

Introduction

Chemistry can be defined as the science that deals with the materials of the universe and the changes that these materials undergo. Chemists are involved in activities as diverse as examining the fundamental particles of matter, looking for molecules in space, synthesizing and formulating new materials of all types, using bacteria to produce such chemicals as insulin, and inventing new diagnostic methods for early detection of disease.

Chemistry is often called the central science and with good reason. Most of the phenomena that occur in the world around us involve chemical changes, changes where one or more substances become different substances. Here are some examples of chemical changes:

1. Wood burns in the air, forming water, carbon dioxide, and other substances.
2. A plant grows by assembling simple substances into more complex substances.
3. The steel in a car rusts.
4. Eggs, flour, sugar, and baking powder are mixed and baked to yield a cake.

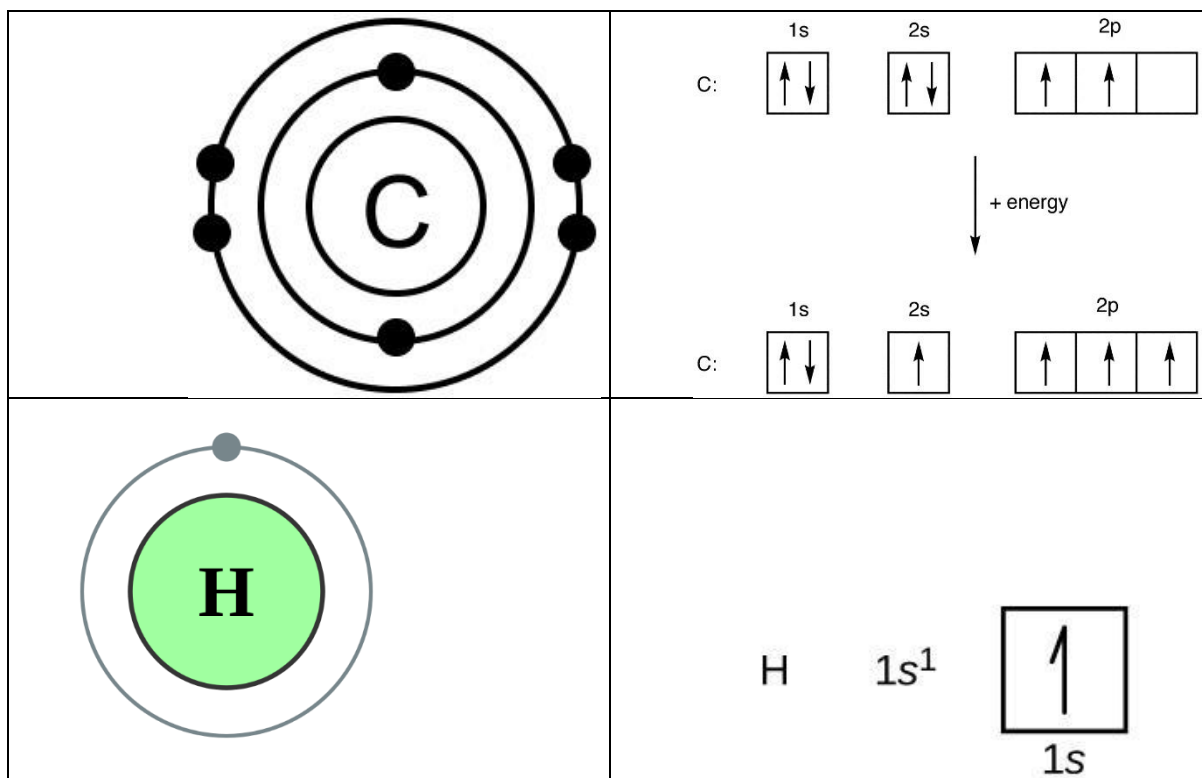
Lecture One

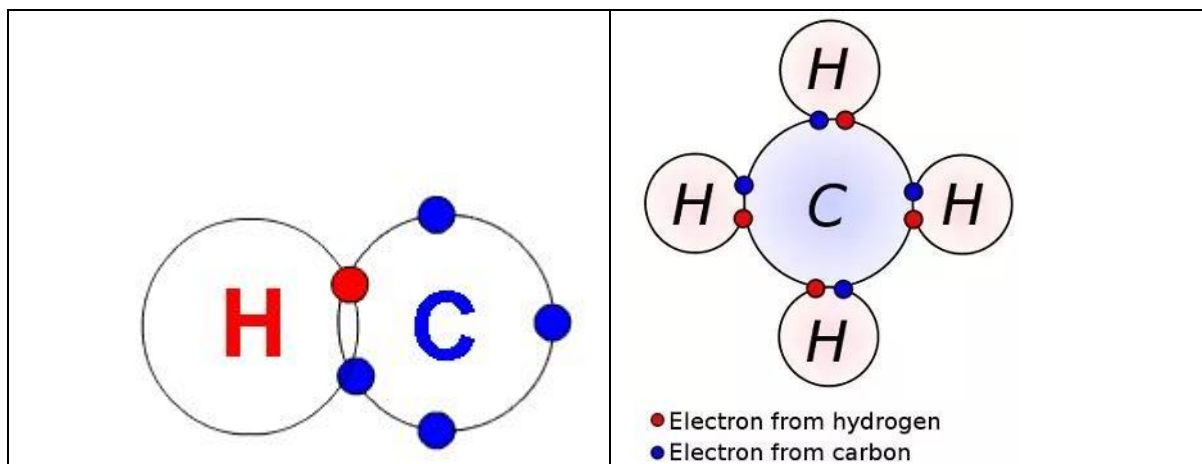
Introduction to Organic Chemistry

Organic Chemistry

Organic chemistry is the study of compounds containing carbon. Carbon (C) has 4 bonds.

The carbon-hydrogen bond (C–H bond) is a chemical bond between carbon and hydrogen atoms that can be found in many organic compounds. This bond is a covalent, single bond, meaning that carbon shares its outer valence electrons with up to four hydrogens. This completes both of their outer shells, making them stable.





The Chemical Bond

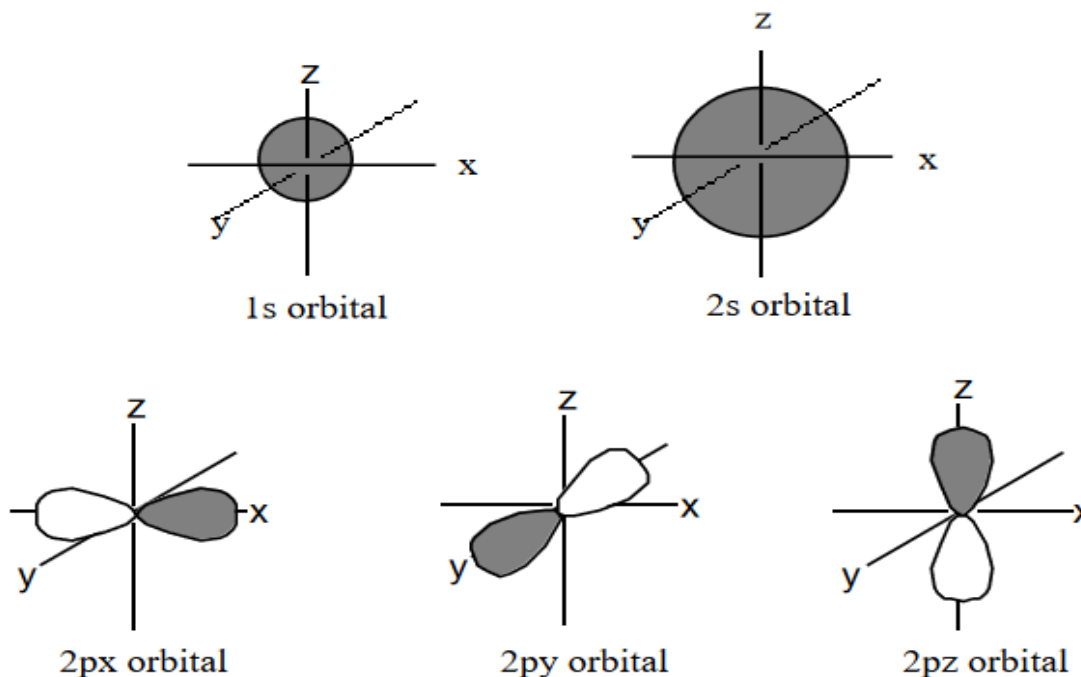
Electrons exist in energy levels that surround the nucleus of the atom. The energy of these levels increases as they get farther from the nucleus. The energy levels are called **shells**, and within these shells are other energy levels, called **subshells or orbitals**., that contain up to two electrons. The calculations from atomic theory give the following results for electron energy and orbitals. The results for the first two energy levels (shells 1 and 2) are the most important for bonding in organic chemistry.

Shell	Orbitals				Total Electrons Possible
	s	p	d	f	
1	1				2
2	2	3			8
3	3	3	5		18
4	1	3	5	7	32

***energy level 1** contains up to two electrons in a spherical orbital called a 1s orbital.

***energy level 2** contains up to eight electrons; two in a 2s-orbital and two in each of three orbitals designated as 2p-orbitals. The p-orbitals have a barbell-type shape and are aligned along the x, y, and z axes. They are

thus called the p_x , p_y , and p_z orbitals.



***energy level 3** contains up to eighteen electrons, two electrons in a 3s orbital, six electrons in the three 3p orbitals, and ten electrons in the five 3d orbitals.

***energy level 4** contains up to thirty-two electrons, two electrons in a 4s-orbital, six electrons in the three 4p-orbitals, ten electrons in the five 4d-orbitals, and fourteen electrons in the seven 4f-orbitals. Electrons fill the lower energy levels first until all of the electrons are used (Aufbau Principle). An element contains the number of electrons equal to its atomic number. For the first and second row elements, the electron configurations are relatively simple.

Bonding

Atoms can become bonded with each other, and their electronic structure governs the type of bond formed. The main two types of bonds that are formed are called ionic and covalent.

Types of bonding

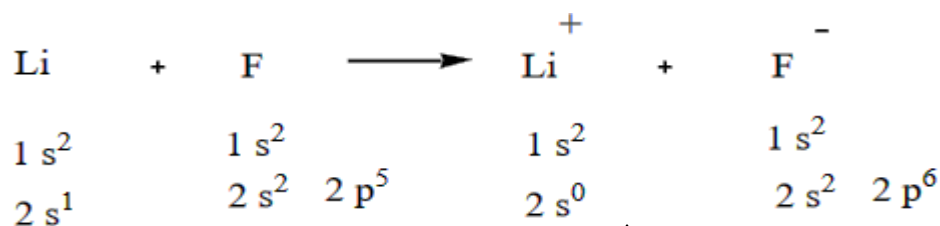
- 1- Ionic bond
- 2- Covalent bond

- a) Polar covalent bond
- b) Nonpolar covalent bond

Ionic Bond

Ionic bonding is important between atoms of vastly different electronegativity. The bond results from one atom giving up an electron while another atom accepts the electron. Both atoms attain a stable Nobel gas configuration.

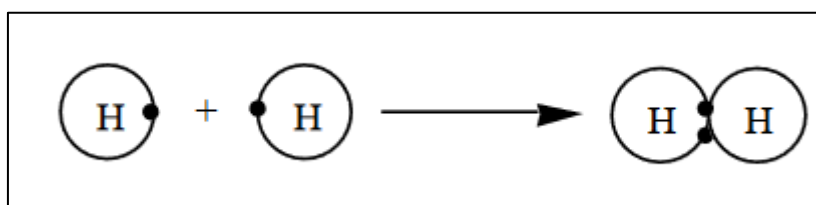
In the compound lithium fluoride, the $2s^1$ electron of lithium is transferred to the $2p^5$ orbital of fluorine. The lithium atom gives up an electron to form the positively charged lithium cation with $1s^2, 2s^0$ configuration, and the fluorine atom receives an electron to form a fluoride anion with $1s^2, 2s^2, 2p^6$ configuration. Thus the outer energy levels of both ions are filled. The ions are held together by the electrostatic attraction of the positive and negative ions.



Covalent Bond

A covalent bond is formed by the sharing of two electrons by two atoms.

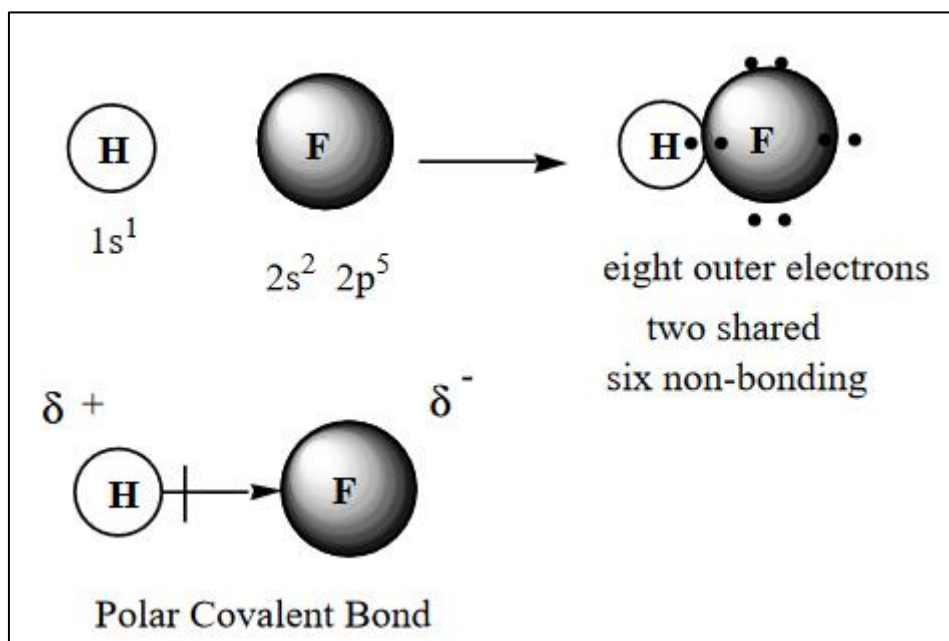
A hydrogen atom possessing the $1s^1$ electron joins with another hydrogen atom with its $1s^1$ configuration. The two atoms form a covalent bond with two electrons by sharing their electrons.



In hydrogen fluoride, HF, the hydrogen $1s$ electron is shared with a $2p^5$ electron in fluorine ($1s^2, 2s^2, 2p^5$), and the molecule is now held together by a covalent

bond. In this case, the fluorine atom is much more electronegative than the hydrogen atom and the electrons in the bond tend to stay closer to the fluorine atom.

This is called a polar covalent bond, and the atoms possess a small partial charge denoted by the Greek δ symbol

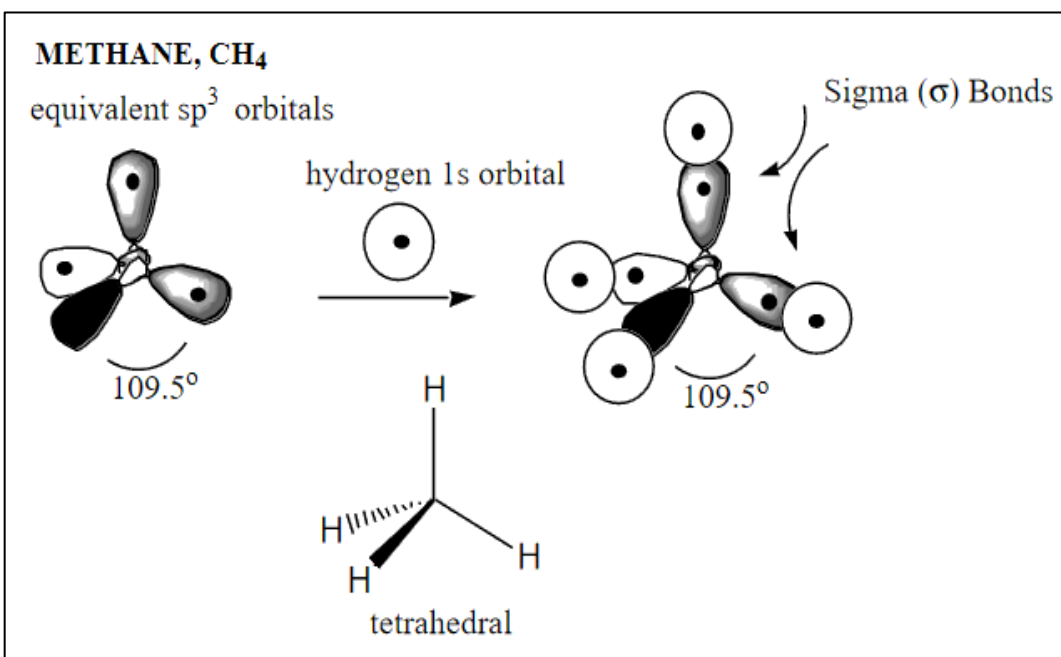
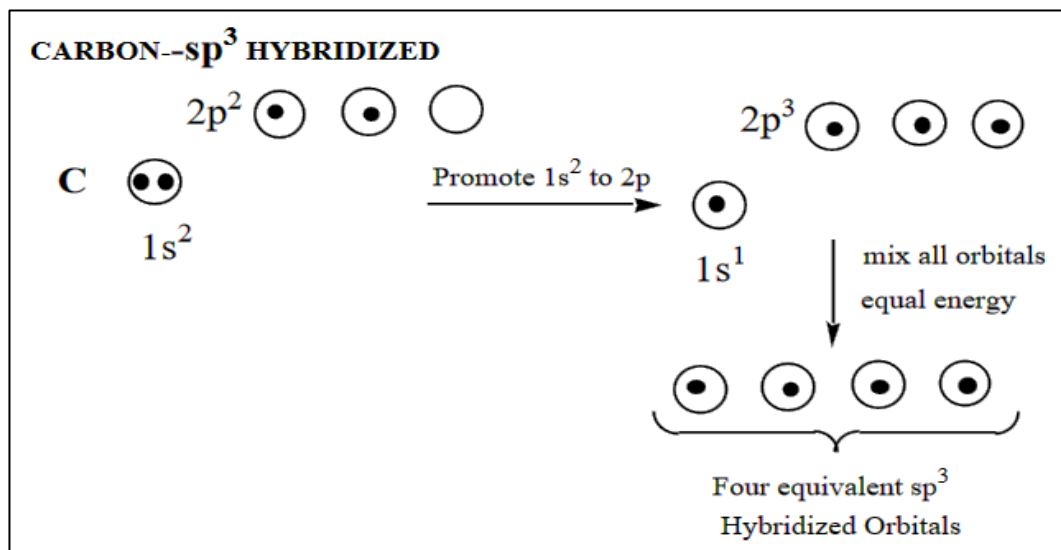


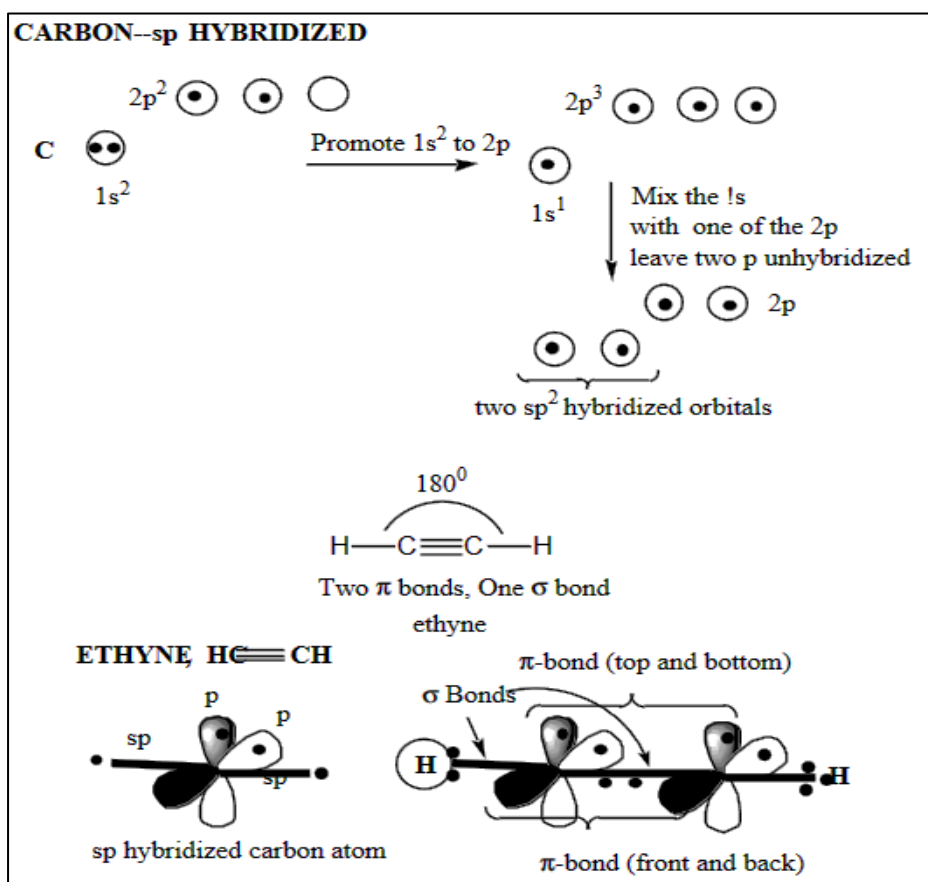
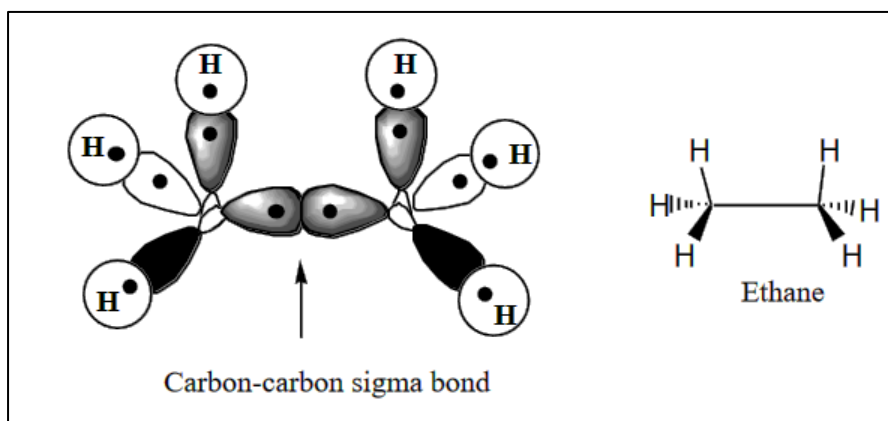
Bonding in Carbon Compounds

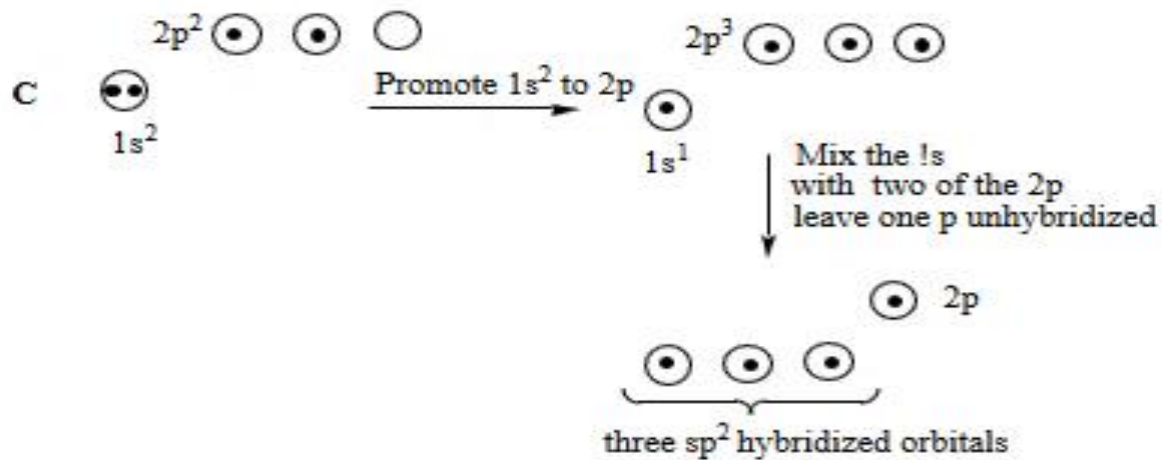
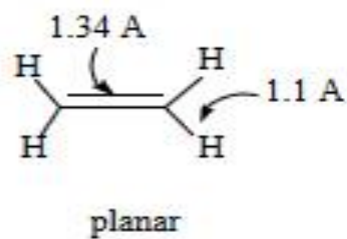
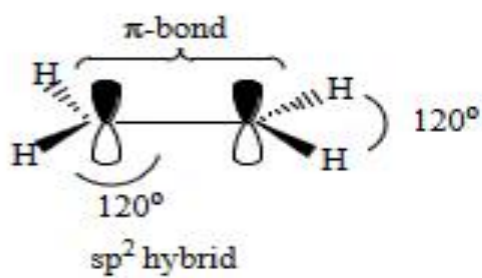
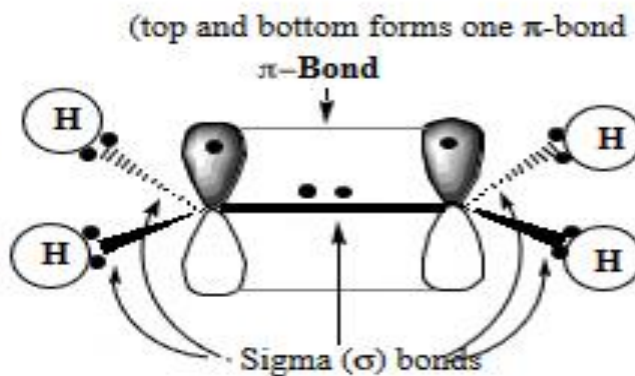
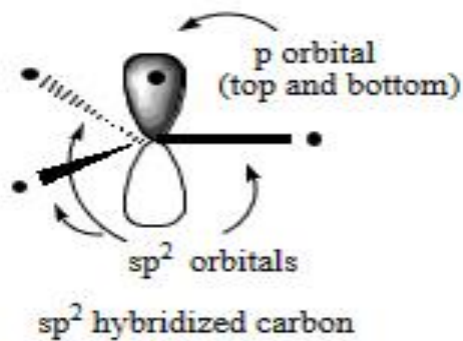
The property of carbon that makes it unique is its ability to form bonds with itself and therefore, allows a large number of organic chemicals with many diverse properties.

Carbon has the property of forming single, double and triple bonds with itself and with other atoms. This multiple-bond ability allows carbon compounds to have a variety of shapes. In all carbon compounds, carbon forms four bonds. The types of bonds used by the carbon atom are known as sigma (σ) and pi (π) bonds.

Different combinations of these bonds lead to carbon single bonds, double bonds and triple bonds.

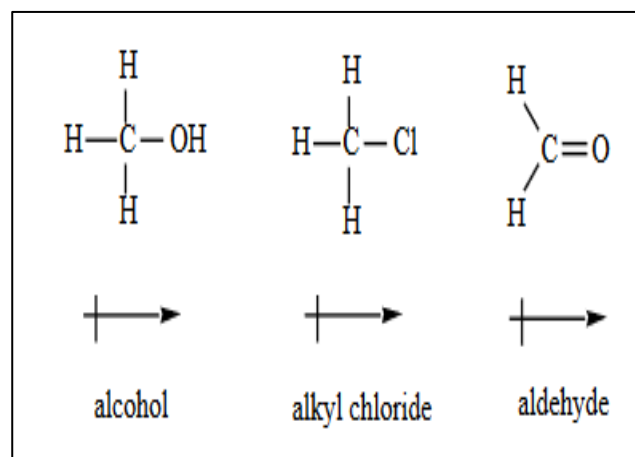




CARBON-- sp^2 HYBRIDIZED**ETHENE $CH_2=CH_2$** 

Polar Covalent Bonds in Carbon

Carbon forms single, double and triple bonds with elements other than carbon. The atoms involved in the bonding are usually oxygen, nitrogen, sulfur and halogens. These elements are more electronegative than carbon and thus attract the electrons to themselves. The bonds are therefore polar covalent bonds.



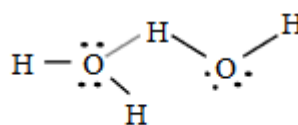
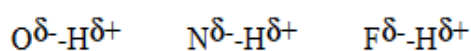
Bonds that contain a separation of charge possess a dipole moment, a property that contributes to the overall polarity of the molecule.

Hydrogen Bonds and Bond Polarity

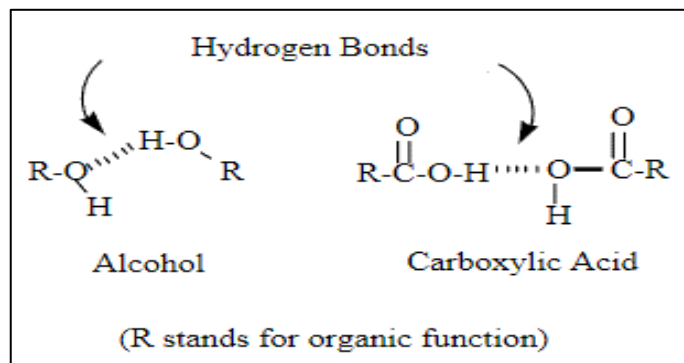
The bonds O-H, N-H and F-H are highly polar covalent bonds because the electronegative draws electrons away from the hydrogen atom.

In every case, the hydrogen atom has a partial positive charge.

Hydrogen bonding in Water



In organic compounds, hydrogen bonding is very important for describing the boiling and solubility characteristics of alcohols and acids, and the concept will be given in more detail in chapters dealing with those types of molecules.



Classification of Organic Compounds

Organic compounds are often classified according to the type (s) of functional groups present. These functional groups are presented in detail in the remaining chapters. The on-sight recognition of functional groups is required for an adequate study of organic chemistry.

Family name	Functional group	Name ending	Simple example
Alkane	C-C	-ane	
Alkene	C=C	-ene	
Alkyne	$\text{C}\equiv\text{C}$	-yne	
Alkylhalid	C-X (Cl,Br,I)	-halide	
Alcohol	C-OH	-ol	
Ether	C-O-C	-ether	
Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{CH} \end{array}$	-al	
Ketone	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$	-one	
Carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$	-oic acid	
Amine	C-NH ₂	-amine	
Benzene			

Hydrocarbon

A compound of carbon and hydrogen is known as hydrocarbon.

•Saturated Hydrocarbon

A hydrocarbon is said to be saturated if it contains only C—C single bonds.

For example: Ethane $\text{CH}_3\text{—CH}_3$

• Unsaturated Hydrocarbon

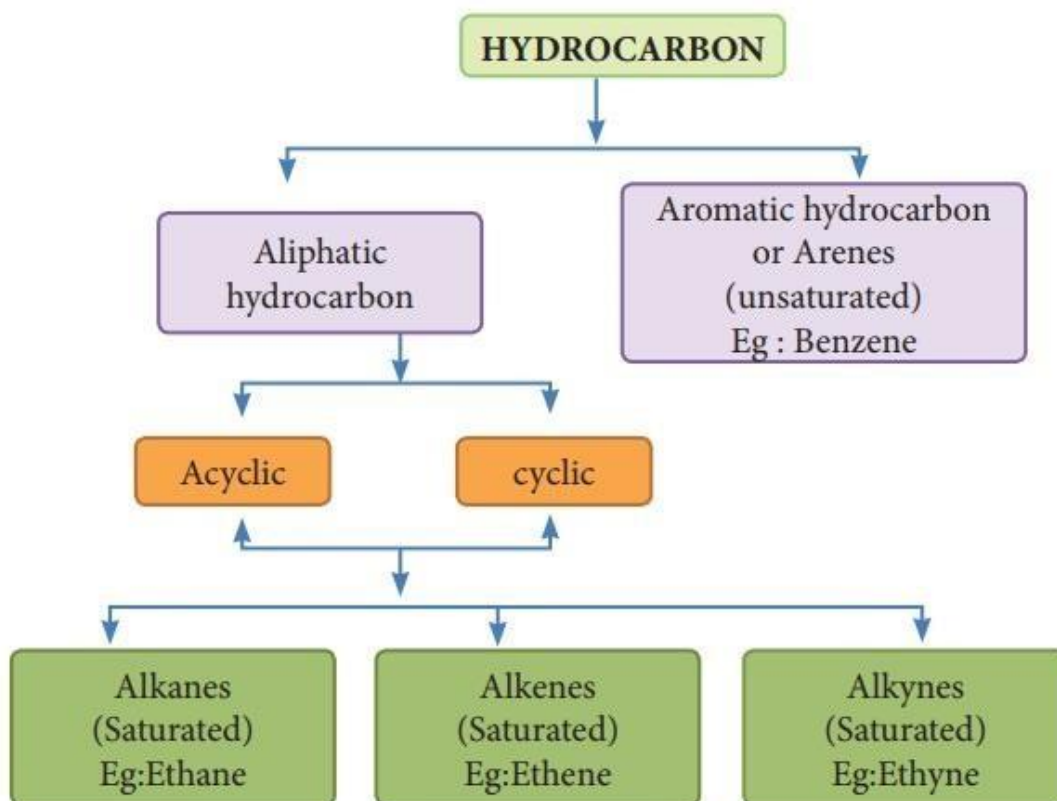
A hydrocarbon is said to be unsaturated if it contains C=C or C≡C multiple bonds.

Example: ethene $\text{CH}_2=\text{CH}_2$

Ethyne $\text{CH}\equiv\text{CH}$

• Aromatic Hydrocarbon

Benzene and its derivatives are called aromatic compounds.



Alkanes

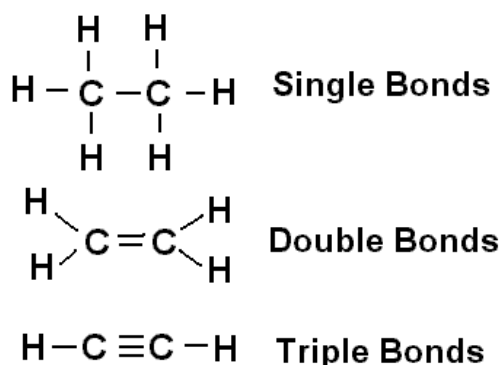
A homologous series of saturated compounds with general molecular formula C_nH_{2n+2} (where n is an integer). Methane CH_4 , ethane C_2H_6 , propane C_3H_8 , butane C_4H_{10} , pentane C_5H_{12} , hexane C_6H_{14} , heptane C_7H_{16} , octane C_8H_{18} , nonane C_9H_{20} , decane $C_{10}H_{22}$, etc.

Alkenes

A homologous series of unsaturated compounds with general molecular formula C_nH_{2n} (n is an integer greater than 1) that contain a double bond. ethene C_2H_4 , propene C_3H_6 , butene C_4H_8 , pentene C_5H_{10} , hexene C_6H_{12} , heptene C_7H_{14} , octene C_8H_{16} , nonene C_9H_{18} , decene $C_{10}H_{20}$, etc.

Alkynes

The alkynes are unsaturated hydrocarbons that contain one triple bond, the general formula of alkynes C_nH_{2n-2} and the triple bond is known as the 'acetylenic bond'. Many alkynes have been found in nature. Ethyne (C_2H_2) is the first member of the alkyne family, with two carbon atoms connected by a triple bond.

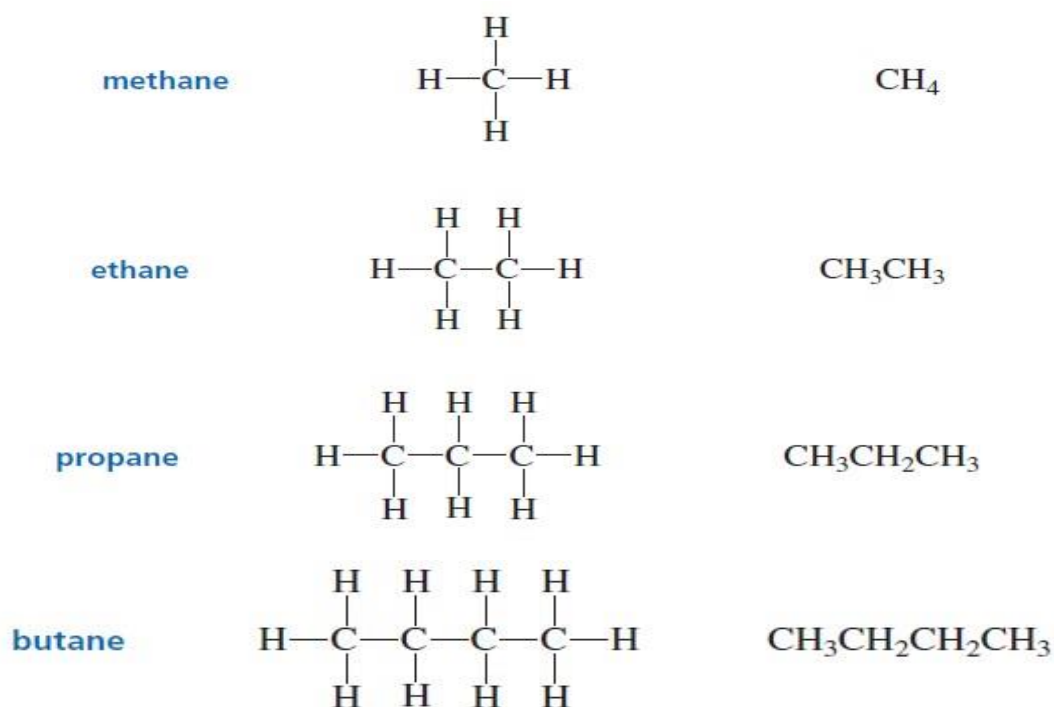


The method of nomenclature is called systematic nomenclature. It is also called IUPAC nomenclature because it was designed by a commission of the

International Union of Pure and Applied Chemistry (abbreviated IUPAC and pronounced “eye-you-pack”) in 1892.

* Find the longest carbon chain in the molecule. This will give you the base of the name:

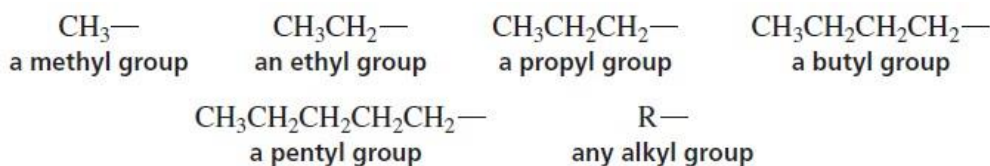
Table 3.1 Nomenclature and Physical Properties of Straight-Chain Alkanes						
Number of carbons	Molecular formula	Name	Condensed structure	Boiling point (°C)	Melting point (°C)	Density ^a (g/mL)
1	CH ₄	methane	CH ₄	-167.7	-182.5	
2	C ₂ H ₆	ethane	CH ₃ CH ₃	-88.6	-183.3	
3	C ₃ H ₈	propane	CH ₃ CH ₂ CH ₃	-42.1	-187.7	
4	C ₄ H ₁₀	butane	CH ₃ CH ₂ CH ₂ CH ₃	-0.5	-138.3	
5	C ₅ H ₁₂	pentane	CH ₃ (CH ₂) ₃ CH ₃	36.1	-129.8	0.5572
6	C ₆ H ₁₄	hexane	CH ₃ (CH ₂) ₄ CH ₃	68.7	-95.3	0.6603
7	C ₇ H ₁₆	heptane	CH ₃ (CH ₂) ₅ CH ₃	98.4	-90.6	0.6837
8	C ₈ H ₁₈	octane	CH ₃ (CH ₂) ₆ CH ₃	125.7	-56.8	0.7026
9	C ₉ H ₂₀	nonane	CH ₃ (CH ₂) ₇ CH ₃	150.8	-53.5	0.7177
10	C ₁₀ H ₂₂	decane	CH ₃ (CH ₂) ₈ CH ₃	174.0	-29.7	0.7299
11	C ₁₁ H ₂₄	undecane	CH ₃ (CH ₂) ₉ CH ₃	195.8	-25.6	0.7402
12	C ₁₂ H ₂₆	dodecane	CH ₃ (CH ₂) ₁₀ CH ₃	216.3	-9.6	0.7487
13	C ₁₃ H ₂₈	tridecane	CH ₃ (CH ₂) ₁₁ CH ₃	235.4	-5.5	0.7546
⋮	⋮	⋮	⋮	⋮	⋮	⋮
20	C ₂₀ H ₄₂	eicosane	CH ₃ (CH ₂) ₁₈ CH ₃	343.0	36.8	0.7886
21	C ₂₁ H ₄₄	heneicosane	CH ₃ (CH ₂) ₁₉ CH ₃	356.5	40.5	0.7917
⋮	⋮	⋮	⋮	⋮	⋮	⋮
30	C ₃₀ H ₆₂	triacontane	CH ₃ (CH ₂) ₂₈ CH ₃	449.7	65.8	0.8097



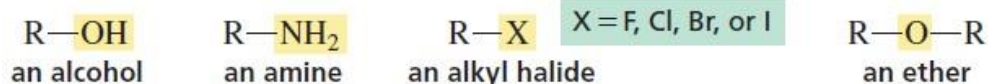
Nomenclature, Preparation and reaction of Alkanes

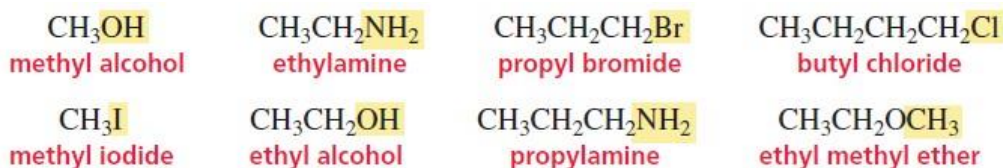
How Alkyl Substituents Are Named

Removing hydrogen from an alkane results in an alkyl substituent (or an alkyl group). Alkyl substituents are named by replacing the “ane” ending of the alkane with “yl.” The letter “R” is used to indicate any alkyl group.

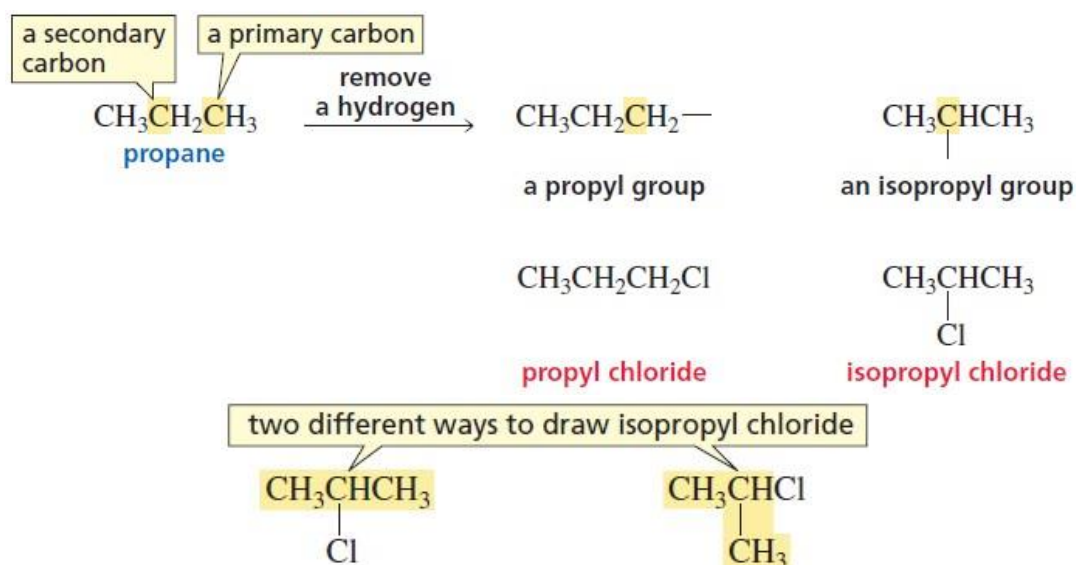


If hydrogen in an alkane is replaced by an OH, the compound becomes an alcohol; if it is replaced by an NH_2 , the compound becomes an amine; if it is replaced by a halogen, the compound becomes an alkyl halide; and if it is replaced by an OR, the compound becomes an ether.

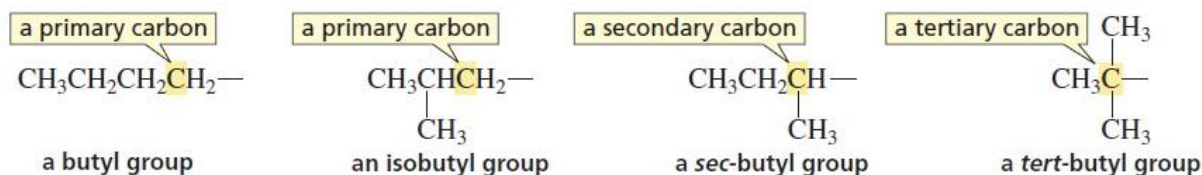




There are two alkyl groups the propyl group and the isopropyl group that have three carbons.



There are four alkyl groups that have four carbons. Two of them, the butyl and isobutyl groups, have a hydrogen removed from a primary carbon. A sec-butyl group has a hydrogen removed from a secondary carbon (*sec-*, sometimes abbreviated *s-*, stands for secondary), and a *tert*-butyl group has a hydrogen removed from a tertiary carbon (*tert-*, often abbreviated *t-*, stands for tertiary). A tertiary carbon is a carbon that is bonded to three other carbons. Notice that the isobutyl group is the only one with an *iso-structural* unit.



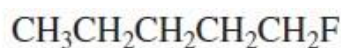
The names of straight-chain alkyl groups often have the prefix “n” (for “normal”) to emphasize that the carbons are in an unbranched chain. If a name does not have a prefix such as “n”, “iso,” “sec,” or “tert,” we assume that the carbons are in an unbranched chain.



butyl bromide

or

n-butyl bromide

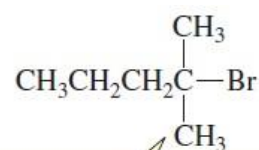
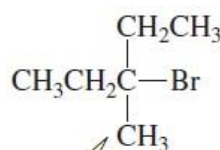
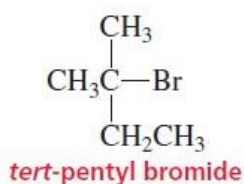
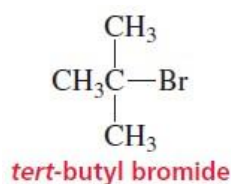


pentyl fluoride

or

n-pentyl fluoride

The prefix “tert” can be used for both *tert*-butyl and *tert*-pentyl compounds because each of these substituent names describes only one alkyl group. The name “*tert*-hexyl” cannot be used because it describes two different alkyl groups.



Both alkyl bromides have six carbon atoms with a bromine attached to a tertiary carbon, but two different compounds cannot be named *tert*-hexyl bromide.

Notice in the following structures that whenever the prefix “iso” is used, the *iso* structural unit is at one end of the molecule, and any group replacing a hydrogen is at the other end:

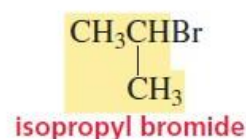
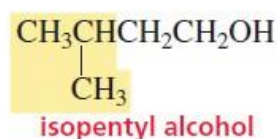
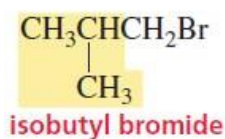
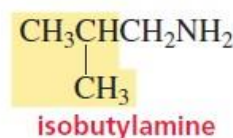
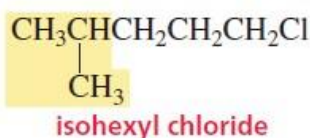
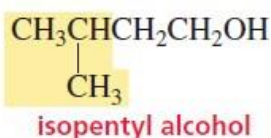
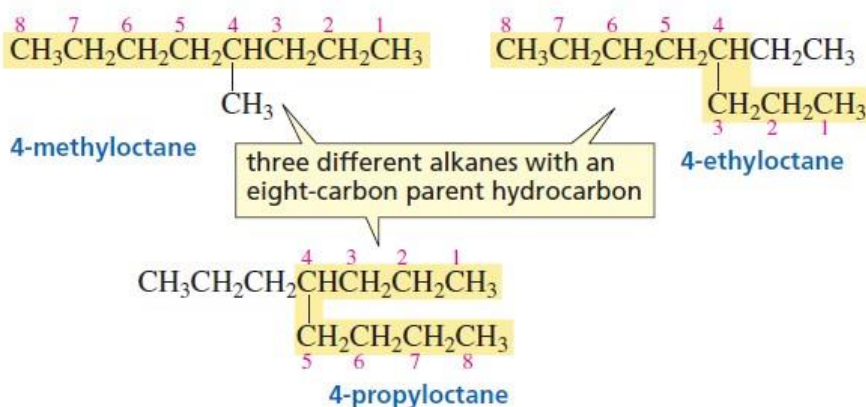


Table 3.2 Names of Some Common Alkyl Groups

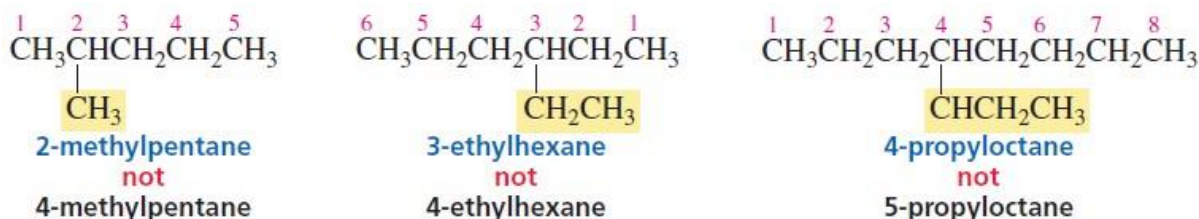
methyl	$\text{CH}_3\text{—}$	isobutyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$	pentyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$
ethyl	$\text{CH}_3\text{CH}_2\text{—}$			isopentyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$
propyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$	sec-butyl	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH—} \\ \\ \text{CH}_3 \end{array}$		
isopropyl	$\begin{array}{c} \text{CH}_3\text{CH—} \\ \\ \text{CH}_3 \end{array}$			hexyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$
butyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$	tert-butyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C—} \\ \\ \text{CH}_3 \end{array}$	isohexyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$

The Nomenclature of Alkanes

- Determine the number of carbons in the longest continuous carbon chain.

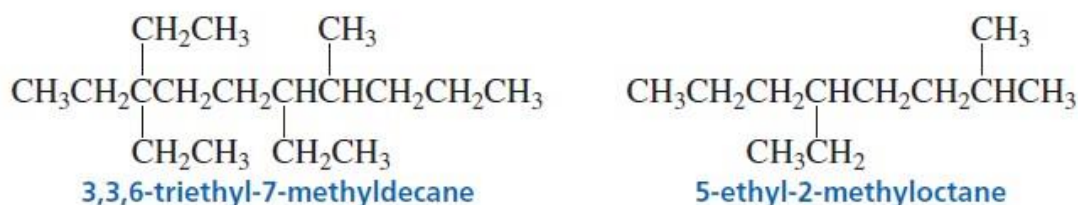
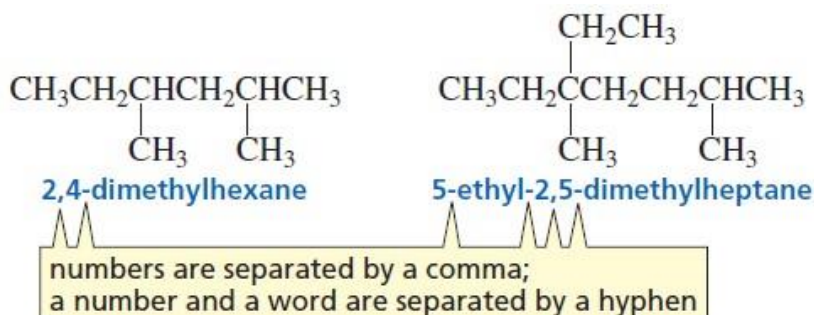


- The name of any alkyl substituent that hangs off the parent hydrocarbon is placed in front of the name of the parent hydrocarbon, together with a number to designate the carbon to which the alkyl substituent is attached.

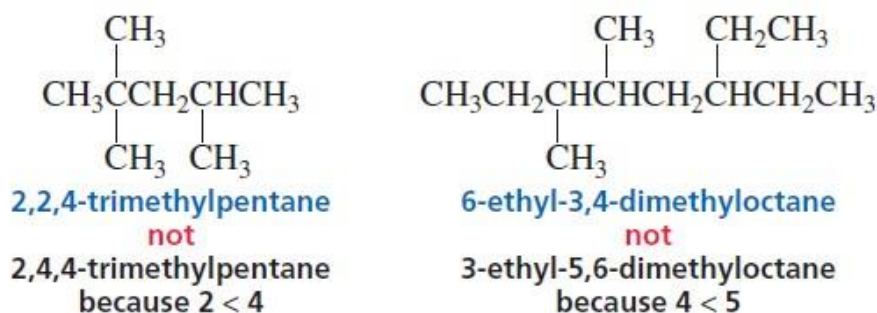


- If more than one substituent is attached to the parent hydrocarbon, the chain is numbered in the direction that will produce a name containing the lowest of the possible numbers. The substituents are listed in alphabetical order, with each substituent preceded by the appropriate number. If two or more substituents are

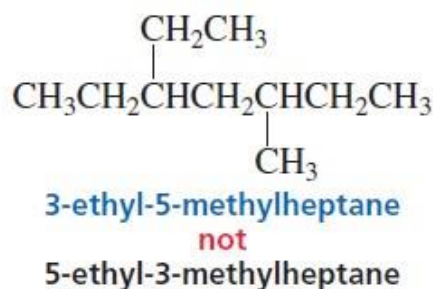
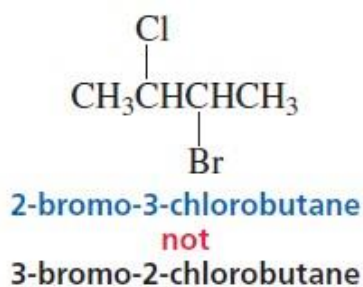
the same, the prefixes “di,” “tri,” and “tetra” are used to indicate how many identical substituents the compound has.



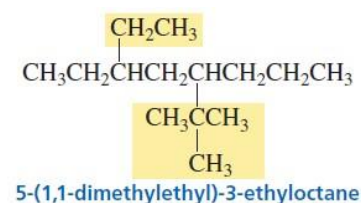
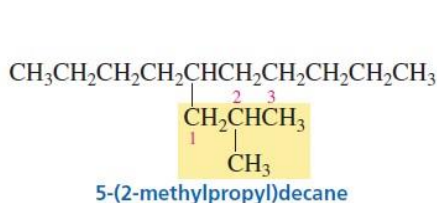
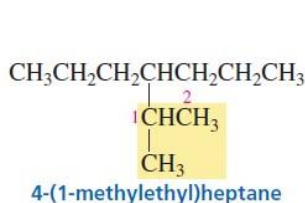
4. When numbering in either direction leads to the same lowest number for one of the substituents, the chain is numbered in the direction that gives the lowest possible number to one of the remaining substituents.



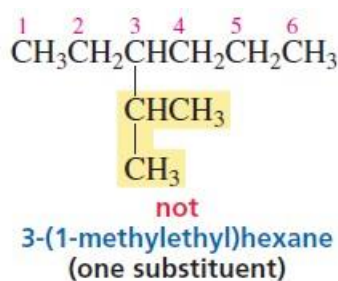
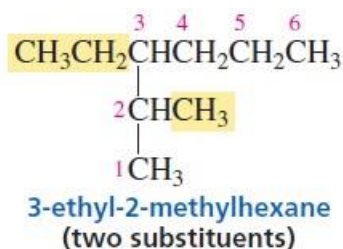
5. If the same substituent numbers are obtained in both directions, the first group listed receives the lower number.



6. Systematic names for branched substituents are obtained by numbering the alkyl substituent starting at the carbon attached to the parent hydrocarbon.

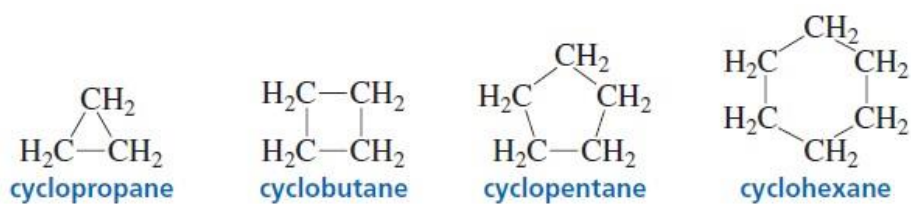


7. If a compound has two or more chains of the same length, the parent hydrocarbon is the chain with the greatest number of substituents.

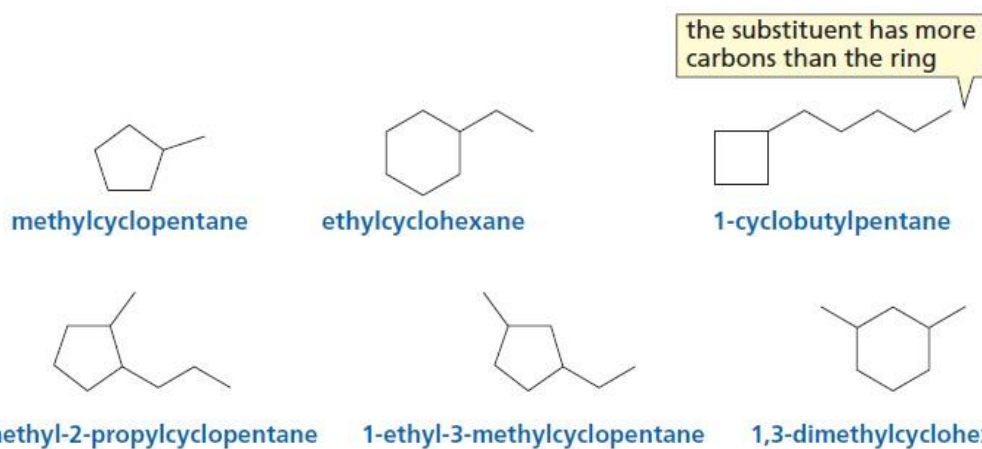
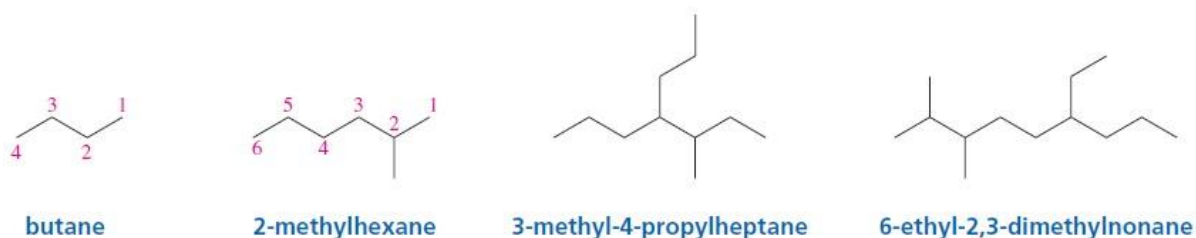


The Nomenclature of Cycloalkanes

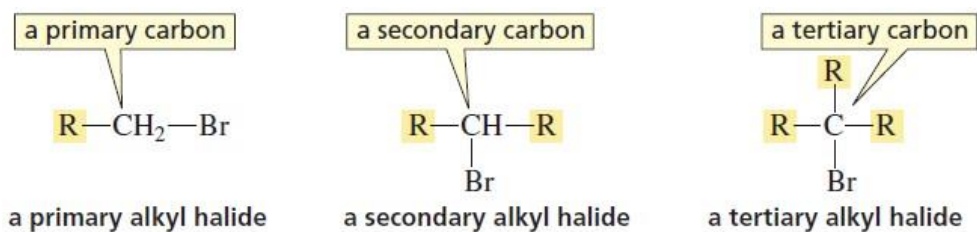
Cycloalkanes are alkanes with their carbon atoms arranged in a ring. Because of the ring, a cycloalkane has two fewer hydrogens than an acyclic (noncyclic) alkane with the same number of carbons. This means that the general molecular formula for a cycloalkane is C_nH_{2n} . Cycloalkanes are named by adding the prefix “cyclo” to the alkane name that signifies the number of carbons in the ring.



Acyclic molecules can also be represented by skeletal structures. In skeletal structures of acyclic molecules, the carbon chains are represented by zigzag lines.



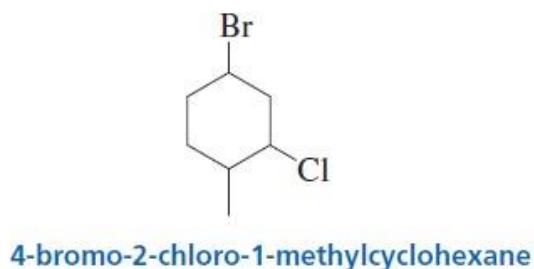
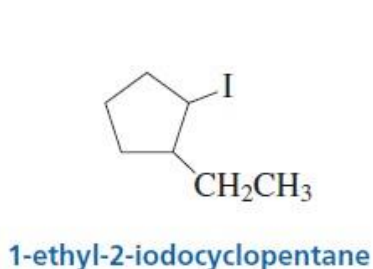
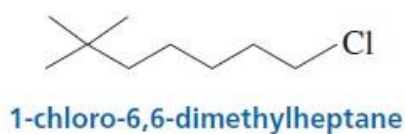
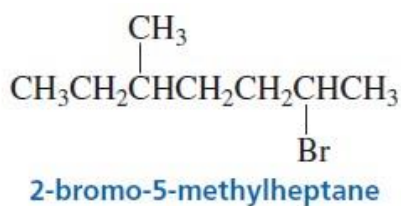
The Nomenclature of Alkyl Halides

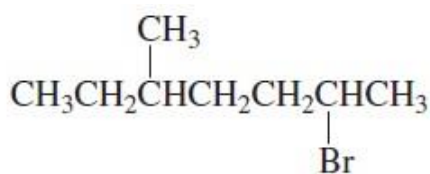


The common names of alkyl halides consist of the name of the alkyl group, followed by the name of the halogen with the “ine” ending of the halogen name (fluorine, chlorine, bromine, and iodine) replaced by “ide” (fluoride, chloride, bromide, and iodide).

	CH_3Cl	$\text{CH}_3\text{CH}_2\text{F}$	$\begin{array}{c} \text{CH}_3\text{CHI} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHBr} \\ \\ \text{CH}_3 \end{array}$
common name:	methyl chloride	ethyl fluoride	isopropyl iodide	sec-butyl bromide
systematic name:	chloromethane	fluoroethane	2-iodopropane	2-bromobutane

In the IUPAC system, alkyl halides are named as substituted alkanes. The prefixes for the halogens end with “o” (that is, fluoro, chloro, bromo, and iodo). Therefore, alkyl halides are also called haloalkanes.

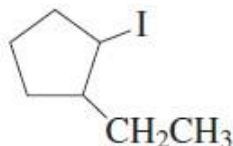




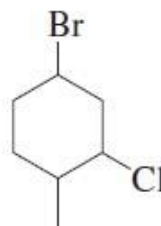
2-bromo-5-methylheptane



1-chloro-6,6-dimethylheptane



1-ethyl-2-iodocyclopentane

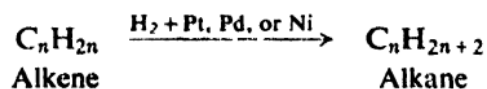


4-bromo-2-chloro-1-methylcyclohexane

Preparation of Alkanes

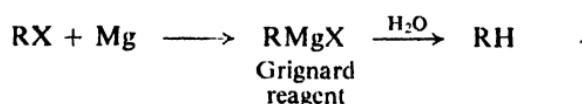
PREPARATION OF ALKANES

1. Hydrogenation of alkenes. Discussed in Sec. 6.3.

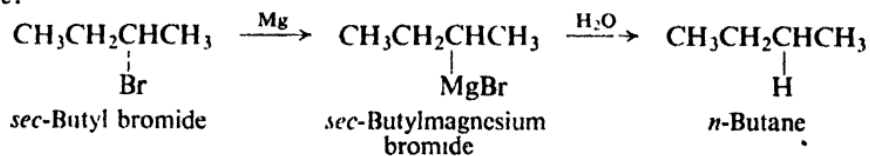


2. Reduction of alkyl halides

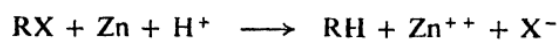
(a) Hydrolysis of Grignard reagent. Discussed in Sec. 3.16.



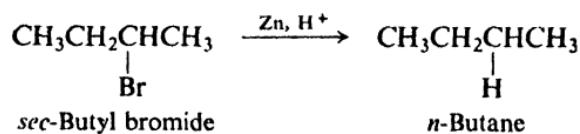
Example:



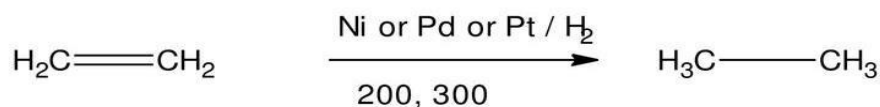
(b) Reduction by metal and acid. Discussed in Sec. 3.15.



Example:



1- Hydrogenation of unsaturated hydrocarbon:



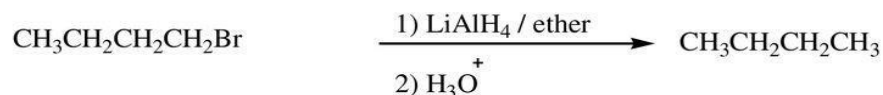
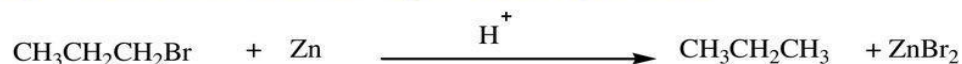
2- Hydrolysis of Grignard reagent

- i) $\text{R}-\text{X} + \text{Mg} \rightarrow \text{RMgX}$ (Grignard reagent)
- ii) $\text{RMgX} + \text{H}_2\text{O} \rightarrow \text{RH} + \text{Mg(OH)X}$



3- Reduction of alkyl halides

a) by metal and acid or by metal hydrides



b) By sodium metal (Coupling reaction)



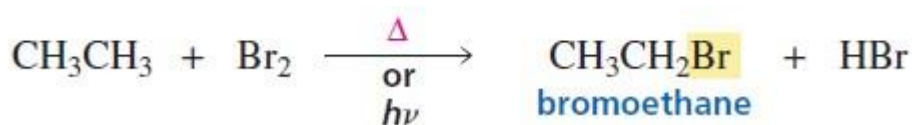
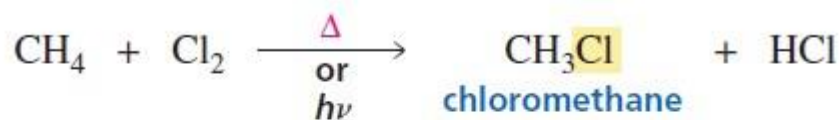
c) By lithium dialkyl cuprate



Reactions of Alkanes

1. The Chlorination and Bromination of Alkanes

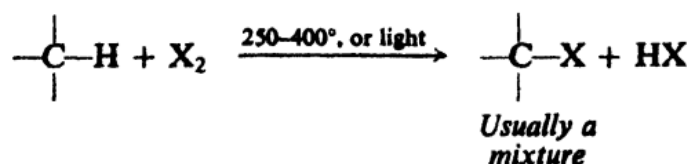
Alkanes react with chlorine (Cl₂) or bromine (Br₂) to form alkyl chlorides or alkyl bromides. These halogenation reactions take place only at high temperatures or in the presence of light. (Irradiation with light is symbolized by *hν*.)



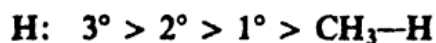
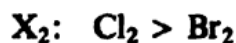
Halogenation and combustion (burning) are the only reactions that alkanes undergo (without the assistance of a metal catalyst). In a combustion reaction, alkanes react with oxygen at high temperatures to form carbon dioxide and water.

REACTIONS OF ALKANES

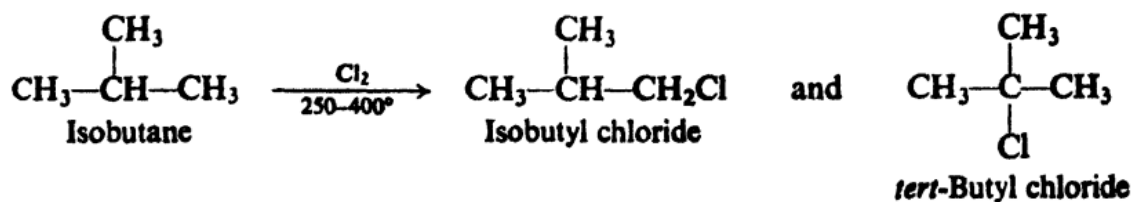
1. Halogenation. Discussed in Secs. 3.19–3.22.

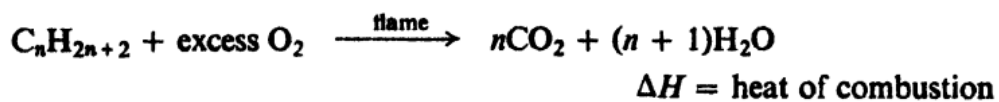


Reactivity



Example:



2. Combustion. Discussed in Sec. 3.30.**Example:****3. Pyrolysis (cracking). Discussed in Sec. 3.31.**