



Chapter 2

Alkanes and Cycloalkanes; Conformational and Geometrical Isomerism

- **Hydrocarbons** are compounds that contain only carbon and hydrogen.

There are three main classes of hydrocarbons, based on the types of carbon–carbon bonds present.

1-**Saturated hydrocarbons** contain only carbon–carbon *single* bonds.

2-**Unsaturated hydrocarbons** contain carbon–carbon *multiple* bonds, double bonds, triple bonds, or both.

3-**Aromatic hydrocarbons** are a special class of cyclic compounds related in structure to benzene.

- Saturated hydrocarbons are known as **alkanes** if they are acyclic, or as
- **cycloalkanes** if they are cyclic.

Hydrocarbons

- **Hydrocarbons** are Organic Compounds, which contain only the two elements **carbon** and **hydrogen**.
- **Aliphatic hydrocarbons** are subdivided into:

- *Saturated hydrocarbons*

- Alkanes; C_nH_{2n+2} (contain *carbon-carbon single bond*)
- Cycloalkanes: C_nH_{2n} (contain *carbon-carbon single bond in a single ring*)

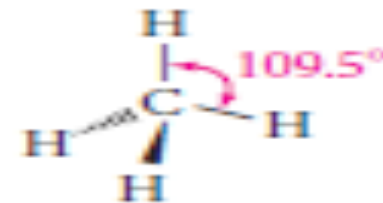
Alkanes and cycloalkanes are so similar that many of their properties can be considered side by side.

- *Unsaturated hydrocarbons*

- Alkenes : C_nH_{2n} (contain *carbon-carbon double bond*)
- Alkynes : C_nH_{2n-2} (contain *carbon-carbon triple bond*)

2.1 The Structure of Alkanes

- Alkanes are hydrocarbons containing only single saturated bonds.
General formula: C_nH_{2n+2} .
- The simplest alkane is methane.
- Its tetrahedral three-dimensional structure .
- Alkanes with carbon chains that are unbranched are called **normal alkanes** or *n*-alkanes.
- Each member of this series differs from the next higher and the next lower member by a $-CH_2-$ group (called a **methylene group**).
- A series of compounds in which the members are built up in a regular, repetitive way like this is called a **homologous series**.



Saturated Hydrocarbons

1. Alkanes

- General formula is C_nH_{2n+2}
- In **alkanes**, the four sp^3 orbitals of carbon repel each other into a TETRAHEDRAL arrangement with bond angles of 109.5° like in CH_4 .
- Each sp^3 orbital in carbon overlaps with the 1s orbital of a hydrogen atom to form a C-H bond.

Saturated Hydrocarbons

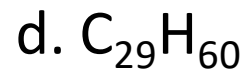
1. Alkanes

Names, Molecular formulas and Number of Isomers of the first ten Alkanes

Name	Molecular Formula	Number of isomers
Methane	CH ₄	1
Ethane	C ₂ H ₆	1
Propane	C ₃ H ₈	1
Butane	C ₄ H ₁₀	2
Pentane	C ₅ H ₁₂	3
Hexane	C ₆ H ₁₄	5
Heptane	C ₇ H ₁₆	9
Octane	C ₈ H ₁₈	18
Nonane	C ₉ H ₂₀	35
Decane	C ₁₀ H ₂₂	75

- Compounds of a **homologous series** differ by *a regular unit* of structure and share *similar properties*.

- **PROBLEM 2.2** Which of the following are alkanes?



2.2 Nomenclature of organic compounds

- In the early days of organic chemistry, each new compound was given a name that was usually based on its source or use.

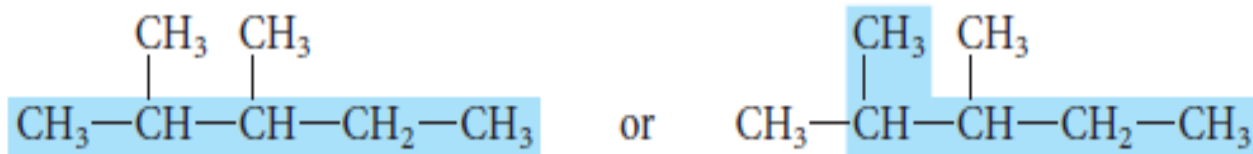
Examples include

limonene (from lemons), α -pinene (from pine trees), coumarin (from the tonka bean, known to South American natives as *cumaru*)

- Internationally recognized systems of nomenclature were devised by a commission of the International Union of Pure and Applied Chemistry; they are known as the IUPAC

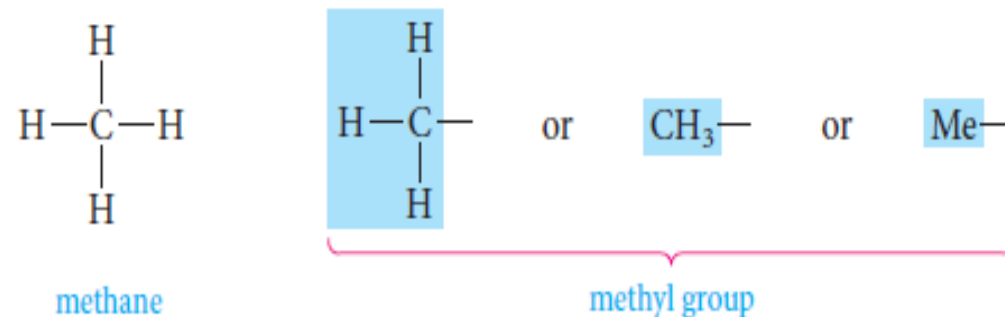
2.3 IUPAC rules for naming alkanes

1. The general name for acyclic saturated hydrocarbons is *alkanes*. The **-ane** ending is used for all saturated hydrocarbons. This is important to remember because later other endings will be used for other functional groups.
2. Alkanes without branches are named according to the *number of carbon atoms*. These names, up to ten carbons, are given in the first column of Table 2.1.
3. For alkanes with branches, the **root name** is that of the longest continuous chain of carbon atoms. For example, in the structure



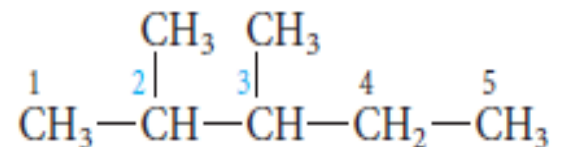
the longest continuous chain (in color) has five carbon atoms. The compound is therefore named as a substituted *pentane*, even though there are seven carbon atoms altogether.

4. Groups attached to the main chain are called **substituents**. Saturated substituents that contain only carbon and hydrogen are called **alkyl groups**. An alkyl group is named by taking the name of the alkane with the same number of carbon atoms and changing the *-ane* ending to *-yl*.



5. The main chain is numbered in such a way that the first substituent encountered along the chain **receives the lowest possible number**. Each substituent is then located by its name and by the number of the carbon atom to which it is attached.

- When two or more identical groups are attached to the main chain, prefixes such as ***di-***, ***tri-***, and ***tetra-*** are used. *Every substituent must be named and numbered*, even if two identical substituents are attached to the same carbon of the main chain.



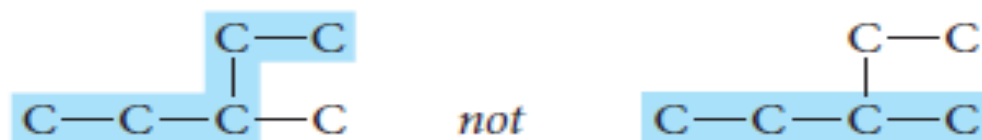
2,3-dimethylpentane

6. If two or more different types of substituents are present, they are listed alphabetically, except that prefixes such as *di-* and *tri-* are not considered when alphabetizing.

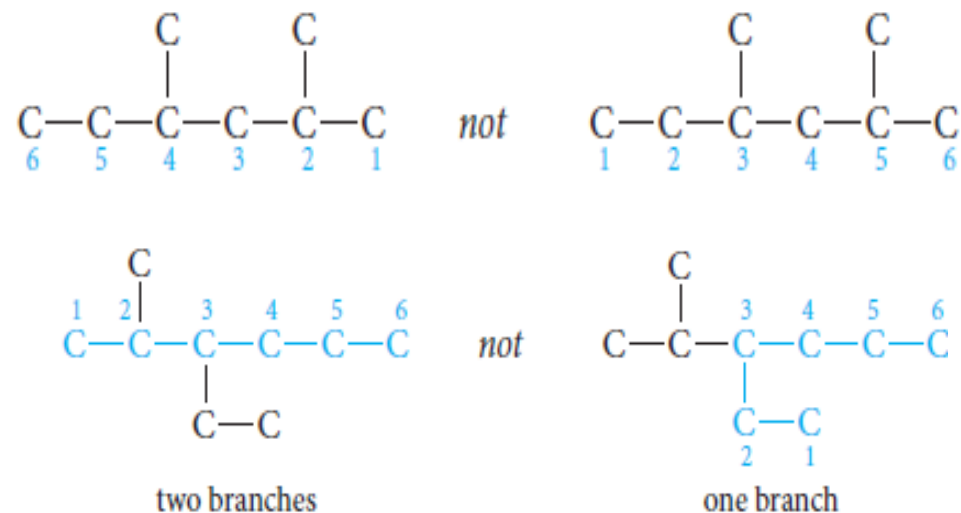
7. Punctuation is important when writing IUPAC names. IUPAC names for hydrocarbons are written as one word. Numbers are separated from each other by commas and are separated from letters by hyphens. There is no space between the last named substituent and the name of the parent alkane that follows it.

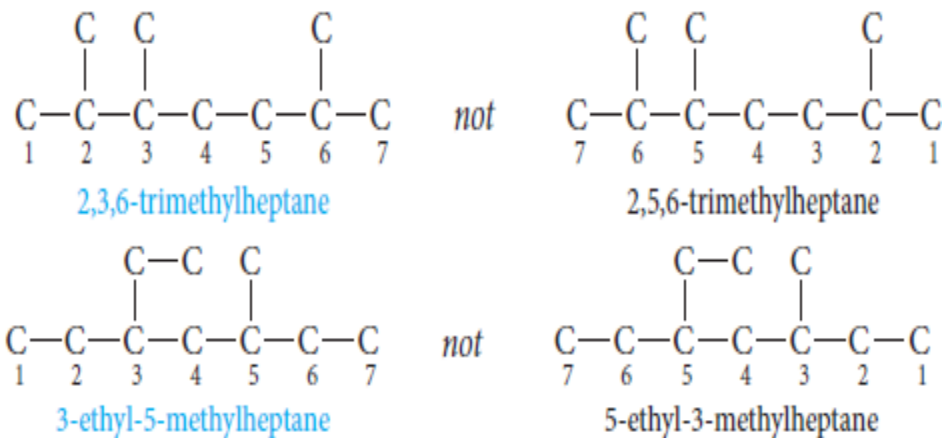
notes

1. Locate the longest continuous carbon chain. This gives the name of the parent hydrocarbon. For example,



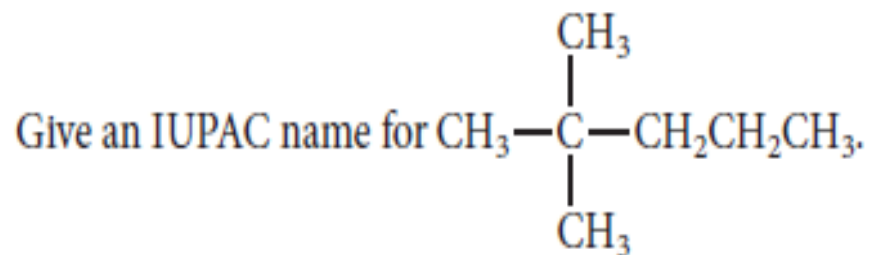
2. Number the longest chain beginning at the end nearest the first branch point. For example,





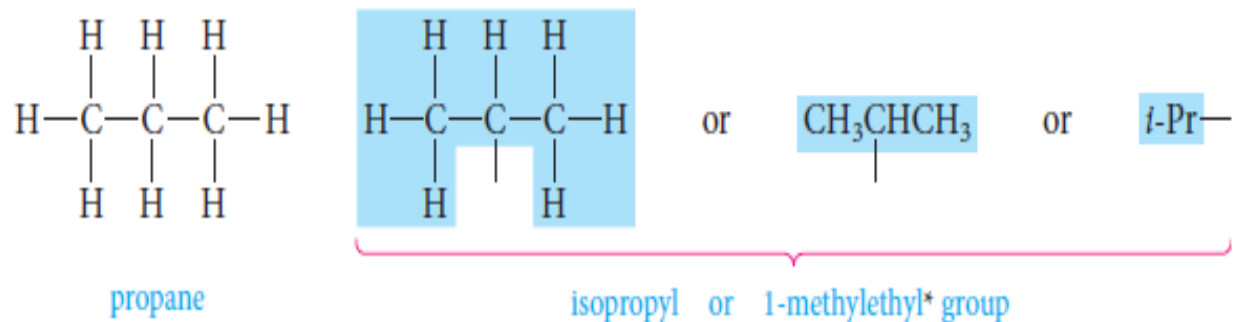
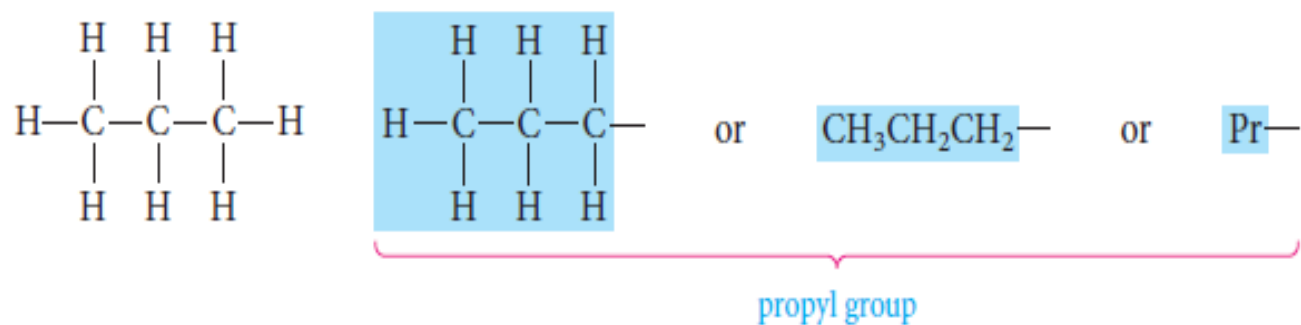
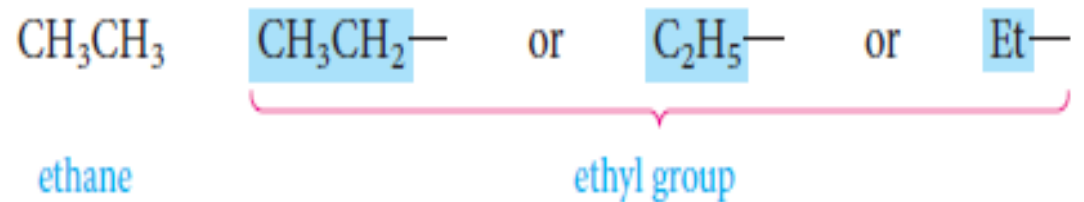
3. Write the name as one word, placing substituents in alphabetic order and using proper punctuation.

Example 2.2

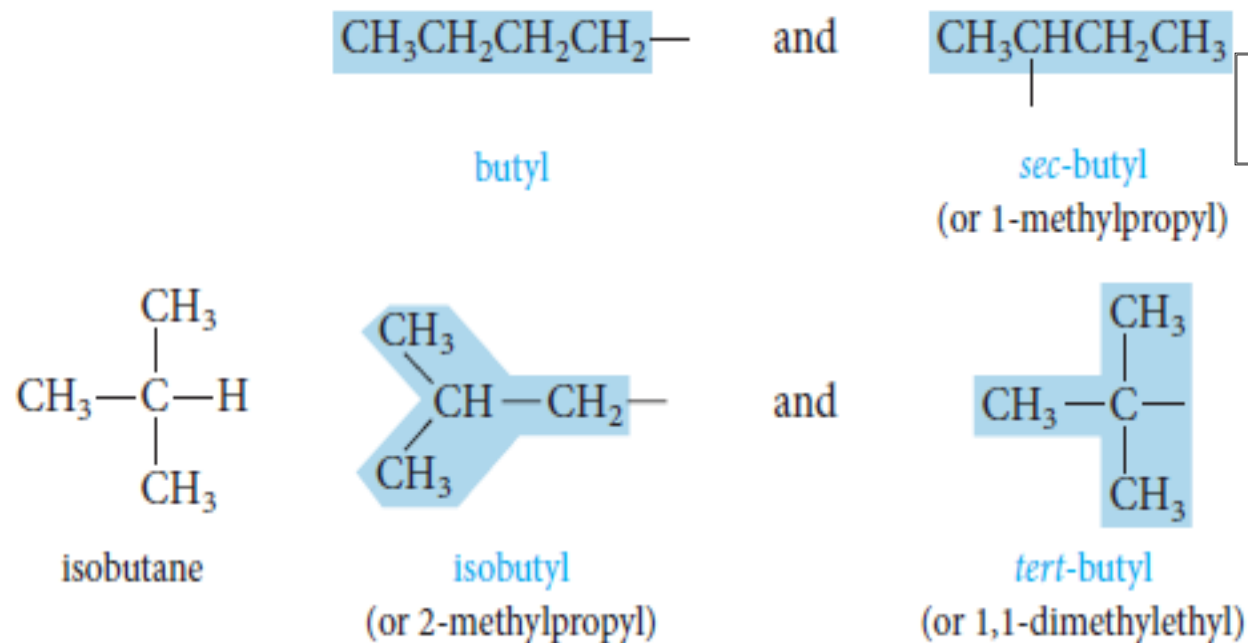


2,2-dimethylpentane

2.4 Alkyl and Halogen Substituents



Classes of Carbons and Hydrogen



- A primary (1°) carbon.
- A secondary (2°) carbon
- A tertiary (3°) carbon
- A quaternary (4°) carbon

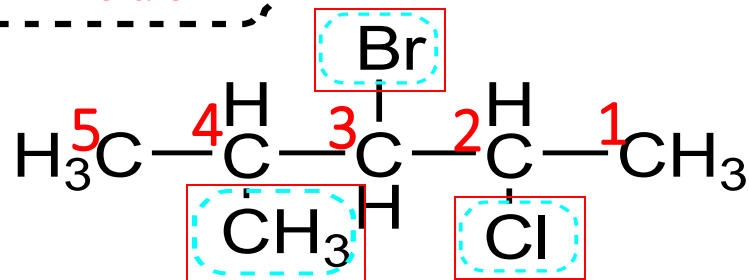
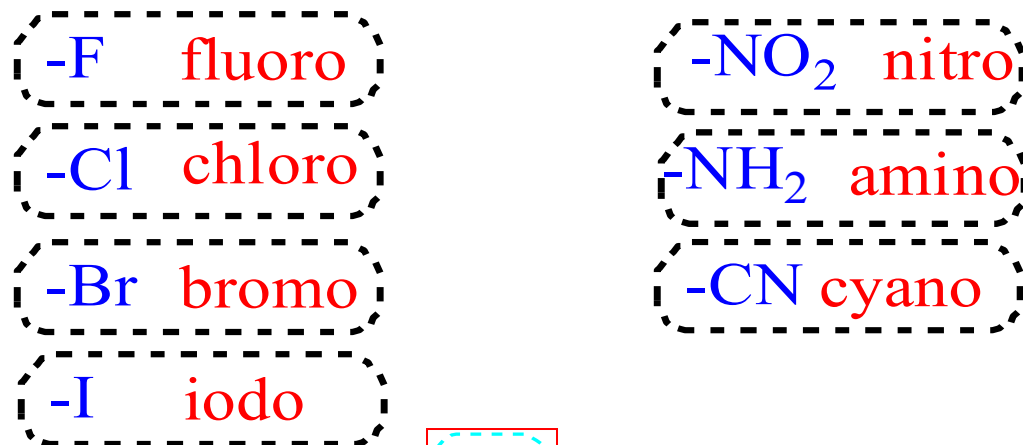
R is the general symbol for an alkyl group.

Halogen substituents are named by changing the *-ine* ending of the element to *-o*.

F-	Cl-	Br-	I-
fluoro-	chloro-	bromo-	iodo-

Give the common and IUPAC names for $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$.

If **substituents other than alkyl groups** are also presents on the parent carbon chain;
all substituents are named alphabetically.

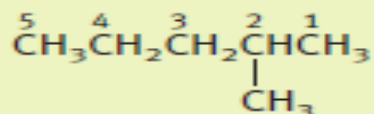


2-chloro
3-bromo
4-methyl

3-bromo -2-chloro -4-methyl pentane

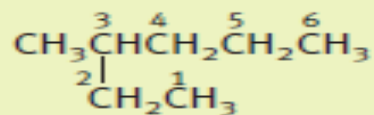
2.5 Use of the IUPAC Rules

Table 2.2 Examples of Use of the IUPAC Rules



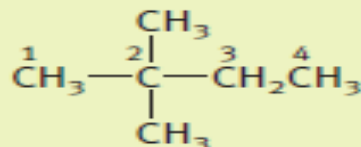
2-methylpentane
(not 4-methylpentane)

The ending *-ane* tells us that all the carbon-carbon bonds are single; *pent-* indicates five carbons in the longest chain. We number them from right to left, starting closest to the branch point.



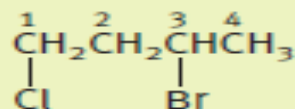
3-methylhexane
(not 2-ethylpentane
or 4-methylhexane)

This is a six-carbon saturated chain with a methyl group on the third carbon. We would usually write the structure as $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$.



2,2-dimethylbutane
(not 2,2-methylbutane
or 2-dimethylbutane)

There must be a number for each substituent, and the prefix *di-* says that there are two methyl substituents.



3-bromo-1-chlorobutane
(not 1-chloro-3-bromobutane
or 2-bromo-4-chlorobutane)

First, we number the butane chain from the end closest to the first substituent. Then we name the substituents in alphabetical order, regardless of position number.

- **PROBLEM 2.8**

Explain why 1,3-difluorobutane is a correct IUPAC name, but 1,3-dimethylpentane is *not* a correct IUPAC name.

Sources of Alkanes

- The two principal sources of alkanes are **petroleum** and **natural gas**.

Petroleum and natural gas constitute the chief sources of

- Alkanes up to 40 Carbons
- Aromatic
- Alicyclic (Cyclic aliphatic hydrocarbons)
- Heterocyclic

Sources of Alkanes

Petroleum Refining

Some components of refined petroleum

Fraction	Boiling range (°C)	Carbon content
Gas	Below 20	C1 – C4
Petroleum ether	20 – 60	C5 – C6
Naphtha	60 – 100	C6 – C7
Gasoline	40 – 200	C5 – C10
Kerosine	175 – 325	C11 – C18
Gas oil	300 – 500	C15 – C40
Lubricating oil, asphalt, petroleum coke and paraffins	Above 400	C15 – C40

2.7 Physical properties and Intermolecular Interactions

Physical Properties of Alkanes, Alkenes and Alkynes

Those properties that can be observed without the compound undergoing a chemical reaction.

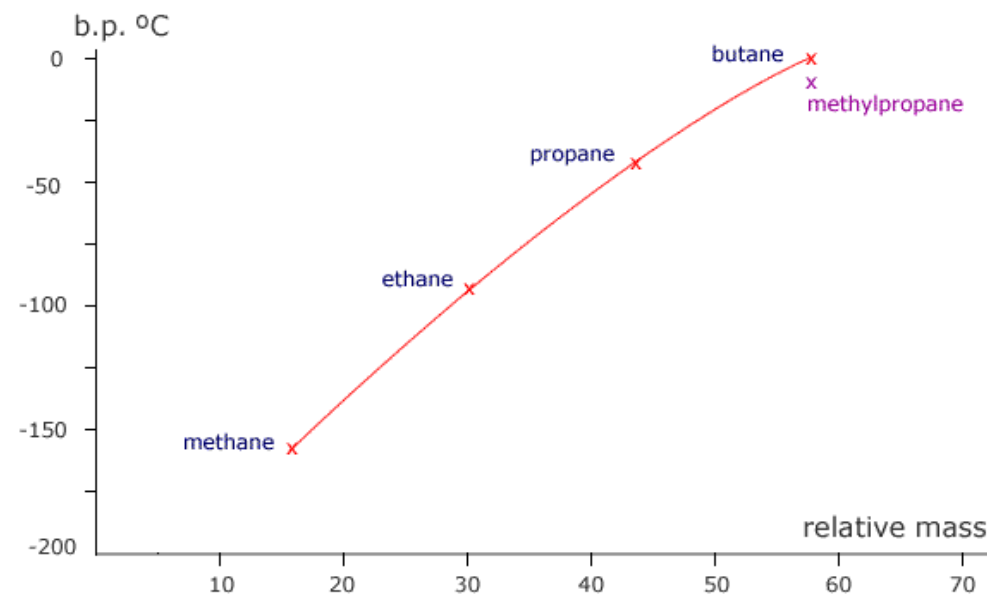
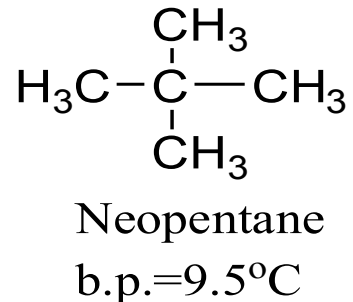
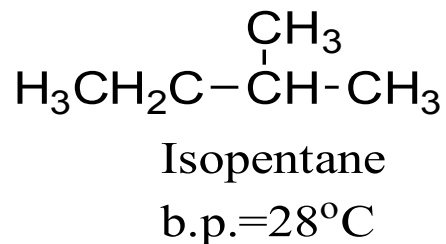
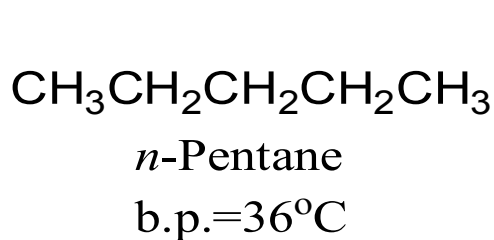
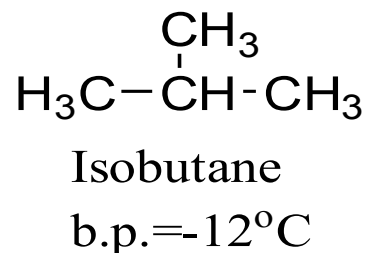
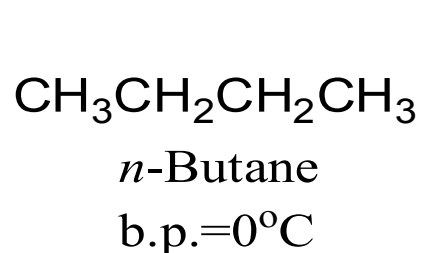
A. Physical States

C1 (C2) to C4 are gases,
C5 to C17 are liquids,
C18 and larger alkanes are wax-like solids.

B. Solubility

- Alkanes, Alkenes and Alkynes are **nonpolar** compounds.
- Their solubility “ **Like dissolve like**”
- Alkanes, Alkenes and Alkynes are **soluble** in the **nonpolar solvents**;
carbon tetrachloride, CCl_4 and benzene,
- Alkanes, Alkenes and Alkynes are **insoluble** in **polar solvents** like **water**.

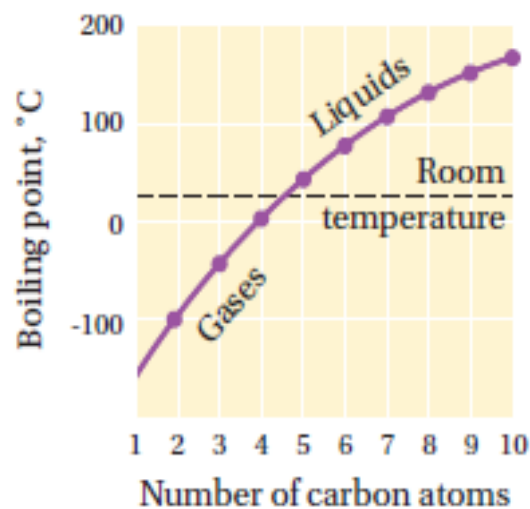
C. Boiling Points



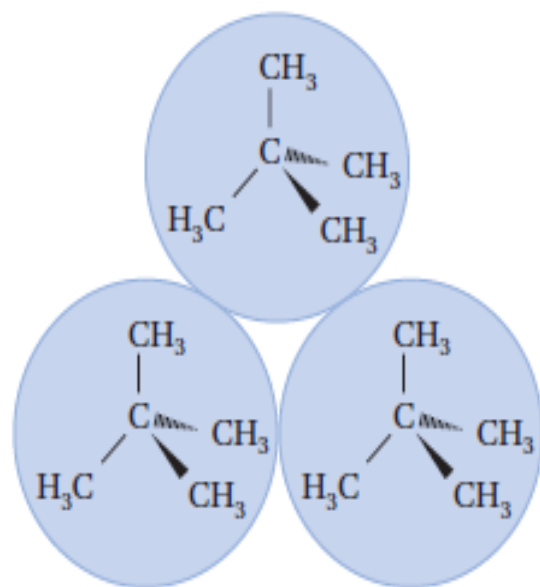
Graph showing boiling point of the alkanes against relative mass

- Intermolecular interactions: H-bond, dipole-dipole and London forces
- Boiling point decreases with increasing branches
- Boiling point increases with increasing molecular weight

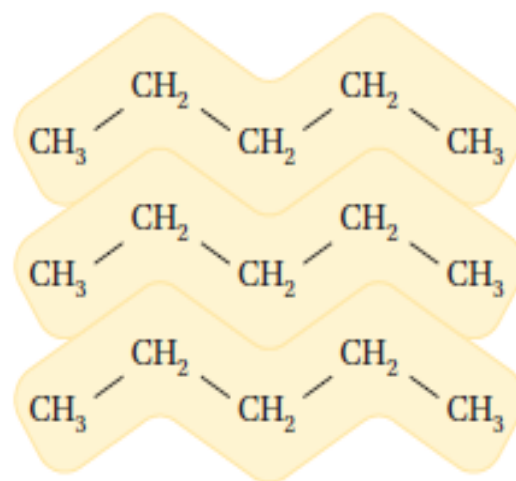
- The boiling points for alkanes rise as the chain length increases and fall as the chains become branched and more nearly spherical in shape.



Name	Formula	Boiling point, °C
pentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	36
2-methylbutane (isopentane)	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	28
2,2-dimethyl- propane (neopentane)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	10



2,2-dimethylpropane
bp 10°C



pentane
bp 36°C

2.9 Cycloalkanes Nomenclature and Conformation

- Cycloalkanes are saturated hydrocarbons that have at least one ring of carbon atoms.
- Cycloalkanes are named by placing the prefix *cyclo-* before the alkane name that corresponds to the number of carbon atoms in the ring.



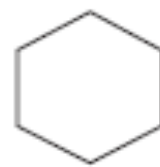
cyclopropane
bp -32.7°C



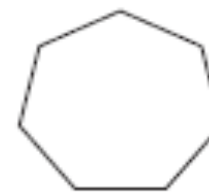
cyclobutane
bp 12°C



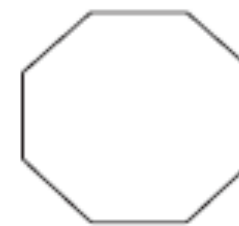
cyclopentane
bp 49.3°C



cyclohexane
bp 80.7°C



cycloheptane
bp 118.5°C

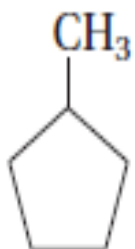


cyclooctane
bp 149°C

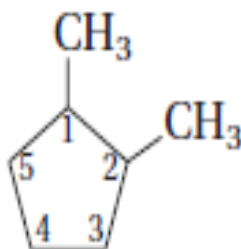
- Nomenclature

- Alkyl or halogen substituents attached to the rings are named in the usual way.
- If only one substituent is present, no number is needed to locate it.
- If there are several substituents, numbers are required. One substituent is always located at ring carbon number 1, and the remaining ring carbons are then numbered consecutively in a way that gives the other substituents the lowest possible numbers

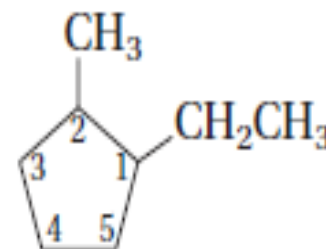
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methylcyclopentane
(not 1-methylcyclopentane)

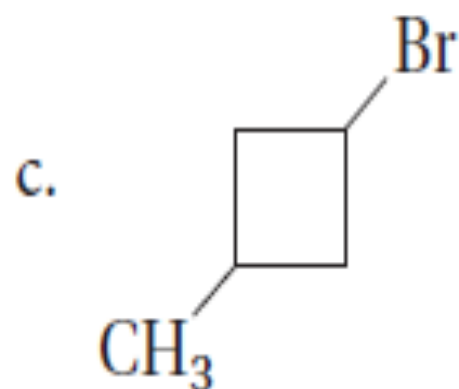
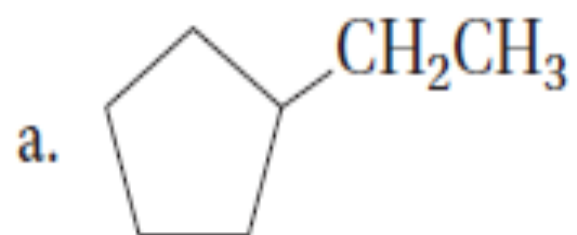


1,2-dimethylcyclopentane
(not 1,5-dimethylcyclopentane)



1-ethyl-2-methylcyclopentane
(not 2-ethyl-1-methylcyclopentane)

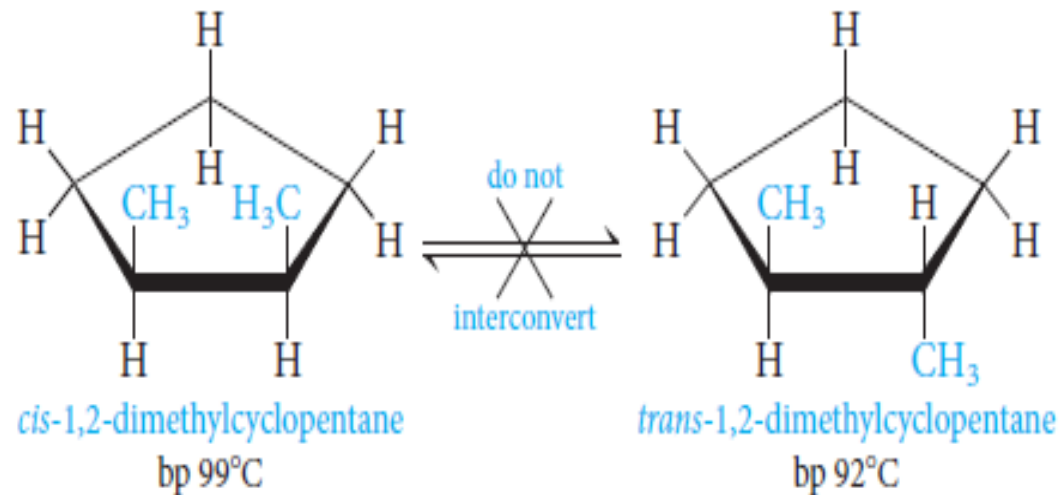
PROBLEM 2.12 Give IUPAC names for



- a. ethylcyclopentane
- b. 1,1-dichlorocyclopropane
- c. 1-bromo-3-methylcyclobutane

2.10 *Cis-Trans* Isomerism in Cycloalkanes

- **Stereoisomerism** deals with molecules that have the same order of attachment of the atoms, but different arrangements of the atoms in space. ***Cis-trans* isomerism** (sometimes called **geometrical isomerism**) is one kind of stereoisomerism, and it is most easily understood with a specific case.

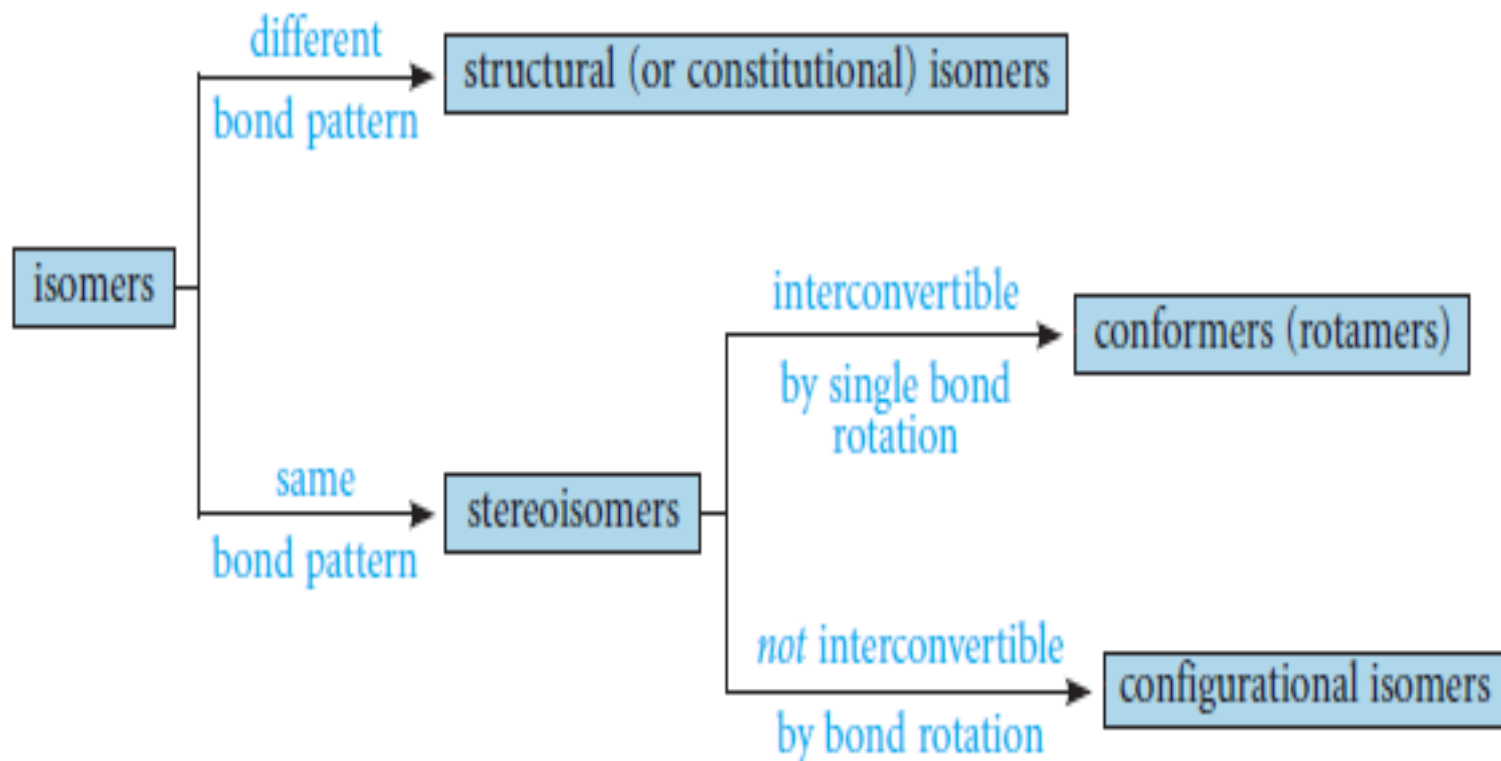


- *Cis*: like groups on same side of ring
- *Trans*: like groups on opposite sides of ring

PROBLEM 2.16 Draw the structure for the *cis* and *trans* isomers of

- 1,3-dibromocyclopentane
- 1-chloro-2-methylcyclopropane

2.11 Summary of Isomerism



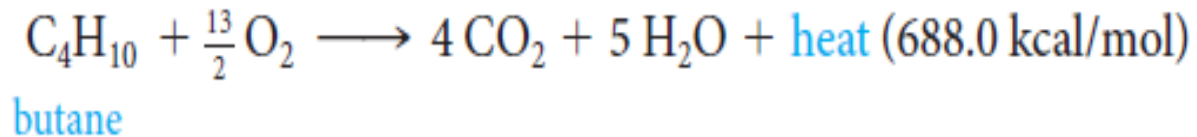
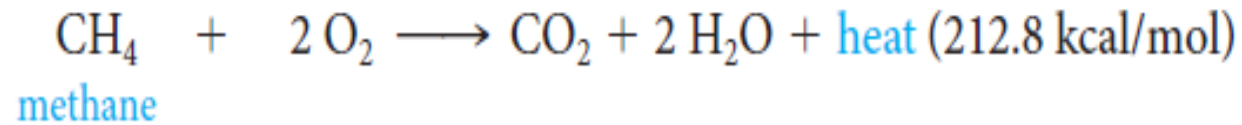
PROBLEM 2.17 Classify each of the following isomer pairs according to the scheme

- a. *cis*- and *trans*-1,2-dimethylcyclohexane
- b. chair and boat forms of cyclohexane
- c. 1-fluoropropane and 2-fluoropropane

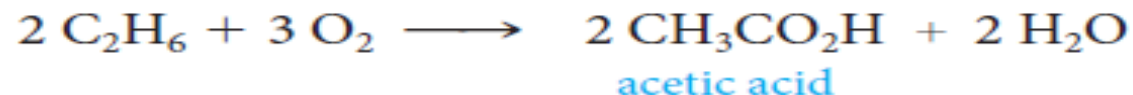
2.12 Reactions of Alkanes

- All of the bonds in alkanes are single, covalent, and nonpolar. Hence alkanes are relatively inert.
- Because of this inertness, alkanes can be used as solvents for extraction or crystallization as well as for carrying out chemical reactions of other substances.

1) Oxidation and Combustion: alkanes as fuels



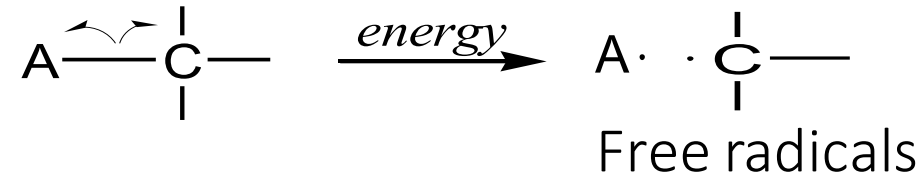
Partial oxidation of hydrocarbon



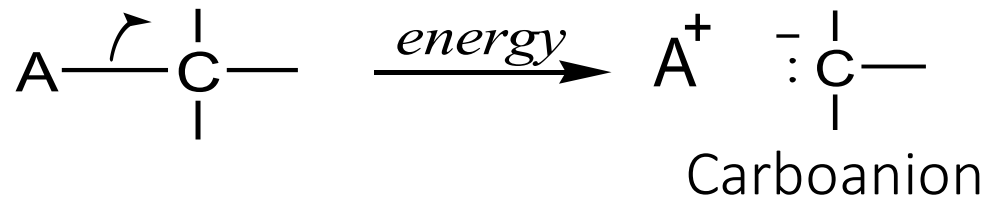
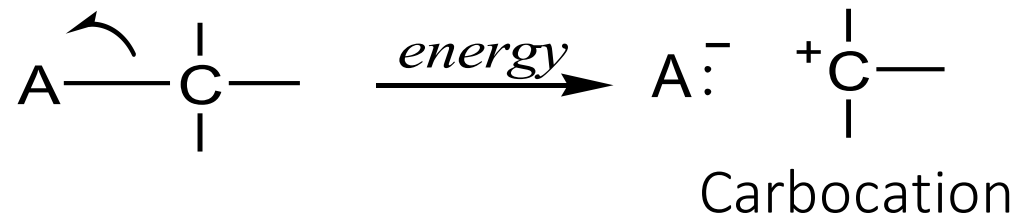
Notations for bond breaking and bond making

- A covalent bond can be broken in either two ways,

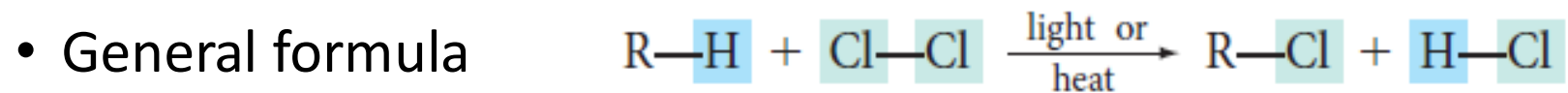
- **Homolytic cleavage.**



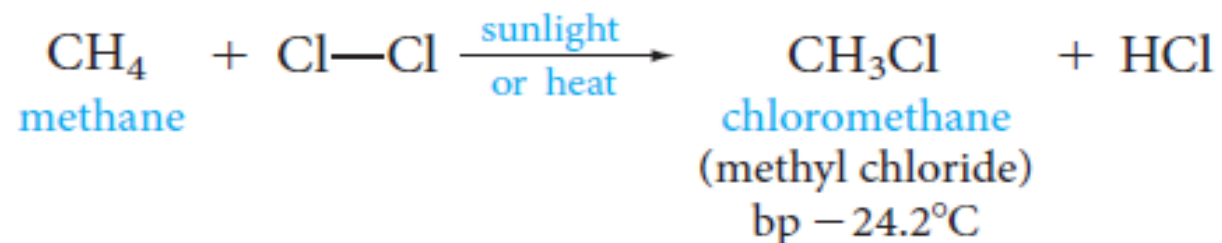
- **Heterolytic cleavage.**



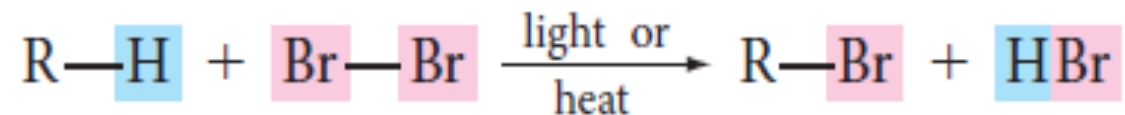
2.12 b Halogenation of alkanes.



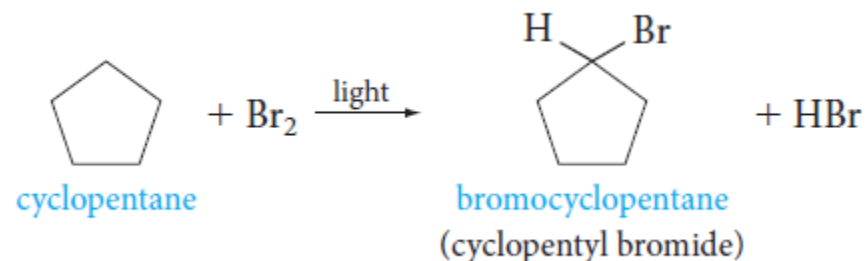
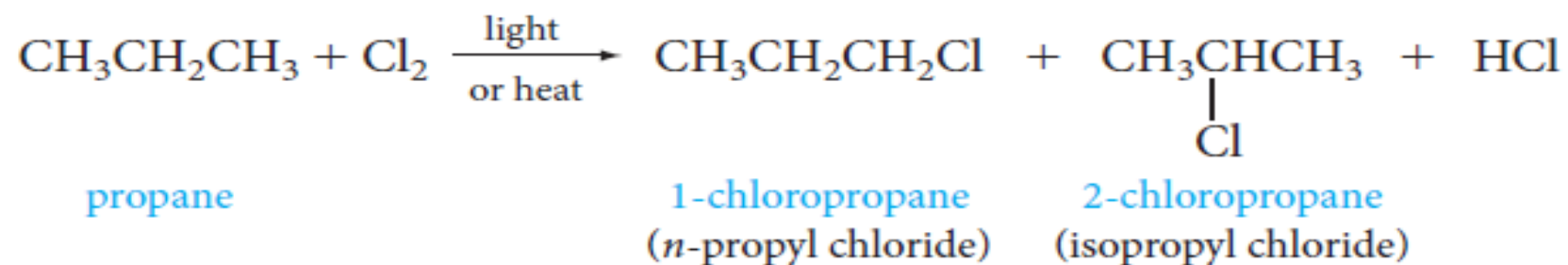
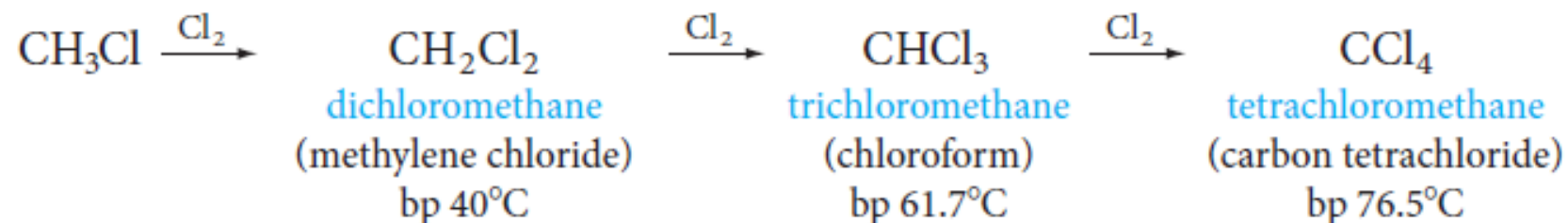
For methane



- The reaction is called **chlorination**. This process is a **substitution reaction**, as a chlorine is substituted for a hydrogen. An analogous reaction, called **bromination**, occurs when the halogen source is bromine.

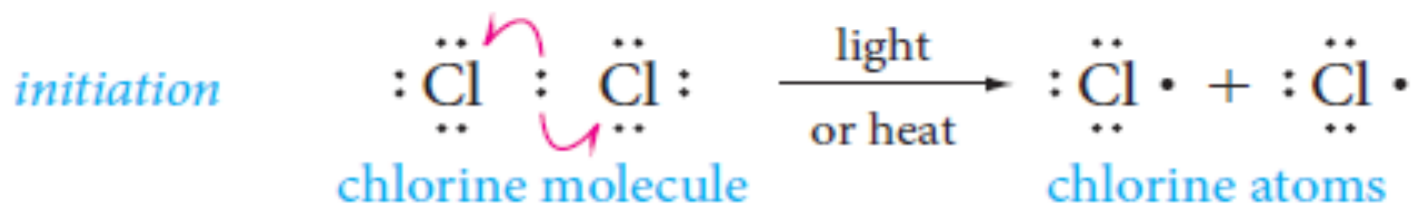


- If excess halogen is present, the reaction can continue further to give polyhalogenated products. Thus, methane and excess chlorine can give products with two, three, or four chlorines

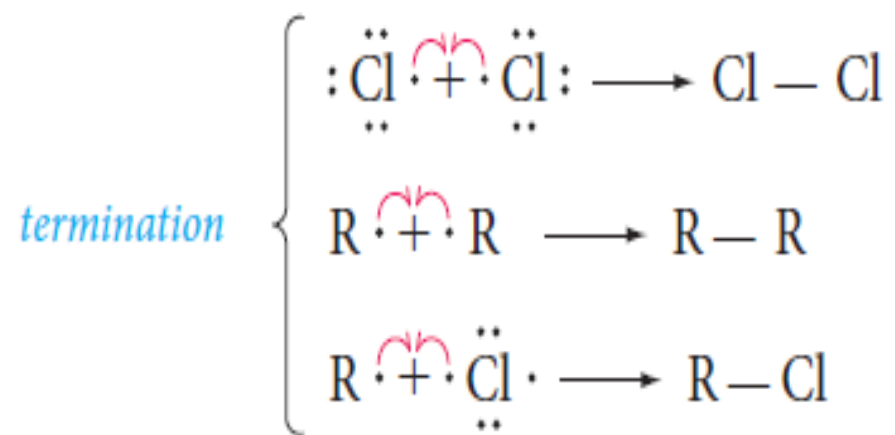
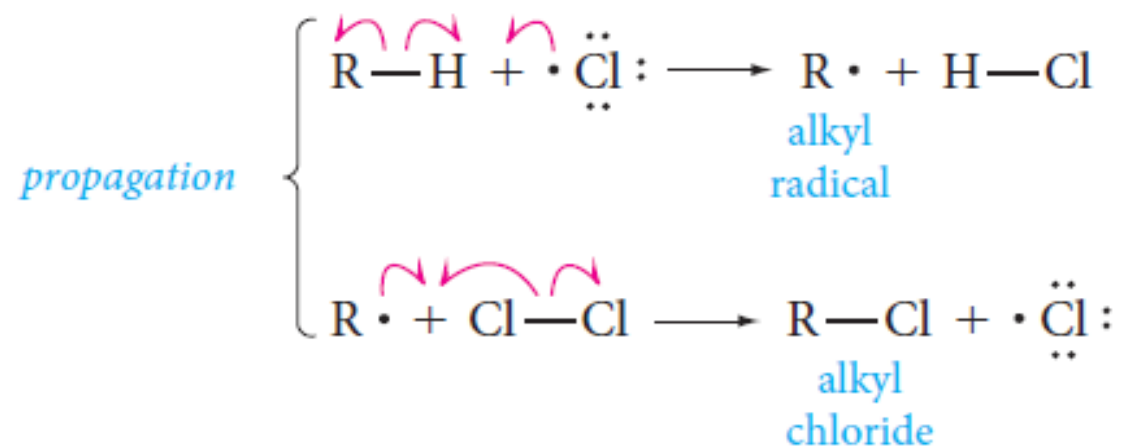


2.13 Free Radical Chain Mechanism of Halogenation

- A **reaction mechanism** is a step-by-step description of the bond-breaking and bond-making processes that occur when reagents react to form products. In the case of halogenation, various experiments show that this reaction occurs in several steps, and not in one magical step. Indeed, halogenation occurs via a **free-radical chain** of reactions.
- The **chain-initiating step** is the breaking of the halogen molecule into two halogen atoms.



The chain-propagating steps are



mechanism for the monochlorination of methane

