C.A.N CHEMISTRY AWESOME NOTES

CHAPTER 5.0: HYDROCARBON

TOPIC	SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
			C1	C2	C3	C4
Hydrocarbon	5.1 Alkanes	a) Define and classify hydrocarbons into: i. Aliphatic and aromatic ii. Saturated and unsaturated	√	√		
		b) Draw structure and name alkane compounds according to IUPAC rules for: i. Straight chain and branched alkanes (parent chain $\leq C_{10}$) ii. Cyclic alkanes ($C_3 - C_6$) iii. Alkyl groups		√		
		c) Explain the following physical properties: i. Boiling points of - Alkanes based on molecular weight - Isomeric alkanes - Alkanes and cycloalkanes ii. Solubility in water and organic solvents			√	√
		d) Write equation for the combustion of alkanes in: i. Excess oxygen ii. Limited oxygen		√		
		e) Explain the halogenation reaction of alkanes		√		
		f) Explain the monosubstitution of alkanes containing equivalent and non-equivalent type of hydrogen atoms			√	
		g) Illustrate the free radical monosubstitution mechanism of alkanes				√
	5.2 Alkenes	a) Draw structures and name alkenes according to the IUPAC nomenclature for: i. Straight chain and branched alkenes - (parent chain $\leq C_{10}$) - Cyclic alkenes ($C_3 - C_6$) - Simple dienes ($C_4 - C_6$)		√		
		b) Explain boiling point of isomeric alkenes				√
		c) Describe the preparation of alkenes through: i. Dehydration of alcohol ii. Dehydrohalogenation of haloalkanes				√
		d) Outline the mechanisms for c(i)				√
		e) Justify major product formed using Saytzeff's Rule				√
		f) Predict the major product of the elimination reaction				√
		g) 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		√		
		h) Predict the products forms according to the Markovnikov's rule				√
		i) Illustrate the mechanism of electrophilic addition of (g) iv and (g) v				√
		j) 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				√
		k) Explain/ Predict 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 $KMnO_4$				√
		l) Identify the position of double bond through: i. Ozonolysis ii. Reaction with hot, acidified $KMnO_4$				√
		m) Explain the unsaturation test for alkenes:				√

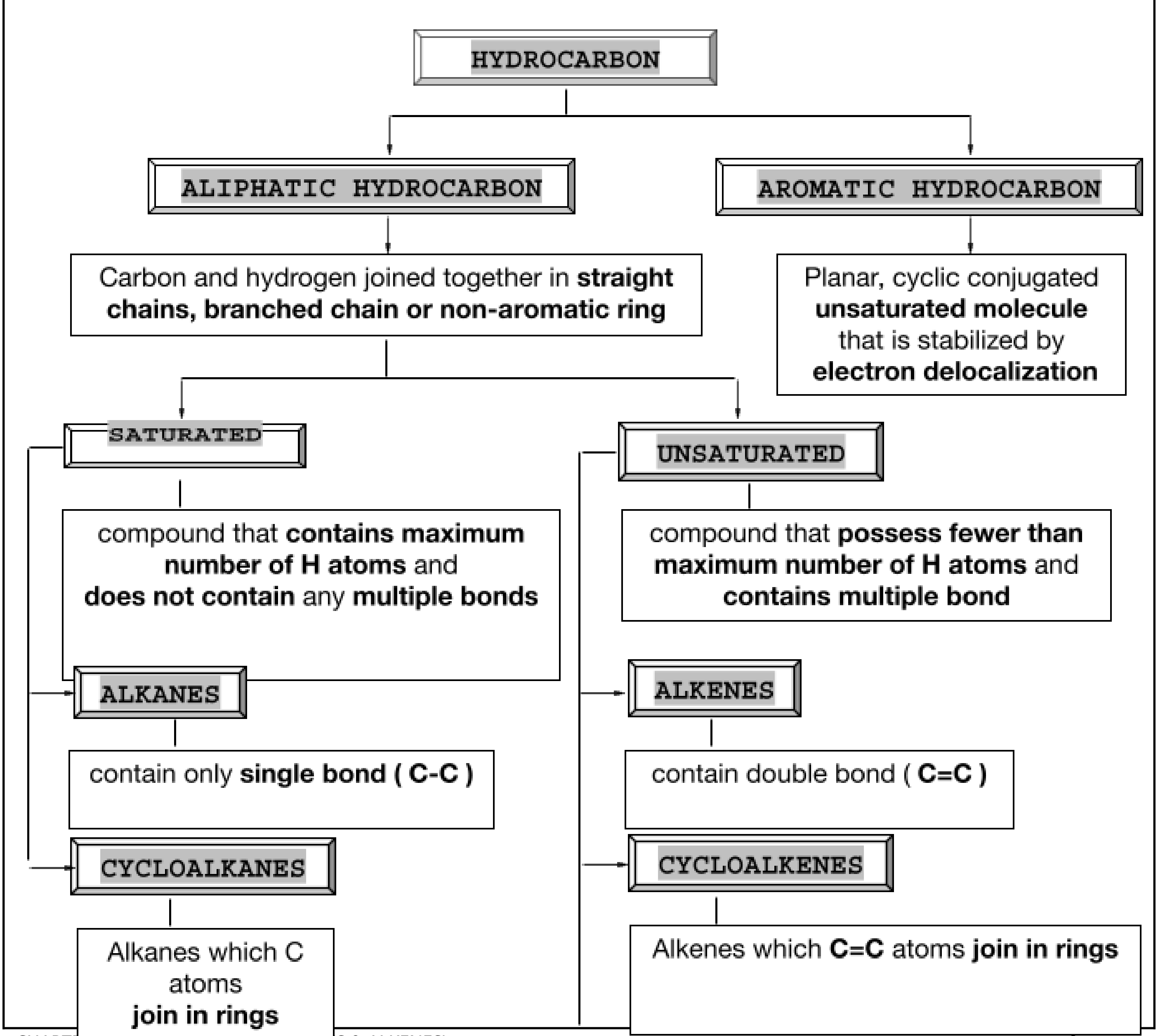
		i. Baeyer's test using dilute $KMnO_4$ solution ii. Bromine in CH_2Cl_2 iii. Bromine water				

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.1 Alkanes	a) Define and classify hydrocarbons into: i. Aliphatic and aromatic **ii.** Saturated and unsaturated	√	√		

INTRODUCTION

HYDROCARBON ► Hydrocarbon is the compound which contains **only carbon and hydrogen**

Classification of Hydrocarbon



ALKYNES

contain triple bond (**C≡C**)

5.1 – ALKANES

It is said to be saturated because it has maximum number of bonded H atoms

SATURATED HYDROCARBON

- All the carbon-carbon in alkanes are **single bond and** each carbon atom in alkanes **is sp^3 hybridised (4 sigma bond)**
- Geometry at **each carbon atom** is **tetrahedral**.
- All bond angles **109.5**

ALKANES (open chain)

CYCLOALKANES (close chain)

EXPLANATION	
Alkanes are organic compounds that consist entirely of **single-bonded carbon and hydrogen** atoms and lack any other functional groups.	**Cyclic alkanes** in which the carbon atoms are arranged in **a ring**. **Same general formula** with **alkenes.** Therefore **cycloalkanes** are **isomeric** with **alkenes.**
General formula:	
C_nH_{2n+2} where n ≥ 1 (n = 1, 2, 3, …)	C_nH_{2n} where n ≥ 3 (n = 3, 4, …)

IUPAC Nomenclature:	
Alkanes **IUPAC** names have the −**ane** suffix.	Cycloalkanes with only **one ring** are named with the prefix **cyclo**− to the names of the alkanes.

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.1 Alkanes	b) Draw structure and name alkane compounds according to IUPAC rules for: i. Straight chain and branched alkanes (parent chain $\leq C_{10}$) ii. Cyclic alkanes ($C_3 - C_6$) **iii.** Alkyl groups		√		

IUPAC NOMENCLATURE OF ALKANES

Nomenclature of Straight Chain (Unbranched) Alkanes

- **Straight chain** or **unbranched alkanes** have their carbon atoms joined together in a **single chain** without any branching.
- Alkanes IUPAC names have the **–ane** suffix.
- General formula: $\mathbf{C_nH_{2n+2}}$ where n=1, 2, 3…

Example:

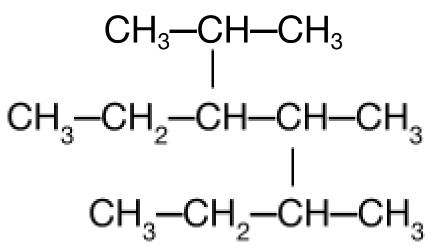
Number of Carbon Atoms	Molecular Formula	Structure	Name
1	CH_4	CH_4	
2	C_2H_6	CH_3CH_3	Methane
3	C_3H_8	$CH_3CH_2CH_3$	Ethane
4	C_4H_{10}	$CH_3(CH_2)_2CH_3$	Propane
5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	Butane
6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	Pentane
7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	Hexane

8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	Heptane
9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	Octane
10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	Nonane
			Decane

IUPAC NOMENCLATURE OF ALKANES

Nomenclature of Branched Chain Alkanes

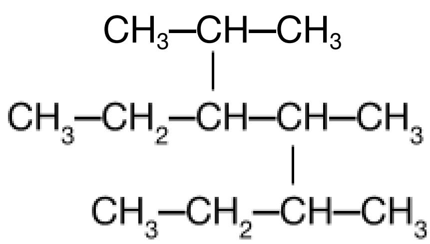
Example:

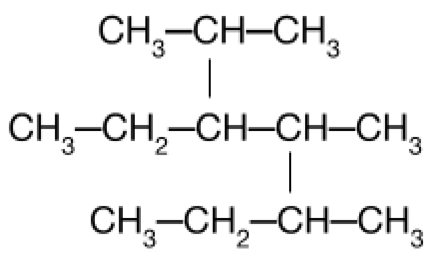


Branched-chain alkanes are named according to the following rules:

1) Find the **longest continuous chain** of C atoms
   ▯ determine the **parent name** for alkanes

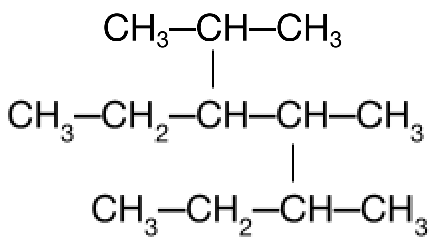
2) If there are two chain of equal length as the parent chain, **choose** the parent **with the greater number of substituent.**

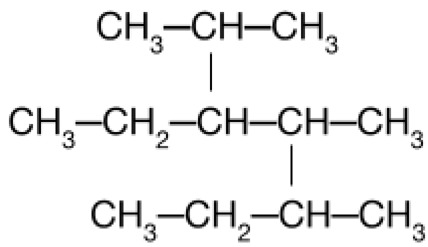




3) Number the longest continuous chain beginning with the end of the chain **nearer the substituent.**

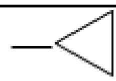
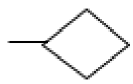
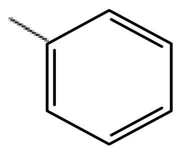
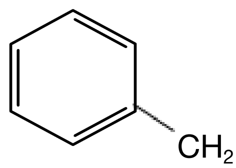
4) If the branching occurs at equal distance from either end of the longest chain, the carbon atoms are numbered from the end of the chain which gives the substituent the lowest possible number.

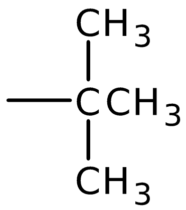
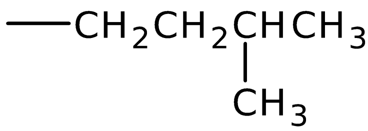
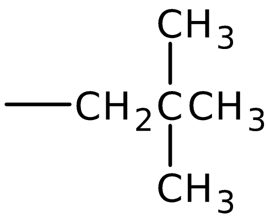




5) Identify the name of the substituent
- Other atom/group attached to the longest chain are called the **substituent group**

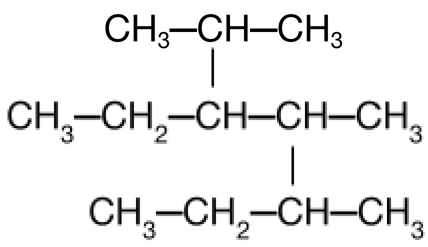
Some Common Substituent Groups

Alkyl Substituent			**Other as Substituent**	
Alkane	**Alkyl**	**Substituent**	**Name**	**Substituent**
Methane	Methyl	$-CH_3$	cyclopropyl	
Ethane	Ethyl	$-CH_2CH_3$	cyclobutyl	
Propane	Propyl	$-CH_2CH_2CH_3$	phenyl	
	Isopropyl	$-CHCH_3$ $\vert$ CH_3	benzyl	
Butane	Butyl	$-CH_2CH_2CH_2CH_3$	Bromo	–Br
	Isobutyl	$-CH_2CHCH_3$ $\vert$ CH_3	Chloro	–Cl
	Sec-butyl	$-CHCH_2CH_3$ $\vert$ CH_3	Fluoro	–F

	Tert-butyl		Iodo	—I
Pentane	Pentyl	—$CH_2CH_2CH_2CH_2CH_3$	Hydroxy	—OH
	Isopentyl		Amino	—NH_2
	Neopentyl		Cyano	—CN
			Nitro	—NO_2

6) Give the **IUPAC** nomenclature for **Alkanes**	
Rule 1	The **position and the name of the substituent** must be written **in front** of the parent chain.
Rule 2	Specify the **locations** of the **substituent** using the numbers assigned to the carbon atom of parent chain.
Rule 3	Use → **hypens (—)** → to separate **number and word** Example: 2—methylhexane Use → **commas (,)** → to separate **number and number** Example: 2,2—dimethyloctane
Rule 4	If **two** or **more substituents** are present, give each substituent a number corresponding to its location on the longest chain. **i.** The substituent should be listed **alphabetically** **ii.** In alphabetizing, the prefixes ▪ di, tri, tetra, sec- and tert- are **ignored** ▪ iso, neo and cyclo are **included**
Rule 5	If **two substituents** are present on the **same carbon atom**, **use the number twice** ▪ **commas** are used to separate numbers from each other
Rule 6	If **two or more identical substituents are present**, use prefixes

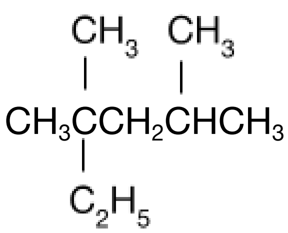
number of identical substituent	prefix
2	
3	
4	



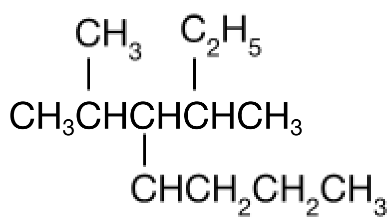
Exercises

1. Name following compounds according to the IUPAC nomenclature:

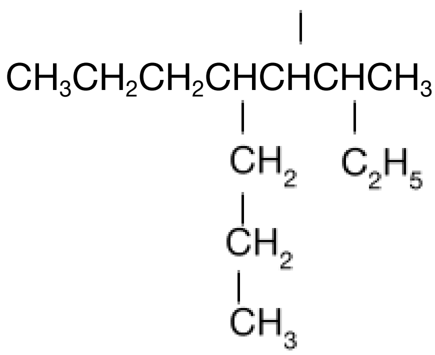
a)



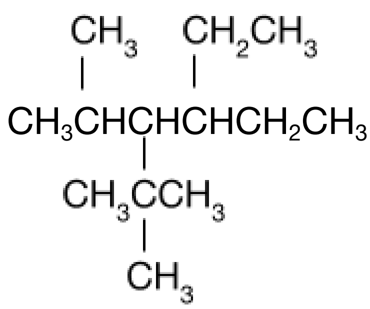
b)



c)



d)



2. Write the structural formula for the following hydrocarbon	
a) 3—methylpentane	b) 1,2—dichloro—3—methylbutane
c) 3—ethyl—2,2,4—trimethylhexane	d) 4—ethyl—2,2—dimethylhexane

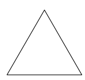
IUPAC NOMENCLATURE OF CYCLOALKANES

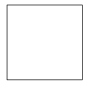
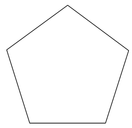
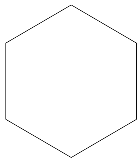
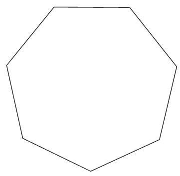
- Cycloalkanes is a **cyclic alkane** in which the carbon atoms are arranged in a **ring.**
- General formula: $\mathbf{C_nH_{2n}}$ where n=3, 4, 5 …..

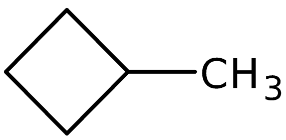
Example:

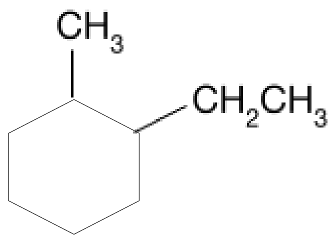
Step 1: Name the parent of cycloalkanes

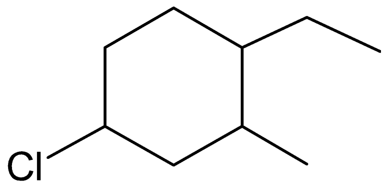
- Cycloalkanes with only one ring are named with the prefix **cyclo—** to the names of the **alkanes** (contain the same number of carbon atoms)

Number of Carbon Atoms	Molecular Formula	Structure	Name
3	C_3H_6		cyclopropane

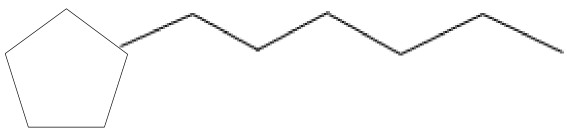
4	C_4H_8		cyclobutane
5	C_5H_{10}		cyclopentane
6	C_6H_{12}		cyclohexane
7	C_7H_{14}		cycloheptane

Step 2: Number the cyclic compounds	
Rule 1	If only **one substituent** is present, it is **not necessary to designate its position.** **Example:** 
Rule 2	If **two substituents are present**, number carbon in the ring **beginning** with the **substituent according to the alphabetical order** follow by giving a possible lowest number to the next substituent. **Example:**

<table>
<tr><td></td><td>
</td></tr>
<tr><td>Rule 3</td><td>When three or more substituents are present, the carbon is numbered with substituent that leads to the lowest set of locants.

Example:

</td></tr>
</table>

<table>
<tr><td colspan="2">Step 3:</td></tr>
<tr><td>Rule 1</td><td>When a single ring system is attached to a single chain with a greater number of carbon atoms, so it is appropriate to name the compounds as cycloalkylalkane

Example:
</td></tr>
<tr><td></td><td></td></tr>
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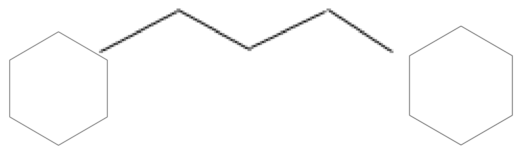
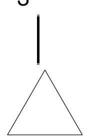
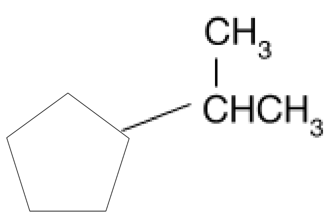
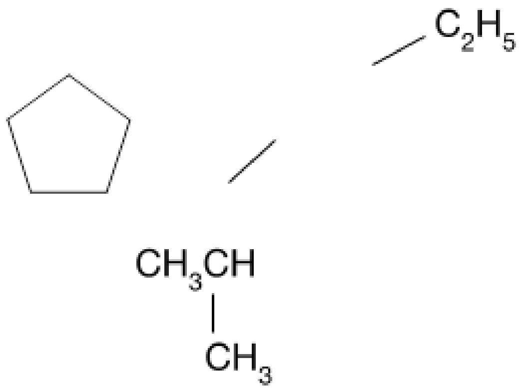
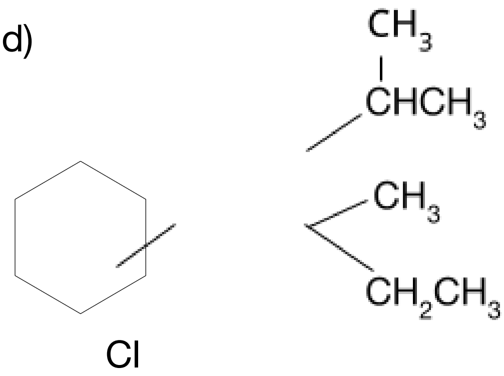
Rule 2	When more than one ring system is attached to a single chain, then it is appropriate to name the compunds as **cycloalkylalkane** **Example:** 

Exercises

Name following compounds according to the IUPAC nomenclature:

a) $CH_3CHCH_2CH_2CH_3$ 	b) 

c) 	d) 

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.1 Alkanes	*c) Explain the following physical properties:* *i. Boiling points of* - *Alkanes based on molecular weight* - *Isomeric alkanes* - *Alkanes and cycloalkanes* ***ii.*** *Solubility in water and organic solvents*			√	√

PHYSICAL PROPERTIES OF ALKANES & CYCLOALKANES

Physical State

At rooms conditions, **25°C** and **1 atm** pressure, for **unbranched alkanes**,

Hydrocarbon	Physical State
$C_1 – C_4$	Gases
$C_5 – C_{17}$	Liquids
C_{18} – more	Solids

Boiling Point

- Depends on the **strength of intermolecular forces** between molecules.
- C-H bond is a non-polar bond. Intermolecular forces between molecules are **Van der Waals forces**.

Factors Effect of Boiling Point

1. Molecular weight / Molar Mass, Mr

- As molecular weight increases;
  - **molecular size bigger,**
  - **larger the surface area** in contact,
  - **stronger Van der Waals forces**,

  ⇒ **higher heat energy required** to overcome the Van Der Waals forces.
  ⇒ higher **boiling points.**

Example:

$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2CH_3$	$CH_2CH_2CH_2CH_2CH_2CH_3$
Butane	Pentane	Hexane
bp = 0°C	**bp = 36°C**	**bp = 79°C**

2. Isomeric Alkanes – Effect of branching chain

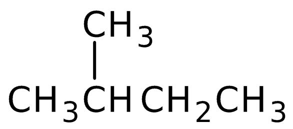
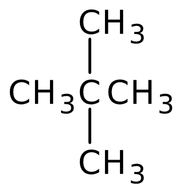
- molecules with **more branches**, become **more compact**,
- **smaller surface area** in contact,
- **weaker Van der Waals** forces,

⇒ **lower heat energy required** to overcome the Van Der Waals forces.
⇒ **lower boiling point.**

REMEMBER!!

- Compare effect of branching chain among the isomers only (same molecular weight)
- Boiling point of branched alkane is higher than straight alkane if number of C is greater

Example:

$CH_3CH_2CH_2CH_2CH_3$		
Pentane	2–methylbutane	2,2–dimethylpropane
bp = 36°C	**bp = 28°C**	**bp = 10°C**

<u>Cyclic Compound</u>

- The boiling points of **cycloalkanes** are 10°C to 15°C **higher than** the **corresponding straight chain alkanes**

<u>Reason:</u>

- the shape is **more compact** and **flat**,
- **intermolecular forces increase** due to the **larger surface area in contact** between molecules.
- **stronger Van Der Waals forces,**
  ⇒ **higher heat energy required** to overcome the Van Der Waals forces.
  ⇒ **higher boiling point compare** to alkanes.

Example:

Cycloalkanes	Boiling Point	Alkane	Boiling Point
Cyclobutane	13°C	Butane	–0.5°C
Cyclopentane	49°C	Pentane	36.3°C

CONCLUSION!!

For same molecular weight,

BOILING POINT: cyclic compound > straight chain > branching chain

Exercises

- Rank the each group of alkanes in order of **increasing boiling point.**

a) $CH_3CH_2CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_3$

b) $CH_3CH_2CH_2CH(CH_3)_2$, $CH_3(CH_2)_4CH_3$, $(CH_3)_2CHCH(CH_3)_2$

c) $CH_3(CH_2)_6CH_3$, $CH_3(CH_2)_5CH_3$, $CH_3CH_2CH_2CH_2CH(CH_3)_2$, $(CH_3)_3CCH(CH_3)_2$

2. Arrange the following alkanes in **decreasing order of boiling points**. Explain.

2,2−dimethylheptane, 4−ethylheptane, 2,2,4,4−tetramethylpentane, nonane

Answer:

Explanation:

- All the compound are same ………………………….
- When the number of branches increases, surface area of molecules …………, strength of Van Der Waals forces also …………………
- ……………… is the highest boiling point because it is …………….. chain and has ……………… surface contact with its molecule.
- ………………………….. has higher boiling point than ………………………… because it has only ……… branch and ………… surface area between its molecules.
- …………………………… has the lowest boiling point because it has the ………… branches, the ……………. surface contact between its molecules.

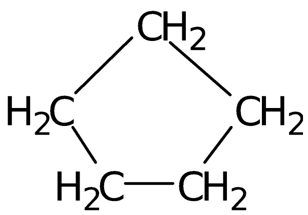
3. Arrange the following alkanes in **ascending order of boiling points**. Explain.

   2-methylbutane, heptane, 3-methylhexane, pentane, 3,3-dimethylpentane

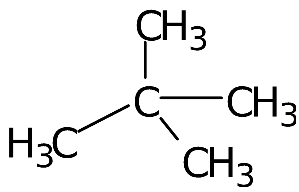
Explanation:

- For molecules with the same molecular weight, branching ………………… surface area and Van der Waals forces, therefore molecules with ……………… branches or …………….. surface area have ………………………boiling points.
- ……………………………, ………………………..... and …………………….. have same and higher molecular mass but ……….............….. is straight chain molecule so it has the highest boiling point. So, greater Van der Waals forces compared than ………………………….. and …………………………
- …………………………….. and ………………………… is branched alkanes, surface area smaller. So the lower Van der Waals forces than …………………
- …………………………….. has more branched, so it has lower boiling point than ……………………………...
- ……………………………… and ……………………… has same and lower molecular mass but ………………………is straight chain molecule so it has the higher boiling point compared than ……………………… (has branched), so greater Van der Waals.

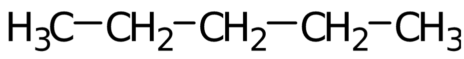
4. Comparing the boiling point of these molecules.
Arrange in order of **decreasing boiling point**. Explain.



(A)



(B)



(C)

Solubility	Ability to intermolecular forces with its solvent (water or organic solvent)

Solubility

Solubility in Water (Polar Solvent)	Solubility in Organic Solvent (Non-Polar Solvent)
Requirement: • Able to **form hydrogen bond** with **water molecules.** (F,O,N attach to H) • Polar molecules can dissolve in polar solvent.	Requirement: • Non polar molecules dissolves in non-polar solvent
Alkanes & cycloalkanes are **insoluble in water** Reason: • **Unable to form hydrogen bond** with water molecule. • **Non-polar molecules.**	Alkanes **soluble in non-polar solvent.** Reason: Can form **intermolecular forces** with **non-polar solvent (benzene, chloroform, carbon tetrachloride** and other hydrocarbon)

C.A.N
CHEMISTRY AWESOME NOTES

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.1 Alkanes	d) Write equation for the combustion of alkanes in: **ii.** Excess oxygen ii. Limited oxygen		√		
	e) Explain the halogenation reaction of alkanes		√		
	f) Explain the monosubstitution of alkanes containing equivalent and non-equivalent type of hydrogen atoms			√	
	g) *Illustrate the free radical monosubstitution mechanism of alkanes*				√

CHEMICAL PROPERTIES OF ALKANES

- Alkanes are generally **inert** towards many chemical reagents.
- This is because carbon and hydrogen have nearly the **same electronegativity.**
  ⇒ the carbon-hydrogen bonds of alkanes are only **slightly polarized**
  ⇒ do not attract nucleophiles or electrophiles.

Reaction of Alkanes → **Combustion** → **Limited Oxygen** / **Excess Oxygen**

Reaction of Alkanes → **Halogenation**

COMBUSTION ⇒ alkanes burnt in air **(oxygen)**

LIMITED OXYGEN	EXCESS OXYGEN
In a **limited supply of oxygen**, combustion of alkanes produces carbon monoxide, **CO** and water, $\mathbf{H_2O}$	Complete combustion **(excess oxygen) of alkanes** produces carbon dioxide, $\mathbf{CO_2}$ and water**,** $\mathbf{H_2O}$
Equation: $CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$	Equation: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $(CH_3)_3CCH_2CH(CH_3)_2 + \frac{25}{2}O_2 \rightarrow 8CO_2 + 9H_2O$

$CH_4 + O_2 \rightarrow C + 2H_2O$	
Product: **$CO + H_2O$ (limited O_2) @** **$C + H_2O$ (very limited O_2)**	**Product:** **$CO_2 + H_2O$**

2. Halogenation of Alkanes ⇒ Type of reaction: **Free Radical Substitution**

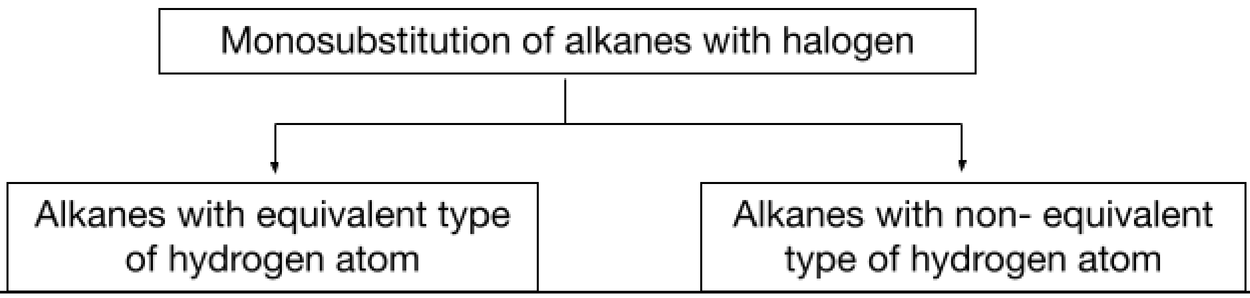
- At room temperature, alkane does not react when mixed with chlorine or bromine in the dark.
- If the mixture is heated to a high temperature **>>100°C** or in the **presence of light** (uv or hv), the hydrogen atoms in the alkane **successively replaced by chlorine or bromine** atoms to produce a mixture of product.
- Function of **uv @ hv: provides the energy needed for homolytic cleavage of halogen molecules to form halogen free radicals.**
- General reaction:

$$R\text{–}H + X_2 \xrightarrow{\text{light or heat}} R\text{–}X + HX$$

** (X = Cl_2, Br_2 only)

TAKE NOTE!!

- *In general, Br_2 is **less reactive** toward alkanes than Cl_2 but **Br_2 is more selective** in the side of attack when it does react.*
- *Formation of **major product only** in bromination.*

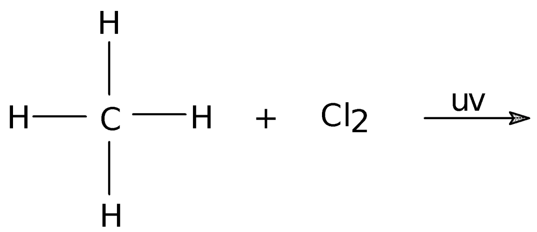


a) Alkanes with equivalent type of hydrogen atom

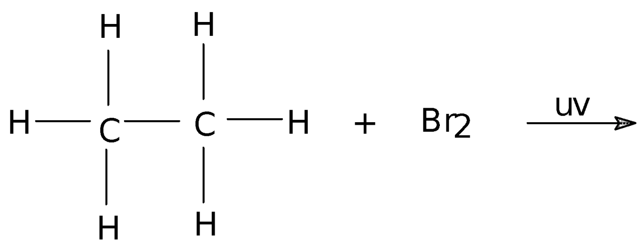
- Alkanes contains equivalent hydrogen atoms.
- Substitution of halogen for hydrogen gives only one product

Example:

1.



2.



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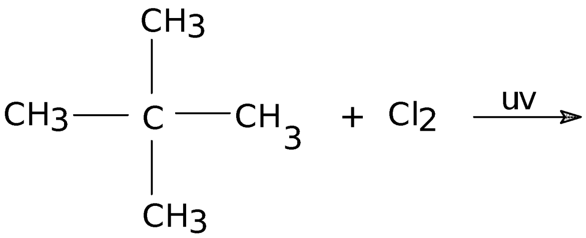


b) Alkanes with non-equivalent type of hydrogen atom

- Unlike methane and ethane, alkanes with more than 2 carbon atoms gives a mixture of products (produce major and minor product)
- The percentage (%) product yield based on the stability of the free radical.

3° free radical > 2° free radical > 1° free radical

Example:

Halogenation of Alkanes (CHLORINATION)

$$CH_3CH_2CH_3 + Cl_2 \xrightarrow{uv}$$

Halogenation of Alkanes (BROMINATION)

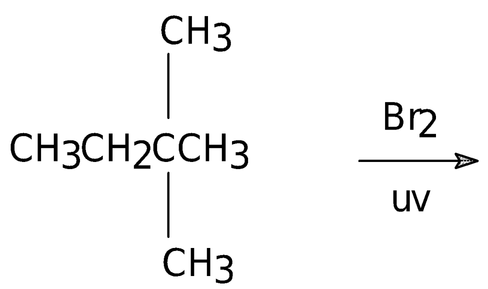
- In general, Br_2 is **less reactive** toward alkanes than Cl_2 but **Br_2 is more selective** in the side of attack when it does react.
- Formation of **major product only** in bromination.

$$CH_3CH_2CH_3 + Br_2 \xrightarrow{uv}$$

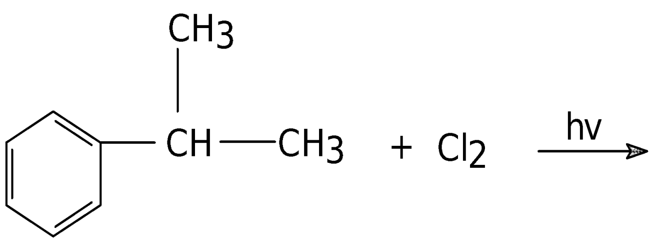
Exercises

Give the product for the reaction below

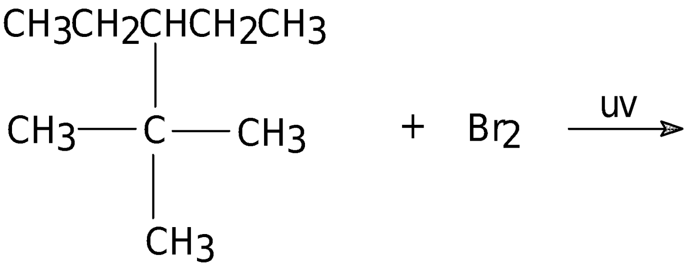
1.



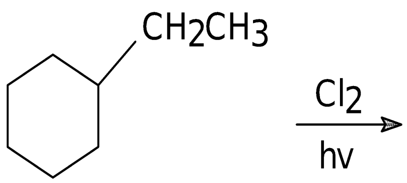
2.



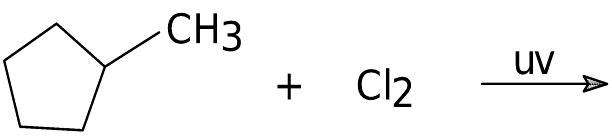
3.



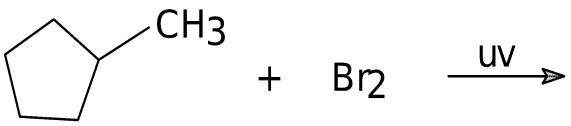
4.



5.



6.



REACTION MECHANISM OF ALKANES

Type of Reaction : **Free Radical Substitution**
Name of Reaction : **Halogenation**

Example

Consider the following monosubstitution reaction:

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

The reaction mechanism:

Step 1: Initiation Step

- **Homolytic fission** of Cl_2 to produce Cl radicals
- Function of **light (uv)** @ **heat** ⇒ **to provide energy for homolytic cleavage.**

Step 2: Propagation Step

- Involve reactions of a **free radical species to produce another species of free radical**.
- Free radical very reactive species

Step 3: Termination Step

- The **reaction stops** when **all free radicals combine with each other.**

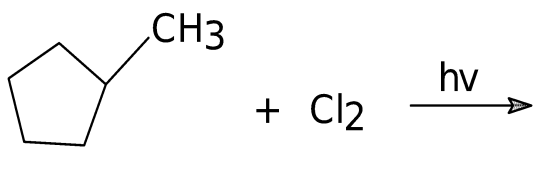
Exercises

PSPM 2014/2015

1. Monobromination of propane gives a mixture of product

   i. Write a chemical equation for this reaction.
   ii. Determine the major product.
   iii. Write the reaction mechanism involved for the formation of major product.

2. Chlorination reaction of certain alkanes can be used for the laboratory preparations, for example in preparation of cyclopentane. Name the type of reaction and show the complete mechanism for the reaction.



PSPM 2012/2013

3. Reaction of 2–methylpropane with chlorine gas in the presence of ultraviolet light forms two monochlorinated products.

   i. Draw the structures of the products.
   ii. Name the mechanism for the formation of the products.
   iii. Draw the most stable free radical formed in this reaction.
   iv. Write reaction equations of the steps for the formation of major products.

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.2 Alkenes	a) Draw structures and name alkenes according to the IUPAC nomenclature for: i. Straight chain and branched alkenes - (parent chain $\leq C_{10}$) - Cyclic alkenes ($C_3 - C_6$) - Simple dienes ($C_4 - C_6$)		√		

5.2 – ALKENES

- General formula: $\mathbf{C_nH_{2n}}$**, n ≥ 2**
- Functional group: **−C=C−**

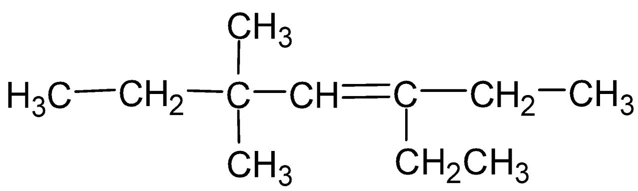
- **Unsaturated** hydrocarbon
- Each carbon atom with double bond is **sp^2 hybridized**
- **Restricted rotation** of carbon-carbon double bond causes **cis-trans isomerism**

IUPAC NOMENCLATURE OF ALKENES

The **IUPAC rules** for naming alkenes are similar to those for alkanes with an additional consideration for the position of its functional group (**double bond**).

Example:

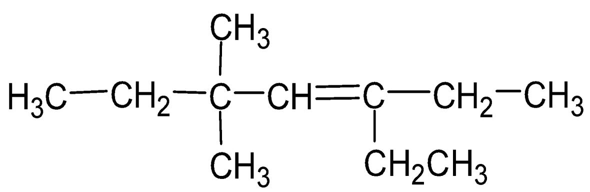
Consider the following alkenes:

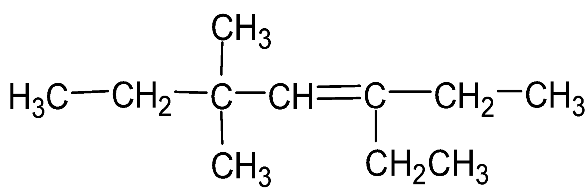


1) Determines the **parent name** by selecting the **longest continuous chain** that **contains the double bond**
   ⇒ change the ending **–ane** to **–ene**

   Parent name:

2) **Number the longest continuous chain** of alkenes.
   ⇒ **begin numbering** at the end **nearer** to the **double bond** **(lowest possible number for double bond)**





<table>
<tr><td colspan="2">3) Give the IUPAC nomenclature for Alkenes</td></tr>
<tr><td>Rule 1</td><td>Indicate the position of the substituent by the number of the carbon atoms to which they are attached.</td></tr>
<tr><td>Rule 2</td><td>The ending of the alkenes with more than one double bond should be change from -ene to:
- diene – if there are two double bonds
- triene – if there are three double bonds

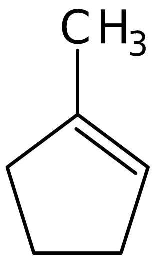
Example:
$H_2C{=}CH{-}CH{=}CH_2$
$H_2C{=}CH{-}CH{=}CH{-}CH{=}CHCH_3$</td></tr>
<tr><td>Rule 3</td><td>For stereoisomeric alkenes, prefix cis and trans are used to distinguish the two isomerism
- same side → cis
- opposite side → trans

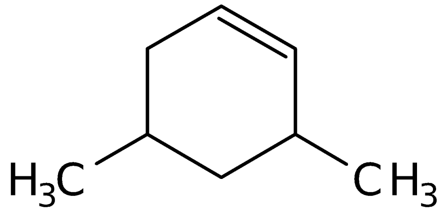
Example:
</td></tr>
</table>

NOMENCLATURE OF CYCLOALKENES

- Number substituted cycloalkenes in the way that gives the carbon atoms of the double bond the **1** and **2** positions and that also gives the substituent groups the **lower numbers at the first point of difference.**

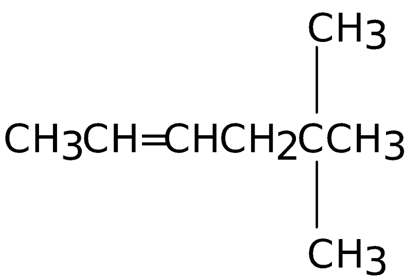
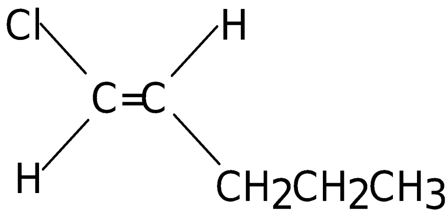
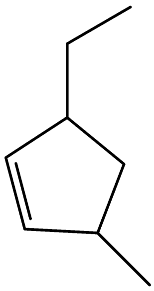
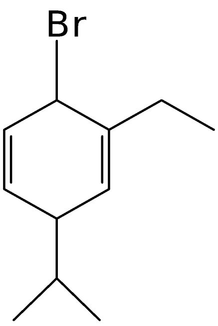
Example:





Exercises

- Name following compounds according to the IUPAC nomenclature:

a) 	b) 
c) 	d) 

- Write the structural formula for the following hydrocarbon

a) 2,3–dimethyl–2–butene	b) 2–methyl–1,3–butadiene

c) 1,2–dibromocyclopentene	d) *trans*–3–methyl–2–pentene

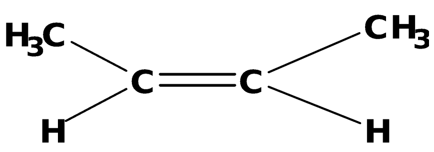
SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.2 Alkenes	*b) Explain boiling point of isomeric alkenes*				√

PHYSICAL PROPERTIES OF ALKENES	
Boiling Point (depends on the **strength of intermolecular forces** between molecules)	⍰ Similar to alkanes, the boiling points of alkenes ● **increase** with increasing molecular weight because – molecular **surface area increases** – strength of **Van der Waals forces** increases ● **decrease** with carbon chain **branching** because – molecular **surface area decreases** – strength of **Van der Waals forces** decreases

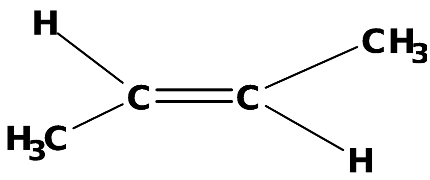
Characteristic of cis-trans isomers

- Both has **similar chemical properties** but **different physical properties.**
- Boiling point: **cis isomer higher than trans isomer.**
- **Reason:**
  - **Cis – isomer** is a ___________ **molecule.**
  - **Trans – isomer** is a _____________ **molecule.**

Hence, **cis – isomers** have **stronger Van der Waals forces** compare to **trans – isomer,** so **boiling point cis – isomer higher** compare to **trans – isomer.**

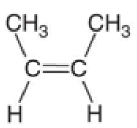
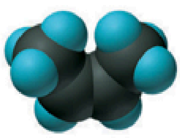
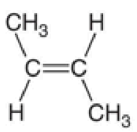
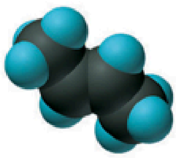


cis – isomer



trans – isomers

Geometric (*cis–trans*) Isomers of 2-Butene

Systematic Name	Condensed Formula	Space-filling Model	Density (g/mL)	Boiling Point (°C)
cis-2-Butene			0.621	3.7
trans-2-Butene			0.604	0.9

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.2 Alkenes	*c) Describe the preparation of alkenes through:* *i. Dehydration of alcohol* *ii. Dehydrohalogenation of haloalkanes*				√
	d) Outline the mechanisms for c(i)				√
	e) Justify major product formed using Saytzeff's Rule				√
	f) Predict the major product of the elimination reaction				√

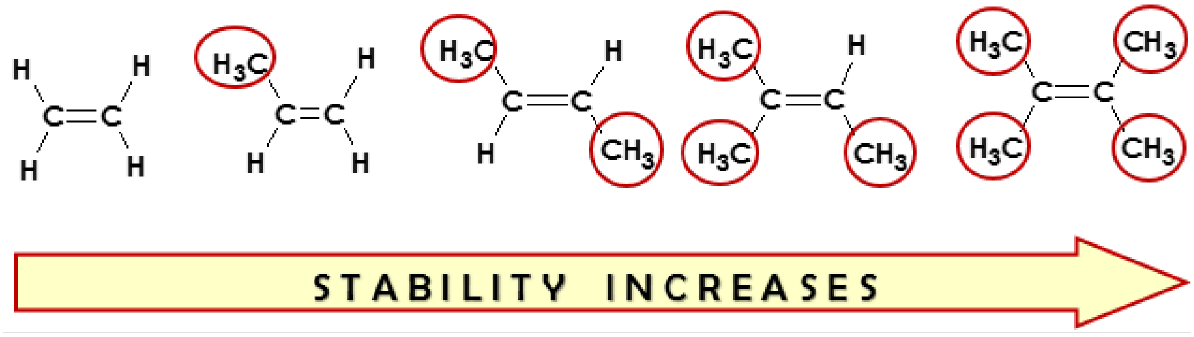
PREPARATION OF ALKENES

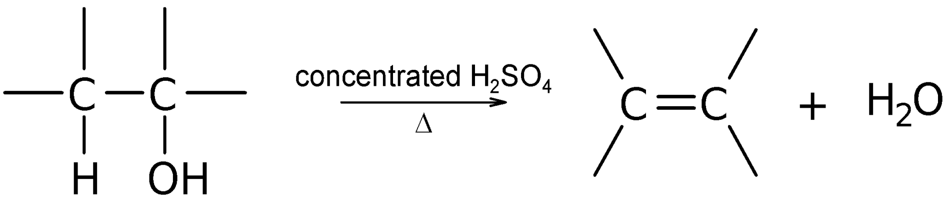
PREPARATION OF ALKENES

- **Dehydration of Alcohols** → loss of **H_2O** from **alcohol**
- **Dehydrohalogenation of Alkyl Halide** → loss of **HX** from **alkyl halide**

Type of Reaction	**Elimination**
Rule Involved	<u>**Saytzeff's Rule:**</u> - The rule that used to determine **major and minor product** of elimination reaction. - In an **elimination reaction**, the **major product** is the most **stable alkene**, commonly the **most highly substituted alkene.**

Example:



Preparation of Alkenes	Explanation and Reaction
1) Dehydration of Alcohols	- **Alcohols** react with **concentrated sulphuric acid** or **phosphoric acid** in the presence of **heat** to form **alkenes** and **water.** - **Reagents: conc H_2SO_4, Δ @ H_3PO_4, Δ** General reaction: 

Example:

i.

$$CH_3CH_2OH \xrightarrow[\Delta]{\text{conc } H_2SO_4}$$

ii.

$$CH_3CH_2CH_2OH \xrightarrow[\Delta]{\text{conc } H_2SO_4}$$

iii.

$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow[\Delta]{\text{conc } H_2SO_4}$$

Application of Saytzeff's Rule:

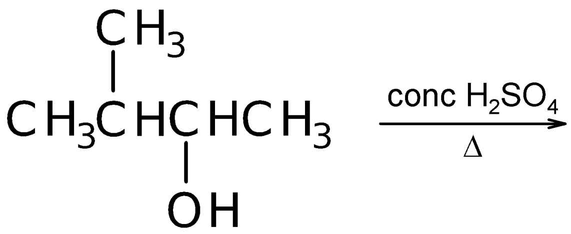
Remember!!!	⇨	states that in an **elimination** reaction alkene with the **most highly substituted double bond** is the **major** product.

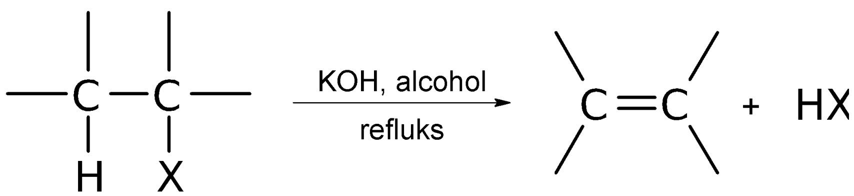
Example:

i.

$$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow[\Delta]{\text{conc } H_2SO_4}$$

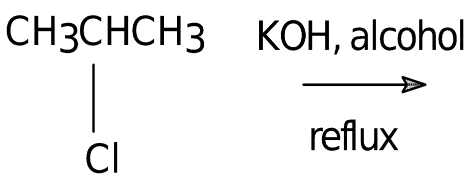
ii.



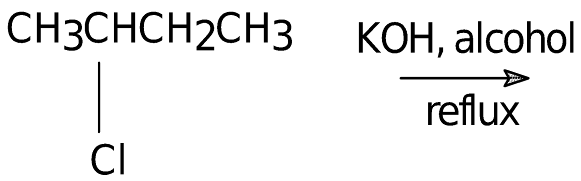
Preparation of Alkenes	Explanation and Reaction
2) Dehydrohalogenation of Alkyl Halide	A **hydrogen atom** and a **halogen** atom are **eliminated** from an **alkyl halide** to form an **alkene.** **Reagents: KOH, alcohol, reflux** Product: **Saytzeff's Rule** is used to determine the **major product.** General reaction: 

Example:

i.



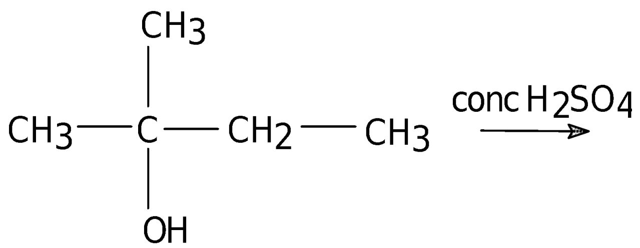
ii.



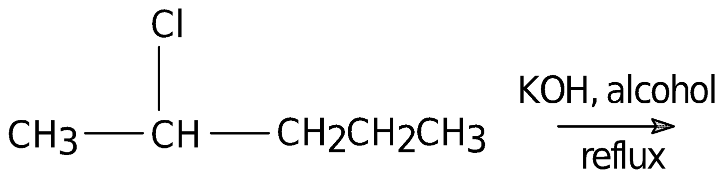
Exercises

1. Draw the structural formulae for the products formed.

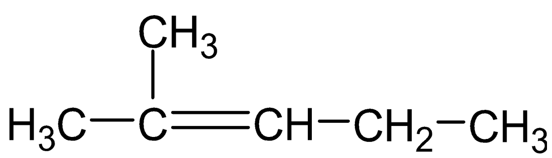
a)



b)



2. By using the suitable reagents, outline the preparation of **2–methyl–2–pentene** from



a) By dehydrohalogenation of alkyl halide.

b) From dehydration of alcohol.

3. i. Write equation to show the preparation of alkenes from

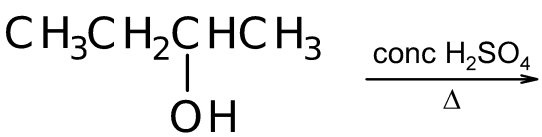
a) 3—chloro—2—methylpentane

b) Isopropyl alcohol

ii. State the rule used in the determining major product

REACTION MECHANISM:
Dehydration of Alcohol

Write mechanism for the formation of major product.



Step 1: Protonation of alcohol

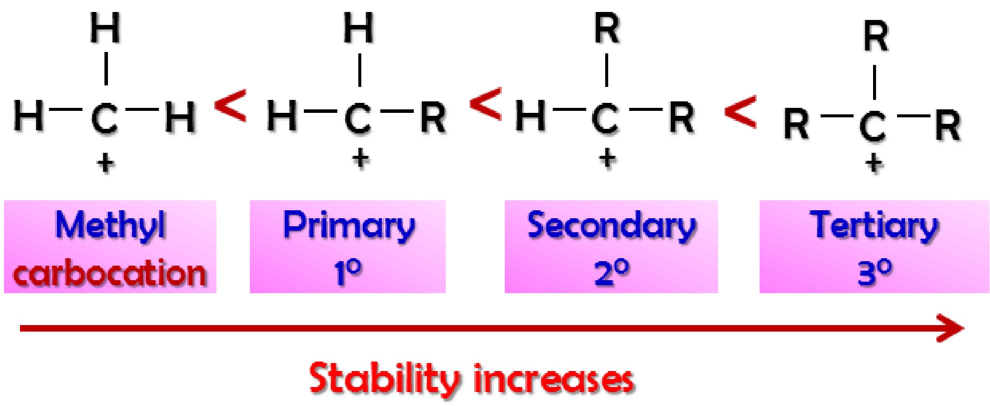
Step 2: Formation of carbocation

Step 3: Formation of alkene

Rearrangement during Dehydration of Alcohol:

⇒ When an unstable carbocation can be transformed into more stable carbocation, a **rearrangement a carbocation** is possible.

⇒ **Stability of carbocation:**



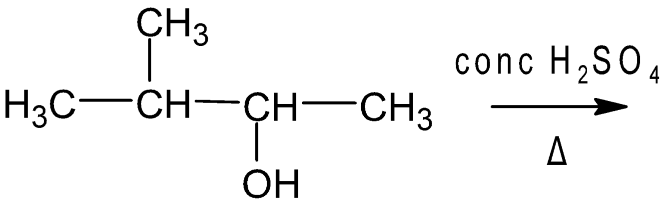
2 types of rearrangement

- **Hydride shift**
- **Methyl shift**

⇒ Because a group migrates from the one carbon to the next, this kind of rearrangement is often called a **1,2–hydride shift @ 1,2–methyl shift**

Example: Rearrangement (Hydride Shift)

Write mechanism for the formation of major product.



Step 1: Protonation of alcohol

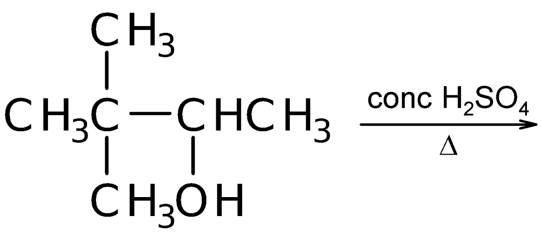
Step 2: Formation of carbocation

Step 3: Rearrangement

Step 4: Formation of alkene

Example: Rearrangement (Methyl Shift)

Write mechanism for the formation of major product.



Step 1: Protonation of alcohol

Step 2: Formation of carbocation

Step 3: Rearrangement

Step 4: Formation of alkene

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.2 Alkenes	g) 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		√		
	h) Predict the products forms according to the Markovnikov's rule				√
	i) Illustrate the mechanism of electrophilic addition of (g) iv and (g) v				√
	j) 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				√

CHEMICAL REACTION OF ALKENES

Addition Reaction of Alkenes

Addition reaction to double bond have these 3 characteristics :

i) The **π bond** of the double bond is broken and two new **single bonds** are formed.

ii) Only **one product** is obtained at the end of the reaction.

iii) The product obtained is a **saturated** organic compound.

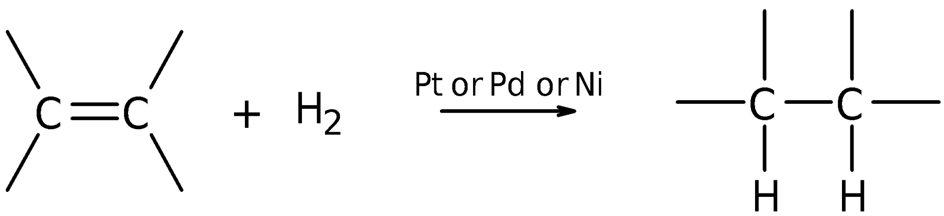
Type of Reaction	**Electrophilic Addition**
Rule	**Markovnikov's Rule** ⇒ In the addition of **HX** to an alkenes, the **hydrogen atom** is **added** to the **carbon of double bond with greater number of hydrogen atoms.**

Reaction

HYDROGENATION

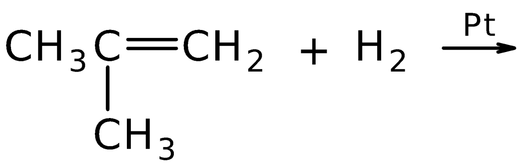
- The reaction of an **alkene** with **hydrogen** in the presence of **catalyst** such as **platinum, nickel** and **palladium** to form alkane.

- **Reagents: H_2, Pt/Pd/Ni (catalyst)**

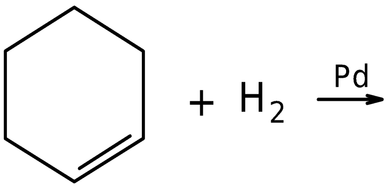


Examples:

i.



ii.



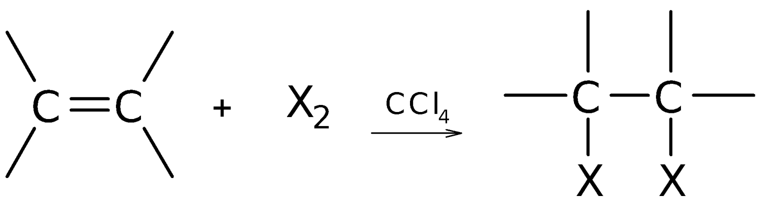
Reaction

2. HALOGENATION
- **HALOGENATION IN INERT SOLVENT (CH_2Cl_2)**
- **HALOGENATION IN AQUEOUS SOLUTION**

HALOGENATION IN INERT SOLVENT (CH_2Cl_2)

- Alkenes react rapidly with **chlorine** or **bromine** in **CH_2Cl_2** at room temperature to form **vicinal dihalides**

- **Reagents: Halogen (Cl_2 or Br_2) in CH_2Cl_2**

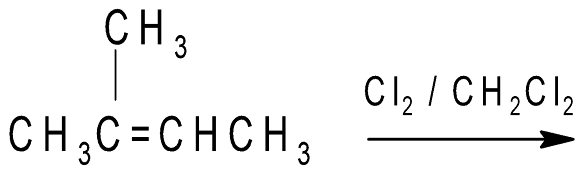


Examples:

i.

$$CH_3CH=CH_2 \xrightarrow{Br_2\ /\ CH_2Cl_2}$$

ii.

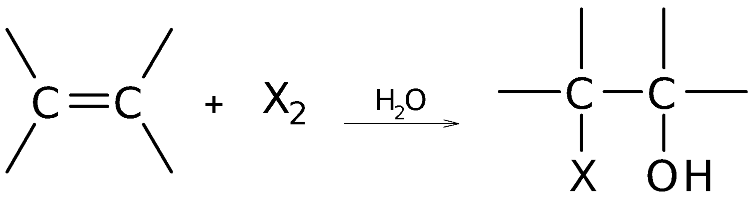


Reaction

HALOGENATION IN AQUEOUS SOLUTION (H_2O)

- Reaction of alkene with **chlorine** or **bromine** in **aqueous solution** produce a **halohydrin**

- **Reagents: Halogen (Cl_2 or Br_2) in H_2O**



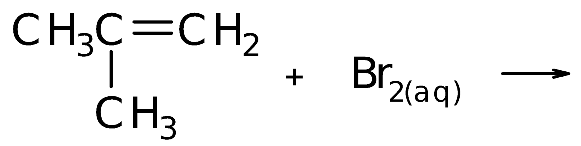
Example:

$$H_2C{=}CH_2 + Cl_{2(aq)} \longrightarrow$$

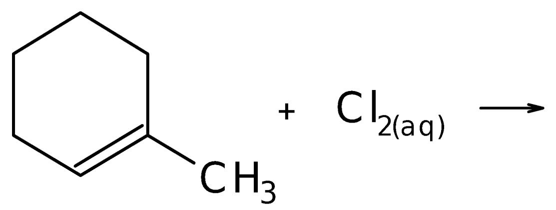
- If the alkenes is **unsymmetrical**, the **halogen (Br or Cl) atom is added** to the **carbon atom** (of the double bond) with the **greater number of hydrogen atoms.**
  ⇒ Follow **Markovnikov's Rule**

Examples:

i.



ii.

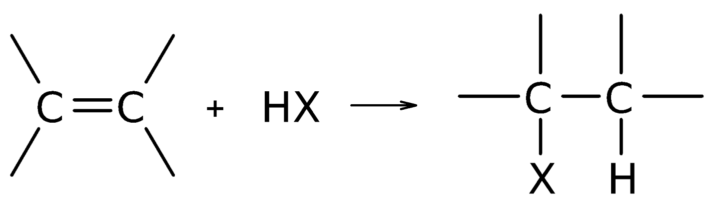


Reaction

3. HYDROHALOGENATION OF ALKENE
- Follow **Markovnikov's Rule**
- Follow **Anti Markovnikov's Rule**

HYDROHALOGENATION OF ALKENE (follow Markovnikov's Rule)

- Addition of hydrogen halides (**HBr, HCl**) to the double bond of alkenes form **haloalkanes**
- **Reagents: HBr or HCl**

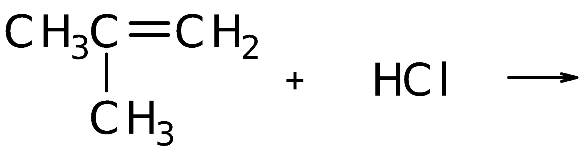


Examples:

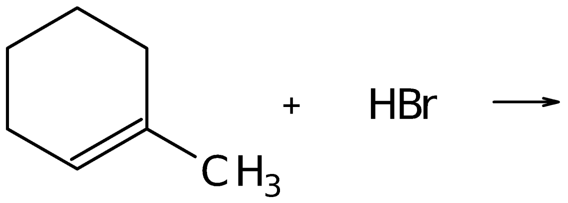
i.

$$CH_3CH{=}CH_2 + HBr \longrightarrow$$

ii.



iii.



Reaction

HYDROHALOGENATION OF ALKENE (follow Anti Markovnikov's Rule)

- When alkenes are treated with **HBr in the presence of peroxides, ROOR** (eg: $\mathbf{H_2O_2}$) the addition occurs in an **anti-Markovnikov's rule**

- **Reagents: HBr, ROOR (eg: $\mathbf{H_2O_2}$)**

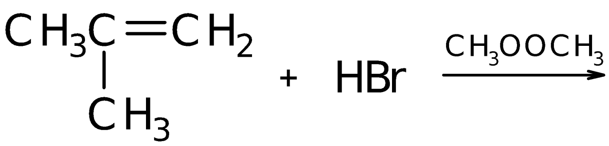
- Rule: **Anti Markovnikov's**
  ⇒ the **hydrogen atom** of HBr **add to the carbon atom** (of the double bond) with **fewer number of hydrogen atom.**

Examples:

i.

$$CH_3CH{=}CH_2 \;+\; HBr \xrightarrow{H_2O_2}$$

ii.



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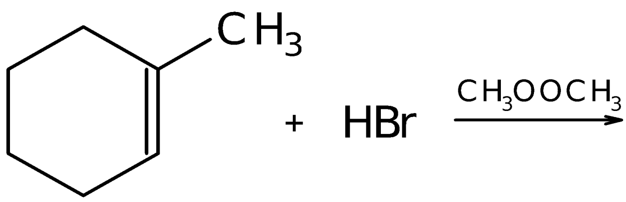


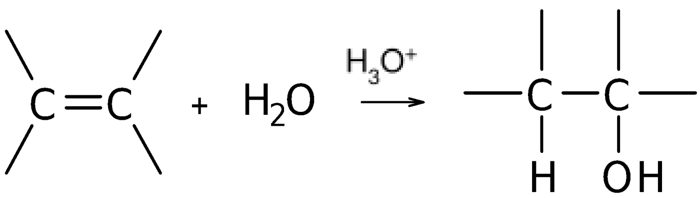
Reaction

4. HYDRATION OF ALKENE @ ACIDIFIED WATER

- **Follow Markovnikov's Rule**

- The **acid-catalyzed** addition of **water** to the **double bond** of an alkene is a **common method for the preparation** of **low molecular weight alcohol.**

- **Reagents: H_2O, H_3O^+**

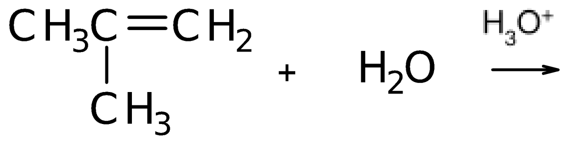


Examples:

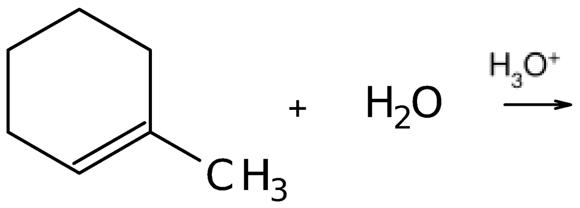
i.

$$CH_3CH{=}CH_2 + H_2O \xrightarrow{H_3O^+}$$

ii.

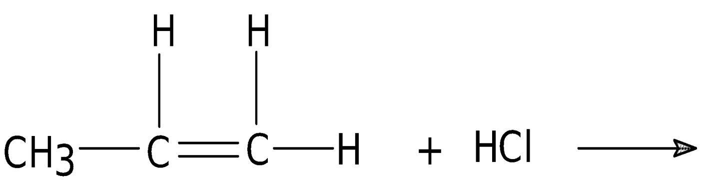


iii.



REACTION MECHANISM (Reaction of Alkenes)
Hydrohalogenation

Write mechanism for the formation of major product.

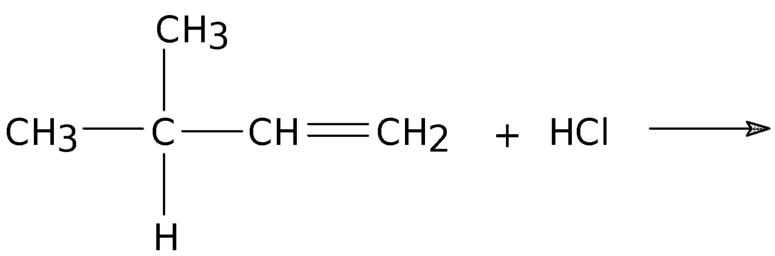


Step 1: Formation of carbocation

Step 2: Nucleophile attack carbocation

Try this!

Write mechanism for the formation of major product.

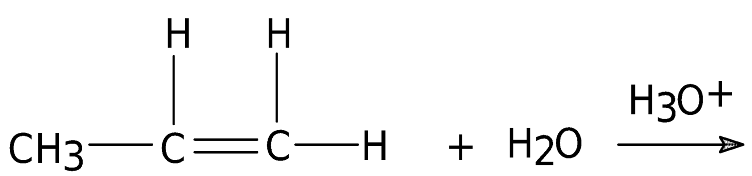


Step 1: Formation of carbocation

Step 2: Nucleophile attack carbocation

REACTION MECHANISM (Reaction of Alkenes)
Hydration (Acidified Water)

Write mechanism for the formation of major product.



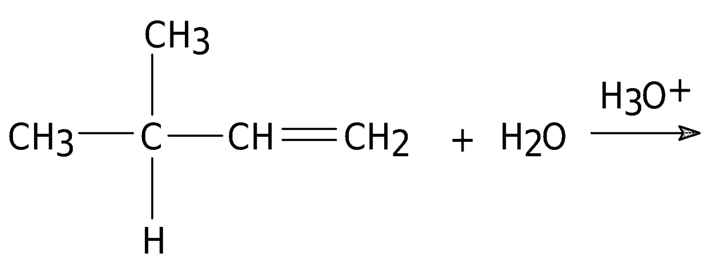
Step 1: Formation of carbocation

Step 2: Nucleophile attack carbocation

Step 3: Loss of proton to form alcohol

Try this!

Write mechanism for the formation of major product.



Step 1: Formation of carbocation

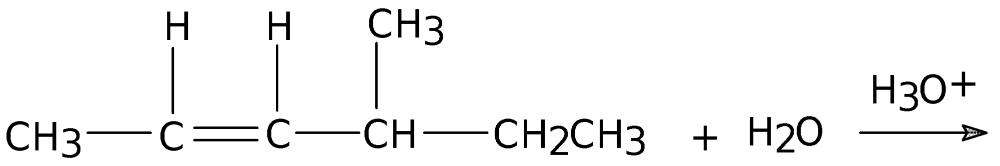
Step 2: Nucleophile attack carbocation

Step 3: Loss of proton to form alcohol

Exercises (Reaction Mechanism)

1. 3–methyl–2–pentene reacts with hydrogen bromide to produce P
   a) Name the type of reaction taken part and give the structures of product P
   b) Show the complete mechanism for the formation of the major product of the above reaction

2. Propose the mechanism for the formation of the major product of the reaction below:



SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.2 Alkenes	k) *Explain/ Predict 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 $KMnO_4$*				√

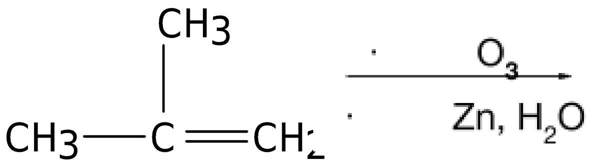
OZONOLYSIS ⇒ **Oxidative cleavage reaction!**

- **Reagents: i. O_3,**
  ii. Zn, H_2O or $(CH_3)_2S$

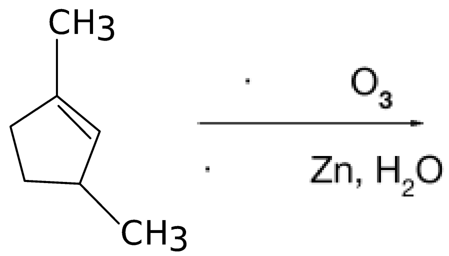
- **Product of reaction: carbonyl**

Examples:

i.



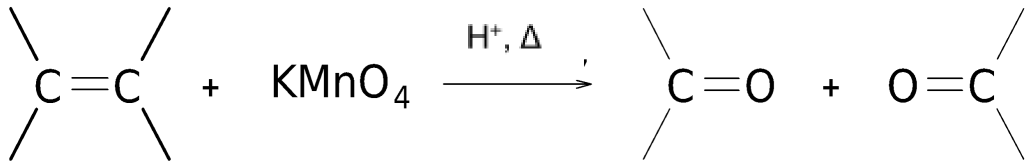
ii.



HOT, ACIDIFIED $KMnO_4$ ⇒ **Oxidative cleavage reaction!**

- When oxidation of the alkene is carried out in acidic solution of $KMnO_4$, **cleavage** of the double bond occurs and carbonyl- containing products are formed.

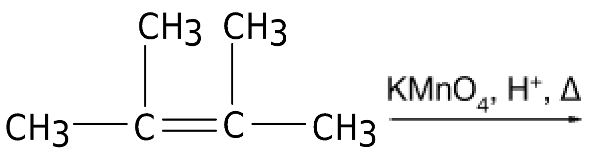
- **Reagents: $KMnO_4$, H^+, Δ @ $K_2Cr_2O_7$, H^+, Δ**



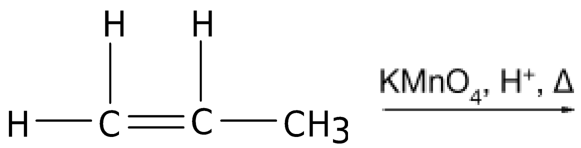
- If the double bond is **tetrasubstituted**, the products are **ketones.**
- If the carbon with double bond is attached to **one hydrogen atom**, the product is **carboxylic acid**.
- If **two hydrogen atoms** are present on one carbon, CO_2 is present

Examples:

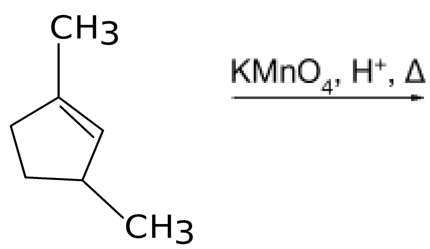
i.



ii.



iii.



SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.2 Alkenes	*I) Identify the position of double bond through:* *i. Ozonolysis* *ii. Reaction with hot, acidified $KMnO_4$*				√

OXIDATIVE CLEAVAGE ⇒ can be used to **establish the location** of the **double bond** in an **unknown alkene.**

Example:

An unknown alkene with the formula **C_6H_{12}** was found to form **propanoic acid** and **propanone** when oxidized with concentrated, hot acidic potassium permanganate permanganate. What is the structure of this alkene?

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
5.2 Alkenes	*m) Explain the unsaturation test for alkenes:* *i. Baeyer's test using dilute $KMnO_4$ solution*				√

	ii. *Bromine in CH_2Cl_2* iii. *Bromine water*				

CHEMICAL TEST FOR ALKENES

Function chemical test ⇒ to **distinguish** between the compound

- Name Test
- Reagents
- Equation
- Observation

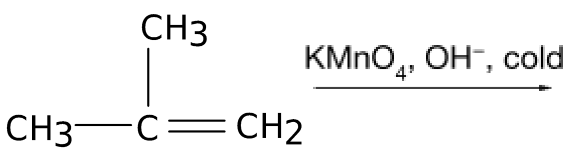
} Very IMPORTANT!!!

Unsaturation Test

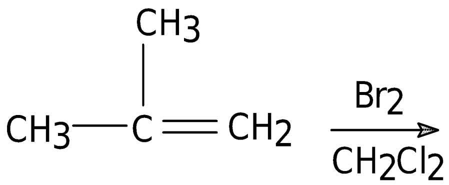
- to determine the presence of C=C
- to distinguish alkene from others compound

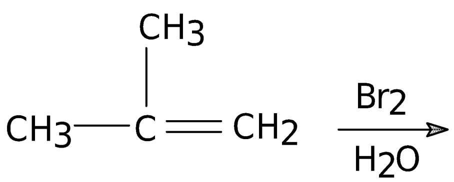
Baeyer's Test | **Bromine Test** | **Bromine water**

- Baeyer's Test

Reagents	**$KMnO_4$, OH^-, cold**
Equation	
Observation	

- Bromine in CH_2Cl_2

Reagents	**Br_2, CH_2Cl_2**
Equation	
Observation	

· Bromine Water	
Reagents	**Br_2, H_2O**
Equation	
Observation	

Exercises

1. Give chemical test to differentiate between cyclohexene and hexane

2. Give one chemical test that can be used to differentiate propane and propene