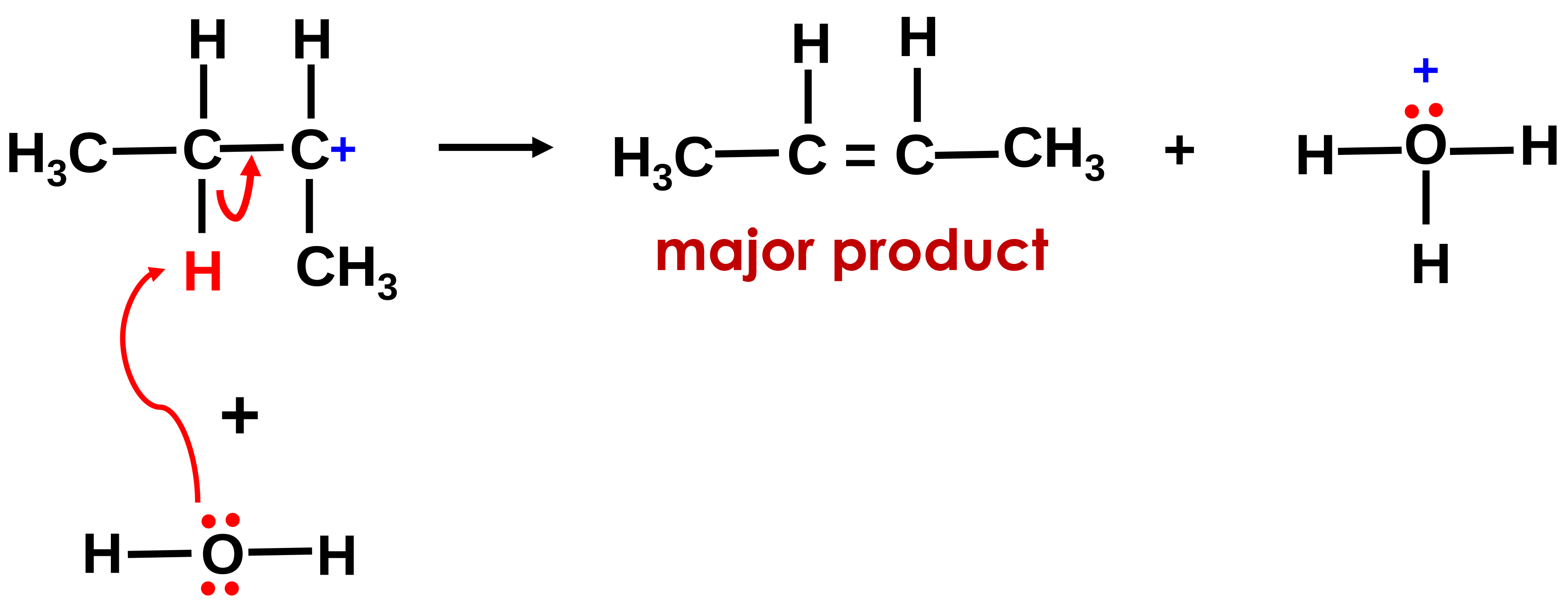
Step 2: Formation of carbocation



carbocation

Step 3: Formation of alkene

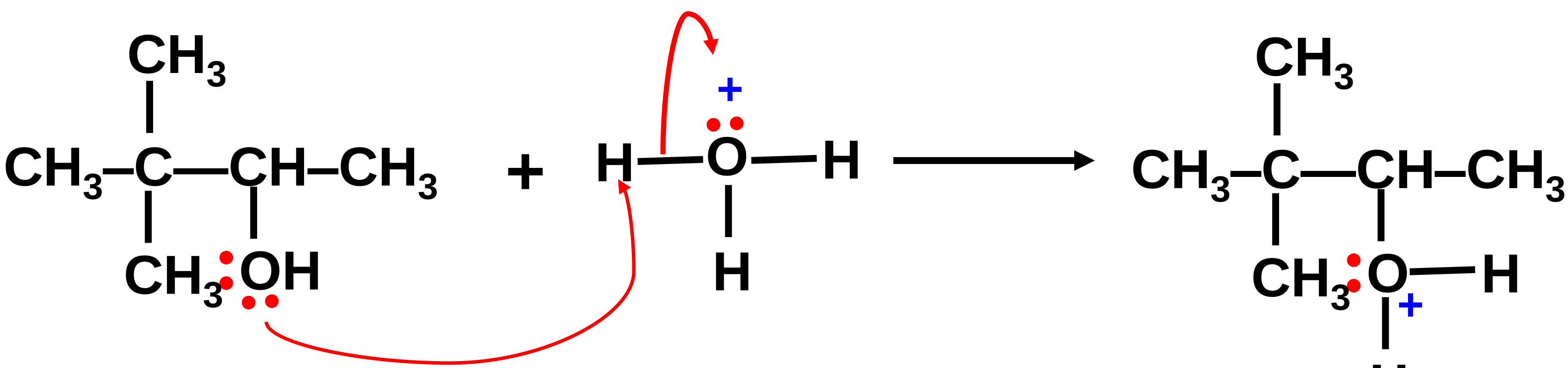
☞ **C atom that adjacent to the carbocation loses proton, H^+**



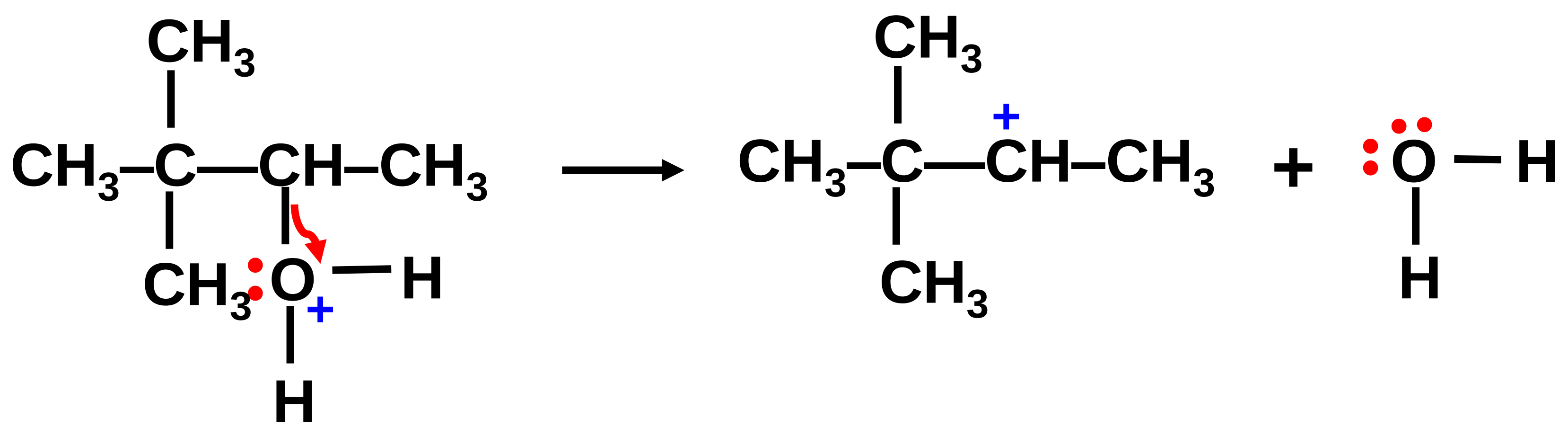
Example 2:

Write the mechanism for the formation of major product for dehydration of 3,3-dimethyl-2-butanol.

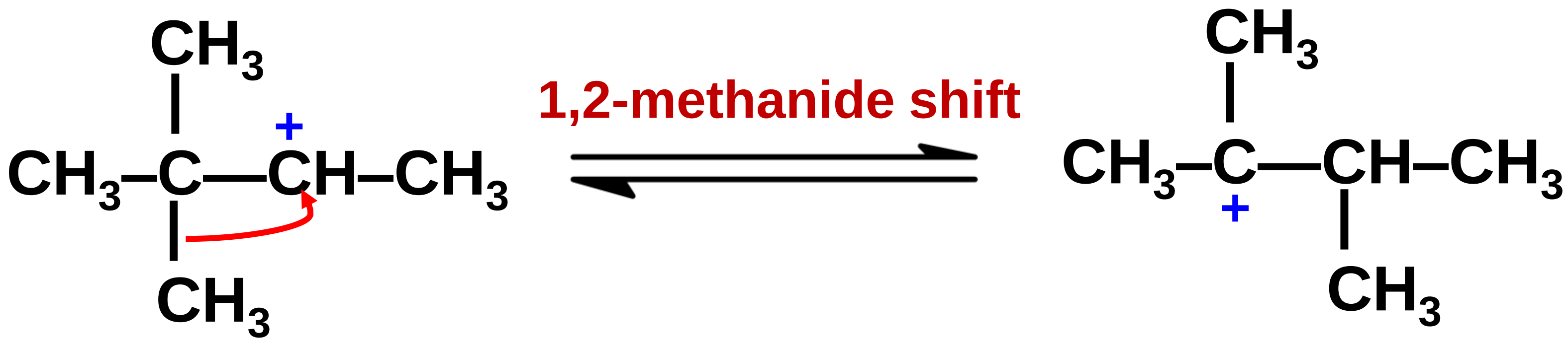
Step 1: Protonation of –OH group



Step 2: Formation of carbocation



Step 3: Rearrangement

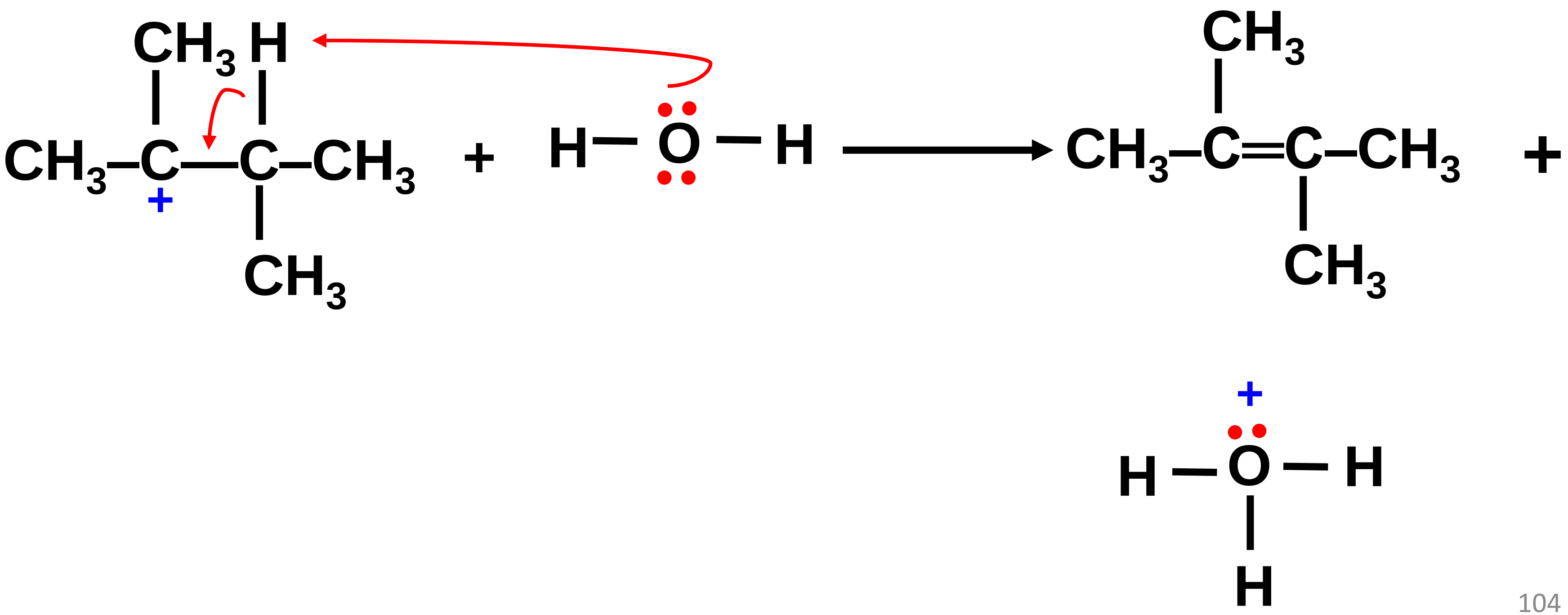


2° carbocation

3° carbocation

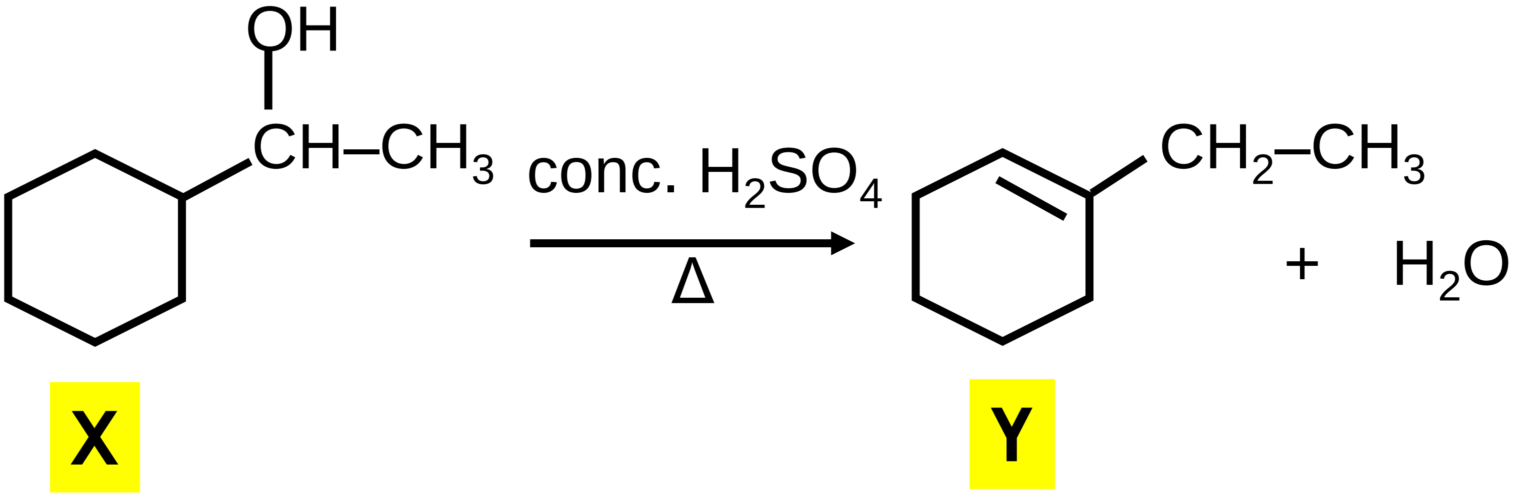
Step 4: Formation of alkene

☞ C atom that adjacent to the carbocation loses proton, H^+

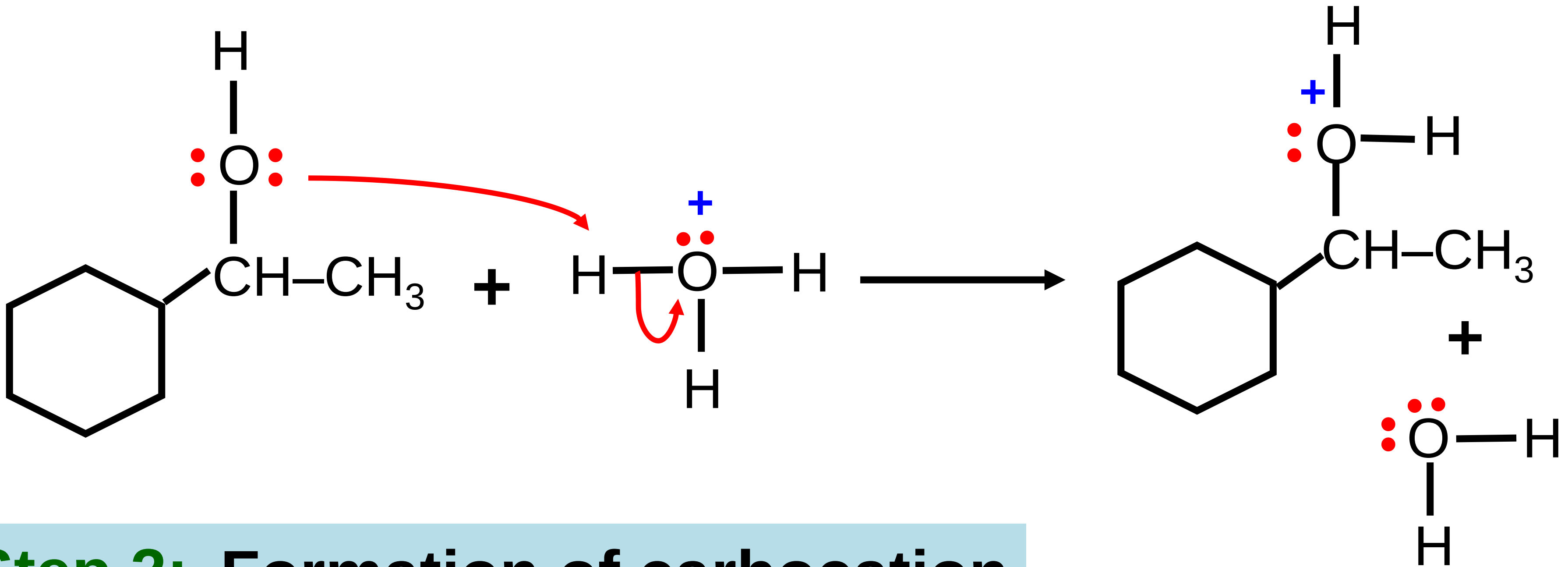


Example 3:

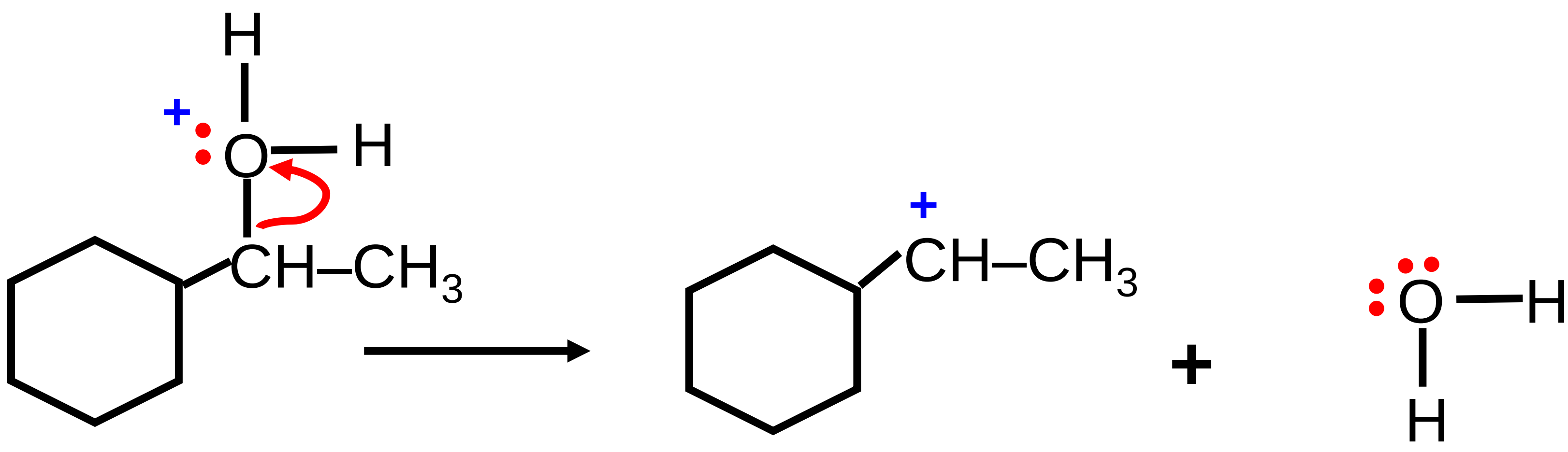
Show the mechanism for the formation of alkene Y from alcohol X.



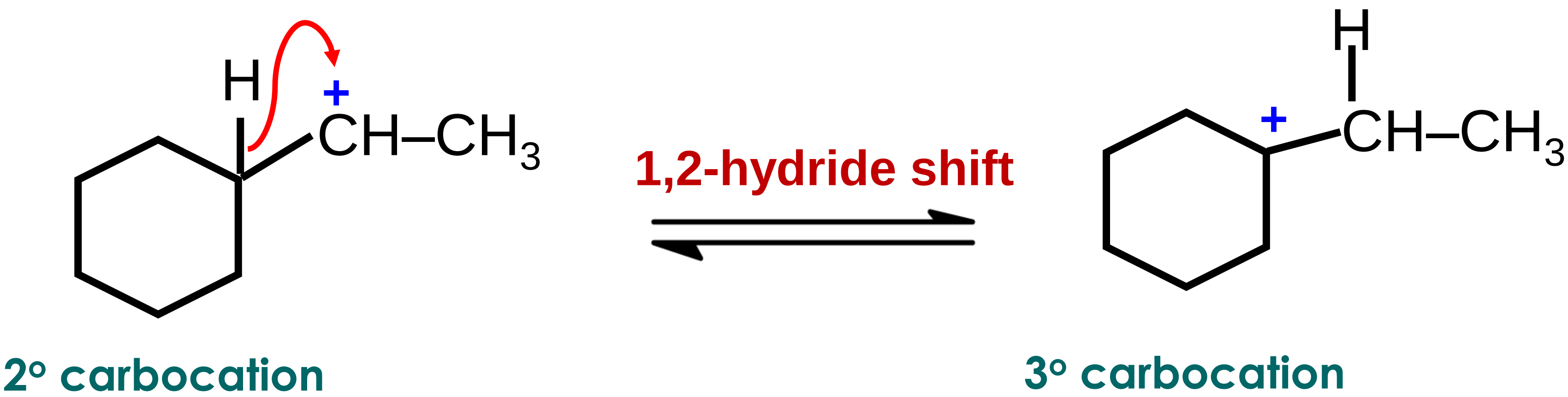
Step 1: Protonation of –OH group



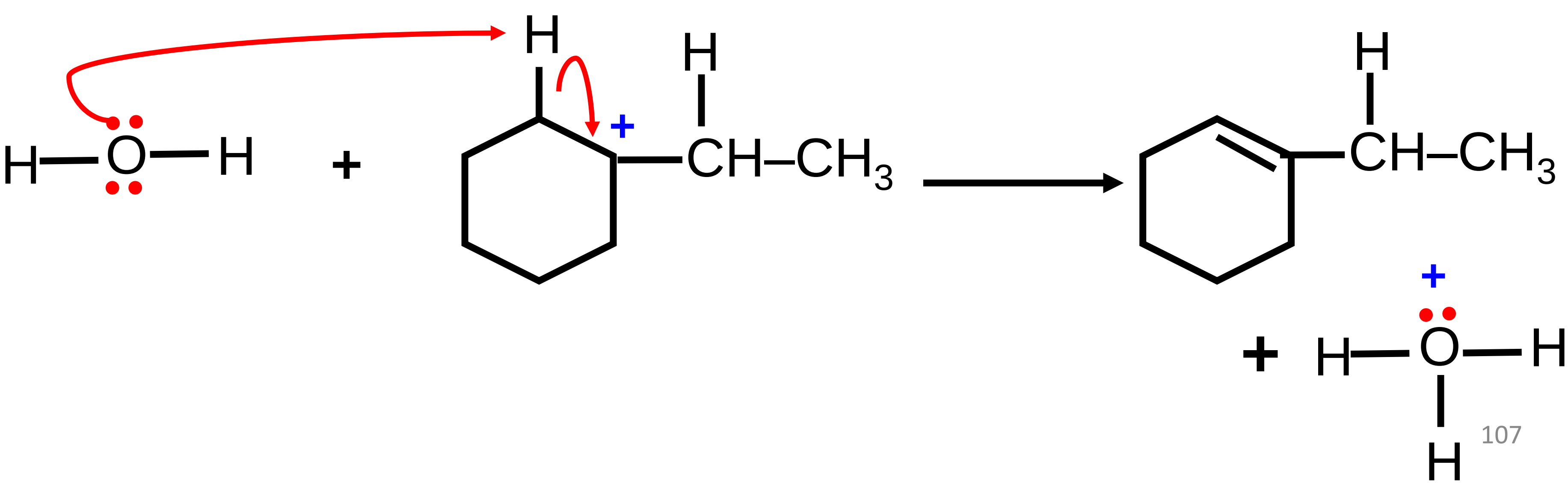
Step 2: Formation of carbocation



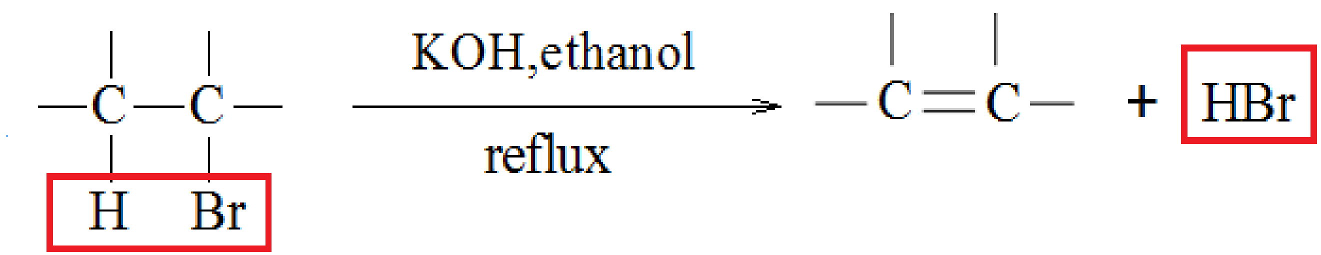
Step 3: Rearrangement



Step 4: Formation of alkene

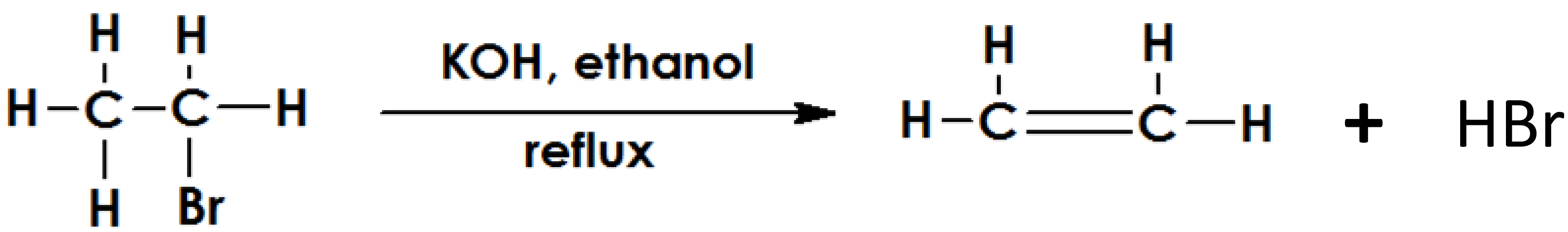


2. Dehydrohalogenation of alkyl halide

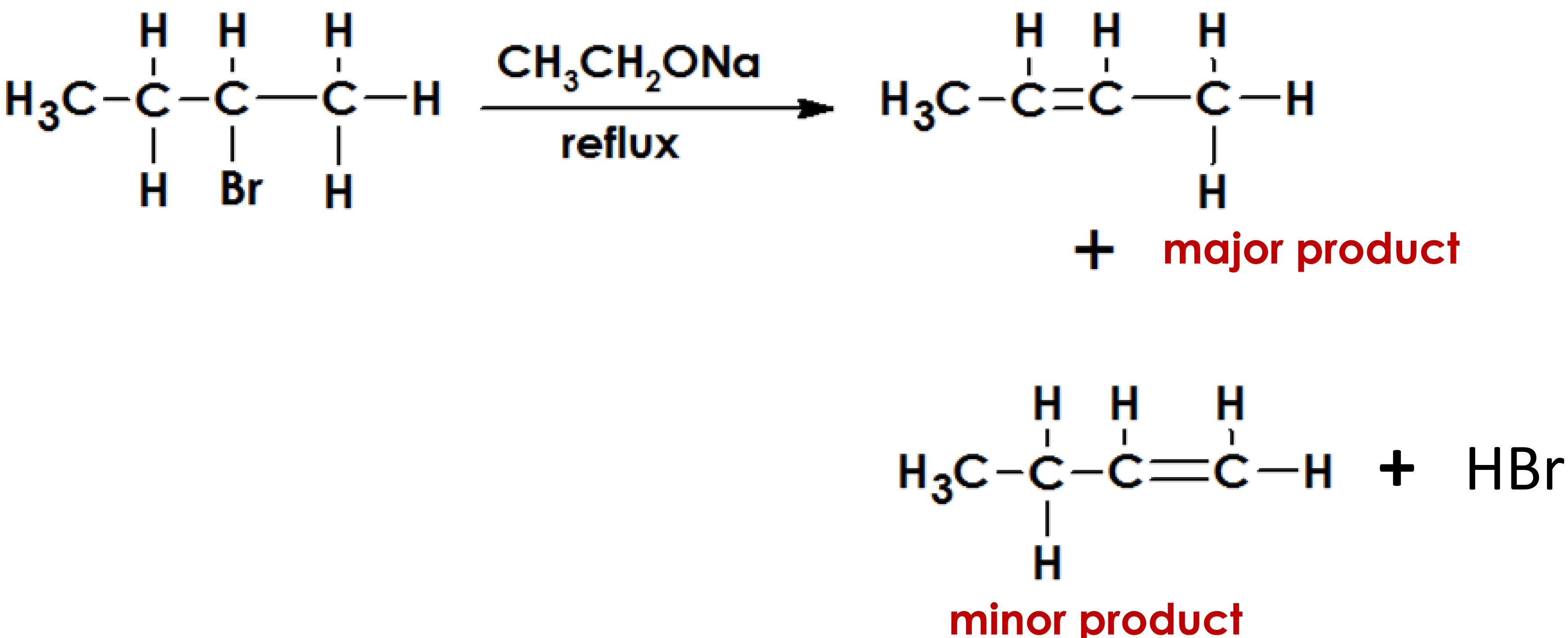
reagents	Alcoholic OH^- @ OR^- e.g: NaOH, KOH, $KOCH_3$, CH_3CH_2ONa
condition	reflux
general equation	

- The reaction produces a mixture of product.
- The **major product** obtained can be predicted by using **Saytzeff's rule**.

Example 1:



Example 2 :



Chemical Properties of Alkenes

CHEMICAL PROPERTIES OF ALKENES

- **1) ELECTROPHILIC ADDITION**
  - catalytic hydrogenation
  - halogenation
    - ☞ in inert solvent
    - ☞ in water
  - hydrohalogenation
  - Acidified water
- **2) OXIDATION**
  - ozonolysis
  - hot, acidified $KMnO_4$
  - cold, dilute alkaline $KMnO_4$ (Baeyer's Test)

Learning Outcomes

(h) Explain the addition reaction of alkenes with:

i. hydrogen in the presence of catalyst;

ii. halogen (Cl_2 or Br_2) in inert solvent (CH_2Cl_2);

iii. halogen (Cl_2 or Br_2) in water;

iv. hydrogen halides (HCl or HBr);

v. acidified water

(i) State Markovnikov's rule

(j) Predict the products formed according to the Markovnikov's rule

(k) Illustrate the mechanism of electrophilic addition of (h) iv and (h) v.

(l) Predict the product of the reaction between alkene and hydrogen bromide in the presence of hydrogen peroxide/ acid peroxide according to anti-Markovnikov's rule.

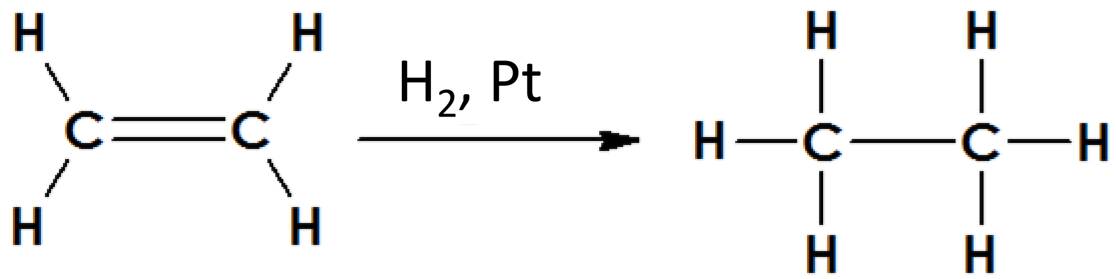
Electrophilic Addition

Catalytic Hydrogenation

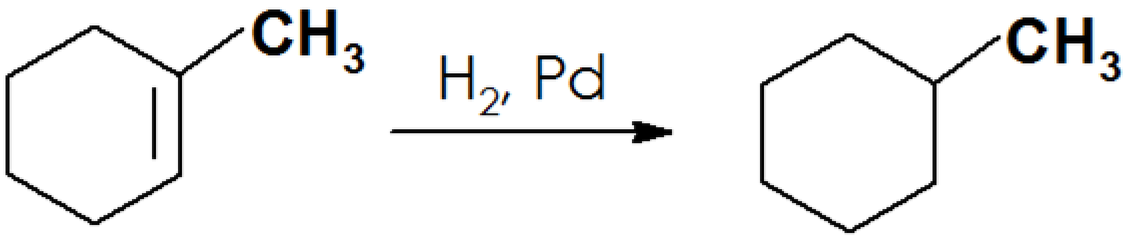
Reagent	H_2 , Pt / Pd / Ni / Pd
Product	alkane

Example:

(i)



(ii)

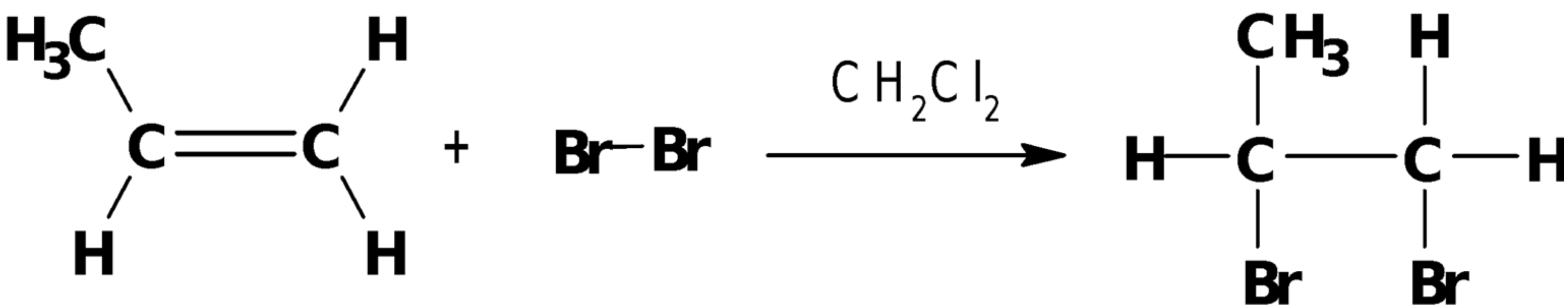


Halogenation in Inert Solvent

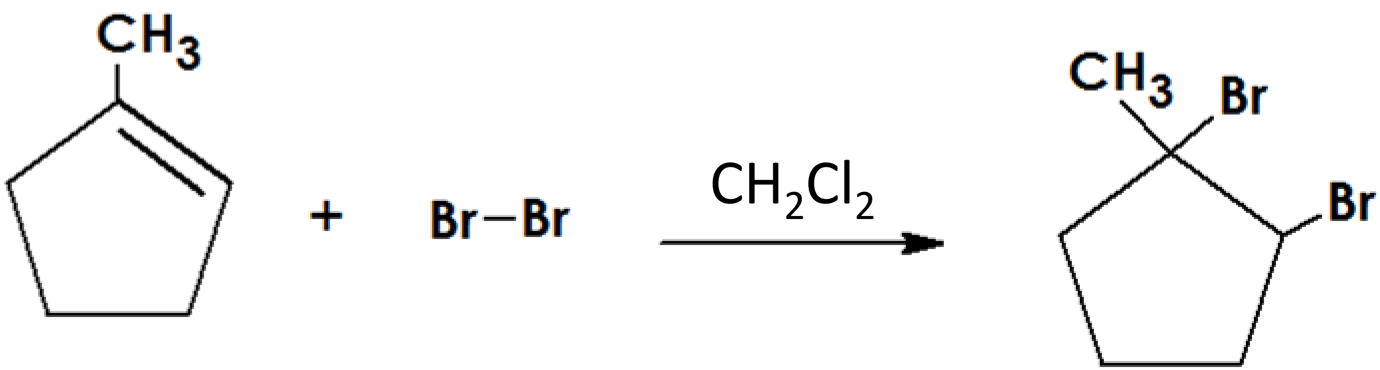
Reagent	X_2, CH_2Cl_2 (X_2 = Cl_2, Br_2)
Product	vicinal dihalide

Example:

(i)

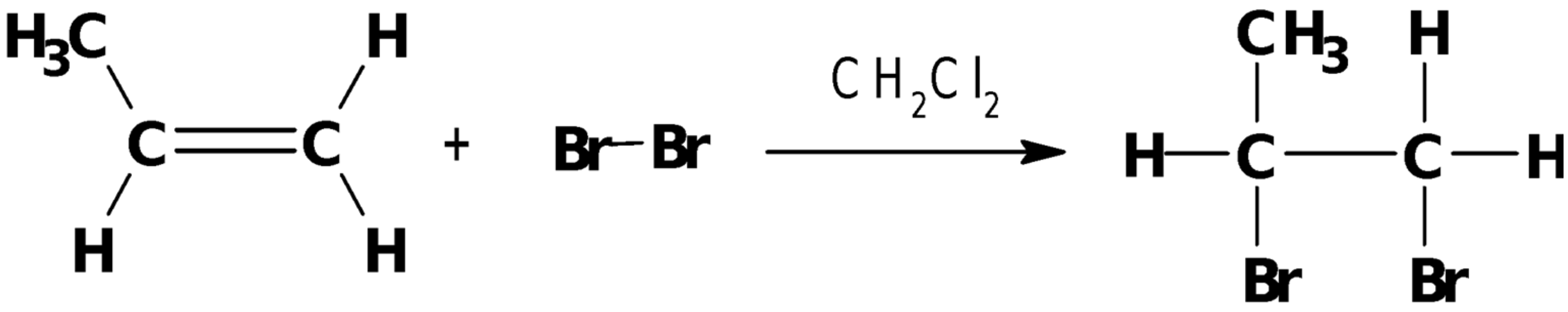


(ii)



Halogenation in Inert Solvent

When the equation below are tested with Br_2 in CH_2Cl_2,



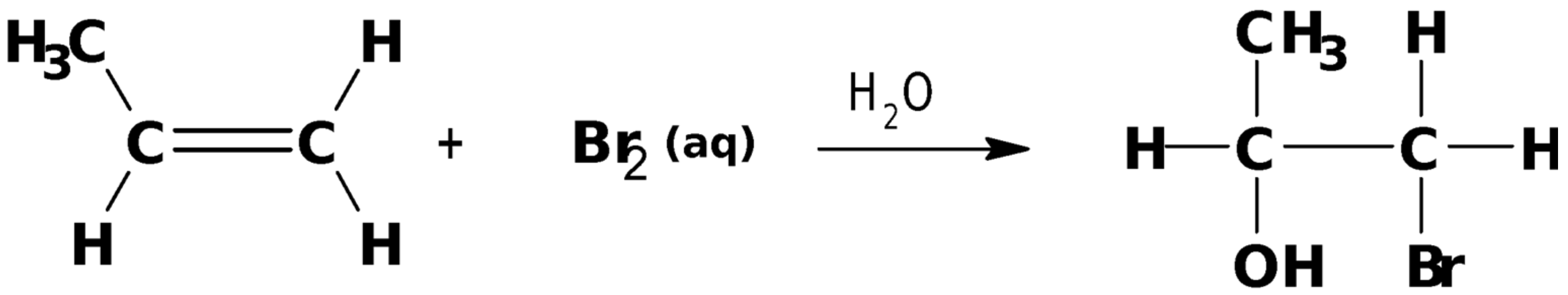
Name of chemical test : **Bromine test**

Observations : **Reddish brown colour of bromine decolourised**

Halogenation in Water

Reagent	X_2, H_2O (X_2 = Cl_2, Br_2)
Product	halohydrin

Example 1:



*****<u>Follow Markovnikov's Rule</u> :**

-OH attach at carbon with fewer no. of H atoms

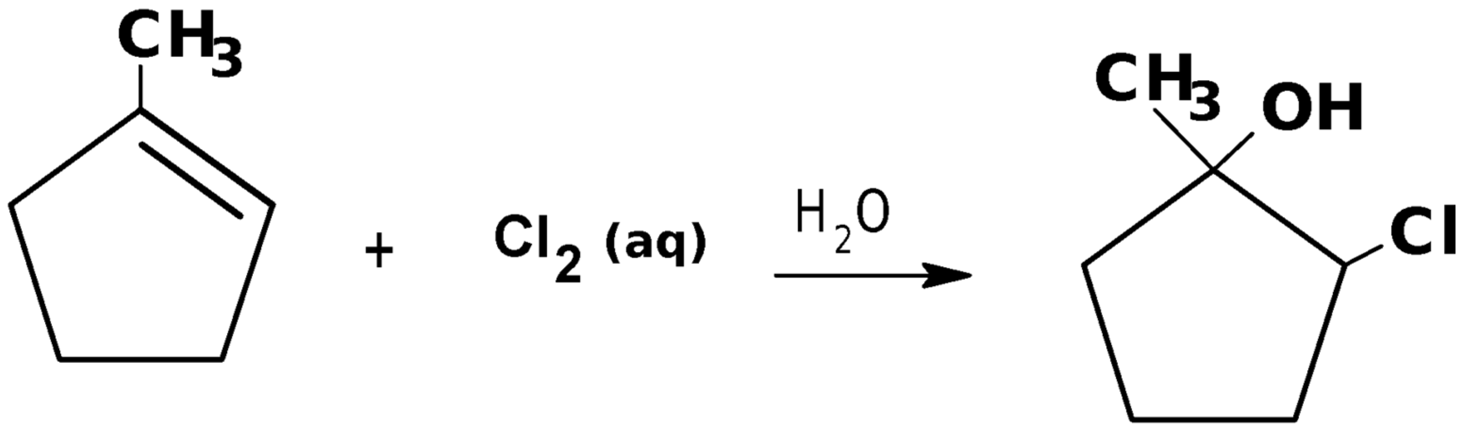
halogen attach at carbon with greater no. of H atoms

Markovnikov's Rule

In the electrophilic addition of alkenes, the electrophile adds to the C atom of the C=C with greater number of H atoms

Halogenation in Water

Example 2:



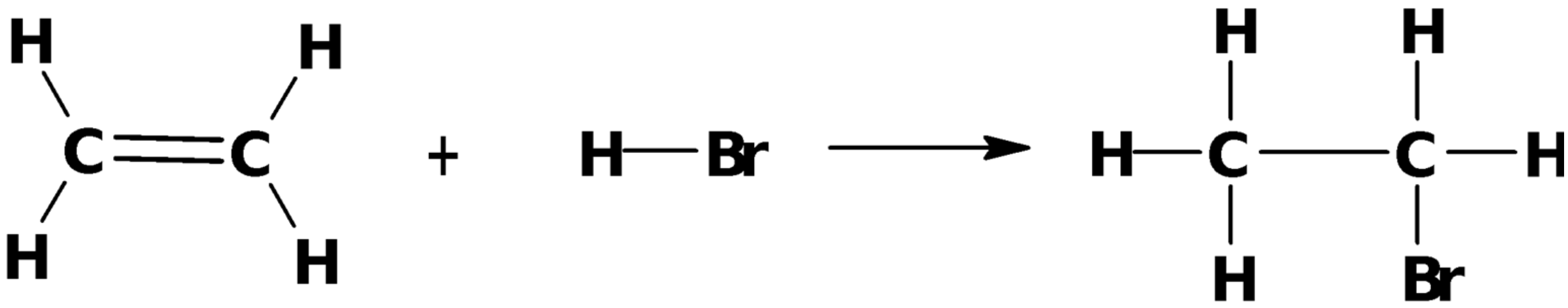
Name of chemical test : **Bromine test**

Observations : **Reddish brown colour of bromine decolourised**

Hydrohalogenation

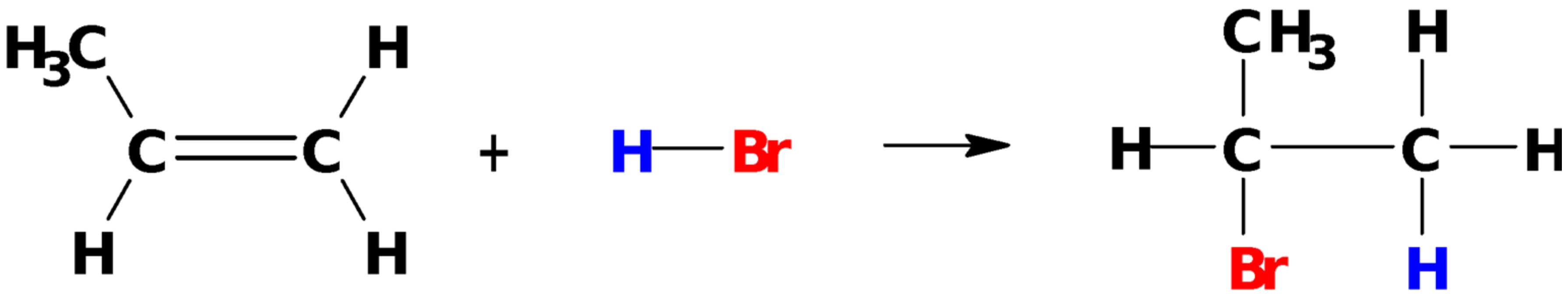
Reagent	HX (X = Cl, Br)
Product	haloalkane
Reactivity	HCl < HBr

Example 1:



Hydrohalogenation

Example 2 :



***<u>Follow Markovnikov's Rule</u> :**

-OH attach at carbon with fewer no. of H atoms

halogen attach at carbon with greater no. of H atoms

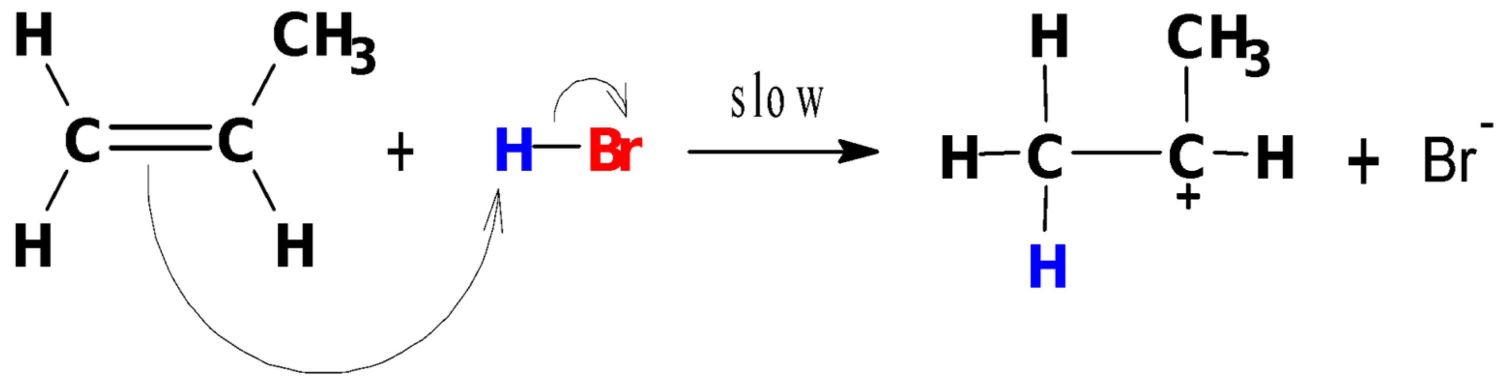
Reaction Mechanism : Hydrohalogenation

Example 1:

Write the mechanism for the hydrohalogenation reaction of propene.

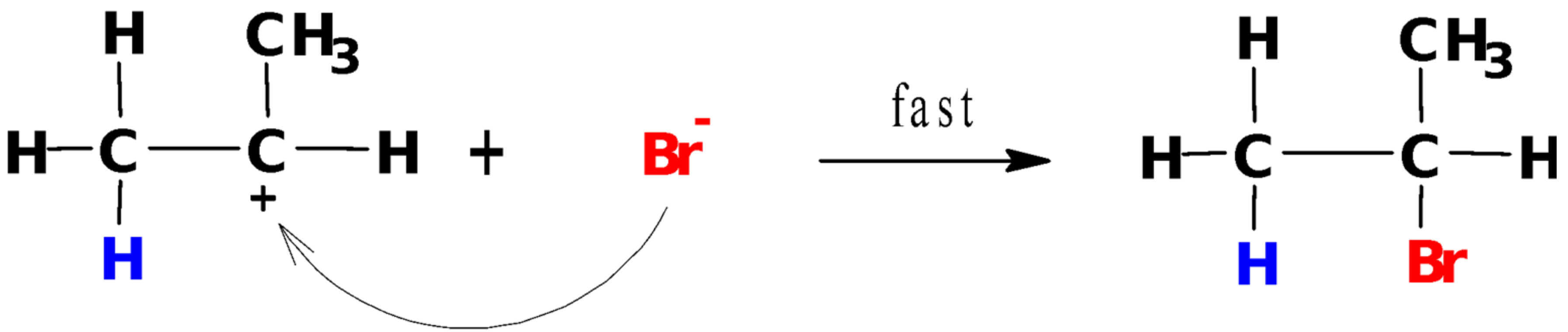
Answer:

Step 1 : Formation of carbocation and halide ion



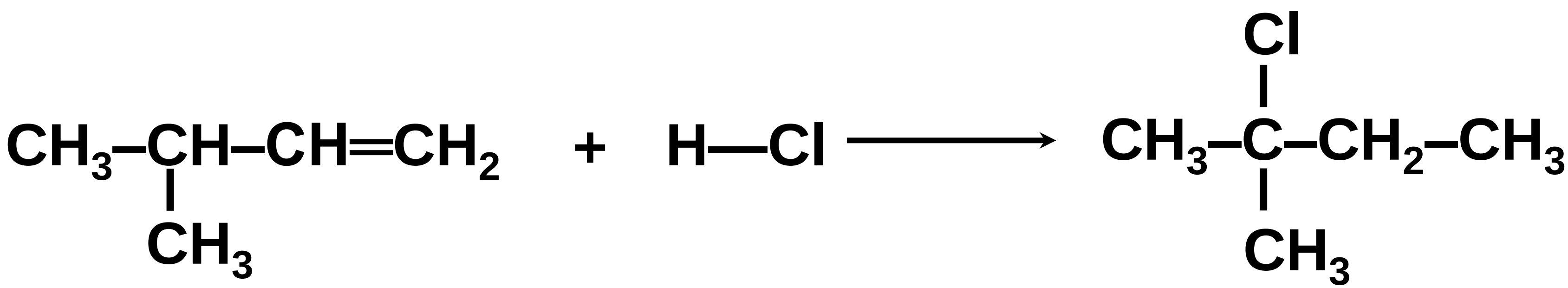
Reaction Mechanism : Hydrohalogenation

Step 2 : Halide ion reacts with the carbocation by donating an electron pair



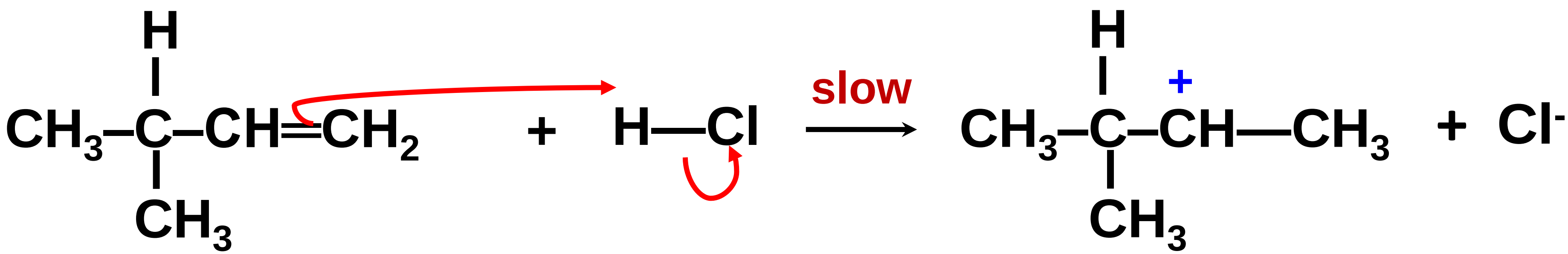
Example 2:

Write the mechanism for the major product of the following reaction:

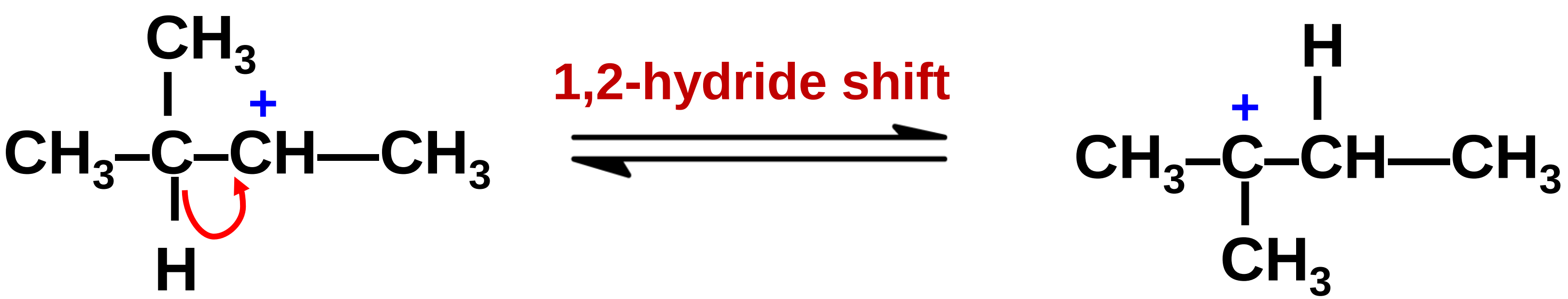


Answer:

Step 1 : Formation of carbocation and halide ion



Step 2 : Rearrangement

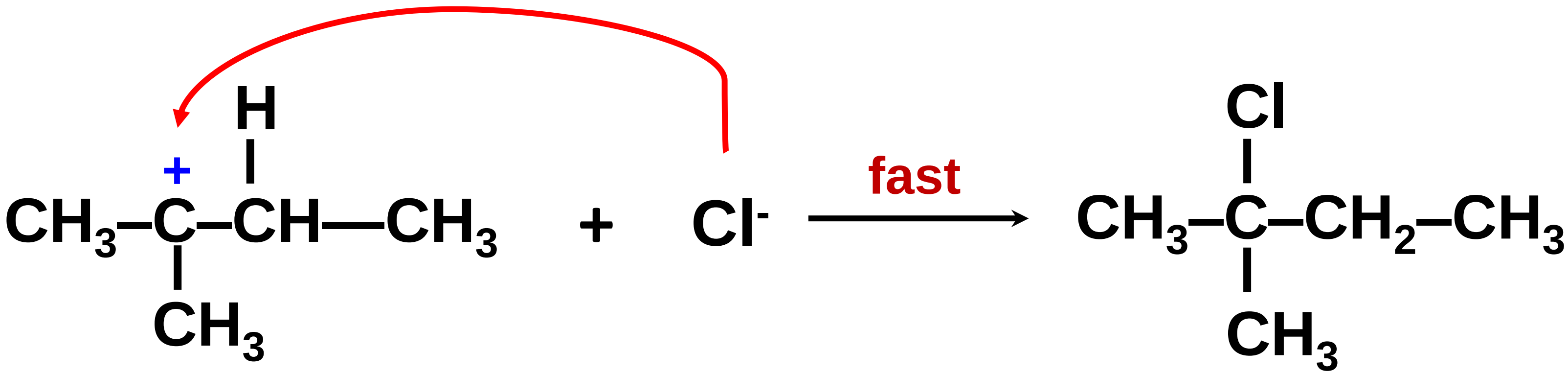


2° carbocation

3° carbocation
(more stable)

Reaction Mechanism : Hydrohalogenation

Step 3 : Halide ion reacts with the carbocation by donating an electron pair



Anti-Markovnikov's Rule

In the presence of peroxides, ROOR (eg: H_2O_2) the addition occurs in an anti-Markovnikov rule

Example :

$$CH_3{-}CH{=}CH_2 \quad + \quad H{-}Br \xrightarrow{H_2O_2} CH_3{-}CH_2{-}\underset{}{\overset{\displaystyle Br}{\overset{|}{C}}}H_2$$

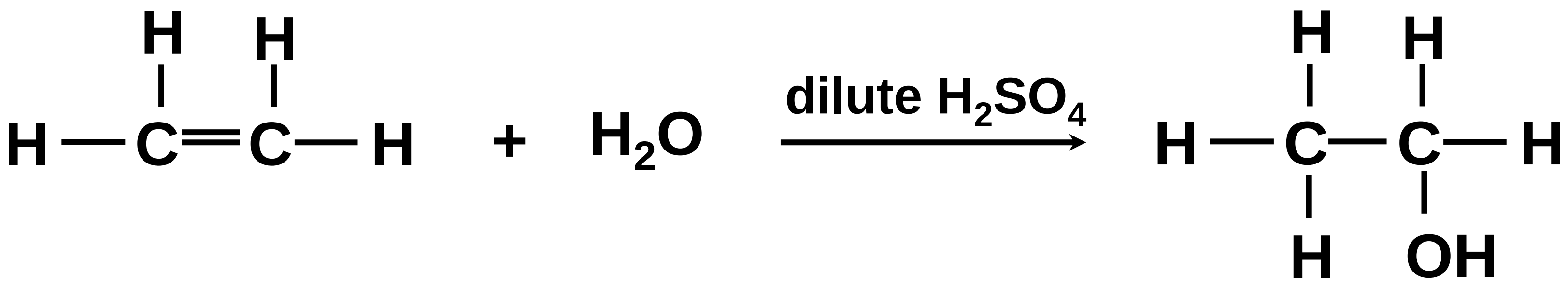
Anti-Markovnikov's Rule :
H atom added to C atom with Less H
(MAJOR product)

*****only occurred in the addition of HBr to an alkene**

Acidified water

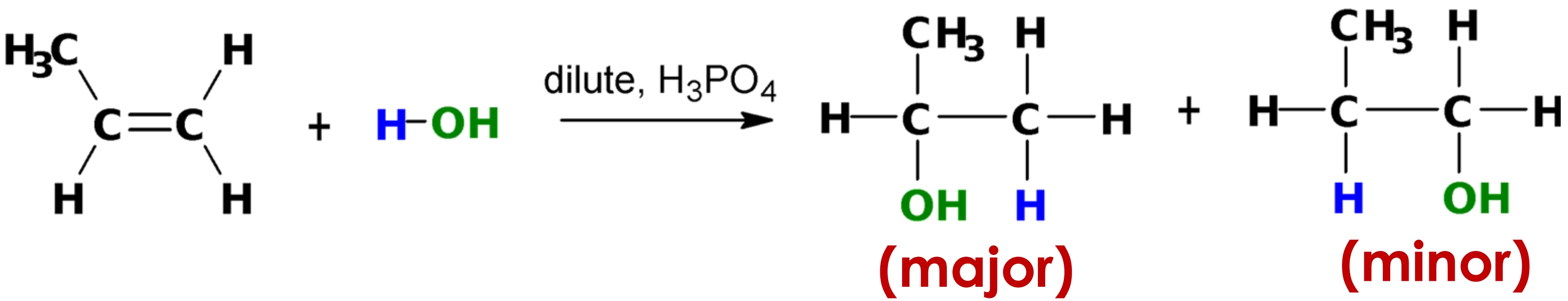
Reagent	H_2O, dilute H_2SO_4 / H_3PO_4
Product	alcohol

Example 1:



Acidified water

Example 2:



***<u>**Follow Markovnikov's Rule**</u> **:**

-OH attach at carbon with fewer no. of H atoms

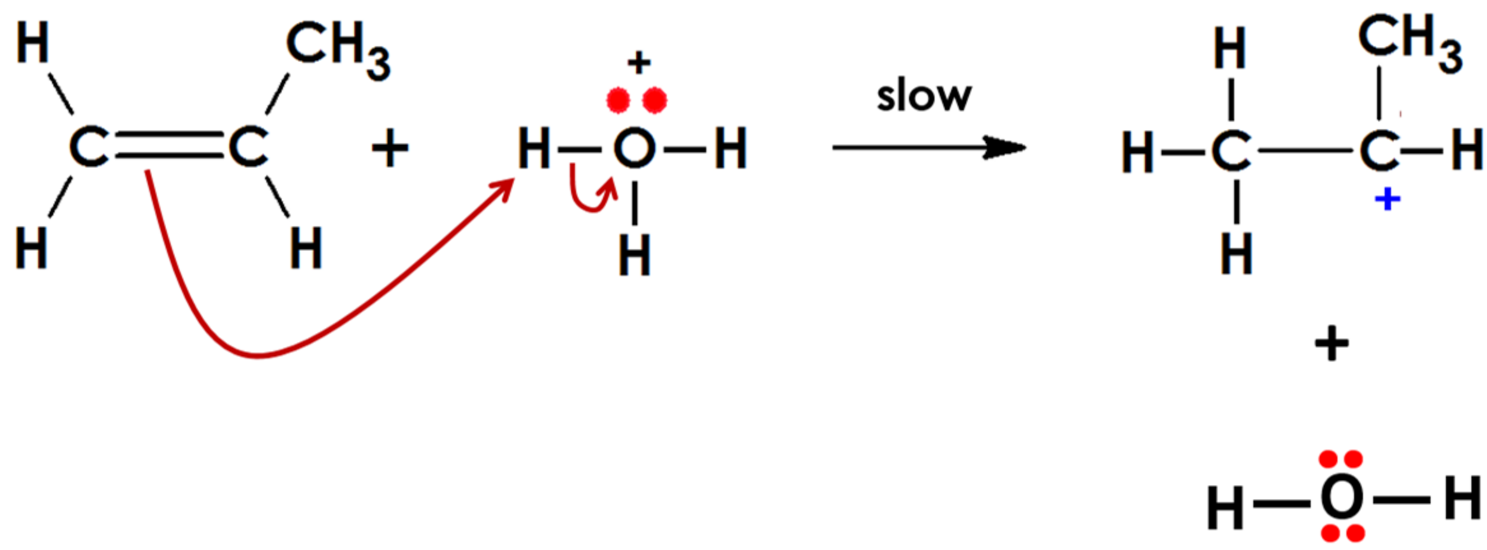
H attach at carbon with greater no. of H atoms

Example 1:

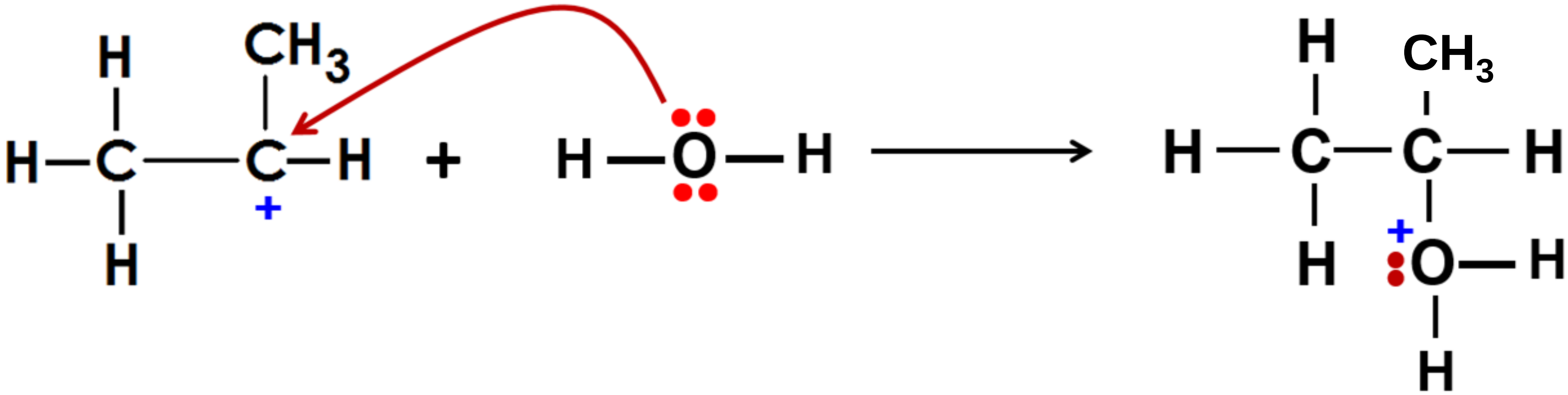
Write the mechanism for the hydration reaction of propene.

Answer:

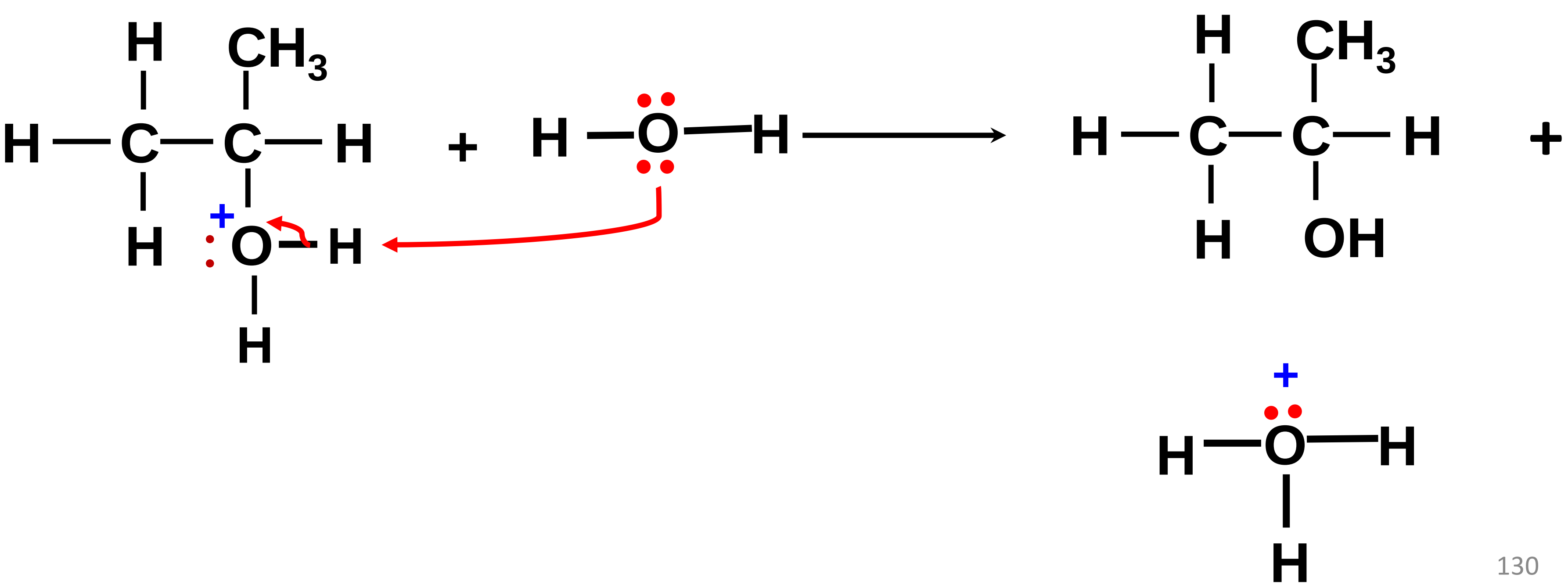
Step 1 : Formation of carbocation



Step 2 : Formation of protonated alcohol

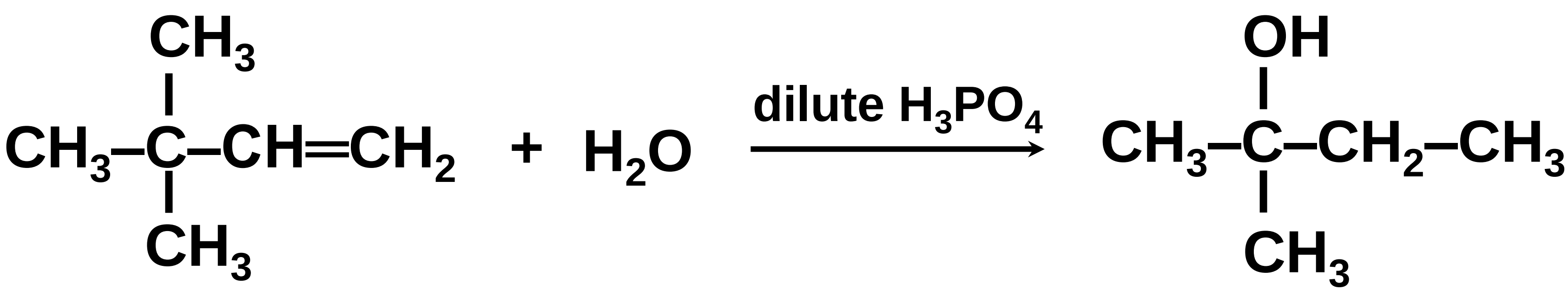


Step 3 : Deprotonation



Example 2:

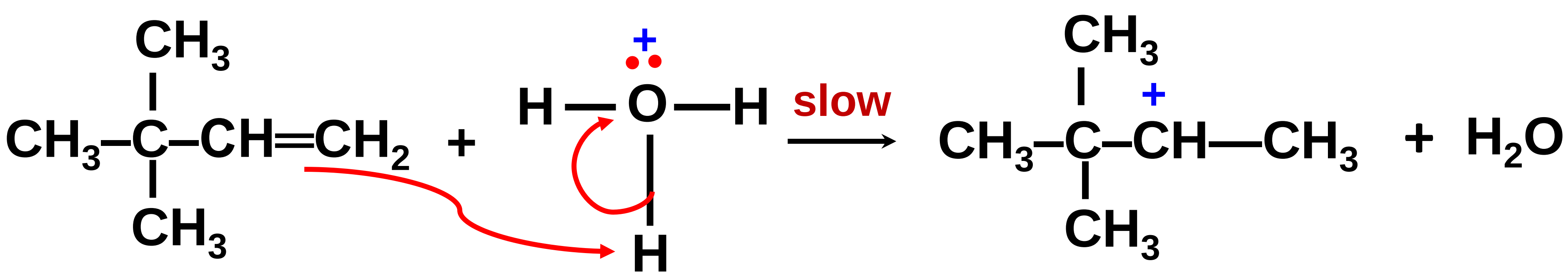
Write the mechanism for the major product for the following reaction:



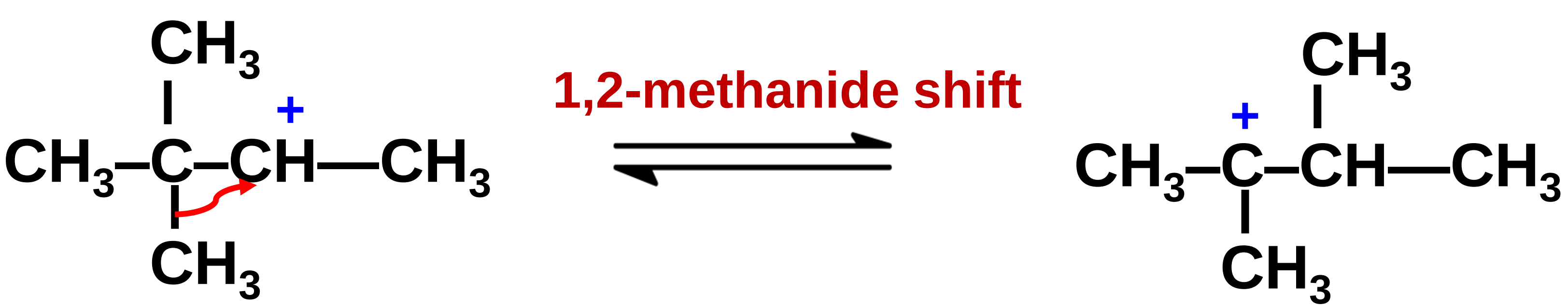
Reaction Mechanism : Acidified water

Answer:

Step 1 : Formation of carbocation



Step 2 : Rearrangement

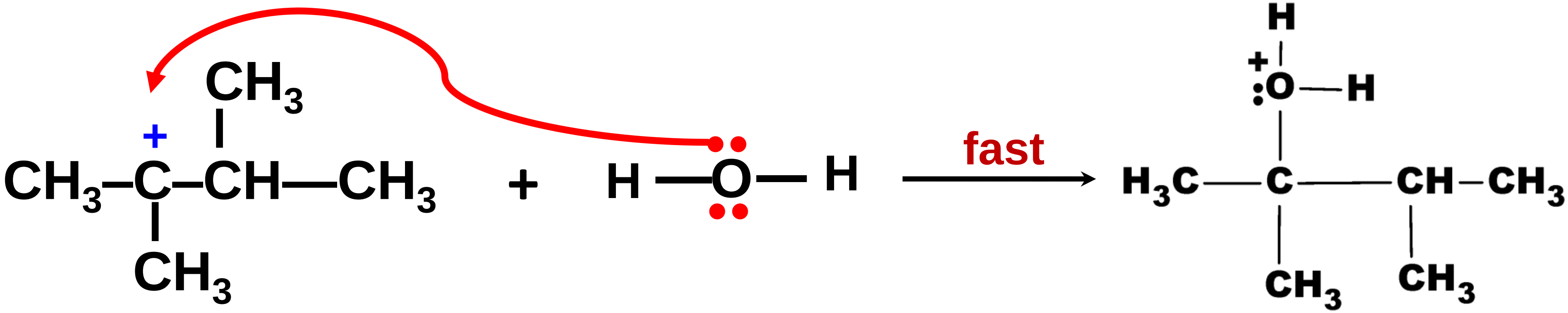


2° carbocation

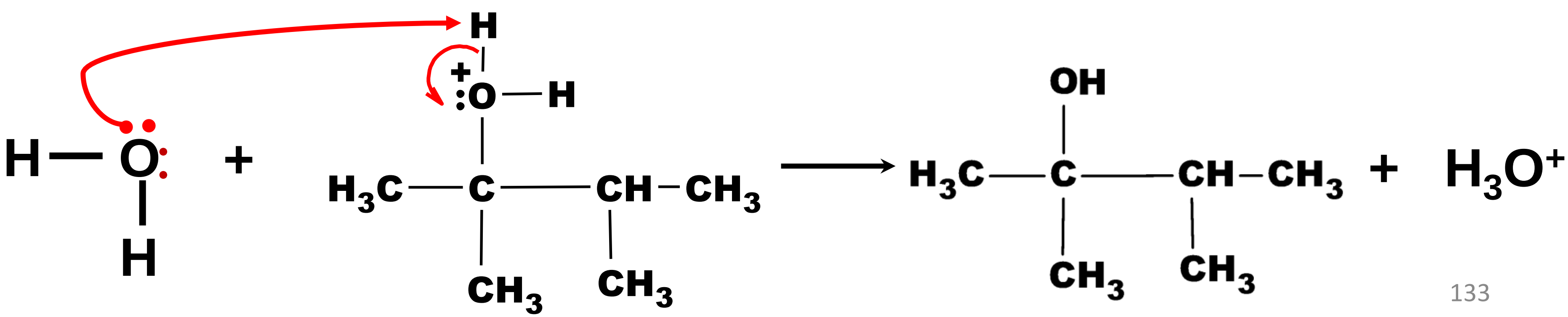
3° carbocation

Reaction Mechanism : Acidified water

Step 3 : Formation of protonated alcohol



Step 3 : Deprotonation



Learning Outcomes

(m) Explain the reaction of alkenes with:

i. O_3 followed by Zn,H_2O or O_3 followed by $(CH_3)_2S$ (ozonolysis);

ii. hot, acidified $KMnO_4$

(n) Predict the position of double bond through:

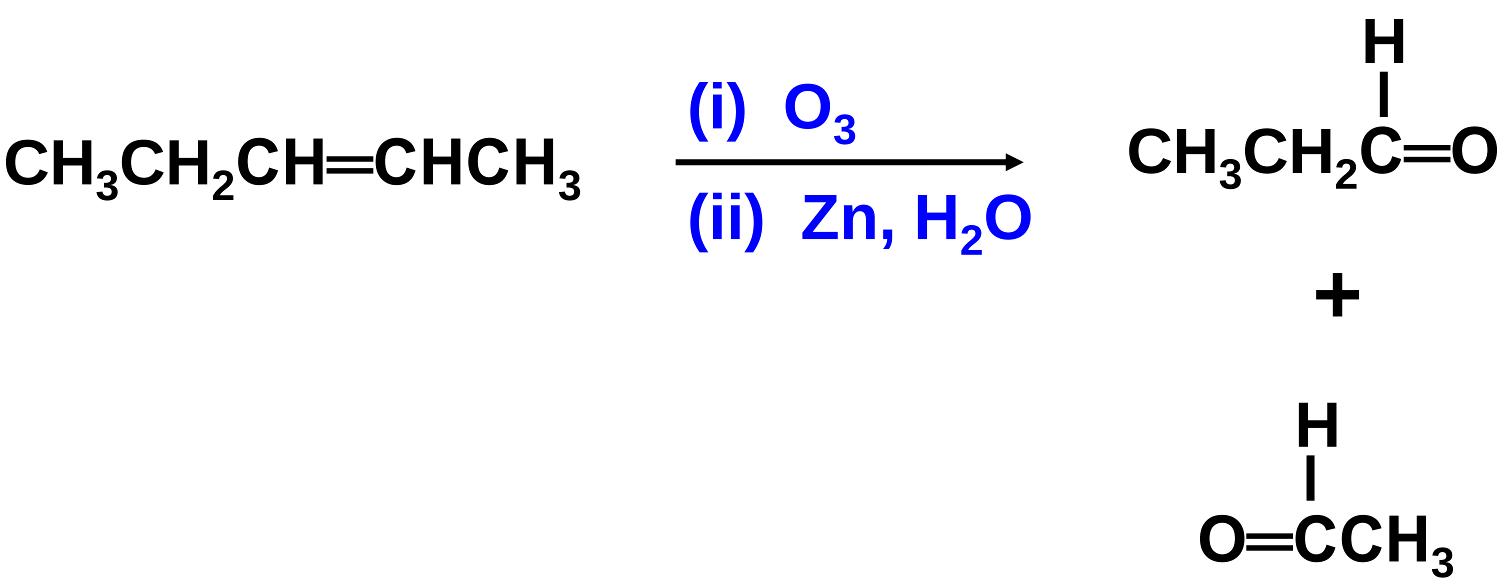
i. ozonolysis

ii. reaction with hot, acidified $KMnO_4$

Ozonolysis

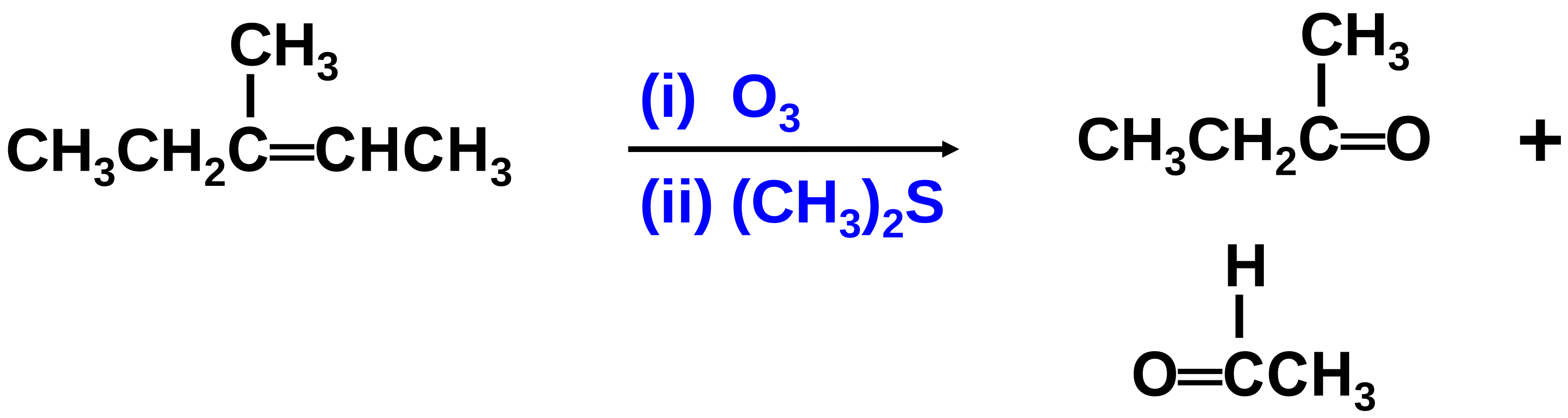
Reagent	(i) O_3 (ii) Zn, H_2O @ $(CH_3)_2S$
Product	aldehyde @ ketone

Example 1 :

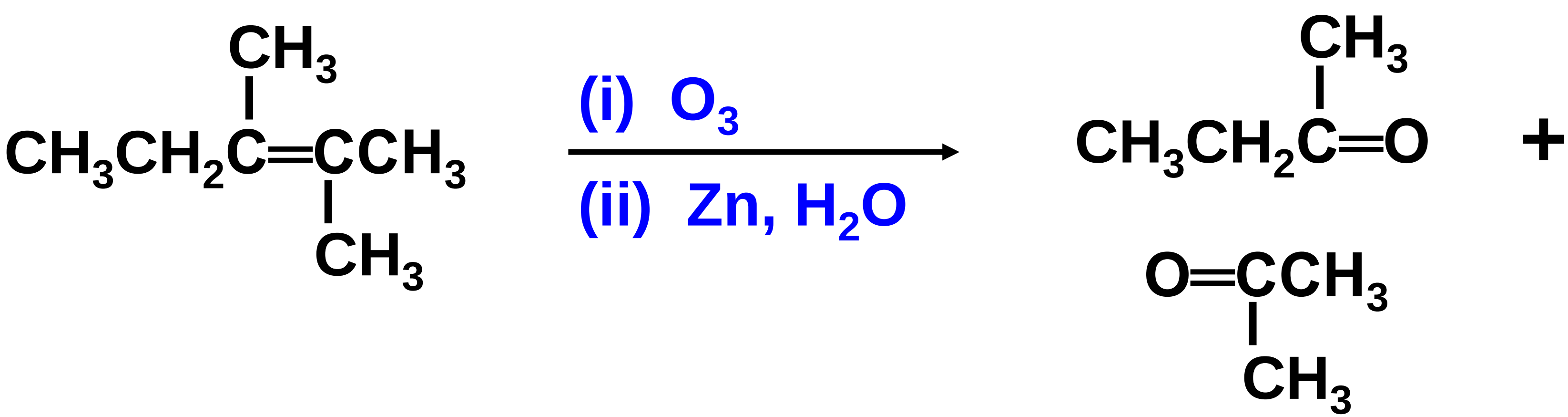


Ozonolysis

Example 2 :



Example 3 :



Ozonolysis

Example 4 :

$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 \xrightarrow[\text{(ii) Zn, } H_2O]{\text{(i) } O_3} CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}O \;+\; O{=}CH_2$$

Example 5 :

$$CH_3CH_2\overset{\overset{\displaystyle H}{|}}{C}{=}CH_2 \xrightarrow[\text{(ii) } (CH_3)_2S]{\text{(i) } O_3} CH_3CH_2\overset{\overset{\displaystyle H}{|}}{C}{=}O \;+\; O{=}CH_2$$

Reaction with hot, acidified $KMnO_4$

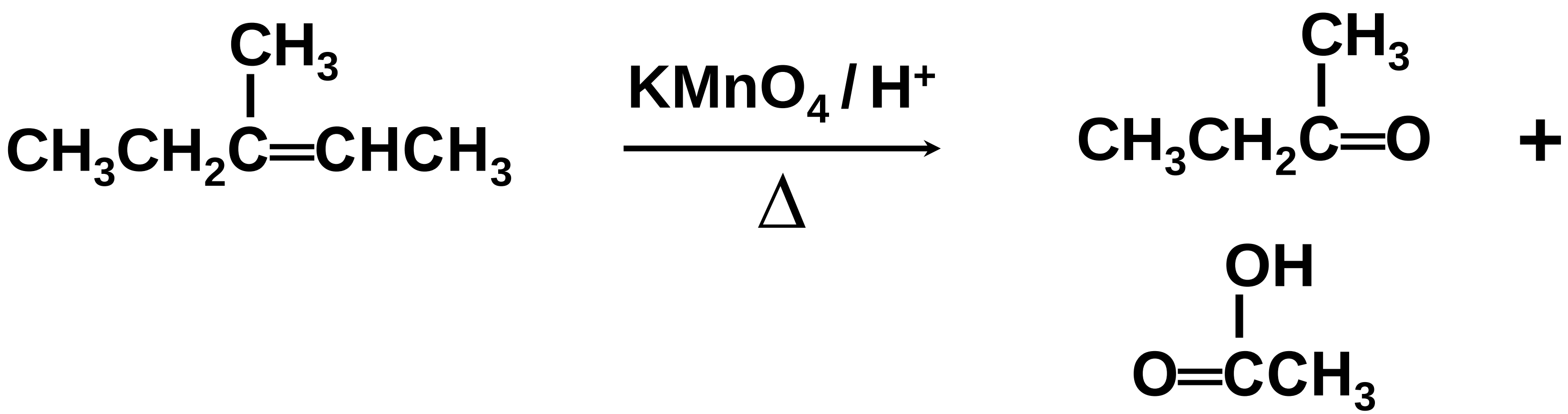
Reagent	$KMnO_4$ / H^+
Condition	heat, Δ
Product	ketone & or carboxylic acid or CO_2 & H_2O

Example 1 :

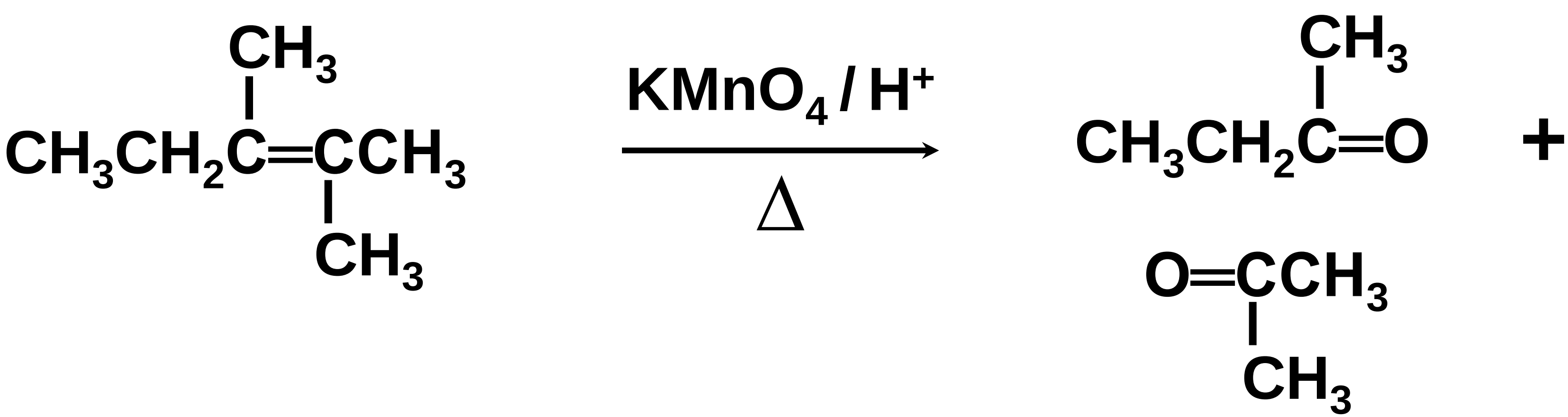
$$CH_3CH_2CH{=}CHCH_3 \xrightarrow[\Delta]{KMnO_4\,/\,H^+} CH_3CH_2\overset{\overset{\large OH}{|}}{C}{=}O \;+\; O{=}\overset{\overset{\large OH}{|}}{C}CH_3$$

Reaction with hot, acidified $KMnO_4$

Example 2 :



Example 3 :



Reaction with hot, acidified $KMnO_4$

Example 4 :

$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 \xrightarrow[\Delta]{KMnO_4\,/\,H^+} CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}O + CO_2 + H_2O$$

Example 5 :

$$CH_3CH_2\overset{\overset{\displaystyle H}{|}}{C}{=}CH_2 \xrightarrow[\Delta]{KMnO_4\,/\,H^+} CH_3CH_2\overset{\overset{\displaystyle OH}{|}}{C}{=}O + CO_2 + H_2O$$

EXAMPLE 1:

Write the structure of alkene that would produce the following products when treated with ozone followed by water, zinc and acid.

CH_3COCH_3 and $CH_3CH(CH_3)CHO$

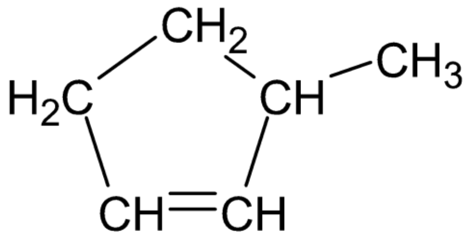
EXAMPLE 2:

Deduce the structural formula of an alkene that gives the following compound when it reacts with ozone in the presence of Zn,H_2O.

$O{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH(CH_3)CH{=}O$

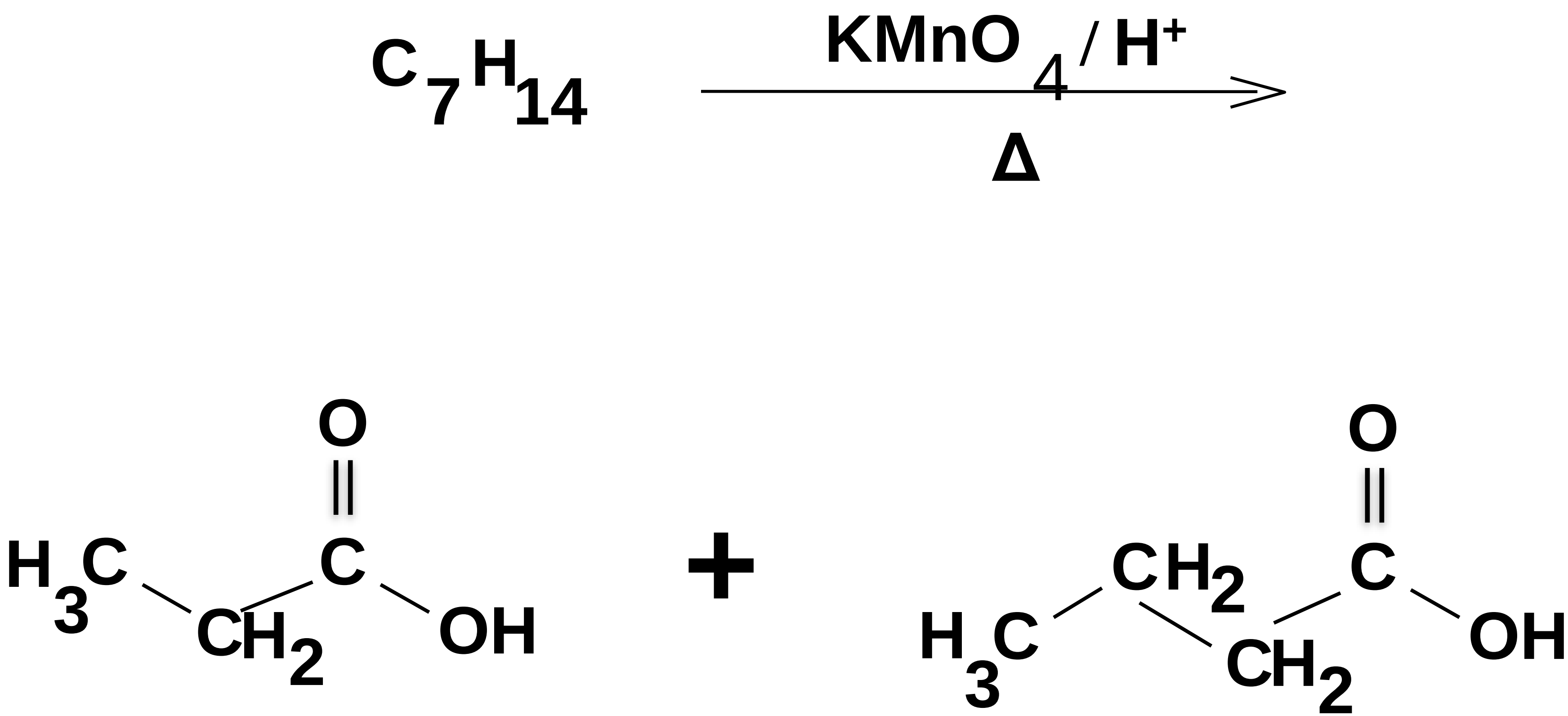
Solution

1) $CH_3CH(CH_3)CH{=}C(CH_3)_2$

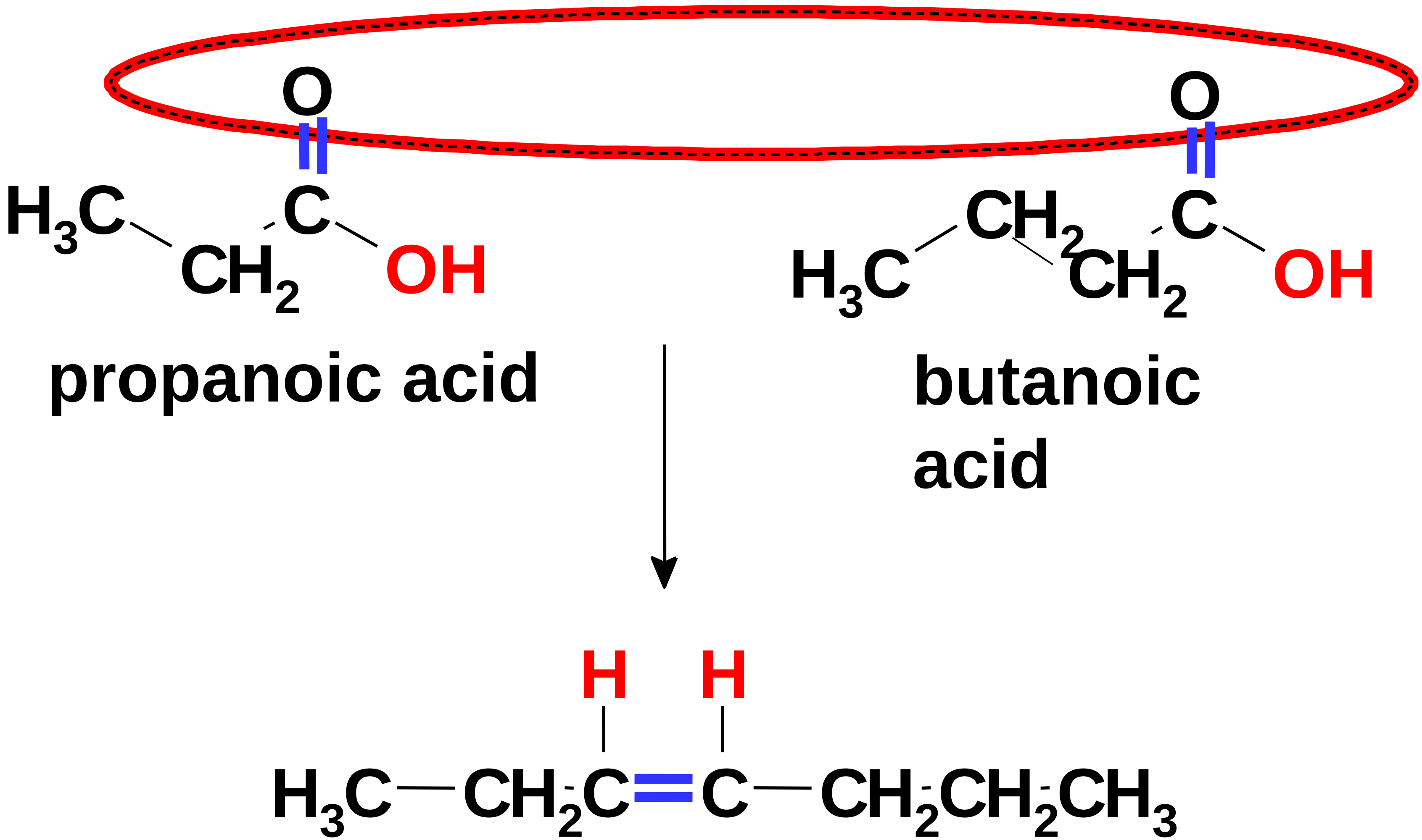
2) 

EXAMPLE 3

- An unknown alkene with the formula C_7H_{14} undergoes oxidation with hot acidic potasium permanganate solution to form propanoic acid and butanoic acid. What is the structure of this alkene?


C_7H_{14}
$KMnO_4 / H^+$
Δ
H_3C
CH_2
C
O
OH
+
H_3C
CH_2
CH_2
C
O
OH

Solution



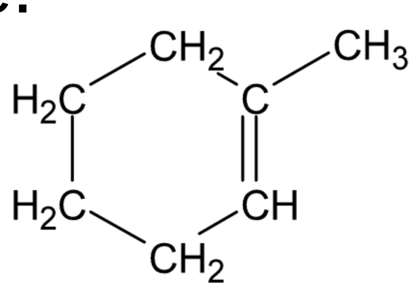
3 -heptene

EXAMPLE 4:

- An unknown alkene undergoes oxidation in hot acidic $KMnO_4$ to give the following product:

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Deduce the structural formula for the unknown alkene.

Ans: 

Chemical Test of Alkenes

Learning Outcomes

o) Explain the unsaturation test for alkenes:

i. Baeyer's test using dilute alkaline $KMnO_4$ solution

ii. bromine in CH_2Cl_2

iii. bromine water

(Experiment 4: Reactions of Aliphatic and Aromatic Hydrocarbons)

p) Explain the preparation of synthetic polymers through addition polymerisation (e.g. polyethylene, poly vinyl chloride, polystyrene, Teflon)

Unsaturation test for Alkenes

There are 3 chemical test to differentiate between an alkanes and alkenes:

i) Baeyer's test using cold, dilute alkaline $KMnO_4$ solution

Baeyer's test

Unsaturation test for Alkenes

ii) Reaction with bromine in CH_2Cl_2

iii) Reaction with bromine water

Bromine test

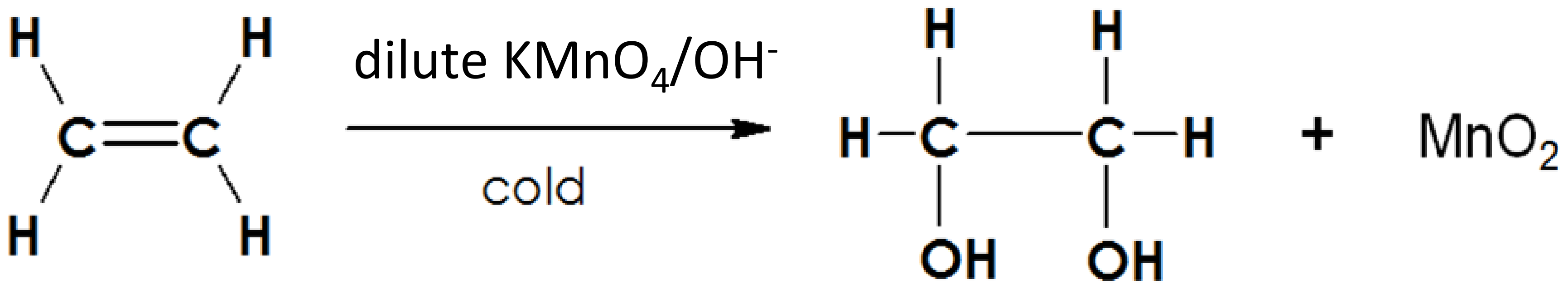
Baeyer's test using cold, dilute alkaline $KMnO_4$

Reagent	dilute $KMnO_4$ / OH^-
Condition	cold
Product	-diols
Name of chemical test	Baeyer's test
Observation	Purple colour of $KMnO_4$ decolourised. Brown precipitate formed. 

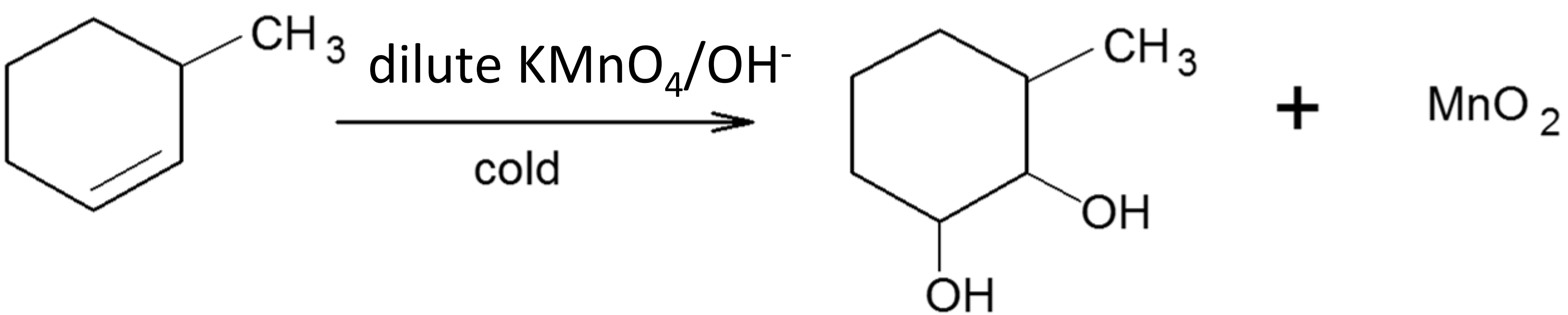
Reaction with Cold, Basic $KMnO_4$

Example :

(i)

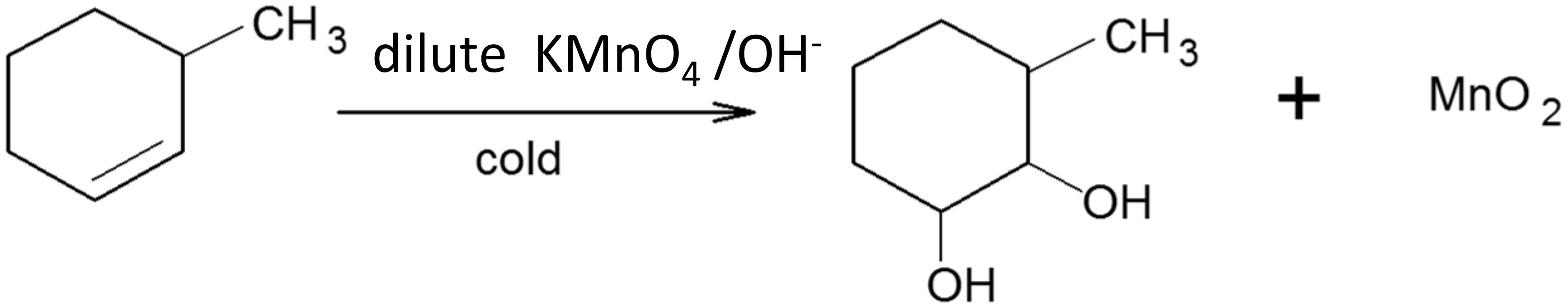


(ii)



Reaction with Cold, Basic $KMnO_4$

When the equation below are tested with cold, basic, dilute $KMnO_4$ ….



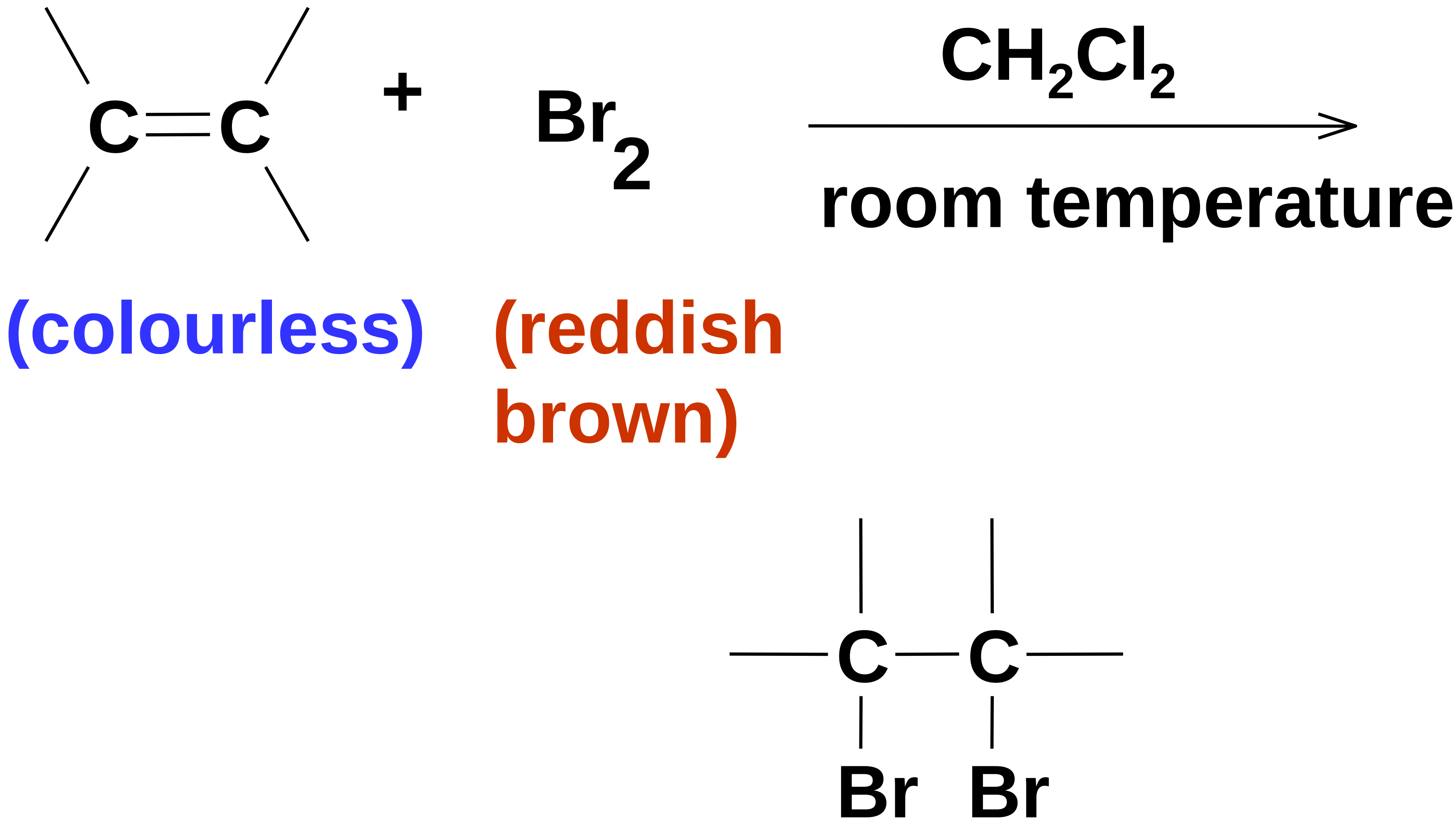
Name of chemical test : **Baeyer's test**

Observations : **Purple colour of $KMnO_4$ decolourised. Brown precipitate formed.**

Bromine in Inert Solvent

Reagent	Br_2, CH_2Cl_2
Product	vicinal dibromo
Name of chemical test	Bromine test
Observation	Reddish brown colour of bromine decolourised 

Bromine Test (Bromine in CH_2Cl_2)



(a colourless compound)

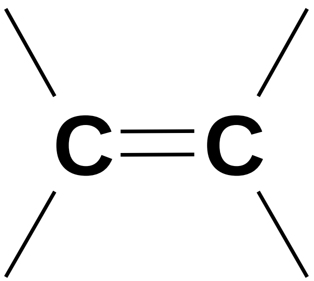
- **When bromine is used for this reaction, it can serve as a test for the presence of carbon-carbon double bonds.**

- **If bromine is added to alkene, the reddish brown color of the bromine disappears almost instantly as long as the alkene is present in excess.**

Bromine Water

Reagent	Br_2, H_2O
Product	halohydrin
Name of chemical test	Bromine test
Observation	Reddish brown colour of bromine decolourised 

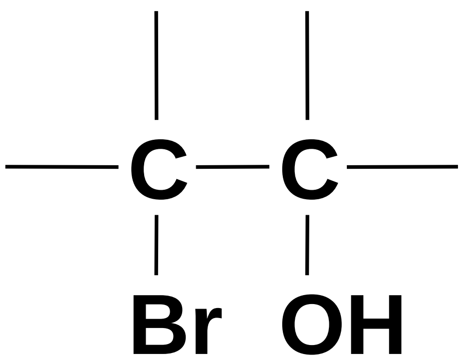
Bromine test (Bromine water)



(colourless)

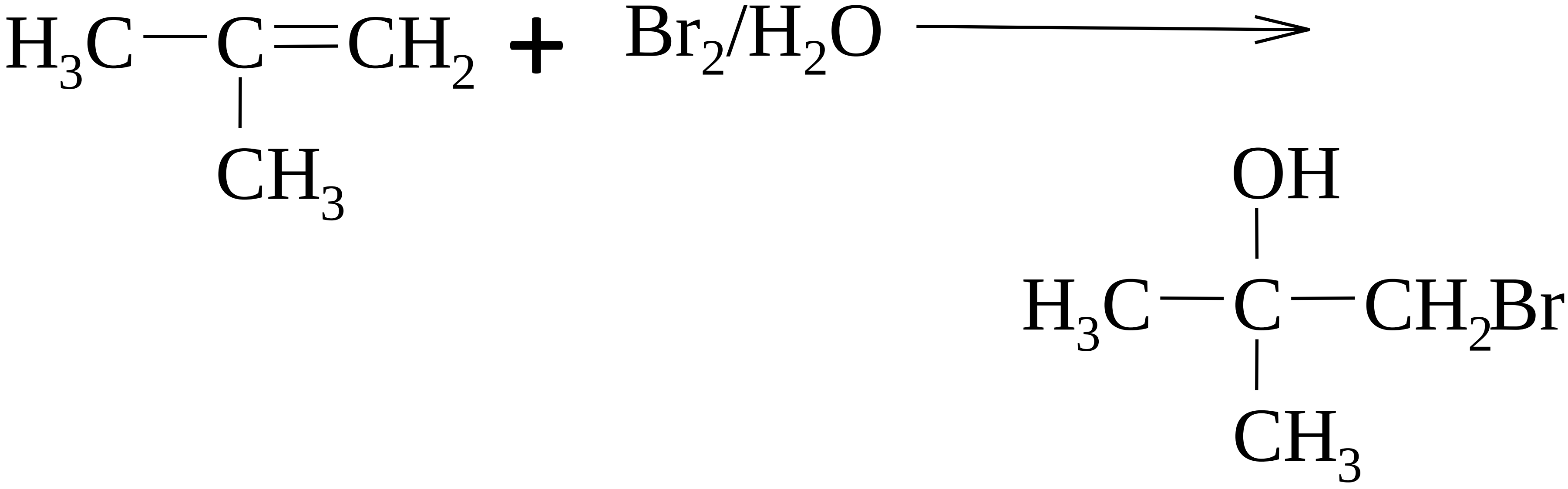
$+ \quad Br_2/H_2O \xrightarrow[\text{room temperature}]{}$

(reddish brown)



(a colourless compound)

Example:



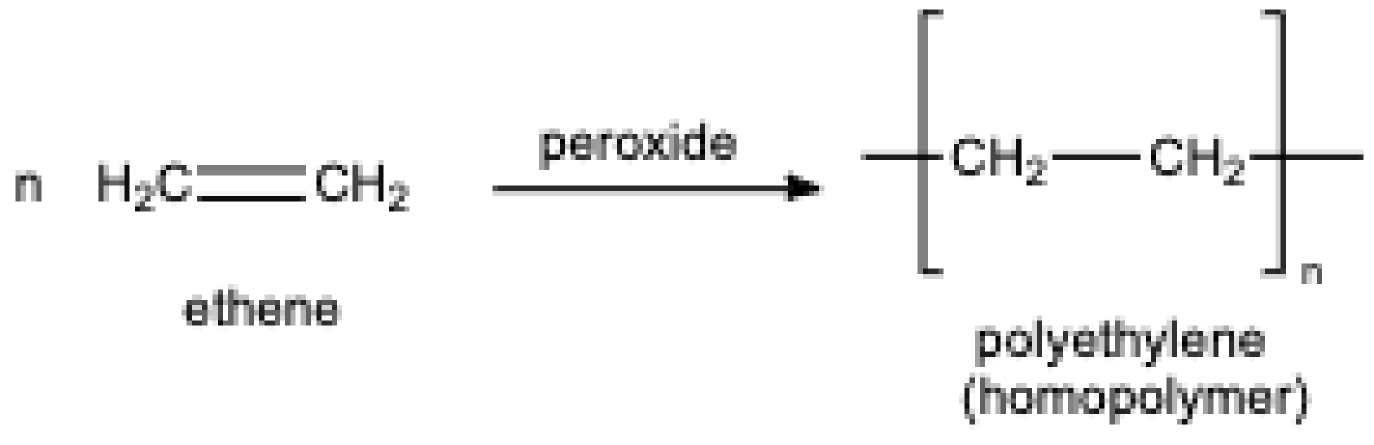
PREPARATION OF SYNTHETIC POLYMERS

ADDITION POLYMERISATION

- The addition reaction in which monomers with double bonds are joined together by covalent bonds to form a large molecule without a loss of smaller molecule.
- C=C are broken and replaced by C-C single bonds. This enables chain formation to form the polymer.
- Peroxide is used as initiator in additional polymerisation

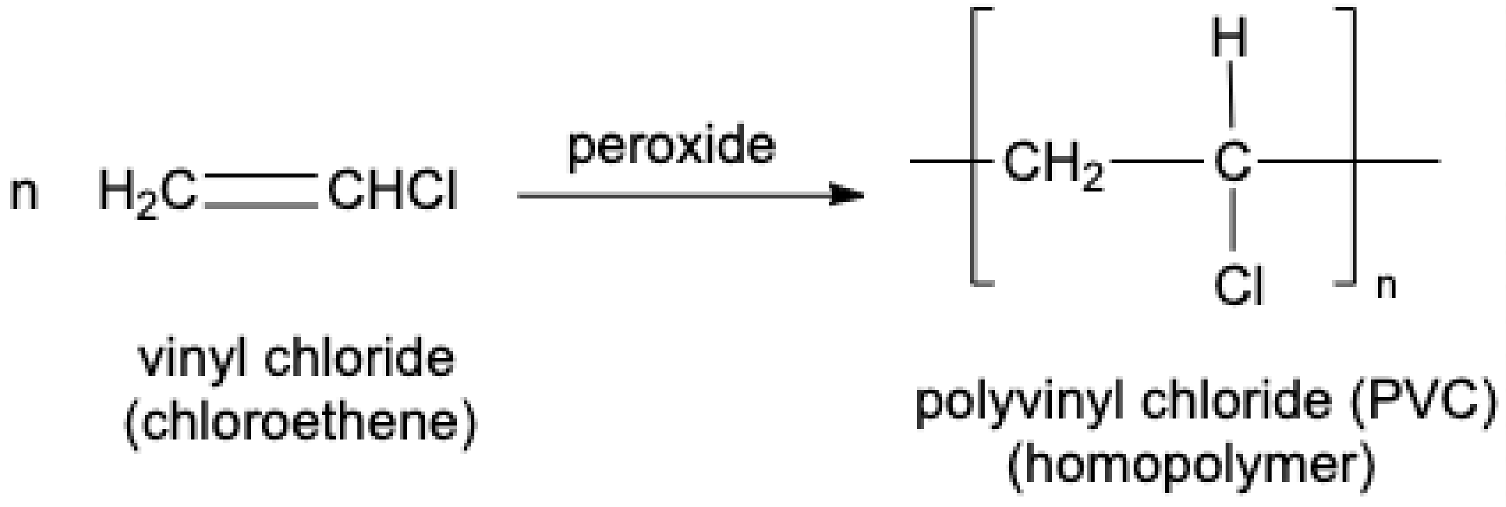
PREPARATION OF SYNTHETIC POLYMERS

ADDITION POLYMERISATION:
POLYETHYLENE



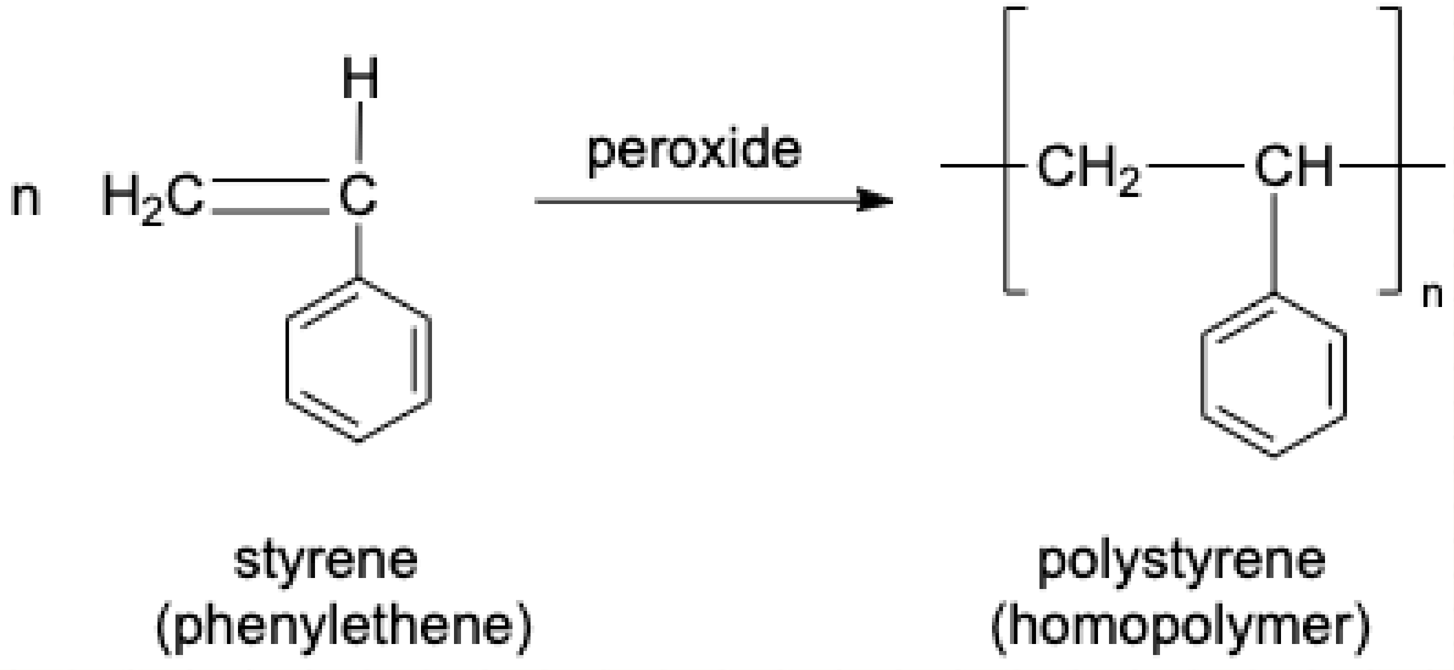
PREPARATION OF SYNTHETIC POLYMERS

ADDITION POLYMERISATION: POLYVINYL CHLORIDE, PVC



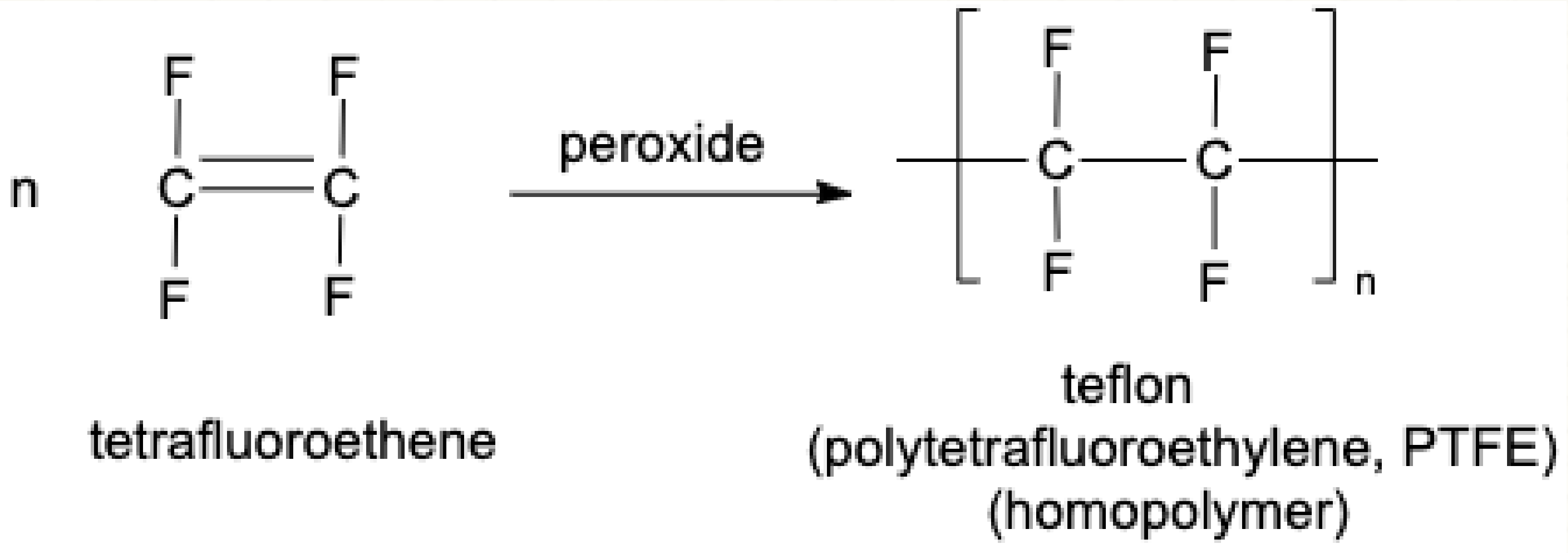
PREPARATION OF SYNTHETIC POLYMERS

ADDITION POLYMERISATION: POLYSTYRENE



PREPARATION OF SYNTHETIC POLYMERS

ADDITION POLYMERISATION: TEFLON



EXERCISE:

1. Give the monomer structure for the following compound

a) $\left[CH_2-CH=CH-CH_2 \right]_n$

b) $\left[CH_2-CBr_2 \right]_n$

2. Predict the structure of this polymer

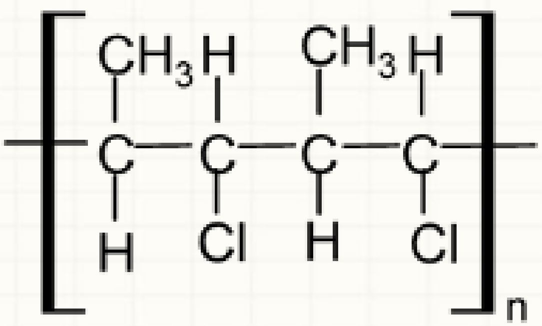
$CH_3CH=CHCl$ and $CH_2=CHCN$

ANSWER:

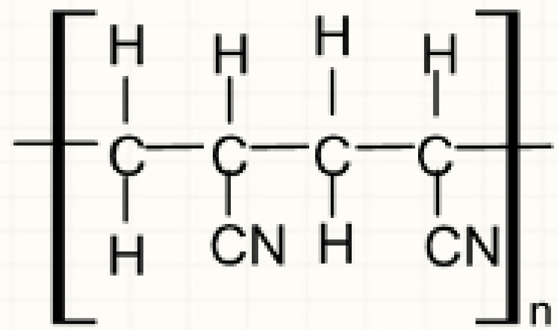
1. a) $H_2C{=}CH{-}CH{=}CH_2$

   b) $H_2C{=}CBr_2$

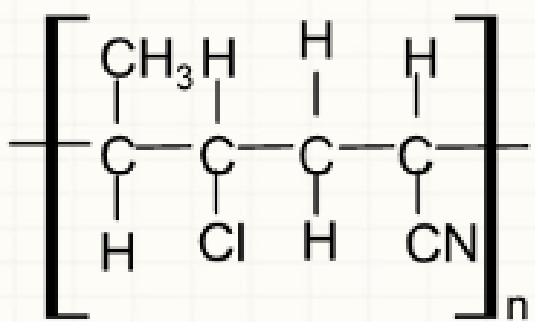
2.



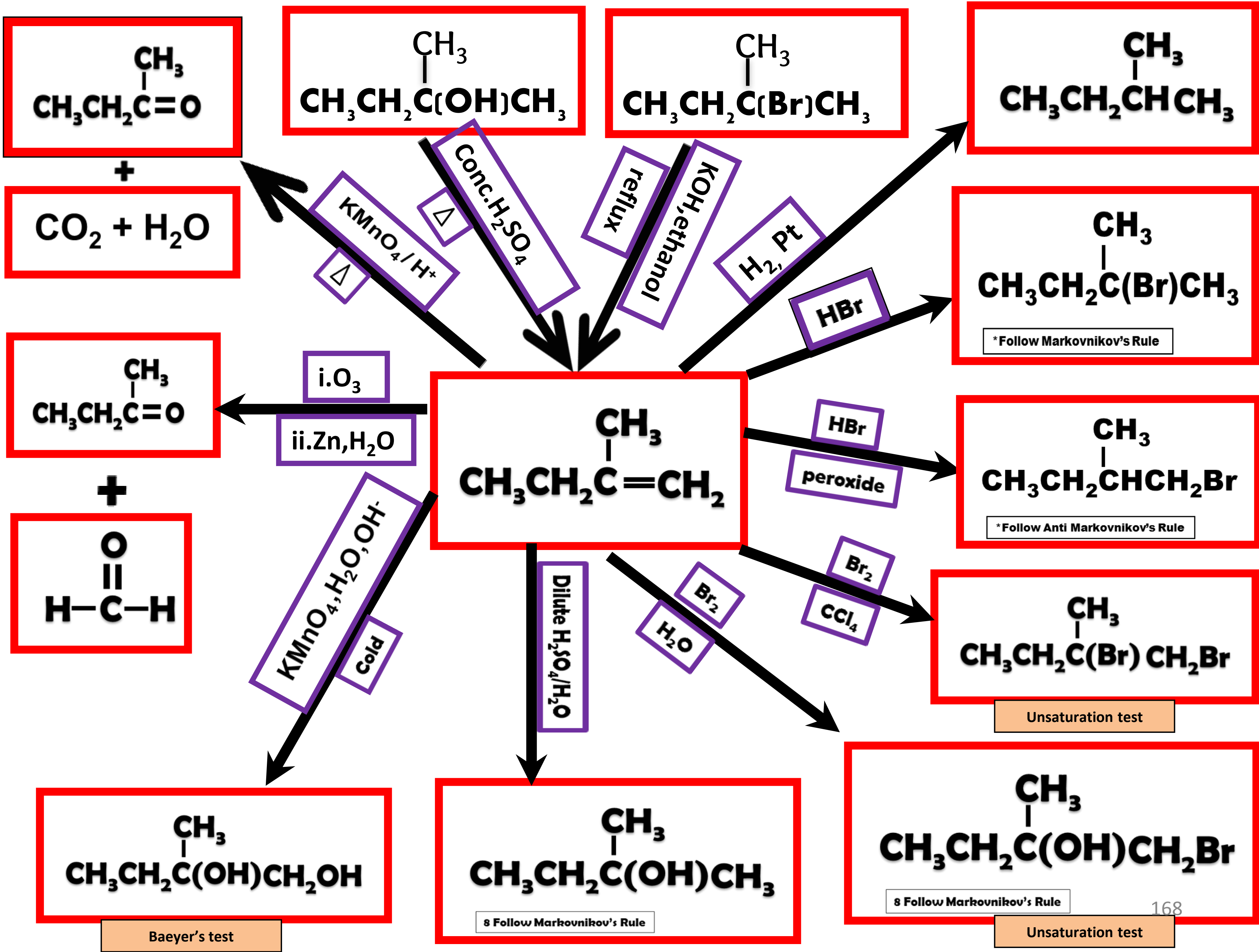
OR



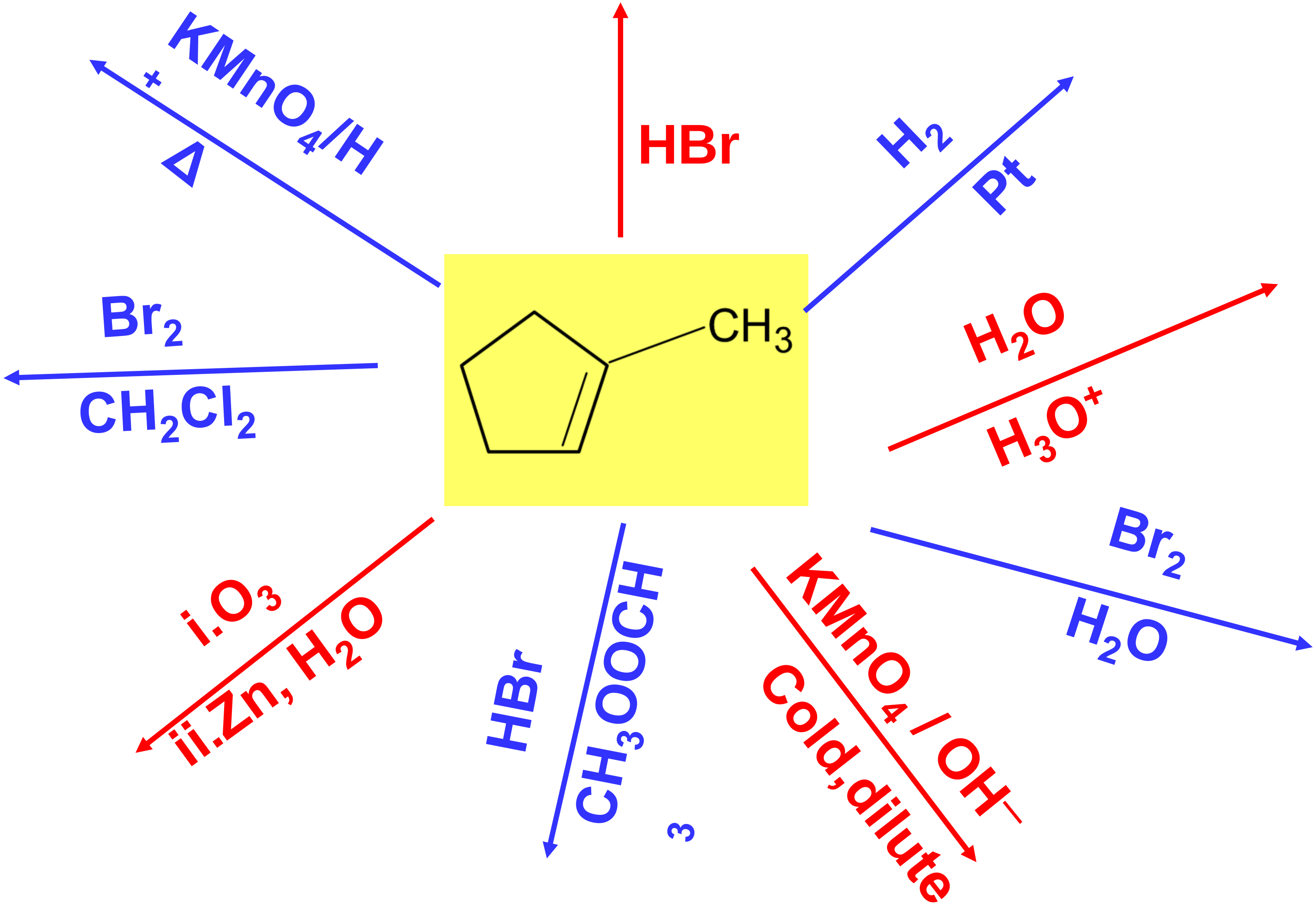
OR



Summary chemical reactions of Alkene


$CH_3CH_2C(CH_3)=CH_2$
$CH_3CH_2C(CH_3)=O$
+
$CO_2 + H_2O$
$KMnO_4/H^+$
Δ
$CH_3CH_2C(OH)(CH_3)CH_3$
Conc.H_2SO_4
Δ
$CH_3CH_2C(Br)(CH_3)CH_3$
reflux
KOH,ethanol
$CH_3CH_2CH(CH_3)CH_3$
H_2, Pt
$CH_3CH_2C(Br)(CH_3)CH_3$
HBr
*Follow Markovnikov's Rule
$CH_3CH_2C(CH_3)=O$
+
$H-C(=O)-H$
i.O_3
ii.Zn,H_2O
$CH_3CH_2CH(CH_3)CH_2Br$
HBr
peroxide
*Follow Anti Markovnikov's Rule
$CH_3CH_2C(Br)(CH_3)CH_2Br$
Br_2
CCl_4
Unsaturation test
$KMnO_4,H_2O,OH^-$
Cold
$CH_3CH_2C(OH)(CH_3)CH_2OH$
Baeyer's test
Dilute H_2SO_4/H_2O
$CH_3CH_2C(OH)(CH_3)CH_3$
8 Follow Markovnikov's Rule
Br_2
H_2O
$CH_3CH_2C(OH)(CH_3)CH_2Br$
8 Follow Markovnikov's Rule
Unsaturation test

LET'S TRY !



CH_3
$KMnO_4/H^+$
Δ
HBr
H_2
Pt
Br_2
CH_2Cl_2
H_2O
H_3O^+
i. O_3
ii. Zn, H_2O
HBr
$CH_3COOOCH_3$
$KMnO_4$ / OH^-
Cold, dilute
Br_2
H_2O

*Glossary

CHAPTER 5 : HYDROCARBON

BIL	TERM	DEFINITION
1.	Aliphatic	Any chemical compound belonging to the organic class in which the atom are connected by single, double, or triple bonds to form nonaromatic structures.
2.	Identical	similar in every detail; exactly alike.
3.	Substituent	an atom or group of atom taking the place of another atom or group or occupying a specified position in a molecule.
4.	Designate	to give something a specific status.
5.	Monosubstitution	A molecule or functional group in which only one hydrogen has been replaced by another atom or group.
6.	Isomeric alkenes	Alkene with same molecular formula but different structure formula.
7.	Restricted rotation	The inhibition of rotation of groups about a bond due to the presence of a sufficiently large rotational barrier to make the phenomenon observable on the time scale of the experiment

BIL	TERM	DEFINITION
8.	slightly	to a small degree; not considerably.
9.	Saytzeff's Rule	The major product in elimination reaction is the most stable alkenes which has the most highly substituted double bond.
10.	1,2-methanide shift	the migration of $-CH_3$ (methanide ion) from the C atom that adjacent to the carbocation.
11.	Markovnikov's Rule	In the electrophilic addition of alkenes, the electrophile adds to the C atom of the C=C with greater number of H atoms
12.	Deduce	arrive at (a fact or a conclusion) by reasoning; draw as a logical conclusion.
13.	monomers	atoms or small molecules that bond together to form more complex structures such as polymers.