For updated version, please click on
http://ocw.ump.edu.my

Organic Chemistry

Alkanes

by
Dr. Seema Zareen & Dr. Izan Izwan Misnon
Faculty Industrial Science & Technology
seema@ump.edu.my; iezwan@ump.edu.my

Alkanes
By Seema Zareen
http://ocw.ump.edu.my/course/view.php?id=152

Expected Outcomes

In the end of this chapter, student will have the ability to:

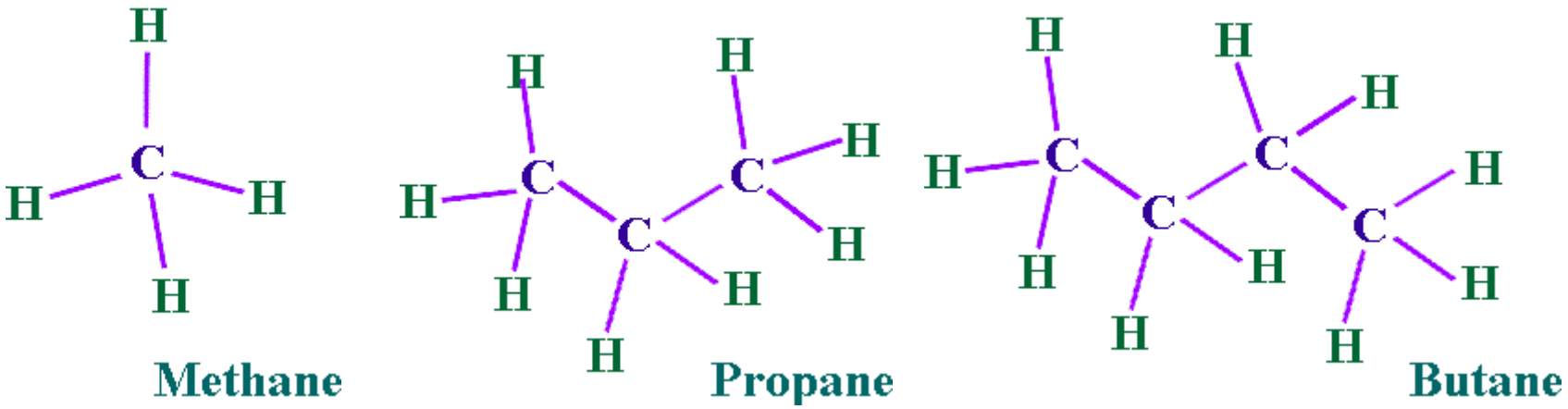
- Classify carbons and hydrogens in alkanes
- Draw and identify IUPAC nomenclature of alkane and cycloalkane compounds
- Describe characteristics and physical properties of alkanes

Contents

- Alkanes
- Physical properties
- Nomenclature
- Alkanes reaction mechanisms

Alkanes

- **Hydrocarbon** chains where all the bonds between carbons are **single bonds** (saturated).
- Name uses the ending –**ane**
- Examples: Meth**ane**, Prop**ane**, But**ane**, Oct**ane**, 2-methylpent**ane**

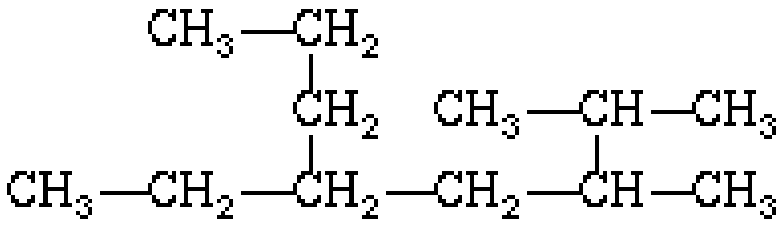


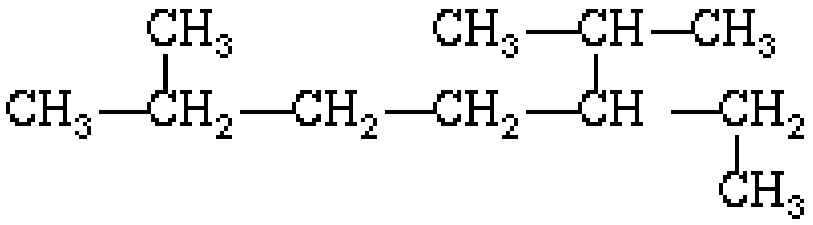
IUPAC Rule for Alkane nomenclature

1. Find and name the **longest continuous carbon** chain. This is called the **parent chain**. (Examples: methane, propane, etc.)
2. **Number the chain**, starting at the end nearest an attached group (**substituent**).
3. Identify and name **groups attached** to this chain. (Examples: methyl-, bromo-, etc.)
4. Designate the **location of each substituent group** with the number of the carbon parent chain on which the group is attached. Place a **dash** between numbers and letters. (Example: 3-chloropentane)
5. Assemble the name, listing groups in **alphabetical order**. The **prefixes** di, tri, tetra etc., used to designate several groups of the same kind, are not considered when alphabetizing. Place a **comma** between multiple numbers. (Example: 2,3-dichloropropane)

Step 1. Find the parent chain.

- Where is the *longest continuous* chain of carbons?



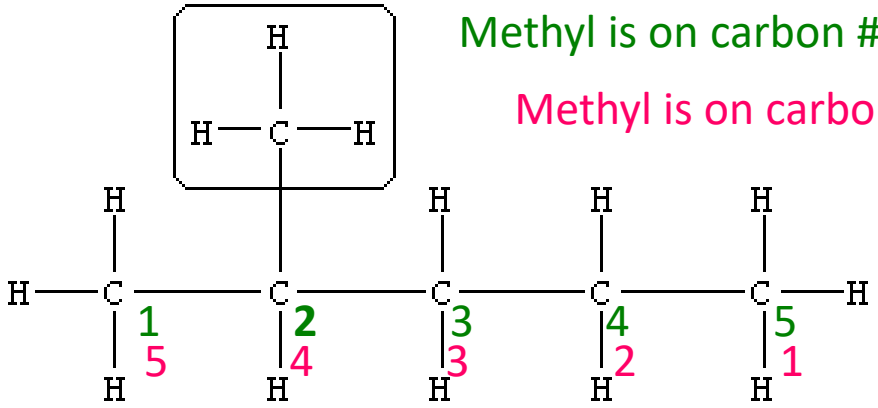


Prefixes for # of Carbons

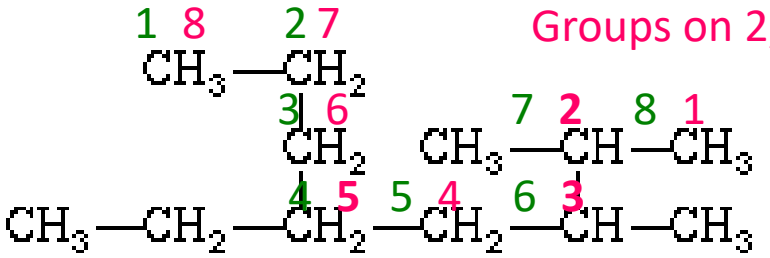
1	Meth	6	Hex
2	Eth	7	Hept
3	Prop	8	Oct
4	But	9	Non
5	Pent	10	Dec

Step 2. Number the parent chain.

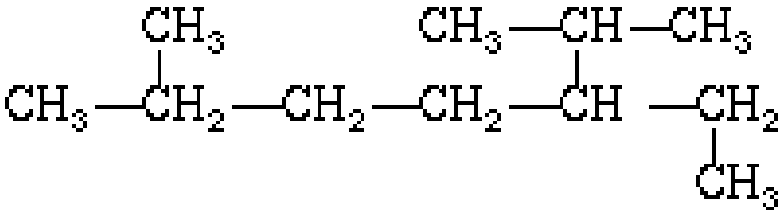
- Number the parent chain so that the attached groups are on the lowest numbers

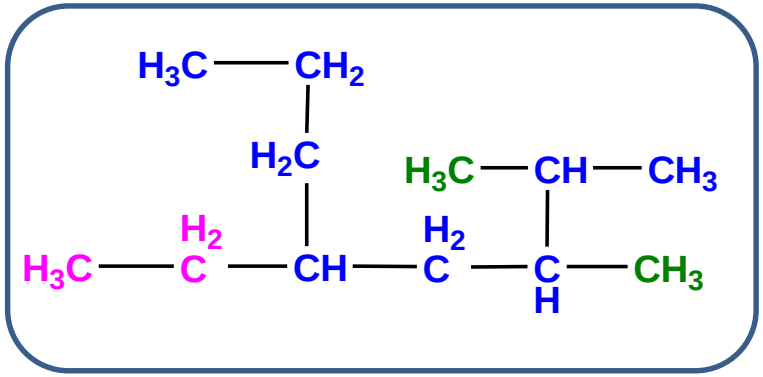


Groups on 4, 6, and 7

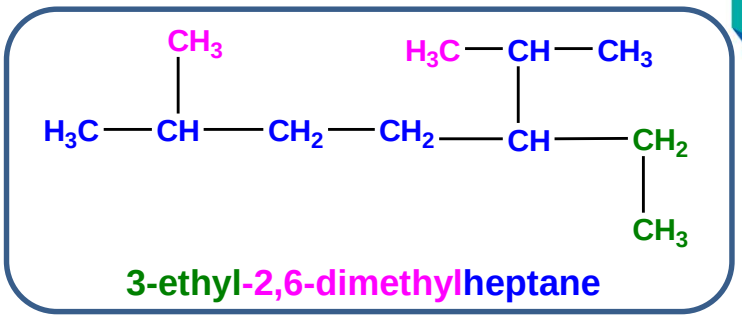


Groups on 2, 3, and 5



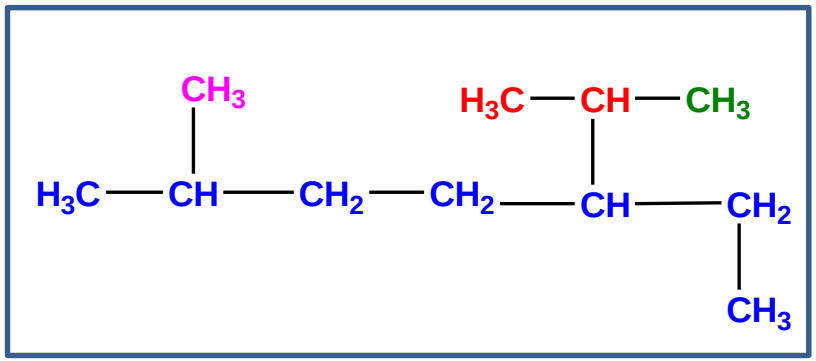


5-ethyl-2,3-dimethyloctane



3-ethyl-2,6-dimethylheptane

OR



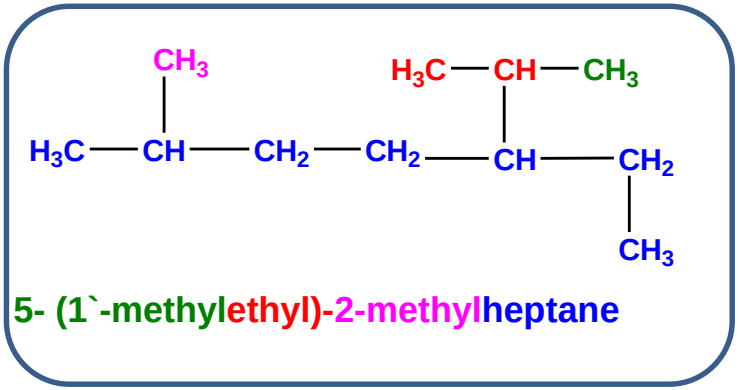
3-ethyl-2,6-dimethylheptane

OR

5- (1`-methylethyl)-2-methylheptane

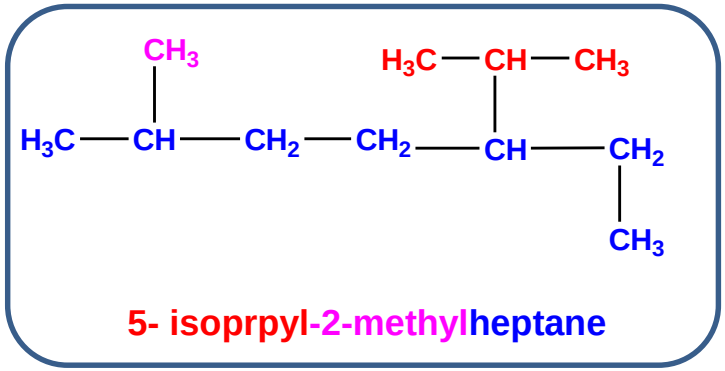
OR

5- isoprpyl-2-methylheptane



5- (1`-methylethyl)-2-methylheptane

OR



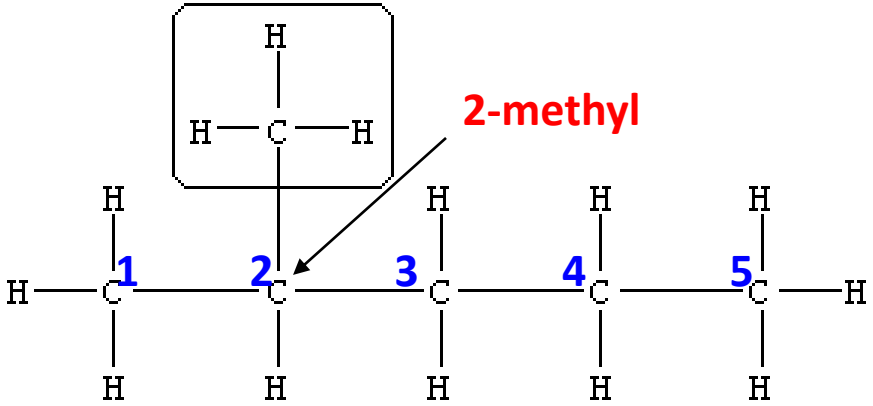
5- isoprpyl-2-methylheptane

Step 3. Name the attached groups.

- Carbon (alkyl) groups
  - Methyl CH_3 -
  - Ethyl CH_3CH_2-
  - Propyl $CH_3CH_2CH_2$ –
- Halogens
  - Fluoro (F-)
  - Chloro (Cl-)
  - Bromo (Br-)
  - Iodo (I-)

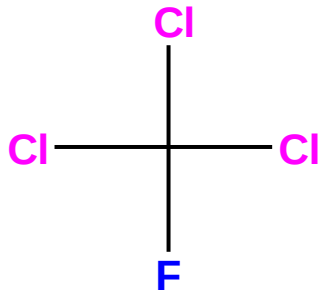
Step 4. Designate where the group is attached to the parent chain.

- Use the numbers of the parent chain from step 2 to designate the location of the attached groups to the parent chain.

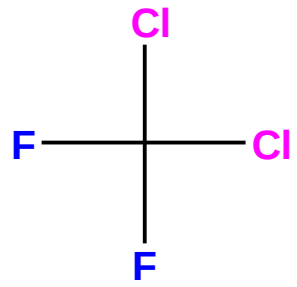


Step 5. Alphabetize the groups, combine like groups, and assemble.

- The prefixes di, tri, tetra etc., used to designate several groups of the same kind
- Prefixes are not considered when alphabetizing (Example: dimethyl = m for alphabetizing)
- Parent chain goes LAST

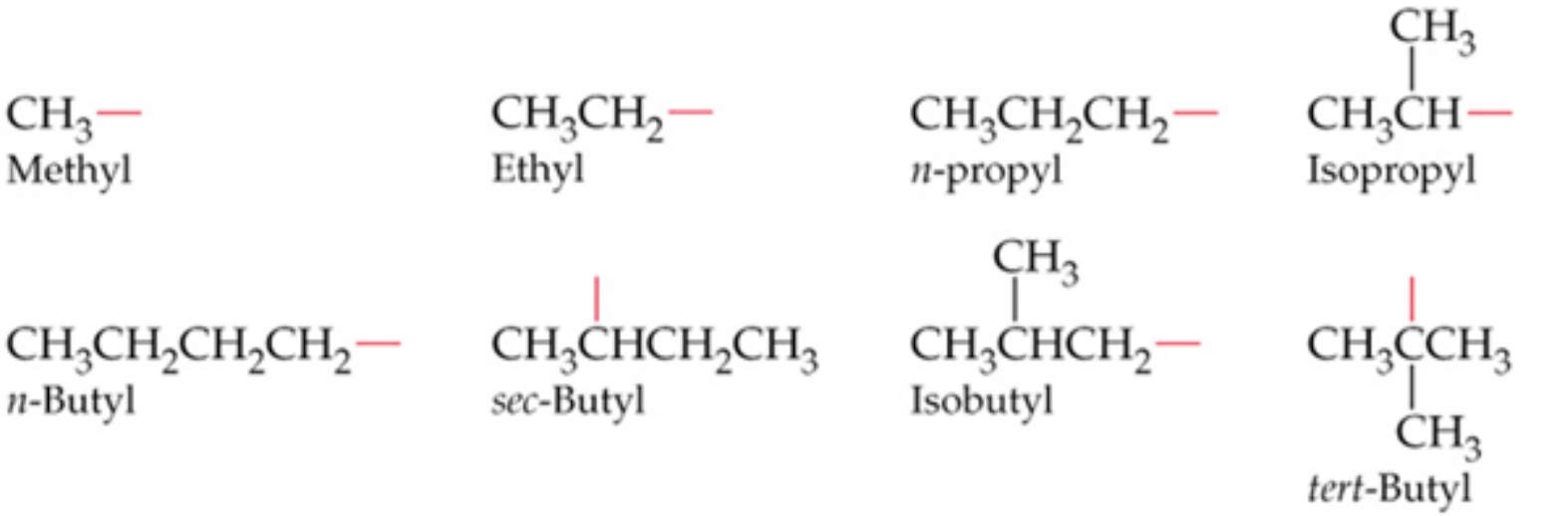


1,1,1-trichloro-1-fluoromethane



1,1-dichloro-1,1-difluoromethane

Some Common Alkyl Groups

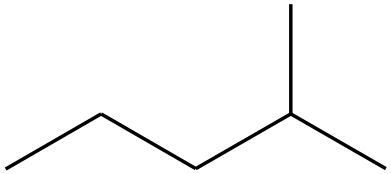


*The red bond shows the connection to the rest of the molecule.

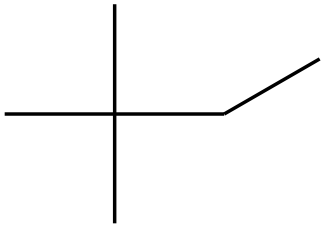
Draw Some Simple Alkanes

- 2-methylpentane
- 3-ethylhexane
- 2,2-dimethylbutane
- 2,3-dimethylbutane

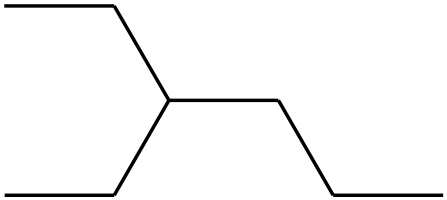
2-methylpentane



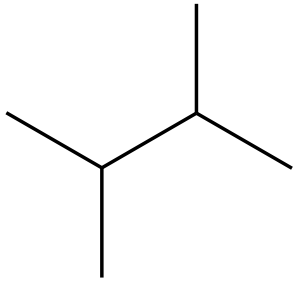
2,2-dimethylbutane



3-ethylhexane

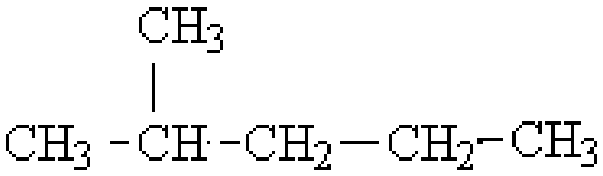


2,3-dimethylbutane

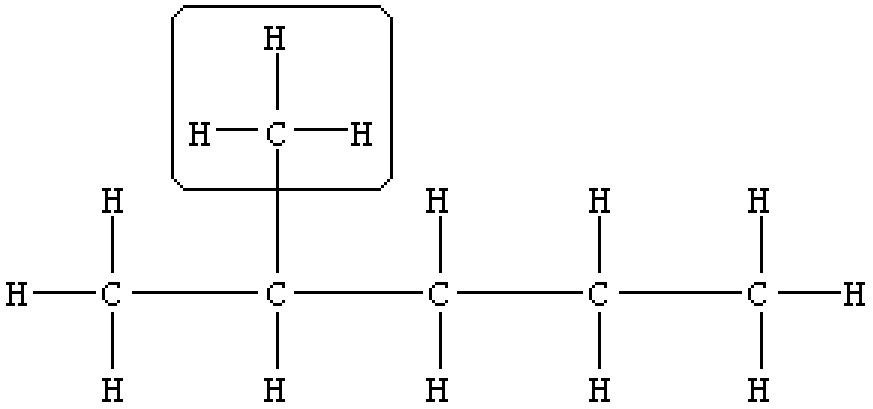


Structural Formulae (Formulas)

- Instead of drawing the bonds, just state how many hydrogens are attached
- NOTE: The bonds are between CARBONS in a parent chain, and not hydrogens.



Structural Formula

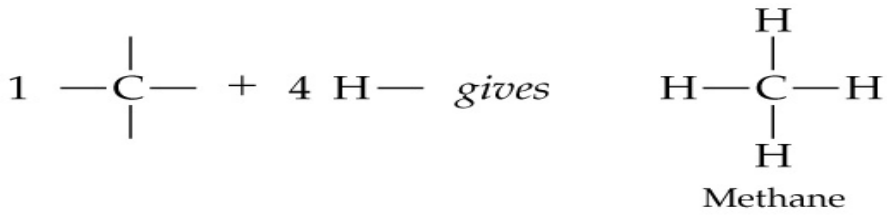


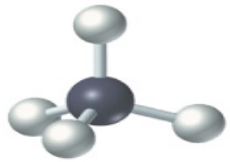
Lewis Structure

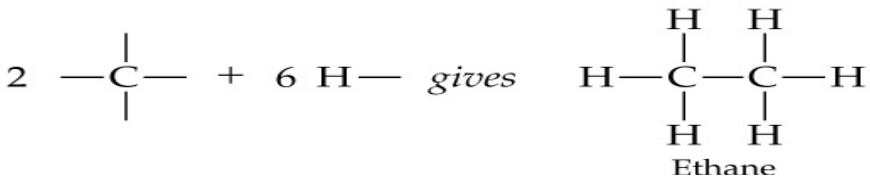
Alkanes

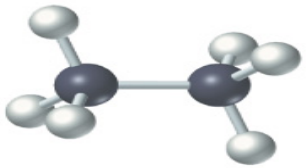
Alkane isomers

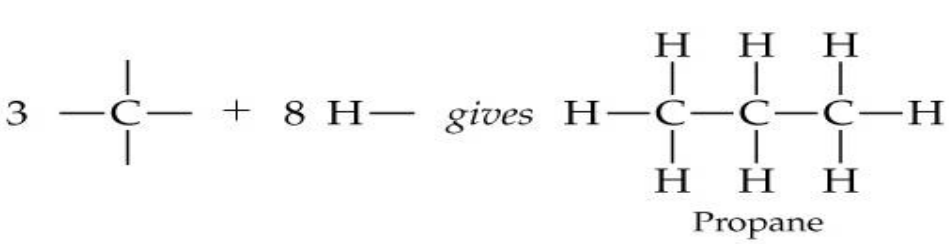
There is only one possible way that the carbons in methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) can be arranged.

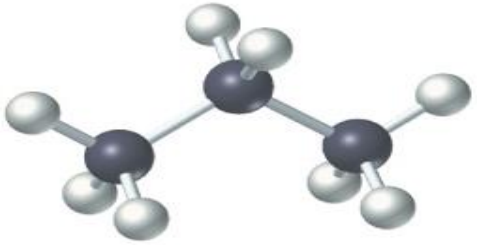




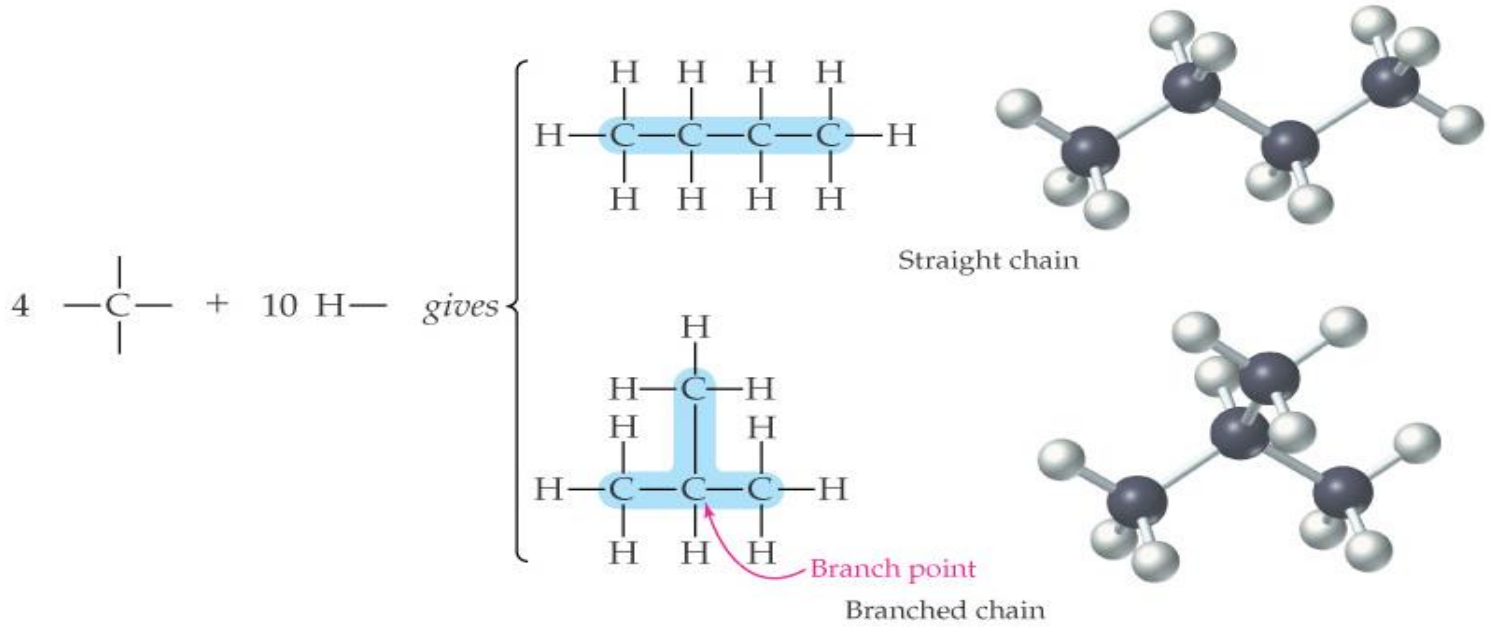








Alkanes



• However, carbons in butane (C_4H_{10}) can be arranged in two ways; four carbons in a row (linear alkane) or a branching (branched alkane). These two structures are two isomers for butane.

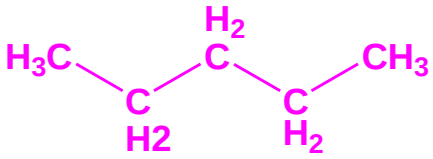
Exercise

- **Draw all possible structural isomers of C_5H_{12}**

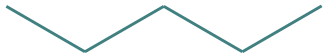
pentane

Condensed Structure $CH_3CH_2CH_2CH_2CH_3$

Lewis Stucture



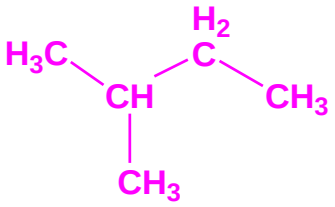
Skeletal Structure



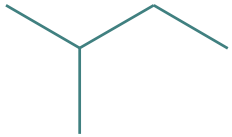
isopentane

Condensed Structure $CH_3CH(CH_3)CH_2CH_2CH_3$

Lewis Stucture



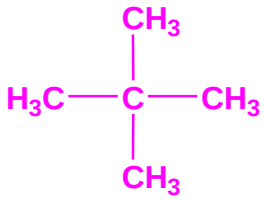
Skeletal Structure



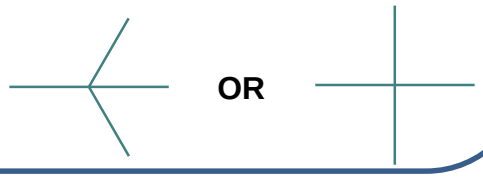
neopentane

Condensed Structure $(CH_3)_3CCH_3$

Lewis Stucture

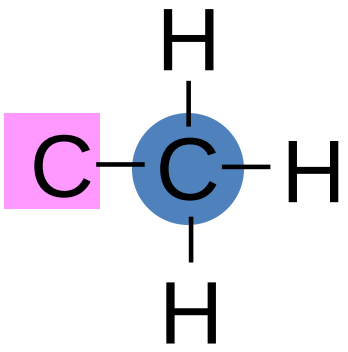


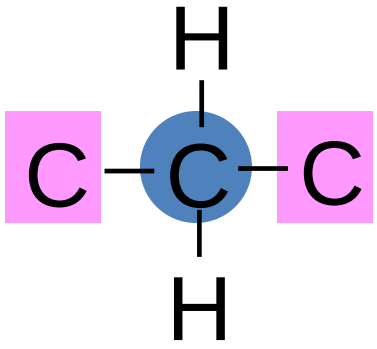
Skeletal Structure

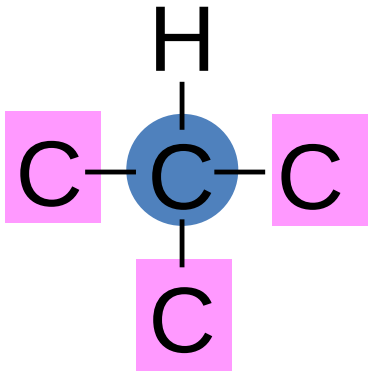


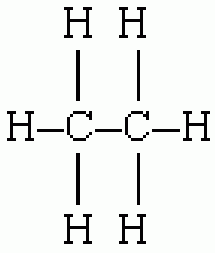
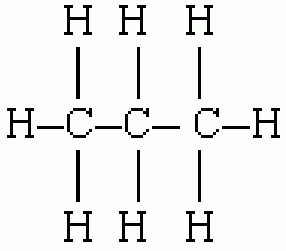
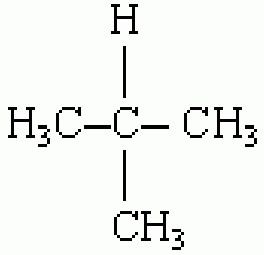
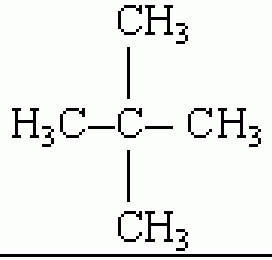
Types of Carbon Atoms

- Primary carbon (1°)
  - a carbon bonded to one other carbon
- Secondary carbon (2°)
  - a carbon bonded to two other carbons
- Tertiary carbon (3°)
  - a carbon bonded to three other carbons

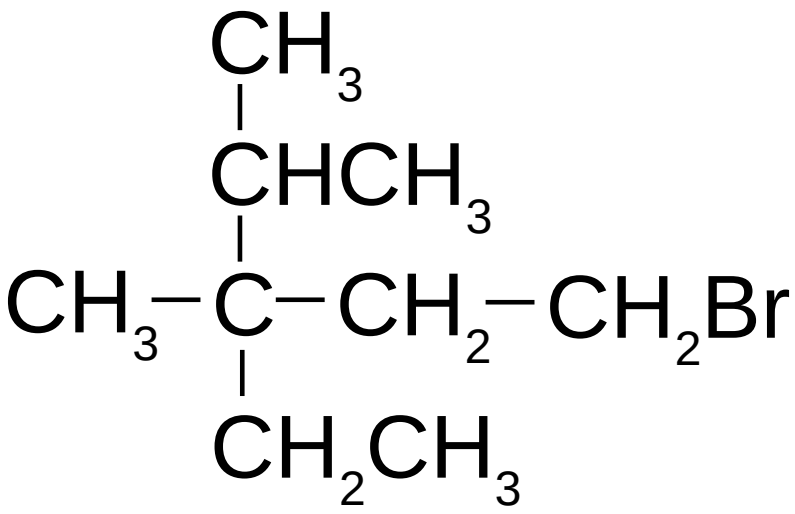


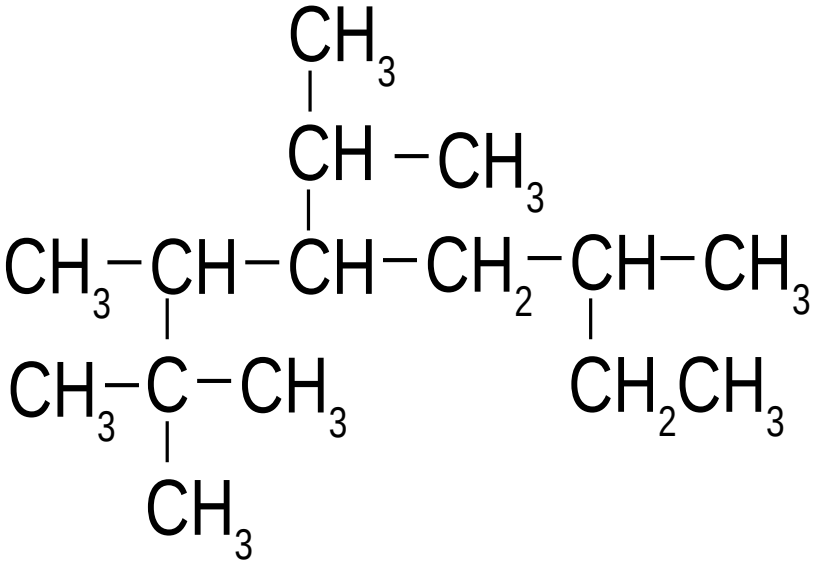


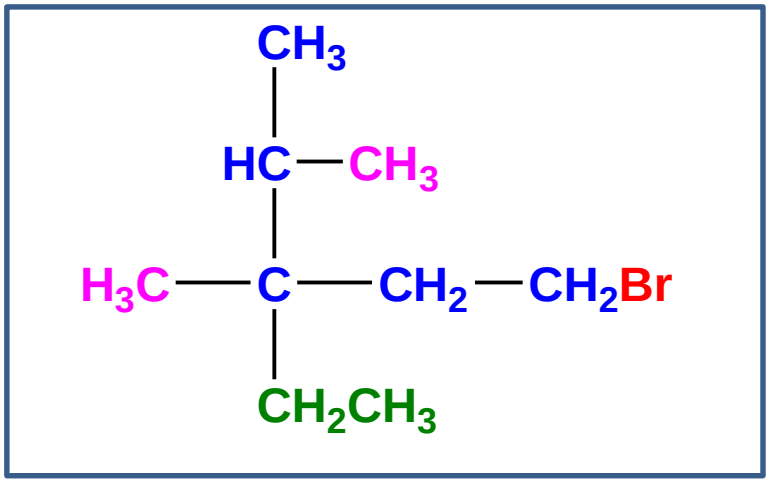


	Each C is attached to <u>one</u> other C atom; therefore, each is a <u>primary</u> C.
	The middle C (C#2) is attached to <u>two</u> other C atoms; therefore, it is a <u>secondary</u> C. (The end C's -- #1 & #3 -- are primary.)
	The top middle C is attached to <u>three</u> other C atoms; therefore, it is a <u>tertiary</u> C. (The three end C's are all primary.) Note that I used a condensed formula here. It doesn't matter. It is up to you to count the C atoms.
	The middle C is attached to <u>four</u> other C atoms; therefore, it is a <u>quaternary</u> C. (The four end C's are all primary.)

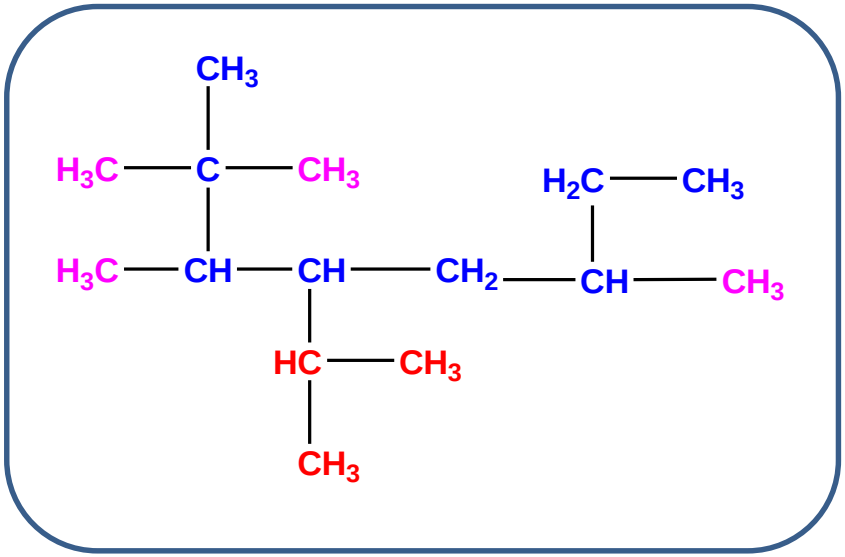
Name the following compounds:



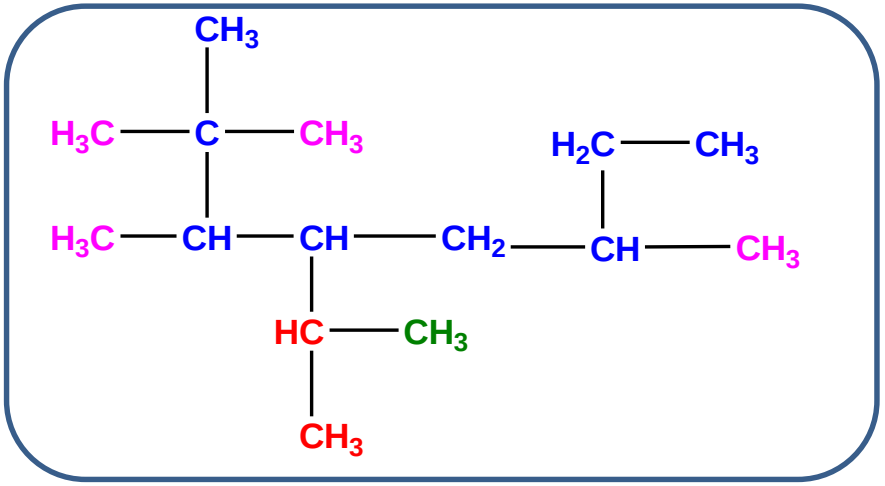




1-bromo-3-ethyl-3,4-dimethylpentane



OR



4-isopropyl-2,2,3,6-tetramethyloctane

4- (1`-methylethyl)-2,2,3,6-tetramethyloctane

Alkanes

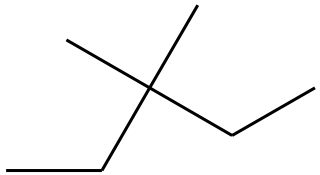
Write the condensed structure for the following compounds:

i. 3,3-dimethylpentane

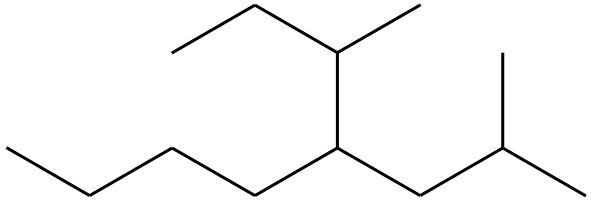
ii. 2-methyl-4-sec-butyloctane

iii. 1,2-dichloro-3-methylheptane

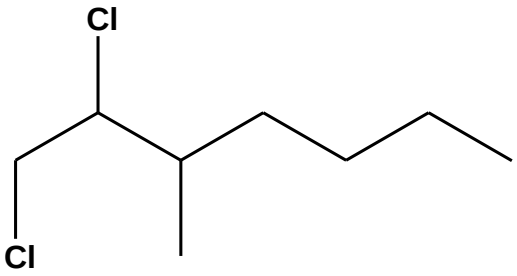
3,3-dimethylpentane



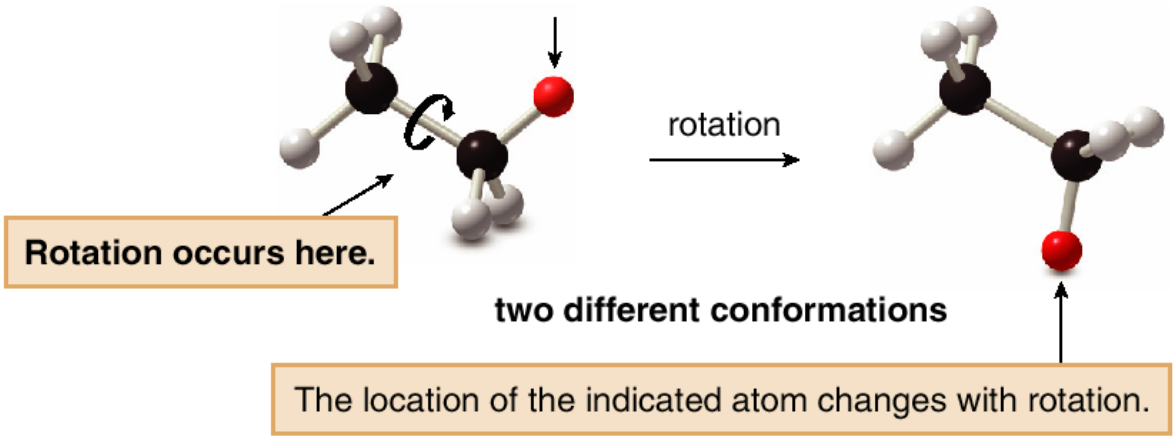
2-methyl-4-sec-butyloctane



1,2-dichloro-3-methylheptane

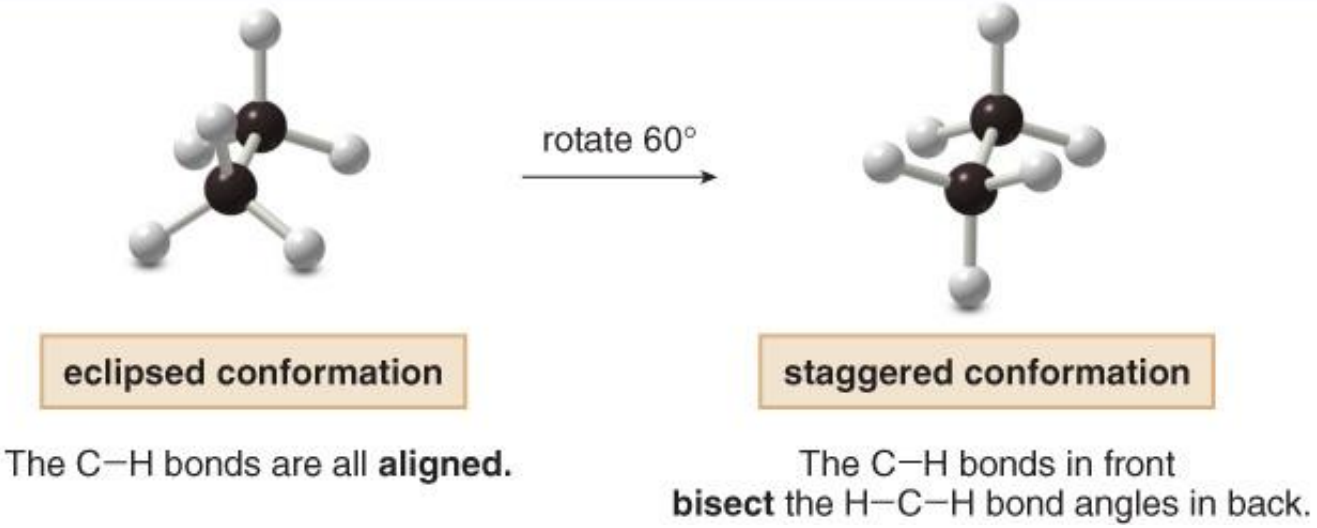


Conformations of acyclic alkanes

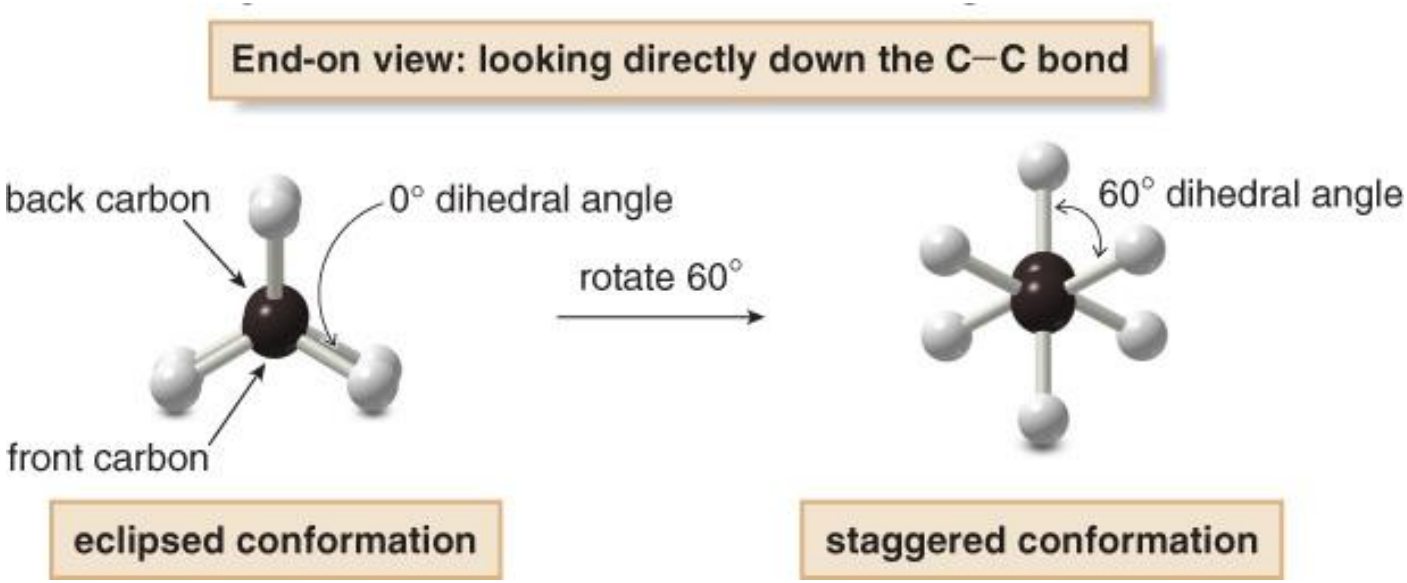


- *Conformations* are different arrangements of atoms that are interconverted by rotation about single bonds.

- Names are given to two different conformations.
- In the **eclipsed conformation**, the C—H bonds on one carbon are directly aligned with the C—H bonds on the adjacent carbon.
- In the staggered conformation, the C—H bonds on one carbon bisect the H—C—H bond angle on the adjacent carbon.



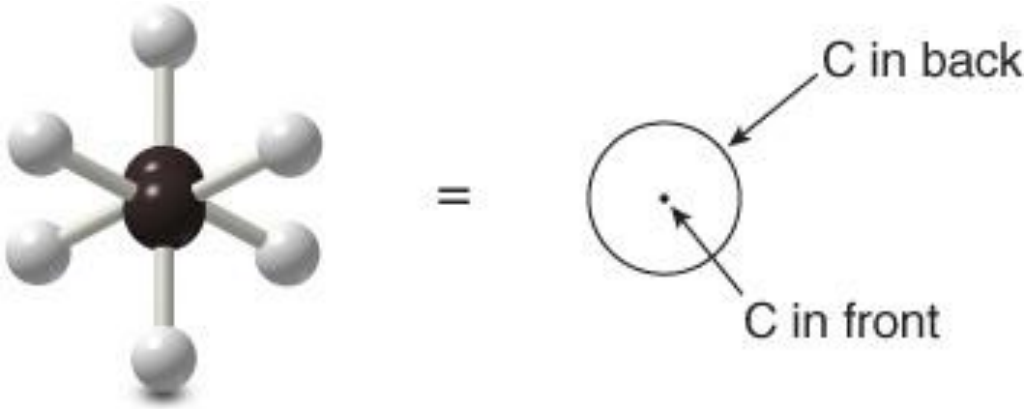
- Rotating the atoms on one carbon by **60° converts an eclipsed conformation into a staggered conformation, and vice versa**.
- The angle that separates a **bond** on one atom from a bond on an adjacent atom is called a **dihedral angle**. For **ethane in the staggered conformation**, **the dihedral angle for the C—H bonds is 60°**. **For eclipsed ethane, it is 0°.**



- End-on representations for conformations are commonly drawn using a convention called a **Newman projection**.

How to Draw a Newman Projection:

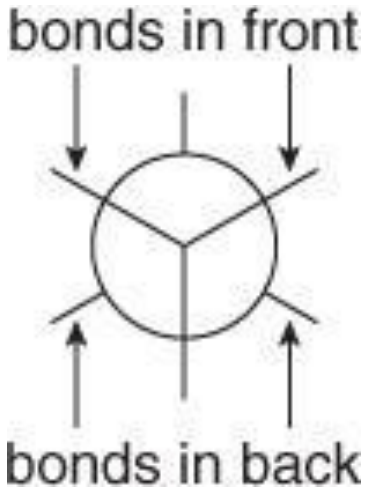
Step 1. Look directly down the C—C bond (end-on), and draw a circle with a dot in the center to represent the carbons of the C—C bond.



Step 2. Draw in the bonds.

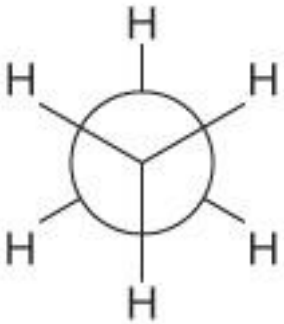
Draw the bonds on the front C as three lines meeting at the center of the circle.

Draw the bonds on the back C as three lines coming out of the edge of the circle.



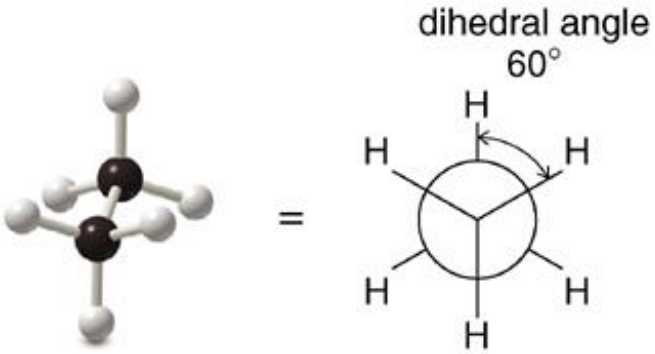
Step 3. Add the atoms on each bond.

=

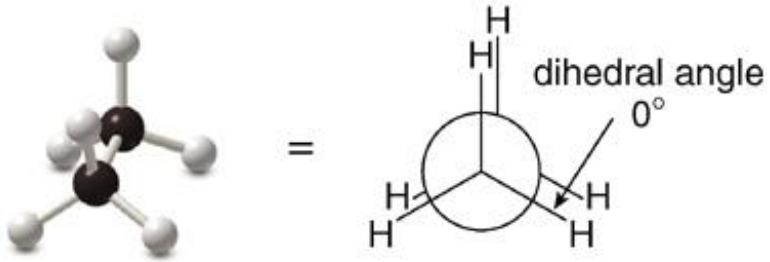


Each C has 3 H's in ethane.

Newman projections for the staggered and eclipsed conformations of ethane



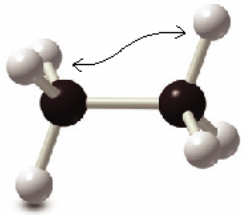
staggered conformation



eclipsed conformation

- The staggered and eclipsed conformations of ethane interconvert at room temperature, but each conformer is not equally stable.
- The **staggered conformations are more stable** (lower in energy) than the eclipsed conformations.
- **Electron-electron repulsion between bonds** in the **eclipsed conformation increases its energy** compared with the **staggered conformation**, where **the bonding electrons are farther apart**.

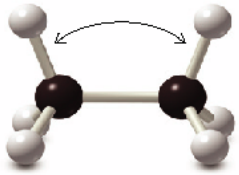
These C—H bonds are farther apart.



staggered conformation
side view

more stable

These C—H bonds are closer together.



eclipsed conformation
side view

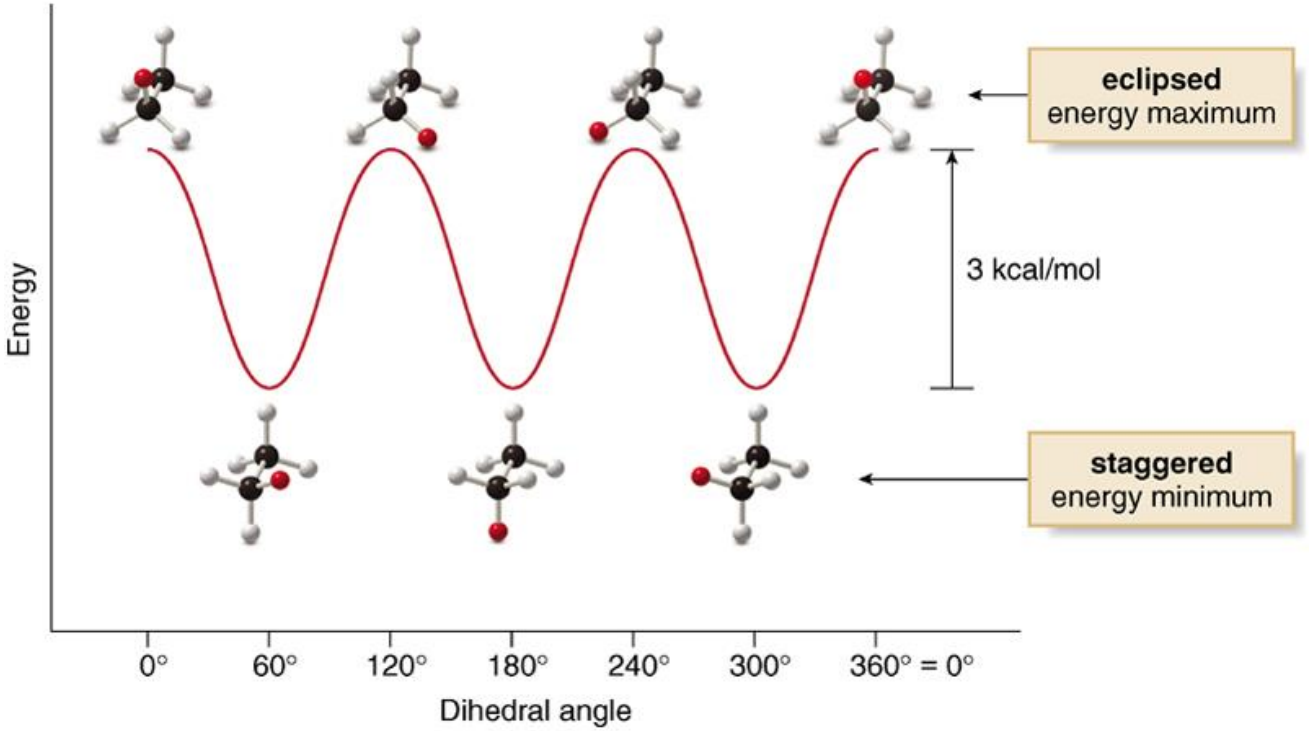
less stable

- The difference in energy between staggered and eclipsed conformers is ~3 kcal/mol, with each eclipsed C—H bond contributing 1 kcal/mol. The energy difference between staggered and eclipsed conformers is called **torsional energy**.
- **Torsional strain** is an increase in energy caused by eclipsing interactions.

Graph: Energy versus dihedral angle for ethane

At any given moment, all ethane molecules do not exist in the more stable staggered conformation; rather, a higher percentage of molecules is present in the more stable staggered conformation than any other possible arrangement.

Each H,H eclipsing interaction contributes 1 kcal/mol of destabilization to the eclipsed conformation.



- Note the position of the labeled H atom after each 60° rotation. All three staggered conformations are identical (except for the position of the label), and the same is true for all three eclipsed conformations.

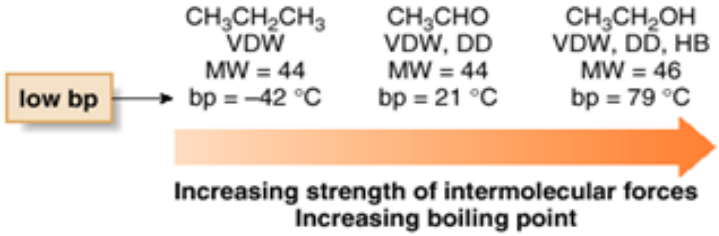
Physical Properties of Alkanes

- **Nonpolar**
- Insoluble in water.
- **Lower density than water.**
- **Low boiling and melting points.**
- **Gases** with 1-4 carbon atoms.
- (methane, propane, butane)
- **Liquids** with 5-17 carbon atoms.
- (kerosene, diesel, and jet fuels)
- **Solids** with 18 or more carbon atoms.
- (wax, paraffin, Vaseline)

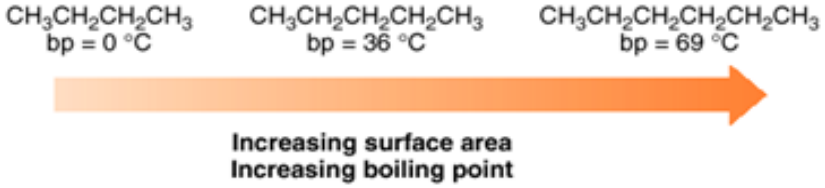
Physical Properties of Alkanes

Physical Properties of Alkanes

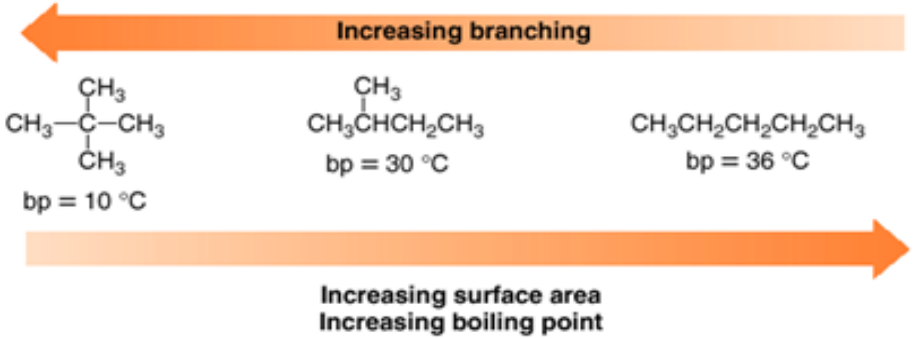
Property	Observation
Boiling point	• Alkanes have low bp's compared to more polar compounds of comparable size.



• Bp increases as the number of carbons increases because of increased surface area.



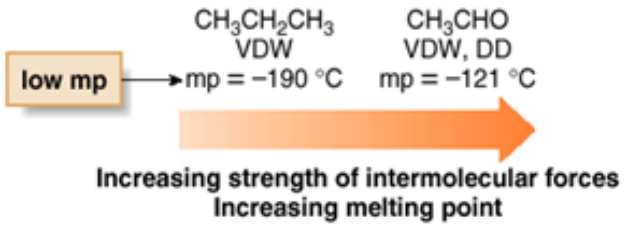
• The bp of isomers decreases with branching because of decreased surface area.



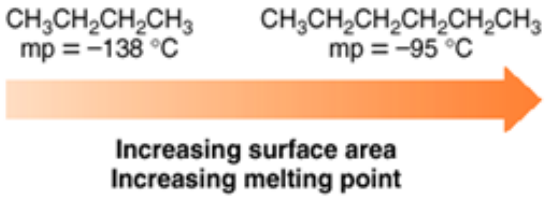
Physical Properties of Alkanes

Continued

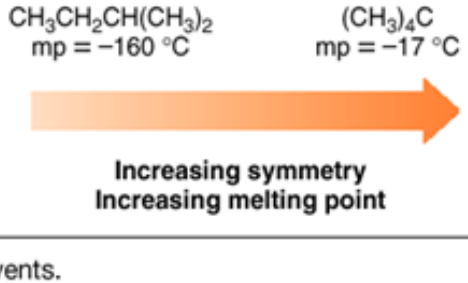
Property	Observation
Melting point	• Alkanes have low mp's compared to more polar compounds of comparable size.



	• Mp increases as the number of carbons increases because of increased surface area.



	• Mp increases with increased symmetry.



Solubility	• Alkanes are soluble in organic solvents. • Alkanes are insoluble in water.

Key: bp = boiling point; mp = melting point; VDW = van der Waals; DD = dipole–dipole; HB = hydrogen bonding; MW = molecular weight

Chemical reactions of Alkanes

- Low reactivity

1- Combustion:

- Alkanes react with oxygen.
- CO_2, H_2O, and energy are produced.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{energy}$$

Chemical reactions of Alkanes

2- Halogenation:

Alkanes react with Halogens.

$CH_4 + Cl_2 \xrightarrow[\text{Heat or light}]{} CH_3Cl + HCl$ Chloromethane

$CH_3Cl + Cl_2 \xrightarrow[\text{Heat or light}]{} CH_2Cl_2 + HCl$ Dichloromethane

$CH_2Cl_2 + Cl_2 \xrightarrow[\text{Heat or light}]{} CHCl_3 + HCl$ Trichloromethane

$CHCl_3 + Cl_2 \xrightarrow[\text{Heat or light}]{} CCl_4 + HCl$ Tetrachloromethane

Sources of Alkanes

- **Natural gas**
  - 90 to 95 percent methane.
  - 5 to 10 percent ethane, and
  - a mixture of other low-boiling alkanes, chiefly propane, butane, and 2-methylpropane.

- **Petroleum**
  - A thick liquid mixture of thousands of compounds, most of them hydrocarbons, formed from the decomposition of marine plants and animals.