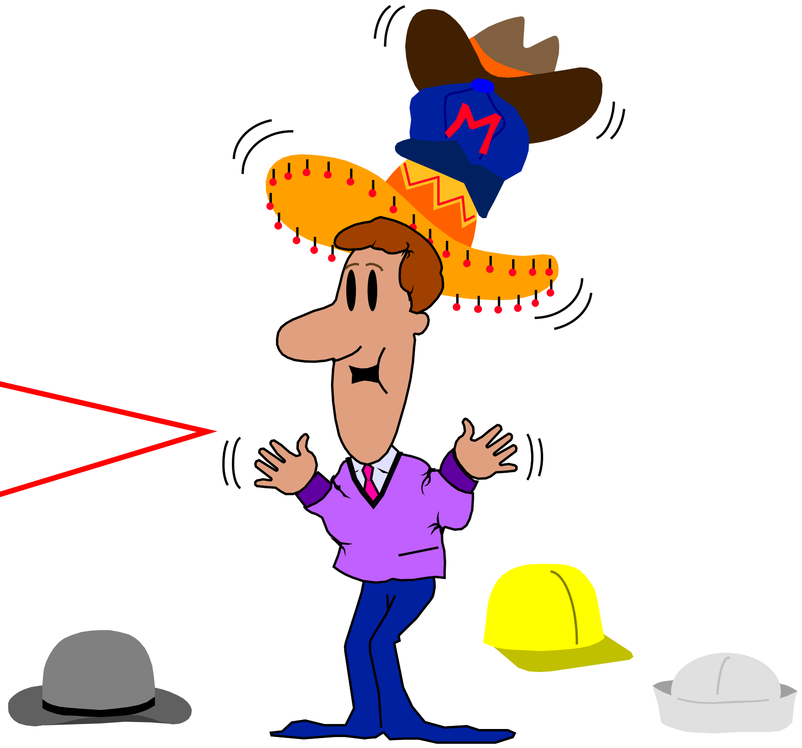
CHAPTER 12: HYDROCARBONS

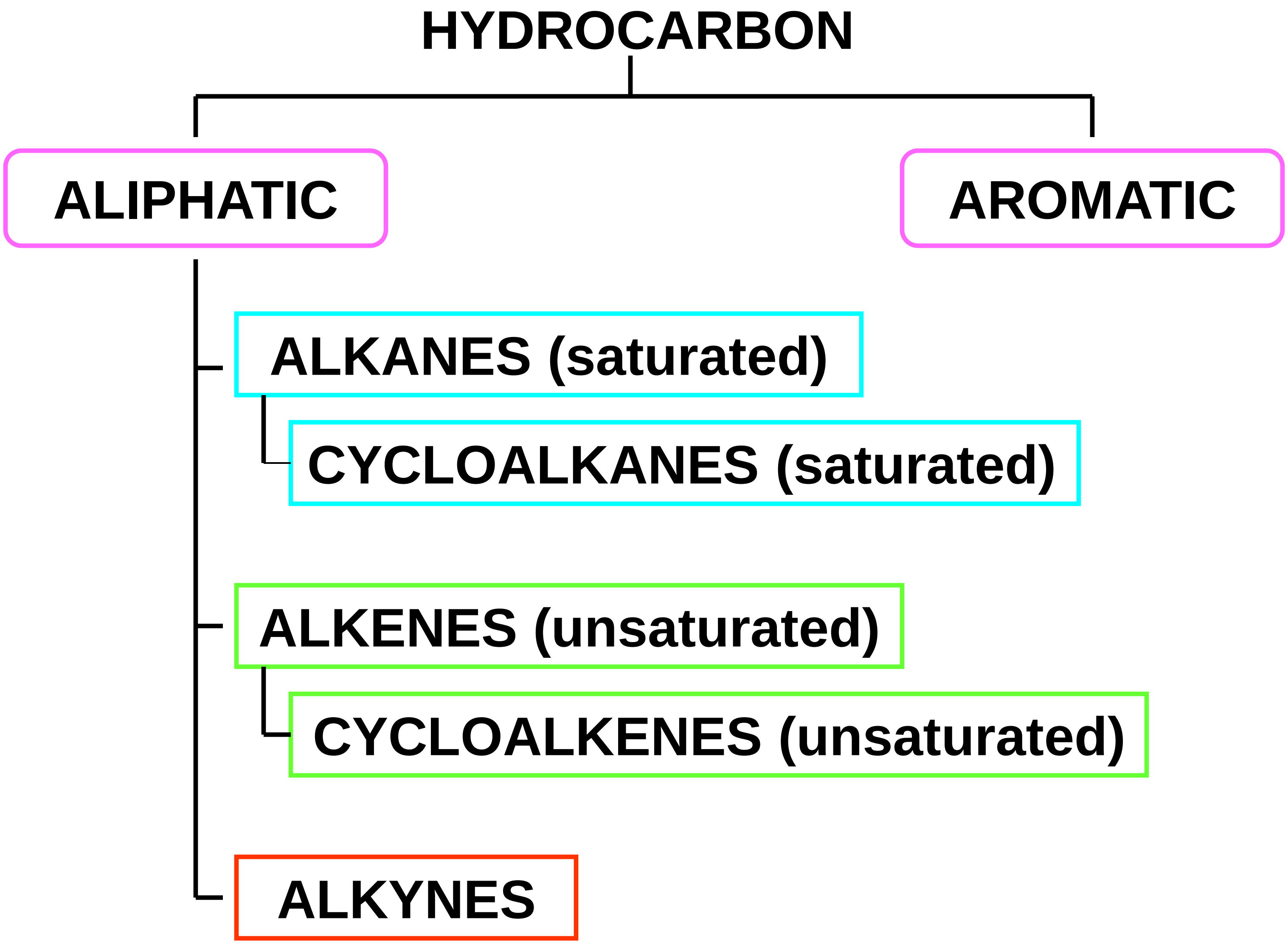
12.1 Alkanes
12.2 Alkenes
12.3 Aromatic Compounds

INTRODUCTION

Hydrocarbon?

are compounds which contain only carbon and hydrogen atoms.




HYDROCARBON
ALIPHATIC
AROMATIC
ALKANES (saturated)
CYCLOALKANES (saturated)
ALKENES (unsaturated)
CYCLOALKENES (unsaturated)
ALKYNES

- Saturated hydrocarbons – contain only single carbon-carbon bonds
- Unsaturated hydrocarbons – contain carbon-carbon double or triple bonds (can accept a number of additional hydrogen atoms to become "saturated")

11.5 Alkane

Learning Outcomes:

1. Describe hydrocarbon
2. Classify hydrocarbon
3. Draw the structure and name straight chain alkanes according IUPAC

Acyclic Alkane

- Aliphatic/open-chain hydrocarbons
- Are saturated hydrocarbon which contain only single covalent bond
- General formula: $\mathbf{C_nH_{2n+2}}$ where **n = 1, 2, 3 …….**
- Each carbon atom is sp^3 hybridized and bonded to four other atoms by single bonds in the form of a tetrahedron. All bond angles are close to 109.5^o
- IUPAC names have the –**ane** suffix

Cycloalkane

- Alkanes which carbon atoms are joined in rings.
- Known as saturated hydrocarbon, because it has the maximum number of bonded hydrogen (only has single bonds).
- General formula: $\mathbf{C_nH_{2n}}$ where **n = 3, 4, 5 ….**

Structural Isomerism

Different compound with the same molecular formula but differ in the order of attachment of atoms

i. Chain/skeletal isomerism

ii. Position isomerism

iii. Functional group isomerism

Exercise:

Draw all possible constitutional isomers for C_5H_{12}.

Answer:

Name	Number of Carbon Atoms	Structure	Molecular Formula
Methane	1	CH_4	CH_4
Ethane	2	CH_3CH_3	C_2H_6
Propane	3	$CH_3CH_2CH_3$	C_3H_8
Butane	4	$CH_3CH_2CH_2CH_3$	C_4H_{10}
Pentane	5	$CH3(CH_2)_3CH_3$	C_5H_{12}
Hexane	6	$CH3(CH_2)_4CH_3$	C_6H_{14}
Heptane	7	$CH3(CH_2)_5CH_3$	C_7H_{16}
Octane	8	$CH3(CH_2)_6CH_3$	C_8H_{18}
Nonane	9	$CH3(CH_2)_7CH_3$	C_9H_{20}
Decane	10	$CH3(CH_2)_8CH_3$	$C_{10}H_{22}$

Table 11.1: The First Ten Unbranched Alkanes

11.5 ALKANE

Learning outcomes

- Draw and name :

  a) alkyl groups

  b) branched alkanes

  c) cyclic alkanes

- State the natural source of alkanes

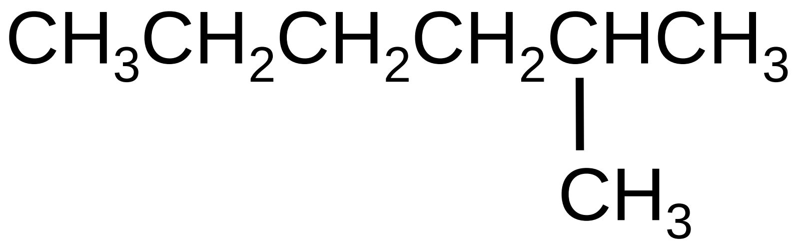
IUPAC Nomenclature

- **IUPAC – International Union of Pure and Applied Chemistry**

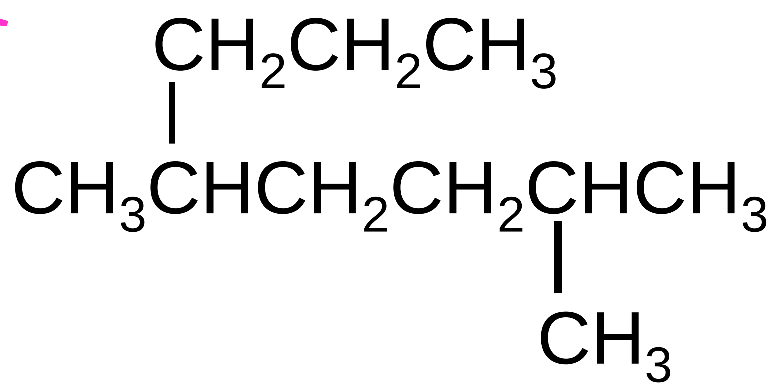
Branched-chain alkanes are named according to the following rules:

Rule 1: Identify the **longest continuous chain** (parent's name)

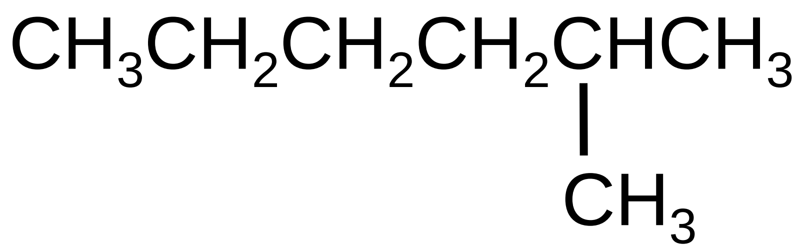
Parent's name:



Parent's name:



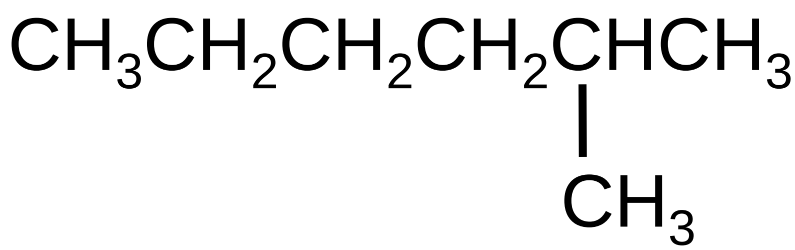
Rule 2: Name the substituent & give a **smaller no.** to the substituent



Substituent:

Rule 3: **Designate** the location of the substituent

* The substituent with its no. is placed in front of parent's name
* Number is separated from words by a hyphen



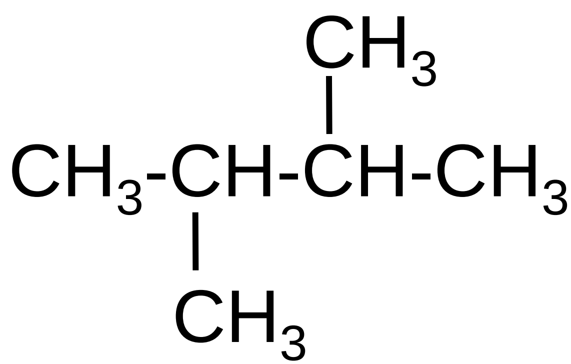
Parent's name:

Substituent:

Name:

Rule 4: Use prefixes **di-, tri-, tetra-** and so on if the same substituent appears more than once.

Commas are used to separate numbers from each other

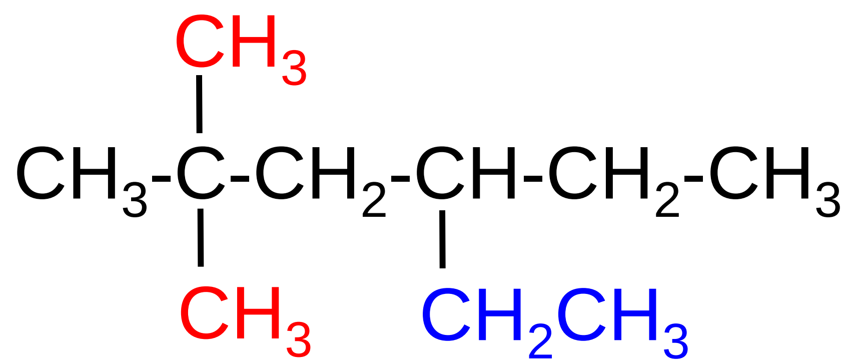


Name:

Rule 5: Arrange the substituents in alphabetical order by assigning small numbers as possible.

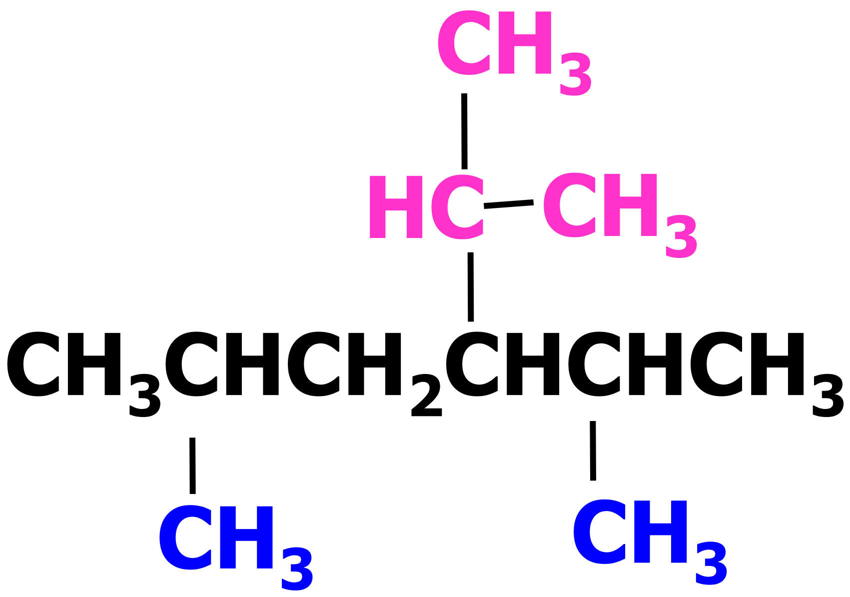
Parent's name: hexane

Substituents:



Name:

Substituents:

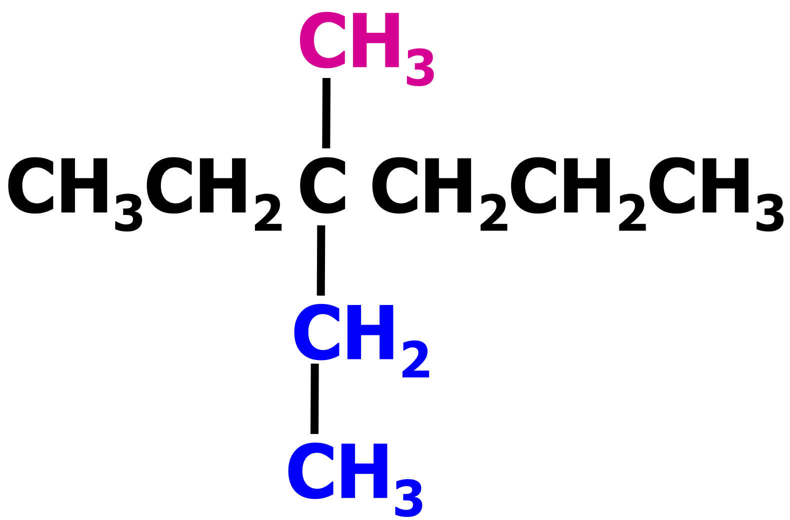


Name:

Keep in mind!

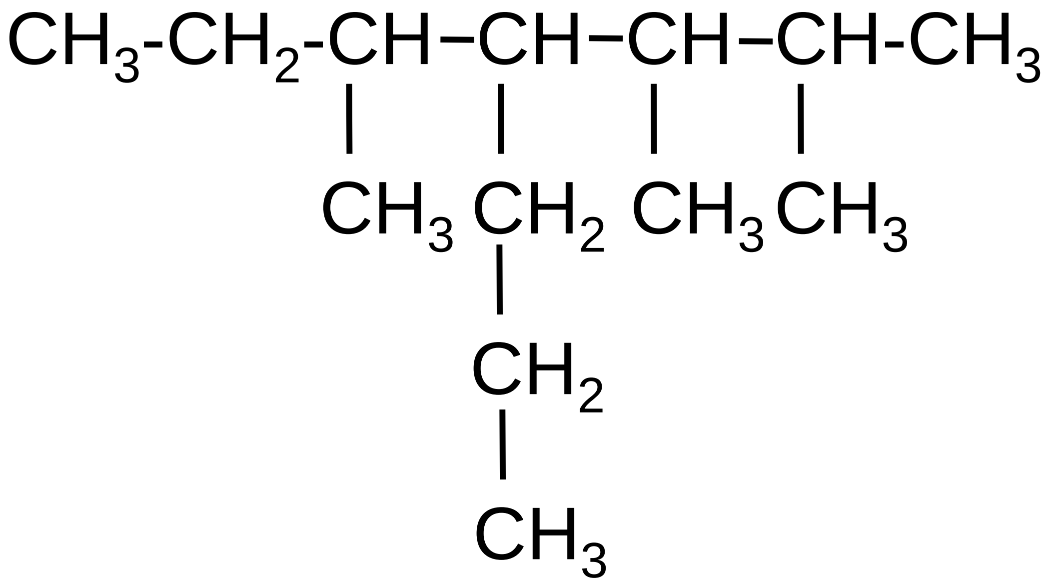
i) In alphabetizing, the prefixes **di, tri, tetra, sec-, tert-** are **ignored except iso** and **neo**.

ii) When two substituents are present on the same carbon atom, use that number twice.



Name:

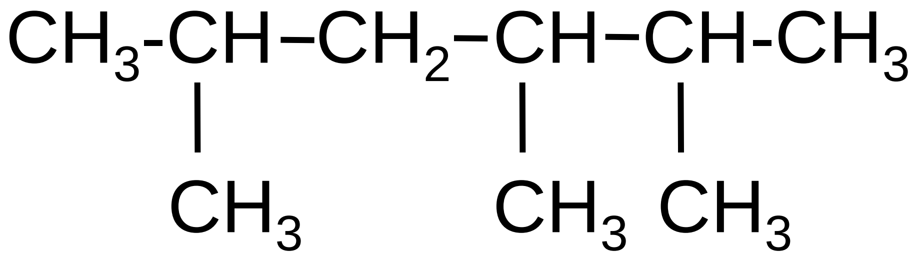
iii) When two chains of equal length compete for selection as the parent chain, choose the chain with the **greatest number** of substituents.



Name :

Name :

iv) When 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.

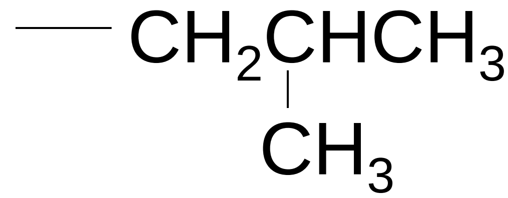
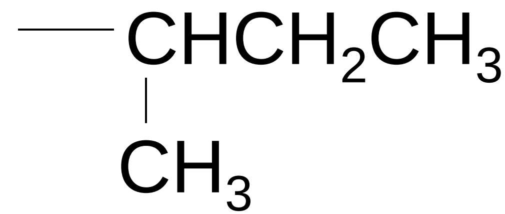
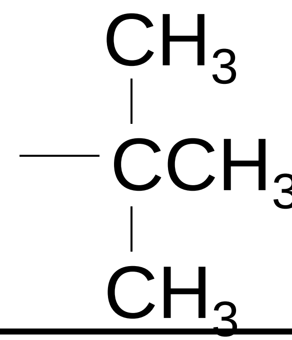
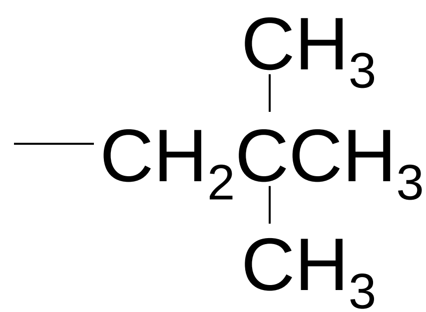


Name :

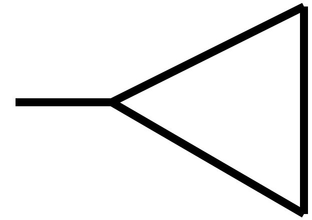
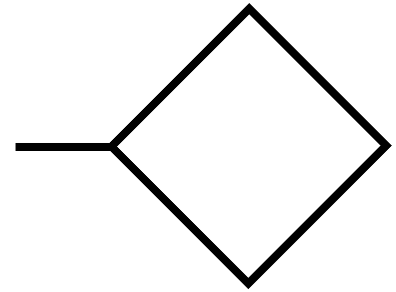
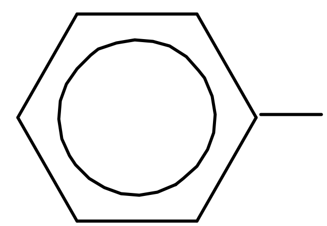
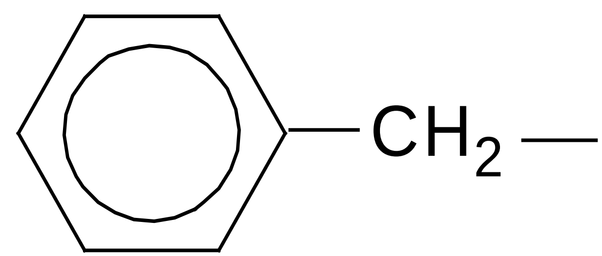
Name :

Some Common Substituent Groups

Name	Substituent
methyl	$-CH_3$
ethyl	$-CH_2CH_3$
propyl	$-CH_2CH_2CH_3$
isopropyl	$-CHCH_3$ $\vert$ CH_3
butyl	$-CH_2CH_2CH_2CH_3$

isobutyl	
sec-butyl	
tert-butyl	
neopentyl	

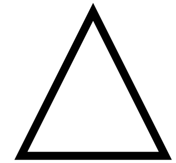
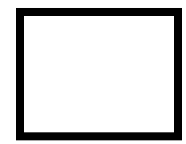
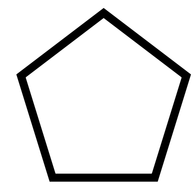
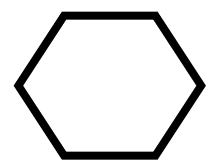
Name	Substituent
bromo	-Br
chloro	-Cl
flouro	-F
iodo	-I
hydroxyl	-OH
amino	$-NH_3$
cyano	-CN
nitro	$-NO_2$

cyclopropyl	
cyclobutyl	
phenyl	$–C_6H_5$ or 
benzyl	

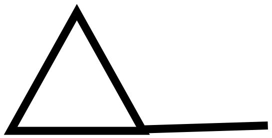
Nomenclature of Cycloalkanes

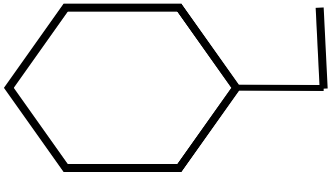
1. Cycloalkanes with only one ring

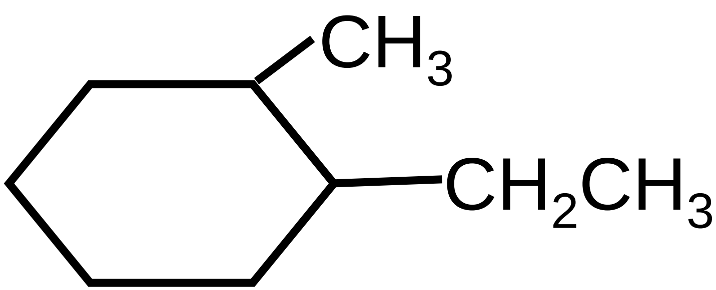
are named by
attaching the **prefix cyclo-** to the names of the alkanes possessing the same number of carbon atoms

Molecular formula	Name	Structural formula
C_3H_6	Cyclopropane	
C_4H_8	Cyclobutane	
C_5H_{10}	Cyclopentane	
C_6H_{12}	Cyclohexane	

2. Cycloalkanes with substituent

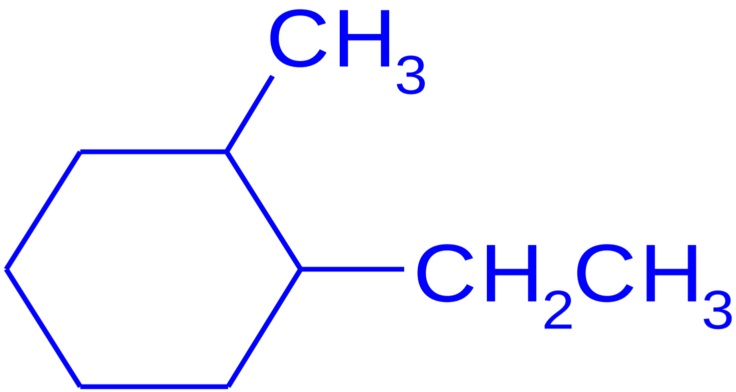


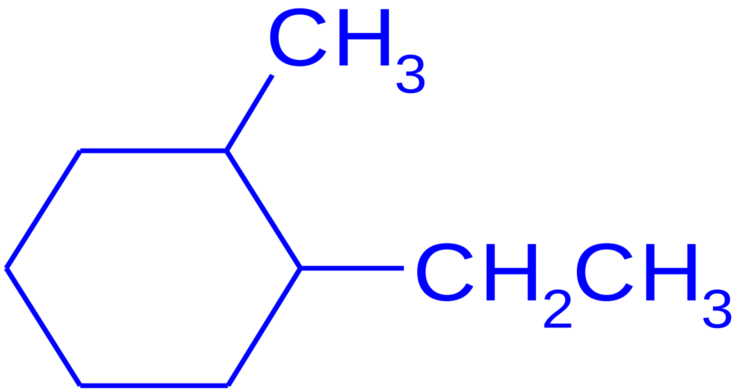


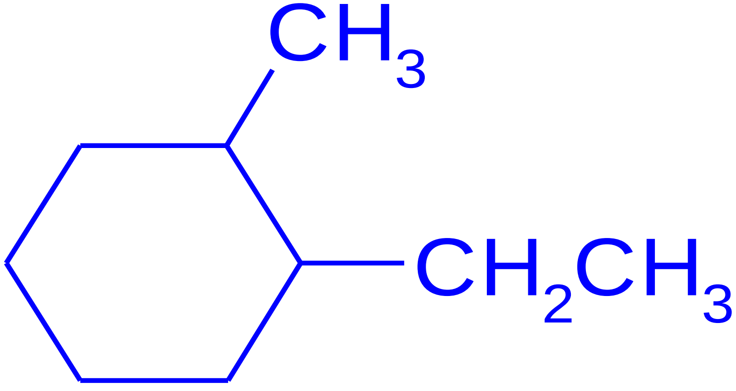


3. When 2 substituents present :
   - Numbered the C beginning with substituent according to the alphabetical order
   - Numbered in the way that gives the next substituent the lowest number possible

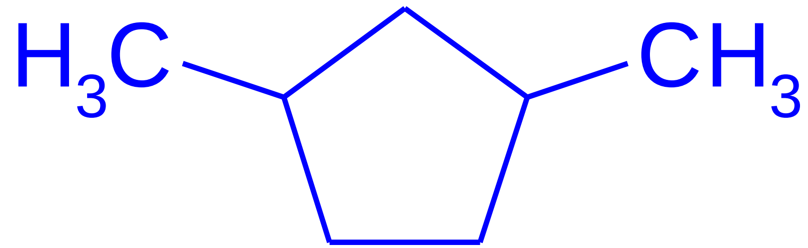
Example 1:

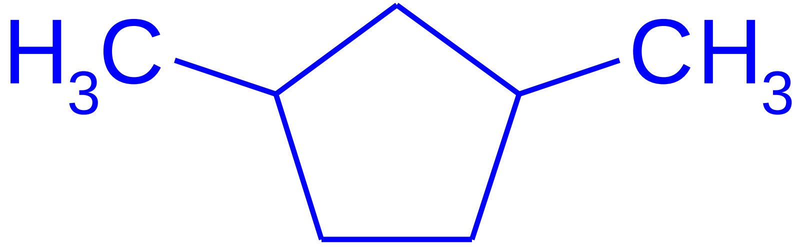






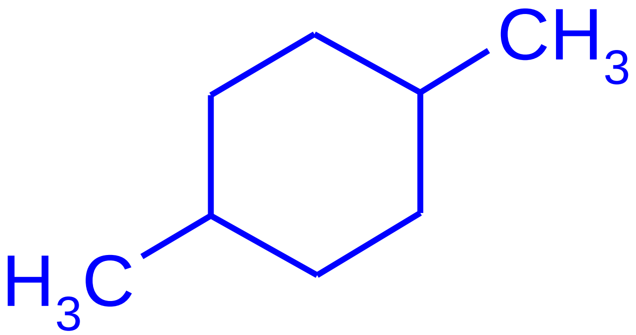
Example 2:

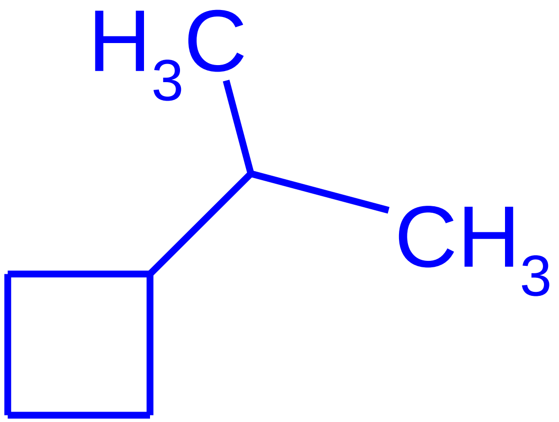


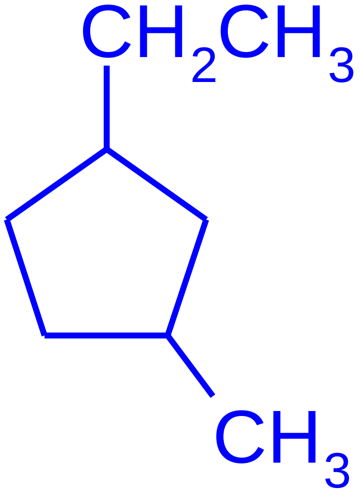


Practice Exercise

Give IUPAC names for the following cycloalkanes :



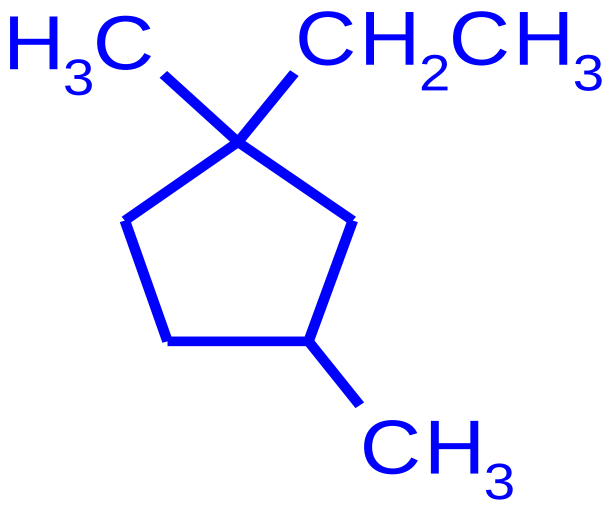


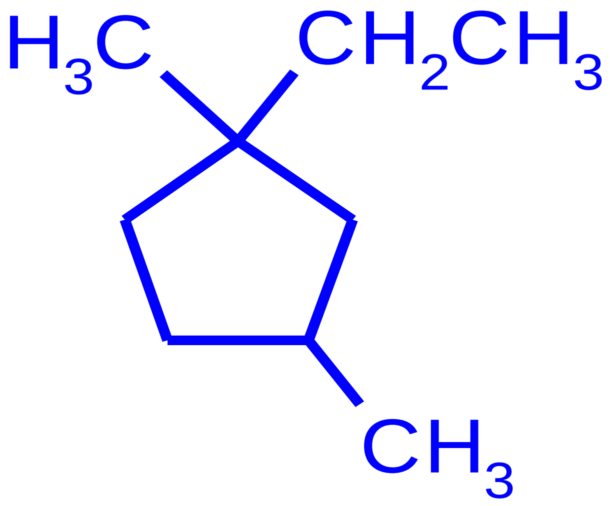


4. When 3 or more substituents present :

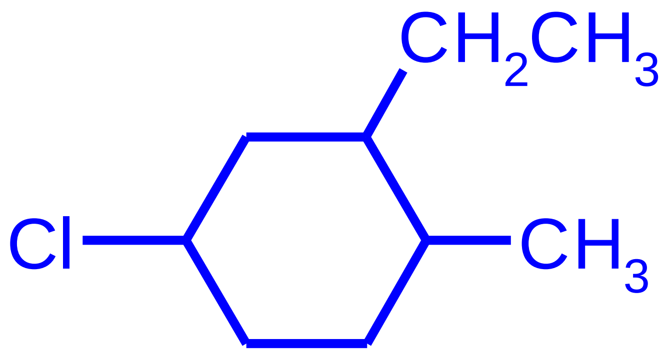
- Begin at the C with substituent that leads to the lowest set of locants

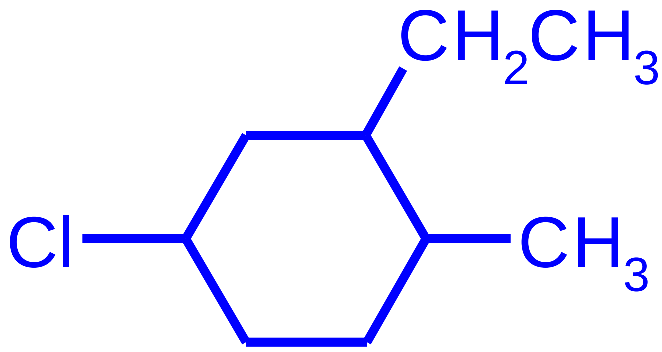
Example 1:



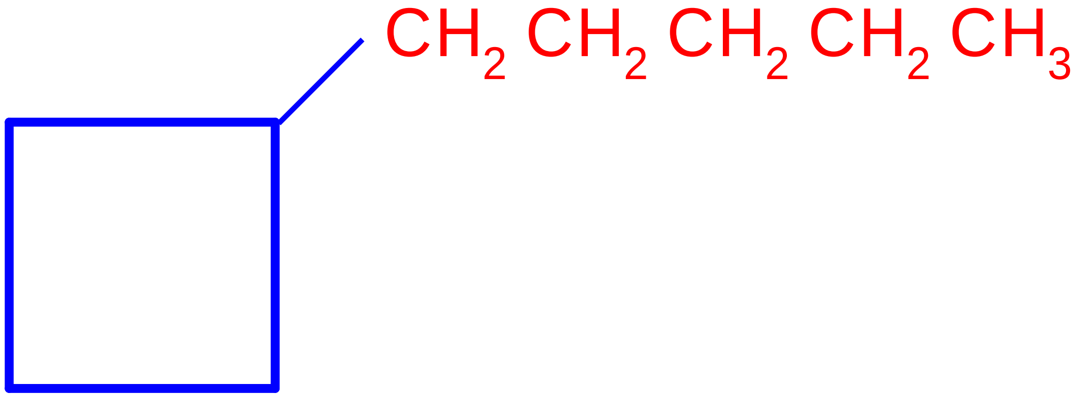


Example 2:

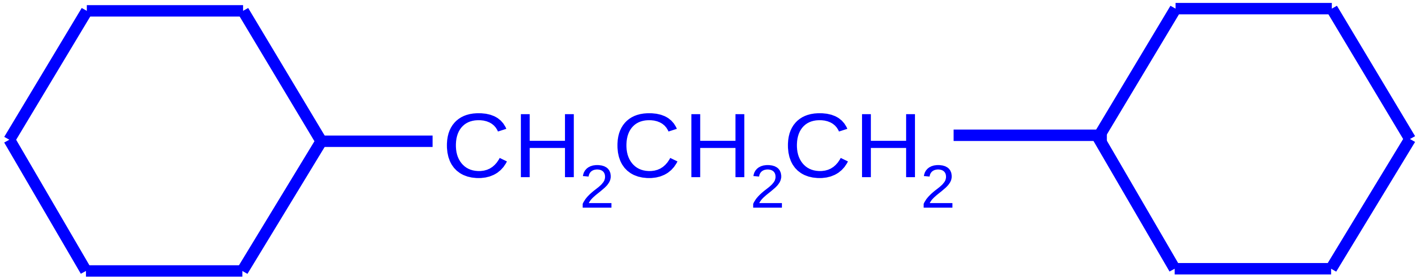




5. Single ring is attached to a chain with greater no. of C atoms : named as *cycloalkyl*alkane



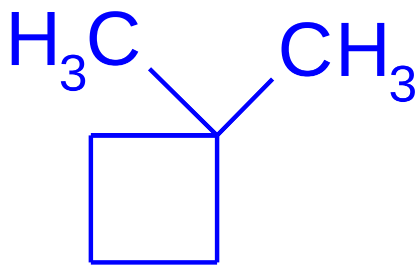
6. When more than 1 ring is attached to a single chain : also named as *cycloalkyl*alkane



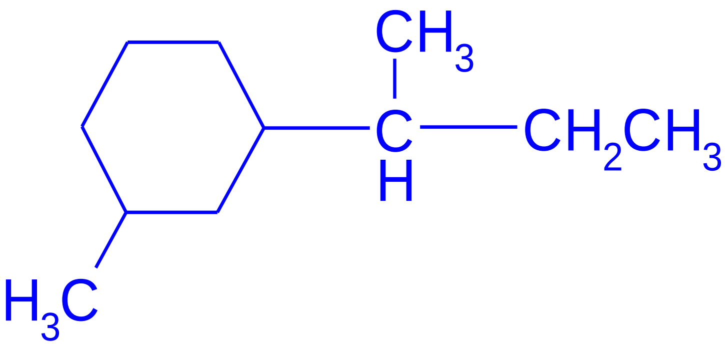
Practice Exercise

Give IUPAC name for the following compounds

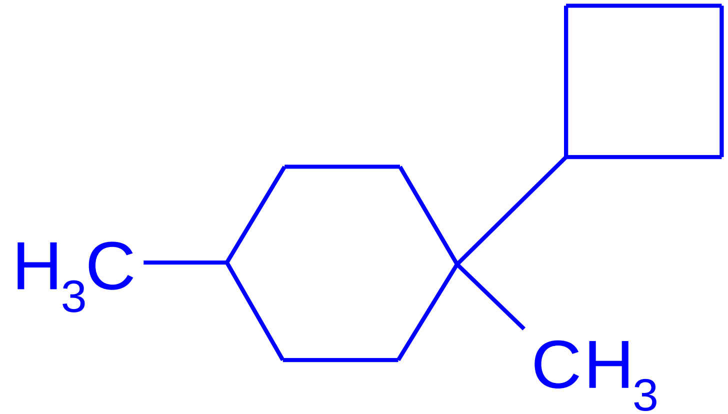
a)



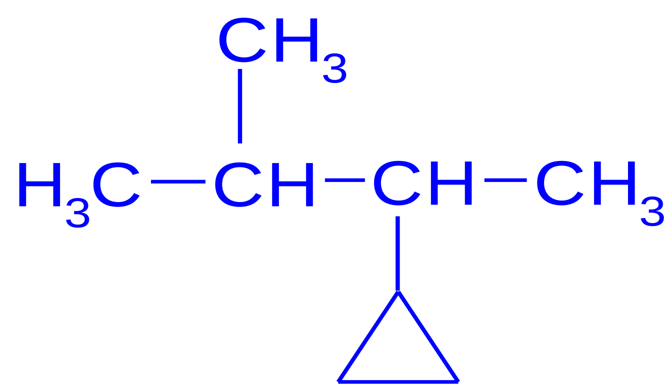
b)



c)



d)



Exercise:

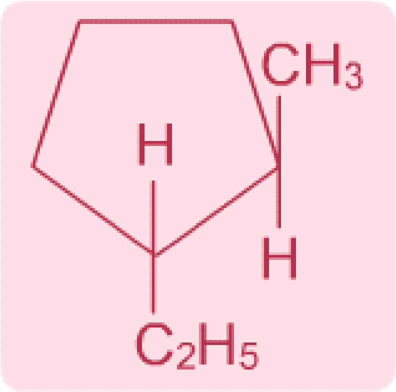
Give the names and molecular formulae of the following alkanes.

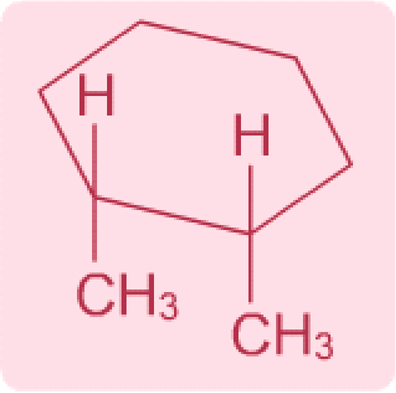
1. $CH_3CH_2CH(CH_3)CH(C_2H_5)CH_2C(CH_3)_2CH_3$

2. $CH_3CH_2C(C_2H_5)_2CH_2CH_2CH_3$

Exercise:

Give the names and molecular formulae of the following cycloalkanes

1. 

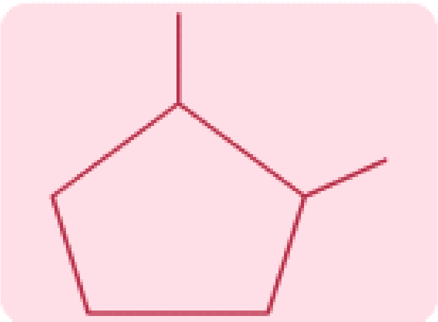
2. 

Exercise:

Consider the following alkanes and choose the right answer.

A. $CH_3(CH_2)_{18}CH_3$

B.



C. $CH_3(CH_2)_6CH_3$

D. $CH_3CH(CH_2)_4CH_3$ with a CH_3 group attached to the CH

E. $CH_3CH_2CH_3$

1. Which two alkanes are isomers?

   Answer: Which compound cannot be represented by the general formula C_nH_{2n+2}?

   Answer:

3. Which of the alkanes has the name octane?

   Answer:

4. Which of them exists as two geometrical isomers?

   Answer:

5. Which alkane is a solid at room tempertaure?

   Answer:

- Sources for alkanes are clearly natural gas and oil.
- Natural gas contains primarily methane and ethane, with some propane and butane.
- Oil is a mixture of liquid alkanes and other hydrocarbons.

11.5 ALKANES

Learning Outcomes:

- Compare boiling points of alkanes
  - based on molecular weight
  - isomeric alkanes
  - alkanes and cycloalkanes
- Solubilty of of alkanes
- Preparation of alkanes
- Describe combustion of alkanes
- Explain the unreactivity of alkanes
- Explain the halogenation of alkanes

PHYSICAL PROPERTIES

Physical state

Boiling Point

Solubility

Physical State

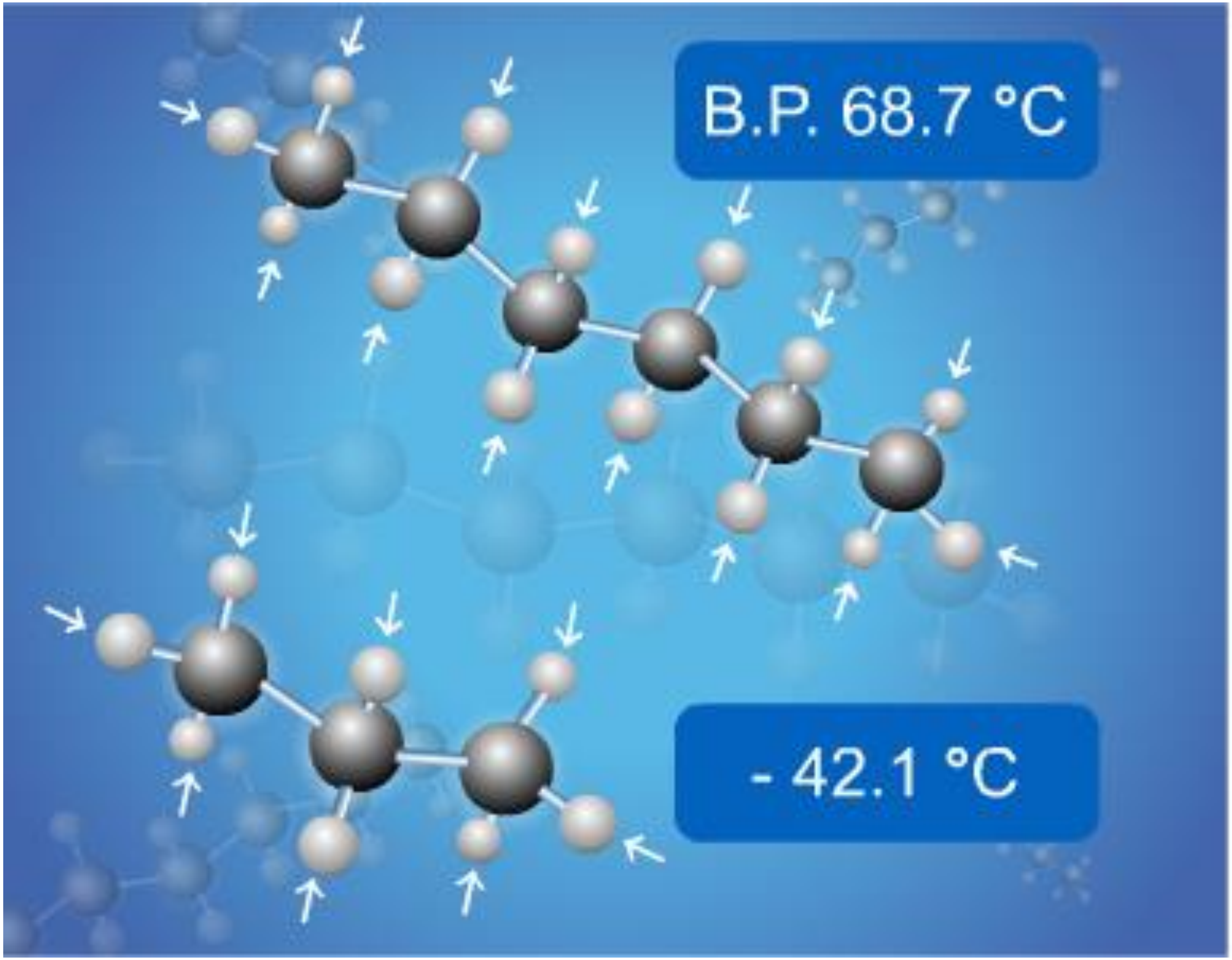
- At 25 ^oC and 1 atm
  - $C_1 – C_4$ (unbranched alkanes) : gases
  - $C_5 – C_{17}$ (unbranched alkanes) : liquids
  - C_{18} - more (unbranched alkanes) : solid

Boiling Points

- Boiling points of the unbranched alkanes show a regular increase with increasing molecular weight.

- Compare the boiling points of
  - Alkanes based on molecular weight
  - Isomeric alkanes
  - Straight vs. cycloalkanes

Alkanes Based on Molecular Weight



- C-H is non polar bond
  - Intermolecular forces exist – London dispersion forces
- Thus,
  - As molecular weight increases,
  - Molecular size increases
  - Molecular surface area increase
  - The Van der Waals forces increase
  - More energy is required to separate molecules from one another
  - Result - a higher boiling point.

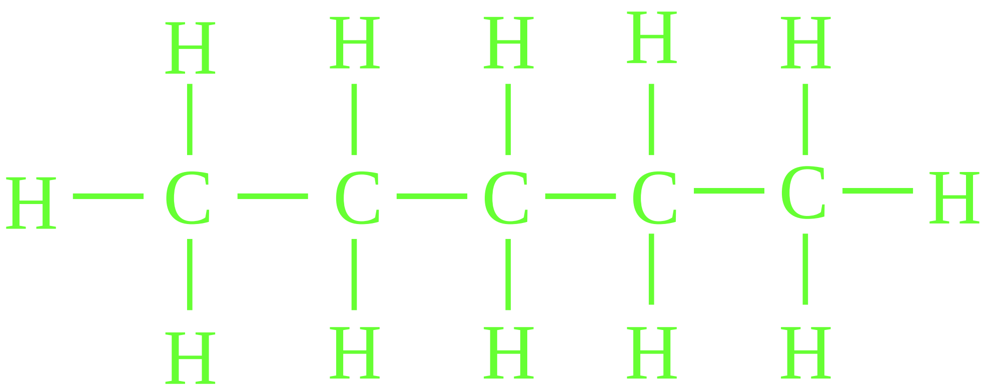
Isomeric Alkanes

- Isomers **differ in their carbon skeleton**.
- Different boiling point due to **branching**.

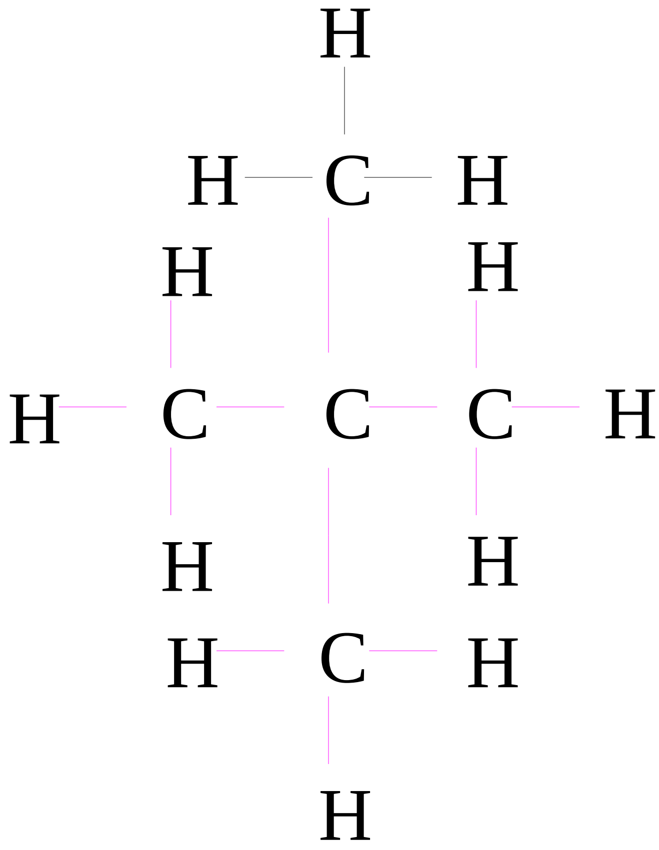
Pentane	2-methylbutane	2,2-dimethylpropane
$CH_3CH_2CH_2CH_2CH_3$	CH_3CHCH_2CH | CH_3	CH_3 | CH_3CCH_3 | CH_3
Bp: 37 ºC	Bp: 28.5 ºC	Bp: 9.0 ºC

Molecular formula: C_5H_{12}

Molecular formula: C_5H_{12}

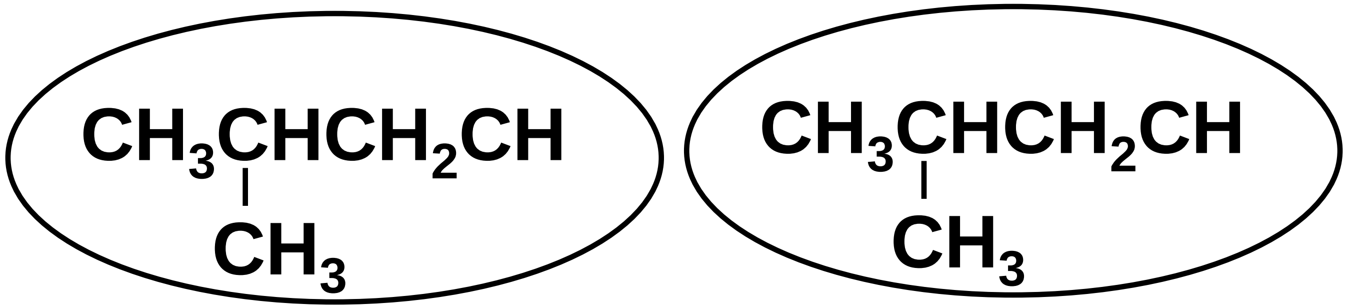


pentane

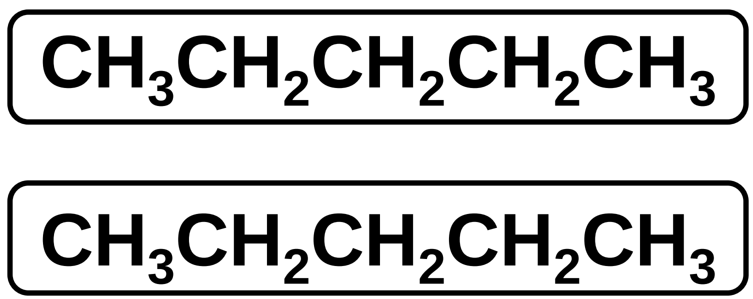


2,2-dimethylpropane

Molecular formula: C_5H_{12}



2-methylbutane



pentane

A branched alkane is **more spherical and** has a **smaller surface area** than an unbranched alkane

- Branched alkane:
  - makes a molecule more compact
  - Surface area reduces
  - The strength of the Van der Waals forces reduce
  - Less energy to break/separate molecule
  - Lower boiling points

Straight Alkane VS Cycloalkanes

- When comparing at the same number of carbon, cycloalkanes has slightly higher boiling point than alkanes.
- The boiling points of cycloalkanes are 10 ^{o}C to 15 ^{o}C higher than the corresponding straight chain alkanes.

Cycloalkane	*Boiling point*	*Alkane*	*Boiling point*
Cyclobutane	13^{o}C	Butane	-0.5^{o}C
Cyclopentane	49^{o}C	Pentane	36.3^{o}C

Reason:

- **Surface area** of cycloalkane is bigger than alkane because the **existance of empty spaces in cyclokanes structure**.
- The **strength of the Van der Waals forces increase**
- **More energy** to break/separate molecule
- **Higher boiling points**

Keep in mind!

- Normally we compare the effect of branching among the isomers only (same molecular formula)
- Boiling point of branched alkane is higher than straight alkane if the molecular weight is greater
- Boiling point of straight alkane is higher than cycloalkane if the number of molecular weight is greater.

Solubility

- Alkanes – less dense than water
- Alkanes and cycloalkanes are almost totally insoluble in water (i*mmiscible)*
  - Non-polar molecule
  - Can form Van der waals forces
  - Unable to form hydrogen bond with H_2O
- Liquid alkanes & cycloalkanes are soluble in one another
- Generally dissolve in non-polar solvents.
- Good solvents for alkanes are benzene, C_6H_6; carbon tetrachloride, CCl_4; chloroform and other hydrocarbons.

Chemical Properties of Alkanes

Non-reactivity of alkanes

- Relatively inert compounds towards many chemical reagents (bases, acids, dehydrating agents and aqueous oxidizing agents).
  - The C–H bond is not polarised (have nearly the same electronegativity)
  - 4 single bonds, all e- have been used up
- Thus, alkanes have no reaction with bases, oxidizing or reducing agents.
- Have no unshared electrons to offer sites for attack by acids.

- Alkanes are unreactive towards polar or ionic reagents but can react with non-polar reagents such as oxygen and bromine.
- The low reactivity of alkanes toward many reagents explain why alkanes were originally called paraffins.
- Reaction of alkanes:
  - Combustion
  - Halogenation

Combustion of Alkane

- Excess oxygen
  – Burnt in air (oxygen) to give carbon dioxide gas, water and heat.

$$C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + y/2\,H_2O + heat$$

$$2C_nH_{(2n+2)} + (3n+1)O_2 \rightarrow 2nCO_2 + 2(n+1)\,H_2O + heat$$

Example:

- Limited oxygen
  - Burnt in limited oxygen to give carbon monoxide, water & heat OR carbon, water & heat.

Example:

$$C_4H_{10(g)} + 9/2O_{2(g)} \longrightarrow 4CO(g) + 5H_2O_{(g)} + Heat$$

$$C_4H_{10(g)} + 5/2O_{2(g)} \longrightarrow 4C_{(s)} + 5H_2O_{(g)} + Heat$$

Halogenation: Free Radical Substitution

- Alkenes react with halogen (Cl & Br) to produce haloalkanes in the presence of light or temperature greater than 100 ^{o}C.

$$R{-}H + X_2 \xrightarrow{h\nu} R{-}X + HX$$

- With alkane, the reaction produces a mixture of haloalkane (alkyl halide) and a hydrogen halide.

- Bromin reacts with alkanes in the same way with chlorine
- Iodine reacts very slow or not at all with alkanes
- The reactions with fluorine are often too fast to control

Example:

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

ii. $$CH_3CH_3 + Cl_2 \xrightarrow{hv} CH_3CH_2Cl + HCl$$

Reaction Mechanism

Mechanism for monochlorination of methane.

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

i. Chain Initiation Step

- The Cl – Cl bond undergo homolytic fission
- The covalent bond breaks to form free radicals with the aid of ultraviolet light or high temperature
- Endothermic process

i. Chain Propagation Step

- The chlorination free radical is very reactive enough to remove hydrogen atom from methane by breaking the C-H bond to form HCl and •CH_3,methyl free radical.
- The •CH_3 then react with Cl_2 molecule to form •Cl and chloromethane (CH_3Cl).
- The •Cl then attack another CH_4 molecule and whole process repeat again. This s called chain reaction.

iii. Chain Termination Step

- The reaction stops when two free radicals collide & combine.
- This reaction is highly exothermic.

Chain Initiation Step

Chain Propagation Step

Chain Termination Step

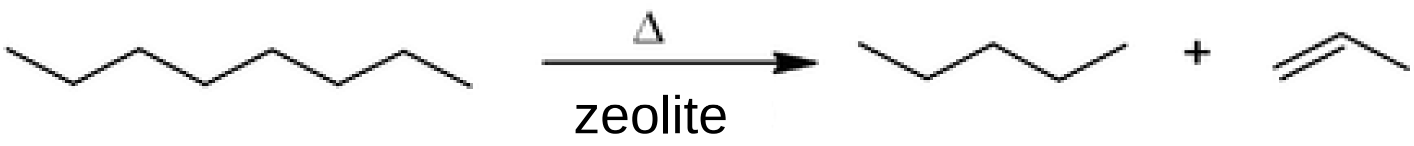
Synthesis of Alkanes

There are 2 method to synthesis alkane:

- ❑ Industrial Method (Cracking of Petroleum)
- ❑ Catalytic Reaction (Hydrogenation)

Cracking of Petroleum

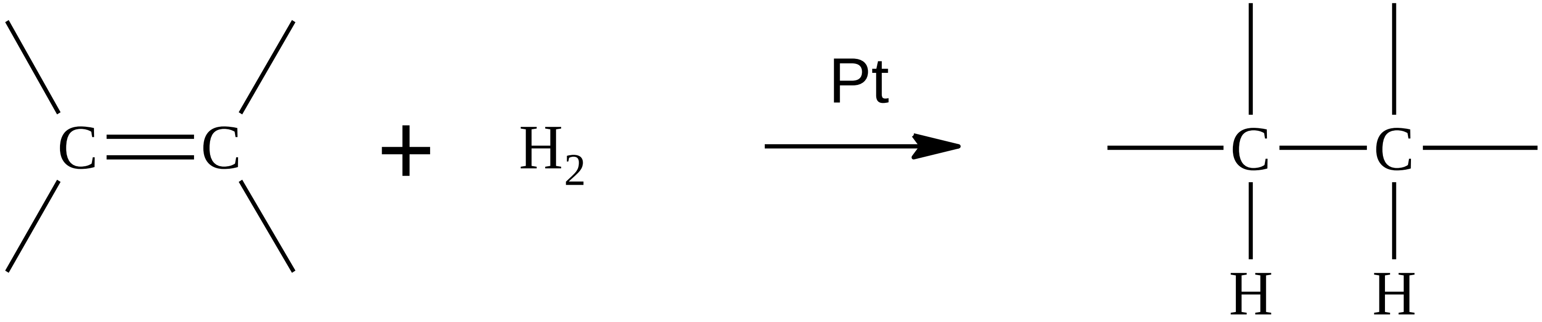
- Large alkanes are broken apart at high temperatures, in the presence of a zeolite catalyst, to give alkenes and smaller alkanes, and the mixture of products is then separated by fractional distillation.
- This is mainly used for the manufacture of small alkenes.
- Example: Cracking of octane to give pentane and propene



Hydrogenation

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

General reaction:



Example:

i)

ii)

The end....