

Chapter One

Hydrocarbons and Alkanes

Alkanes are saturated hydrocarbons — each carbon holds the maximum number of hydrogen atoms). Alkanes contain only carbon-carbon single bonds. – General formula: C_nH_{2n+2} (no rings). Most chemical reactions require a functional group “handle” to proceed. Since alkanes don’t really have functional groups, they aren’t very useful in many biologically important processes. Since alkanes undergo combustion easily, they are a good source of energy (e.g., gasoline). Alkanes also provide the raw materials for the production of many other more complex substances (plastics, etc.).

Physical Properties of Alkanes

- Since alkanes are composed of relatively nonpolar C—C bonds and C—H bonds, alkanes are nonpolar molecules.
- Because they have only weak attractions for each other, they tend to have lower melting points and boiling points than other organic compounds of comparable molecular weights.
- The straight chain alkanes make up a homologous series in which each members differs from a previous member by having one additional CH_2 group. In a homologous series, the physical properties are closely related and vary in a systematic way.

- The general rule when judging solubility is “like dissolves like” — polar substances mixes with polar substances, nonpolar with nonpolar, but not polar with nonpolar.
- Alkanes (nonpolar) are insoluble in water (polar), and since they are less dense than water, they float (e.g., oil slicks).
- Alkanes and other substances that do not dissolve in water are often referred to as being hydrophobic (“water fearing”).
- Liquid alkanes of high molecular weight serve as emollients (skin softeners) to replace oils washed away by bathing or swimming. – Vaseline is a semisolid mixture of alkanes.

Some Common Alkanes

- **Methane, CH₄**

major component of natural gas (~85%), which is produced by bacterial decomposition of organisms in the absence of oxygen (marsh gas, cow flatulence). – burns cleanly, so is useful for cooking, odorless — ethanethiol is added to make natural gas leaks detectable.

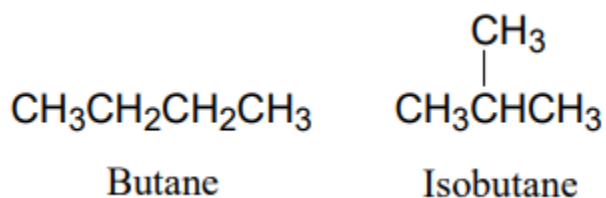
- **Ethane, CH₃CH₃ (C₂H₆)**

a minor component of natural gas (~10%).

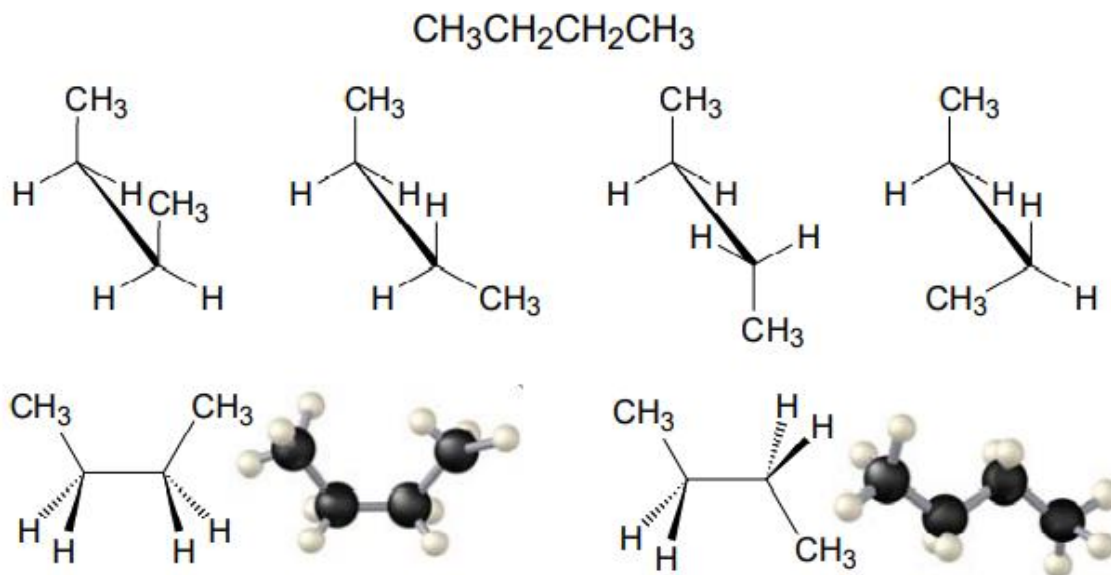
- **Propane, CH₃CH₂CH₃ (C₃H₈)** — used as an industrial fuel, and in home heating and cooking.

- **Butane, CH₃CH₂CH₂CH₃ (C₄H₁₀)** – cigarette lighters – Butane is an unbranched (normal) alkane. There is also a branched alkane with the

formula C_4H_{10} , having a three-carbon chain with a one-carbon group connected to the middle. – We must give the other isomer a different name: $CH_3CH(CH_3)CH_3$ [or $CH_3CH(CH_3)_2$] is named isobutane (or 2-methylpropane). – Butane and isobutane are structural isomers of each other.

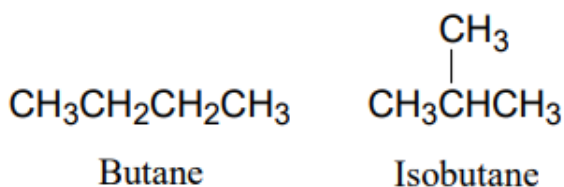


• **Conformation** — the different arrangements of atoms in space achieved by rotation about single bonds. • Structures which are related to each other by rotation around a single bond are the same molecule.

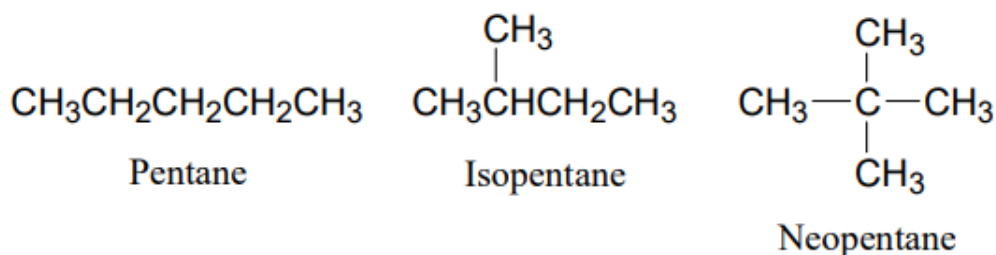


Alkane Nomenclature • Straight-chain alkanes are named by combining a prefix which indicates the number of carbon atoms in the chain, and a suffix indicating the functional group of the molecule.

When alkanes are branched, things get more complex. Remember there are two isomers of C_4H_{10} :



- There are three isomers of C_5H_{12} :



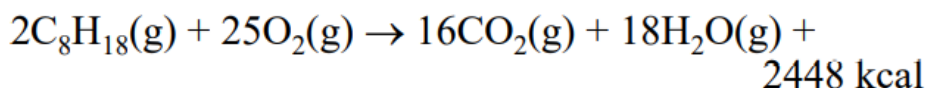
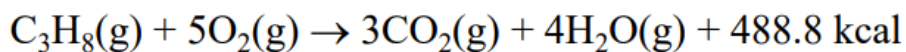
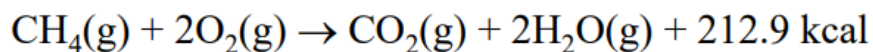
IUPAC System of Chemical Nomenclature

- The system of nomenclature used to name organic compounds was developed by the International Union of Pure and Applied Chemistry (IUPAC). – A root identifies the longest continuous chain of carbon atoms. – A suffix identifies the main functional group in the molecule. – A set of prefixes identifies the numbers and positions of the substituents (groups which are attached to the longest chain). (Alkyl groups are substituents which contain a carbon chain.)

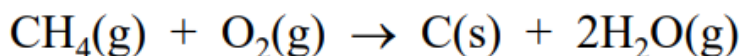
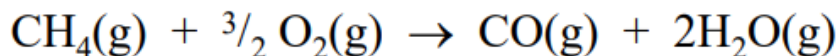
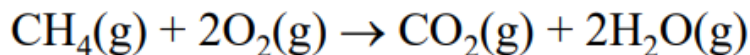
Alkane Reactions

- Alkanes are the least reactive of all organic compounds. They do not usually react with strong acids or bases, or with most oxidizing or reducing agents.

- They do, however, burn very easily in combustion reactions, releasing a great deal of energy:



- In the absence of enough oxygen for complete conversion to carbon dioxide, some common waste products are generated in the incomplete burning of alkanes:



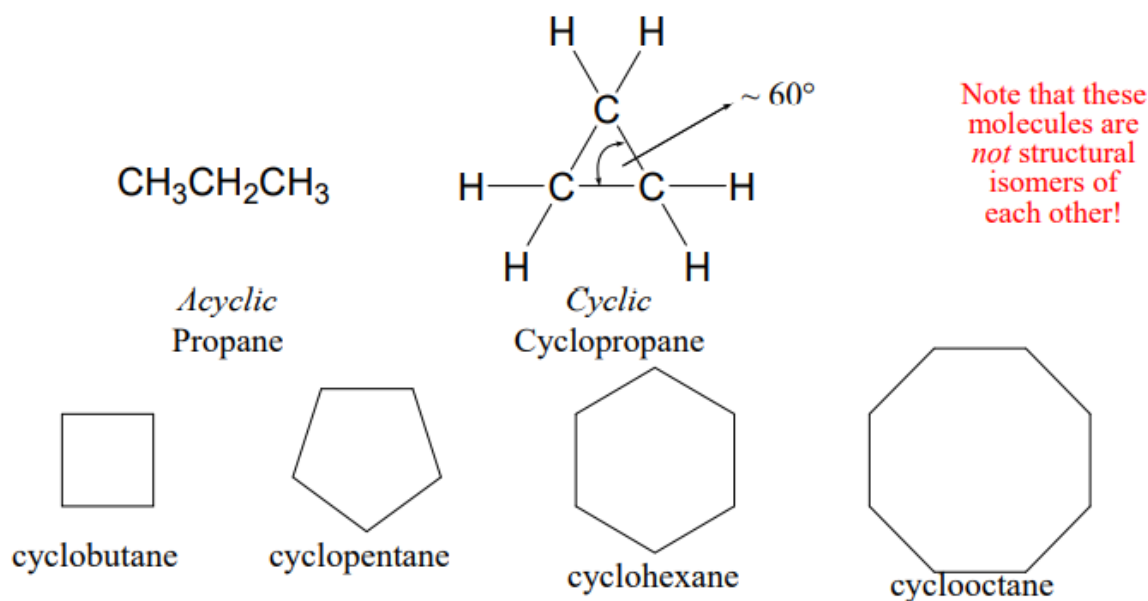
– CO, carbon monoxide, is poisonous, colorless, and odorless. In the exhaust train of most cars, a catalytic converter converts CO to CO₂.

– Solid elemental carbon produces engine deposits; but this reaction is done to produce lampblack, which is used in some ink pigments.

Chapter Two

Cycloalkanes

Alkanes may also possess cyclic structures in addition to the straight- and branched-chain acyclic molecules we have already seen. • General formula: C_nH_{2n} (for one ring)



Cycloalkane Nomenclature

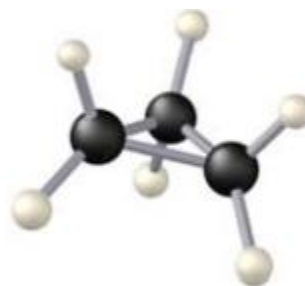
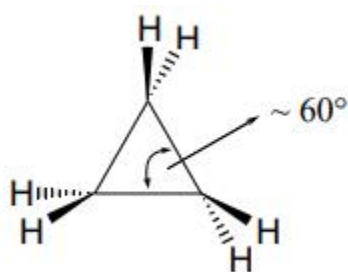
When naming cycloalkanes, the ring is taken to be the longest chain; the prefix cyclo- is added to the normal root + -suffix.

- When mono-substituted cycloalkanes are named, it is not necessary to specify the position number, since all positions in the ring are equivalent.

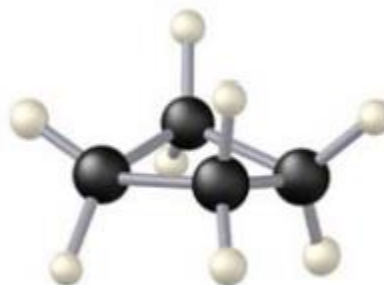
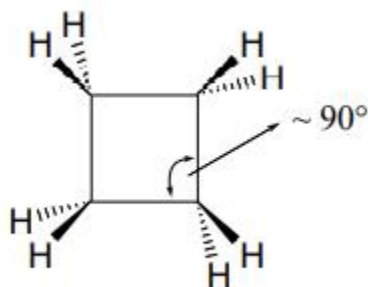
- When more than one substituent is located on a ring, the numbering begins at the carbon to which the group is attached which comes first in alphabetical order, and then proceeds in a direction which gives the lowest possible number to the next attached group.

The Shape of Cycloalkanes

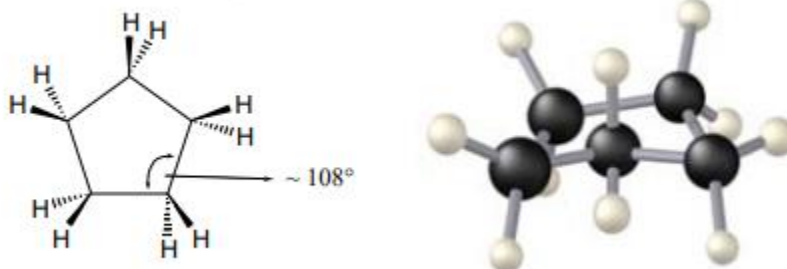
- Cyclopropane has bond angles of 60° , which is bent far away from the “normal” 109.5° bond angles of straight-chain alkanes. It is a flat molecule.



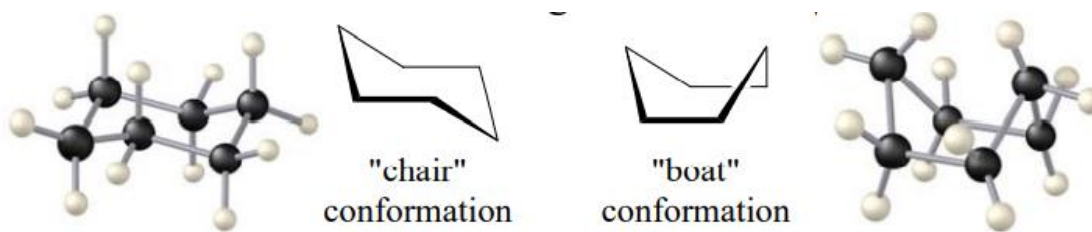
- Cyclobutane has bond angles of about 90° ; it is also less stable than a “normal” alkane. It is mostly flat, but there is some slight puckering of the ring.



Cyclopentane has bond angles of about 108° ; it forms a mostly flat but slightly puckered ring. Cyclopentane rings are very common in nature.



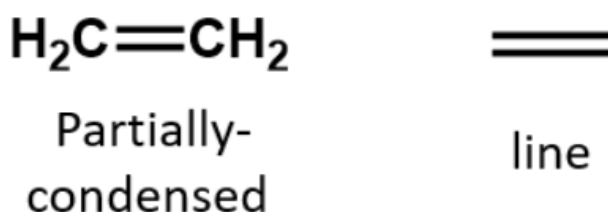
If cyclohexane were flat, the bond angles would be about 120° ; but this molecule can adopt a “chair” or “boat” conformation in which the bond angles are 109.5° . Cyclohexane rings are extremely common.



Chapter Three

alkenes are hydrocarbons with one or more carbon-carbon double bonds ($R_2C=CR_2$), while alkynes are hydrocarbons with one or more carbon-carbon triple bonds ($R-C\equiv C-R$). Collectively, they are called unsaturated hydrocarbons, which are defined as hydrocarbons having one or more multiple (double or triple) bonds between carbon atoms. As a result of the double or triple bond nature, alkenes and alkynes have fewer hydrogen atoms than comparable alkanes with the same number of carbon atoms.

In an alkene, the double bond is shared by the two carbon atoms and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious, ie the condensed formula for ethene is CH_2CH_2 . The double or triple bond nature of a molecule is even more difficult to discern from the molecular formulas. Note that the molecular formula for ethene is C_2H_4 , whereas that for ethyne is C_2H_2 . Thus, until you become more familiar the language of organic chemistry, it is often most useful to draw out line or partially-condensed structures, as shown below:



Properties of Alkenes

The physical properties of alkenes are similar to those of the alkanes. Table 8.1 shows that the boiling points of straight-chain alkenes increase with increasing molar mass, just as with alkanes. For molecules with the same

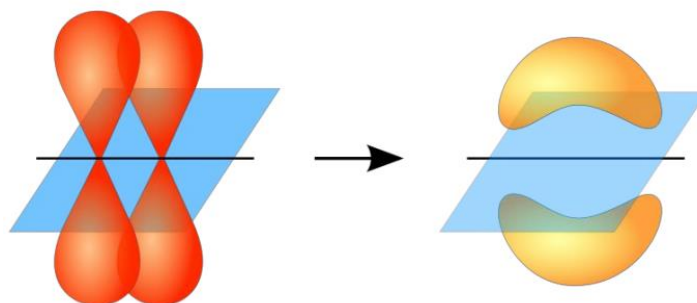
number of carbon atoms and the same general shape, the boiling points usually differ only slightly, just as we would expect for substances whose molar mass differs by only 2 u (equivalent to two hydrogen atoms). Like other hydrocarbons, the alkenes are insoluble in water but soluble in organic solvents

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C ₂ H ₄	CH ₂ =CH ₂	-169	-104
propene	C ₃ H ₆	CH ₂ =CHCH ₃	-185	-47
1-butene	C ₄ H ₈	CH ₂ =CHCH ₂ CH ₃	-185	-6
1-pentene	C ₅ H ₁₀	CH ₂ =CH(CH ₂) ₂ CH ₃	-138	30
1-hexene	C ₆ H ₁₂	CH ₂ =CH(CH ₂) ₃ CH ₃	-140	63
1-heptene	C ₇ H ₁₄	CH ₂ =CH(CH ₂) ₄ CH ₃	-119	94
1-octene	C ₈ H ₁₆	CH ₂ =CH(CH ₂) ₅ CH ₃	-102	121

Geometric Isomers

Within alkane structure there is free rotation about the carbon-to-carbon single bonds (C–C). In contrast, the structure of alkenes requires that the carbon atoms form a double bond. Double bonds between elements are created using p-orbital shells (also called pi orbitals). These orbital shells are shaped like dumbbells rather than the circular orbitals used in single bonds. This prevents the free rotation of the carbon atoms around the double bond, as it would cause the double bond to break during the rotation (Figure 8.7). Thus, a single bond is analogous to two boards nailed together with one nail. The boards are free to spin around the single nail. A double bond, on the other hand, is analogous to two boards nailed together with two nails. In the

first case you can twist the boards, while in the second case you cannot twist them.

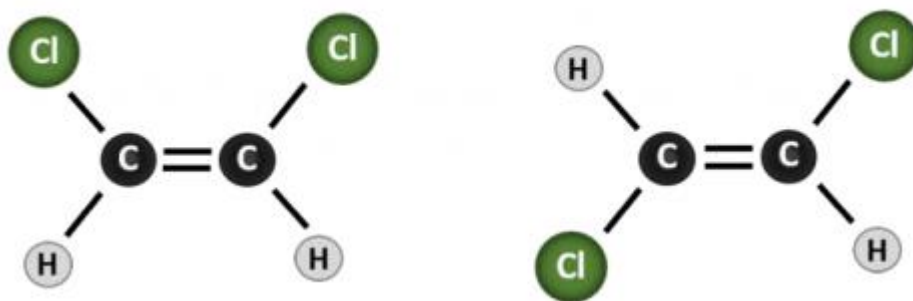


The fixed and rigid nature of the double bond creates the possibility of an additional chiral center, and thus, the potential for stereoisomers. New stereoisomers form if each of the carbons involved in the double bond has two different atoms or groups attached to it. For example, look at the two chlorinated hydrocarbons in Figure 8.8. In the upper figure, the halogenated alkane is shown. Rotation around this carbon-carbon bond is possible and does not result in different isomer conformations. In the lower diagram, the halogenated alkene has restricted rotation around the double bond. Note also that each carbon involved in the double bond is also attached to two different atoms (a hydrogen and a chlorine). Thus, this molecules can form two stereoisomers: one that has the two chlorine atoms on the same side of the double bond, and the other where the chlorines reside on opposite sides of the double bond.

Cis-Trans Nomenclature

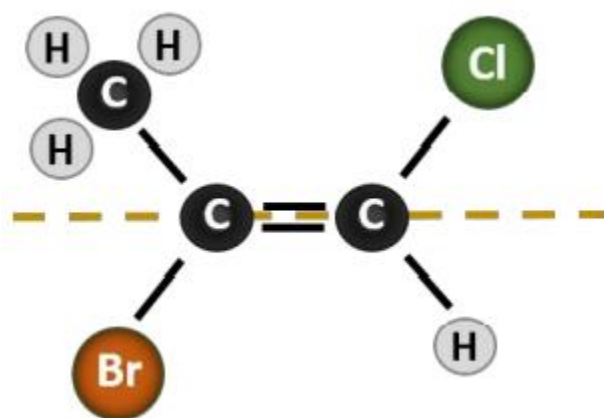
The cis-trans naming system can be used to distinguish simple isomers, where each carbon of the double bond has a set of identical groups attached to it. For example, in Figure 8.8b, each carbon involved in the double bond,

has a chlorine attached to it, and also has hydrogen attached to it. The cis and trans system, identifies whether identical groups are on the same side (cis) of the double bond or if they are on the opposite side (trans) of the double bond. For example, if the hydrogen atoms are on the opposite side of the double bond, the bond is said to be in the trans conformation. When the hydrogen groups are on the same side of the double bond, the bond is said to be in the cis conformation. Notice that you could also say that if both of the chlorine groups are on the opposite side of the double bond, that the molecule is in the trans conformation or if they are on the same side of the double bond, that the molecule is in the cis conformation. To determine whether a molecule is cis or trans, it is helpful to draw a dashed line down the center of the double bond and then circle the identical groups, as shown in figure 8.9. Both of the molecules shown in Figure 8.9, are named 1,2-dichloroethene. Thus, the cis and trans designation, only defines the stereochemistry around the double bond, it does not change the overall identity of the molecule. However, cis and trans isomers often have different physical and chemical properties, due to the fixed nature of the bonds in space.



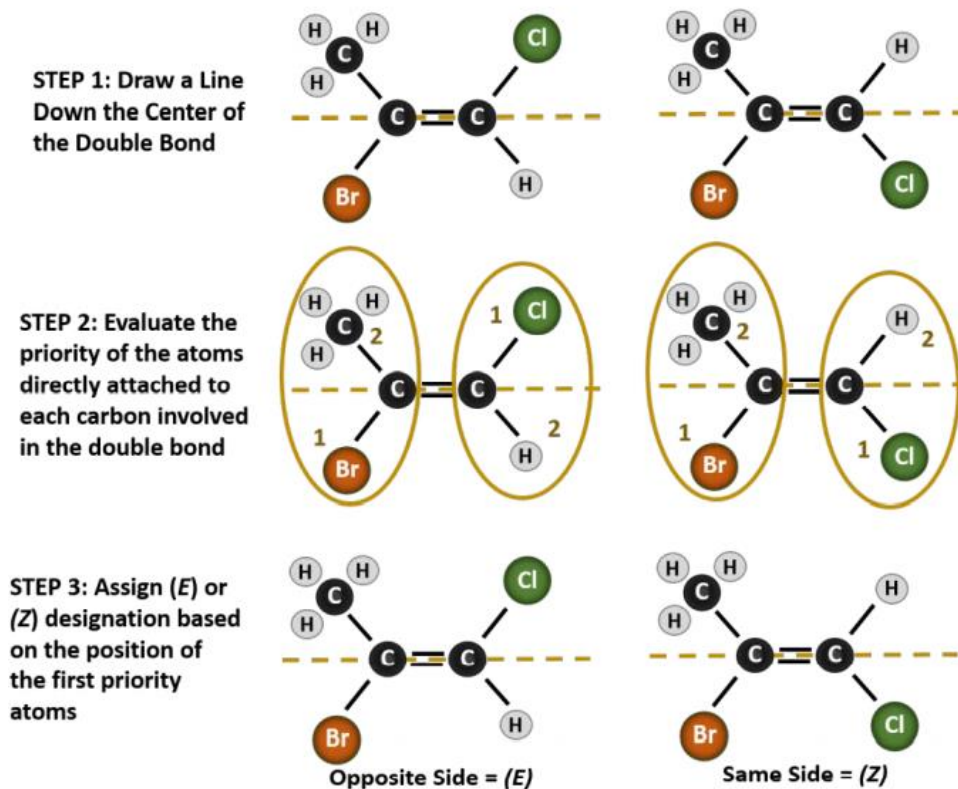
E-Z Nomenclature

The situation becomes more complex when there are 4 different groups attached to the carbon atoms involved in the formation of the double bond. The cis-trans naming system cannot be used in this case, because there is no reference to which groups are being described by the nomenclature. For example, in the molecule below, you could say that the chlorine is trans to the bromine group, or you could say the chlorine is cis to the methyl (CH_3) group. Thus, simply writing cis or trans in this case does not clearly delineate the spatial orientation of the groups in relation to the double bond.



Naming the different stereoisomers formed in this situation, requires knowledge of the priority rules. Recall from chapter 5 that in the Cahn-Ingold-Prelog (CIP) priority system, the groups that are attached to the chiral carbon are given priority based on their atomic number (Z). Atoms with higher atomic number (more protons) are given higher priority (i.e. $\text{S} > \text{P} > \text{O} > \text{N} > \text{C} > \text{H}$). For this nomenclature system the designations of (Z) and (E) are used instead of the cis/trans system. (E) comes from the German word entgegen, or opposite. Thus, when the higher priority groups are on the opposite side of the double bond, the bond is said to be in the (E)

conformation. (Z), on the other hand, comes from the German word *zusammen*, or together. Thus, when the higher priority groups are on the same side of the double bond, the bond is said to be in the (Z) conformation.



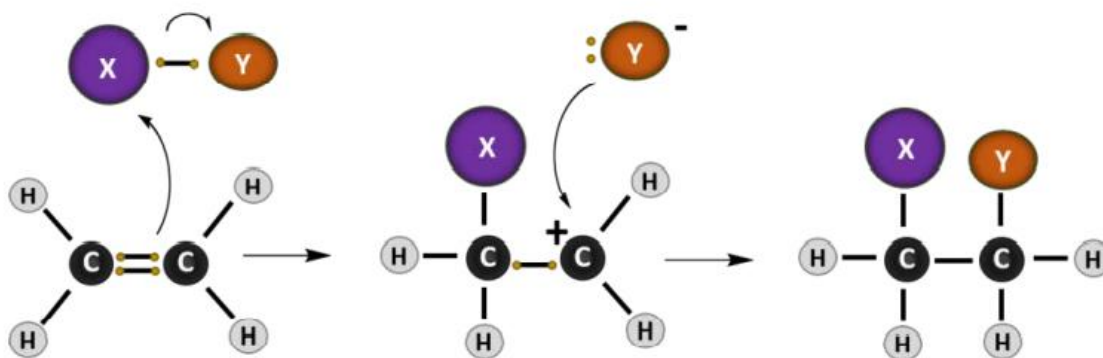
Reactions of Alkenes

As we saw in Chapter 7, small alkanes can be formed by the process of thermal cracking. This process also produces alkenes and alkynes. In comparison to alkanes, alkenes and alkynes are much more reactive. In fact, alkenes serve as the starting point for the synthesis of many drugs, explosives, paints, plastics and pesticides. Alkenes can undergo five major types of reactions: (1) Combustion Reactions, (2) Addition Reactions, (3) Elimination Reactions, (4) Substitution Reactions, and (5) Rearrangement Reactions. Since combustion reactions were covered heavily in Chapter 7,

and combustion reactions with alkenes are not significantly different than combustion reactions with alkanes, this section will focus on the later four reaction types.

Addition Reactions

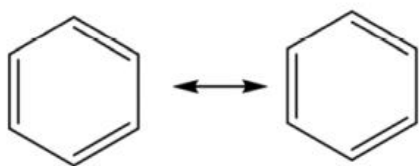
Most reactions that occur with alkenes are addition reactions. As the name implies, during an addition reaction a compound is added to the molecule across the double bond. The result is loss of the double bond (or alkene structure), and the formation of the alkane structure. The reaction mechanism of a reaction describes how the electrons move between molecules to create the chemical reaction. Note that in reaction mechanism diagrams, curved arrows are used to show where electrons are moving. The reaction mechanism for a generic alkene addition equation using the molecule X-Y is shown below:



Chapter Four

Alkynes

Benzene Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons. Aromatic hydrocarbons are compounds that contain a benzene ring structure. The simplest aromatic compound is benzene (C_6H_6) and it is of great commercial importance, but it also has noteworthy deleterious health effects (see “To Your Health: Benzene and Us”). The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14} — eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. This is due to the resonance structure formed from the alternating double bond structure of the aromatic ring.



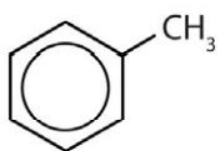
The benzene ring structure is stabilized by resonance. One of the few reactions that benzene rings will undergo are substitution reactions.

Benzene is a liquid that smells like gasoline, boils at $80^\circ C$, and freezes at $5.5^\circ C$. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product

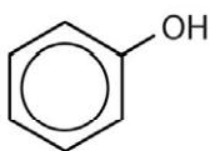
formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called aplastic anemia, in which there is a decrease in the numbers of both the red and white blood cells.

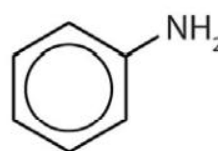
Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated below.



Toluene



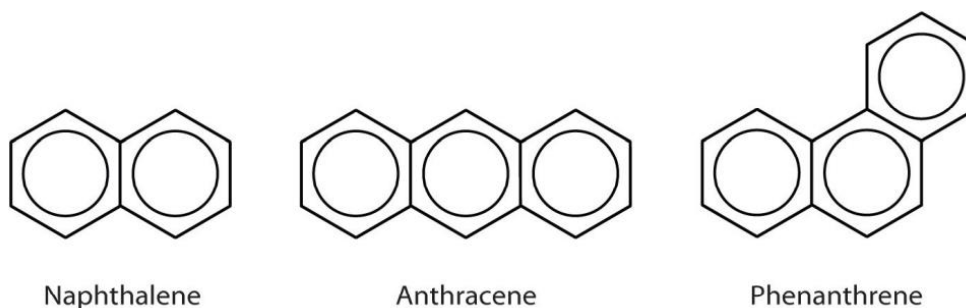
Phenol



Aniline

Polycyclic Aromatic Hydrocarbons

Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs). An aromatic hydrocarbon consisting of fused benzene rings sharing a common side.



The three examples shown here are colorless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odor and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, including cholesterol and the hormones, estrogen and testosterone, contain the phenanthrene structure.

Substitution Reactions

Due to the high reactivity of alkenes, they usually undergo addition reactions rather than substitution reactions. The exception is the benzene ring. The double-bonded structure of the benzene ring gives this molecule a resonance structure such that all of the carbon atoms in the ring share a continually rotating partial bond structure.

Thus, the overall structure is very stable compared to other alkenes and benzene rings do not readily undergo addition reactions. They behave more similarly to alkane structure and lack chemical reactivity. One of the few

types of reactions that a benzene ring will undergo is a substitution reaction. Recall from Chapter 7 that in substitution reactions an atom or group of atoms is replaced by another atom or group of atoms. Halogenation is a common substitution reaction that occurs with benzene ring structures. In the diagram below, notice that the hydrogen atom is substituted by one of the bromine atoms.

