SCH 2108: CHEMISTRY II LECTURE NOTES

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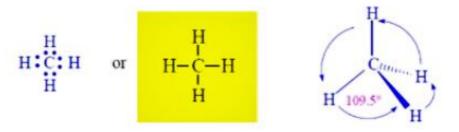
ORGANIC CHEMISTRY

Organic chemistry covers a large class of molecules, all of which contain carbon and hydrogen.

Other elements can also be found in molecules that are considered to be organic, such as nitrogen, oxygen, sulfur, and phosphorous.

Unique properties of Carbon

 Carbon is tetravalent i.e it has four valence electrons and therefore can form four strong covalent bonds with other carbon atoms or other elements (H₂, N₂, S, Br etc.). Eg CH₄



The arrangement of atoms, which is a tetrahedron with angles of 109.5° between hydrogens.

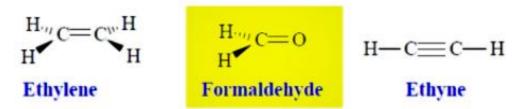
The arrangement in space about the central carbon can be explained in very simple terms. Each covalent bond contains two electrons and constitutes a region of negative charge. Since four such regions in space must repel one another, they will be as far apart as possible and this puts the hydrogens at the corners of a tetrahedron.

Catenation is the ability of carbon to form very long chains of interconnecting C-C bonds.

Carbon-carbon bonds are strong, and stable and this property allows carbon to form an almost infinite number of compounds; in fact, there are more known carbon-containing compounds than all the compounds of the other chemical elements combined except those of hydrogen (because almost all organic compounds contain hydrogen as well).

CH3-CH2-CH2-CH2-CH2-CH3

 Carbon can form multiple bonds including double (alkenes -C=C-), or triple bonds with other carbon atoms (alkynes -C=C-) or other elements e.g Nitrogen.



 Carbon can also form an enormous variety branched compounds and rings of various sizes.



Hydrocarbons

Hydrocarbons are compounds composed only of carbon and hydrogen atoms.

Hydrocarbons provide the backbone of all organic compounds.

Each carbon atom in a hydrocarbon forms a total of four bonds.

These bonds are combinations of single bonds with hydrogen atoms and single or multiple bonds with other carbon atoms.

Hydrocarbons are classified into alkanes (carbon atoms in the structure are joined by single bonds), alkenes (at least two carbon atoms in the structure are joined by a double bond), and alkynes (at least two carbon atoms in the structure are joined by a triple bond).

Organic Compounds occur as:

- Straight chains: aliphatic
- Branched compounds
- Rings

Formulas for representation of hydrocarbons

 A two-dimensional structural formula of a hydrocarbon shows all of the atoms with all of their bonds in the plane of the page.



 A condensed structural formula includes all of the atoms but uses line bonds to emphasize the main structural characteristics of the molecule. Eg., for Heptane

Taking out the lines representing the carbon-carbon bonds condenses this formula to:

Since heptane has five repeating —CH₂— groups, called methylene groups. The formula can be further condensed to:

 Bond-line formulas represent the carbon atoms as the intersection of lines and as line ends. You assume all the hydrogen atoms needed to complete carbon's valences.



nonane

NOMENCLATURE OF HYDROCARBONS

Organic compounds are arranged into classes according to the particular functional groups that they contain.

Members of each class of compounds share common chemical and physical characteristics.

The names of organic compounds are assigned according to the class of the compound as determined by the functional groups.

IUPAC Guidelines on nomenclature of organic compounds

Although called *trivial names* are known for many organic compounds, they are used colloquially and where it is simplest.

However, a **systematic nomenclature** system that chemists use has been adopted by the International Union of Pure and Applied Chemistry (IUPAC) and is internationally accepted as the standard.

Under this system one name fits one structure, and each name identifies a structure unambiguously.

- 1. A systematic name consists of three parts:
 - A prefix: appears before the stem name, and indicates a substituent on the chain (a substituent may be regarded as a group replacing hydrogen in the parent alkane).
 - A stem: identifies the longest carbon chain (parent alkane): It is the main part of
 the name, or it gives an indication of the particular alkane on which the name is
 based and indicates the number of carbon atoms in the longest carbon chain
 present in the compound.

For rings the word "cyclo" is added before the stem name

A suffix: identifies the type of compound and appears at the end .eg A suffix ane on the name of an organic compound indicates an alkane.

A suffix -ane on the name of an organic compound indicates an alkane, -ene alkenes and -yne for alkynes

NB: Before the stem name, a prefix indicates a substituent (a substituent may be regarded as a group replacing hydrogen in the parent alkane).

Both the nature and position of a substituent must be indicated and are included in the name.

No of carbons	Parent/stem name	Alkane	Ring
1C	Meth	Methane	
2C	Eth	Ethane	
3C Prop		Propane	cyclopropane
4C	But	Butane	cyclobutane
			U.

5C	Pent	Pentane	cyclopentane
6C	Hex	Hexane	cyclohexane
7C	Hept	Heptane	cycloheptane
8C	Oct	Octane	cyclooctane
9C	Non	Nonane	cyclononane
10C	Dec	Decane	cyclodecane
11C	Undec	Undecane	undecane
12C	Dodec	Dodecane	cyclododecane

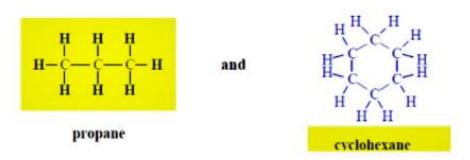
Common prefixes for substituents derived from alkanes

For any alkane, the corresponding group is termed an alkyl substituent.

No of carbons	Prefix/substituent name name	Formula		
1C	Methyl	-CH ₃		
2C	Ethyl	-CH ₂ CH ₃		
3C	Propyl	-CH ₂ CH ₂ CH ₃		
4C	Butyl	-CH ₂ CH ₂ CH ₂ CH ₃		
5C	Pentyl	-CH ₂ CH ₂ CH ₂ CH ₂ CH ₃		
6C	Hexyl	-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃		
R-H	R-	-alkyl		

Steps followed when naming organic Compounds

 Give the parent name for the structre by counting the number carbons in the longest chain or ring. Eg: longest chain 3c = propane, ring 6C = cyclohexane



Number the carbon atoms along the chain to give the lowest number for the position of the substitutuent.

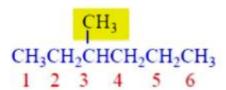
3. Next name the substituent and indicate its position (by a prefix)

The name of the prefix is methyl comes from methane: it is an alkyl substituent.

Position of the prefix = 2

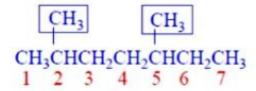
unambiguous name is 2-methylhexane

The compound we have named is different



3-methylhexane

For multiple substituents give each substituent a number to indicate its position, and
indicate the number substituents by the appropriate prefix: di: two, tri: three, tetra: four
etc.



Substituents: Methyl

No of substituents: 2

Preffix: di

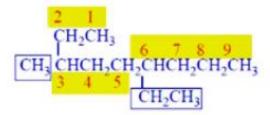
Position: 2, 5

IUPAC name: 2,5-dimethylheptane

NB: The name is not 3,6-dimethylheptane because adding the position no on the of substiteuents in2,5-dimethylheptane (2+5= 7) gives a lower number than in 3,6-dimethylheptane (3+6=9)

The numbers are separated by a "comma" while a "hyphen" separates numbers from words (i.e., the substituent and the parent alkane), words are linked and not broken with spaces

When more than one substituent is present, the alphabetical order is followed; E.g.,



Longest chain: 9 carbons; nonane

Substituents and positions methyl: 3 and ethyl: 6

Name 6-ethyl-3-methylnonane

(e comes before m alphabetically)

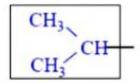
NB: The lowest numbers are used for any possible choices

6. The multiplier "di" is not considered in the alphabetizing. Hence, the name of the following alkane is 5-ethyl-2,3-dimethylheptane:

When two or more subtsituents are attached on the same carbon, the number indicating the position is repeated in the name. E.g.,

The correct name is 5-ethyl-2,2-dimethylheptane (both the methyl substitutents are attached to carbon number 2)

8. Some trivial nomenclature is retained for simple branched substituents. Eg.,



is called the isopropyl group

Examples:

4-isopropylheptane

4-isopropyl-3-methylheptane

This compound can be represented as:

other common trivially named substituents include:

secondary)

written as (CH3)3C- is tertiary-butyl or tert-butyl; tert is an

abbreviation for tertiary

Therefore trivial naming of substituents is as follows:

CH₃- CH₃-

primary (1°): 1 carbon bonded to carbon attached to chain.

secondary (2°): 2 carbons bonded to carbon attached to chain

tertiary (3°): 3 carbons bonded to carbon attached to chain

When substituents are halogen atoms, the prefixes fluoro, chloro, iodo, and bromo are used to denote the substituents. Eg.,

CH₃CH₂CH₂CH₂Br; Bromobutane

10. In ring structures the prefix cyclo- indicates presence of a ring of carbon atoms.

Such compounds are termed cycloalkanes.

4 carbon ring: Cyclobutane

6 carbon ring: cyclohexane

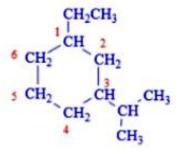
cyclopropane

methylcyclopentane

In these examples, all carbons are identical and they are not numbered.

However, sometimes numbering is necessary to define the name unambiguously and to assign the position bearing the substituent as 1.

Where more than one substituent is on the ring, the positions of the substituents must be specified in the name, e.g.



1-ethyl-3-isopropylcyclohexane.

NB: The numbering around the ring so as to give the substituents must give the lowest number.

Skeletal structures are more commonly used for cyclic compounds - the above examples become:



Alternatively, hybrids of the two conventions are often used, e.g.

Example: Name the following compound

ALKANES

There are various subdivisions in the classification of hydrocarbons.

Alkanes is a family of hydrocarbons saturated hydrocarbons in which carbons atoms are linked by single bonds.

This means that they are saturated with hydrogen, and that they do not react with hydrogen.

They are saturated because the carbon atoms are bonded to maximum no of hydrogen atom.

Also called paraffins from the Latin parum affinis, meaning "little affinity implying a lack of reactivity).

They are also referred to as aliphatics (from the Greek word aleiphar meaning "fat or oil").

Alkanes belong to a homologus series of organic compounds in which the members differ by a constant molecular mass of 14 that is CH2.

A homologous series is a group of organic compounds having similar structure and similar chemical properties in which the successive compound differs by CH2 group

The general formula for alkanes is C_nH_{2n+2}. Where n= is an integer 1, 2,

When the carbon atoms of a hydrocarbon are linked end to end, we refer to them as being straight chain compounds; a better description is unbranched chain to distinguish branched chain possibilities.

The simplest compound is methane.

No of carbons	Alkane	General Formula	Structural formula
1C	Methane	CH4	CH4
2C	Ethane	C2H6	СН3СН3
3C	Propane	C3H8	СН3СН2СН3
4C	Butane	C4H10	СН3СН2СН2СН3
5C	Pentane	C5H12	
6C	Hexane	C6H14	
7C	Heptane	C7H16	
8C	Octane	C8H18	
9C	Nonane	C9H20	
10C	Decane	C10H22	

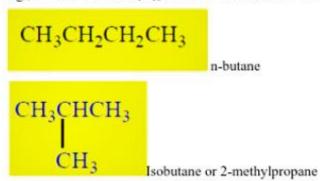
11C	Undecane	
12C	Dodecane	

ISOMERISM

Constitutional or structural isomerism: is the existence of compounds such that they have same molecular formula but differ from each other in the arrangement of attachment of the atoms in the structure.

Consequently, these are molecules which are fundamentally different from each other, having different amounts of branching in their chains or different positions of functional groups or even possessing entirely different functional groups.

Eg., For the formula C4H10 two formulas can be obtained;

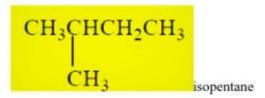


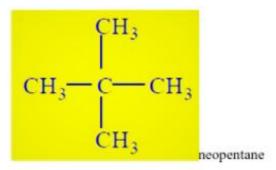
('n-' indicates a normal straight chain arrangement while the 'iso-' indicates an arrangement containing a (CH₃)₂CH- group).

These isomers have differing physical and chemical properties.

Now consider the next highest member of the alkane family, pentane C5H12.

Thus CH3CH2CH2CH2CH3 is pentane or n-pentane,





These are constitutional isomers of pentane, having the same molecular formula C5H12.

Stereoisomerism: the molecules have atoms attached together in the same order, but differ from each other in their spatial (three-dimensional) arrangement.

You will find that your understanding of this topic will be greatly helped by looking at and building three-dimensional models of the different molecules.

There are two types of stereoisomerism:

- · geometric (commonly known as cis- trans)
- · optical isomers

1. Geometric isomers (cis-trans isomers)

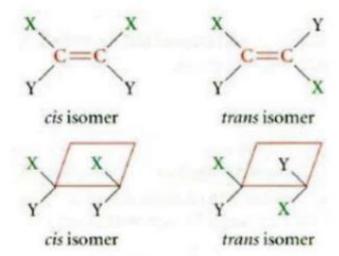
When there is some constraint in a molecule that restricts the free rotation of bonded groups, they become fixed in space relative to each other.

Where there are two different groups attached to each of the two carbon atoms that have restricted rotation, this gives rise to two different three-dimensional arrangements of the atoms known as geometric isomers.

The restriction on rotation can be caused by a double bond or a cyclic structure as shown below.

Cis- refers to the isomer that has the same groups on the same side of the double bond or ring,

trans- is the isomer that has the same groups on opposite sides, or across the point of restricted rotation.



These prefixes are given in italics before the name of the compound. Examples

Optical isomers: are molecules that differ three-dimensionally by the placement of substituents around one or more atoms in a molecule.

Optical isomers were given their name because they were first able to be distinguished by how they rotated plane-polarized light.

These molecules are not necessarily locked into their positions, but cannot be converted into one another, even by a rotation around a single bond.

For example, consider the following two molecules.



In the molecule on the left, the chlorine is oriented upward, and in the molecule on the right, the chlorine is oriented downward.

(These molecules are presented in Wedge-Dash Notation).

CYCLOALKANES

In ring structures the prefix cyclo- indicates presence of a ring of carbon atoms are formed when terminal carbon atoms in a straight or branched alkane are joined.

These have the general formula CnH2n. Examples are:

cyclobutane formed from butane:

$$CH_3$$
 CH_3 $-2H$ CH_2 CH_2 CH_2 CH_2 CH_2

Cyclohexane formed from hexane:

$$\begin{array}{c} \operatorname{CH_2} & \operatorname{CH_2} &$$

Physical properties of alkanes and cycloalkanes:

Alkanes are colourless

They are water-insoluble.

Their boiling point increases with increase in molecular weight, e.g.

	CH ₄	n-C4H ₁₀	n-C7H ₁₆	n-C ₁₀ H ₂₂
bp (°C)-162	0	98	3	174

1-4 C: Gaese

5-16C: liquids

>18C: solids

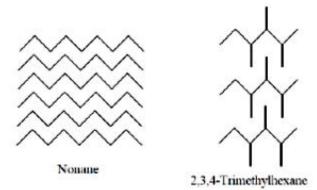
Unbranched hydrocarbons have higher boiling points than their branched isomers.

For example:

n-pentane

2,2-dimethylpropane

The unbranched chain alkanes can align themselves more closely, and hence develop stronger intermolecular forces and associations than are possible when branching of the chain is present. The greater the association between the molecules, the higher the boiling point Compare the neatly packed nonane with its constitutional isomer 2,3,4trimethylhexane:



Chemical properties of alkanes and cycloalkanes:

As their alternative name 'paraffin' implies, alkanes are inert to most common chemical reagents, including:

- · Strong acids
- Strong alkalis
- Oxidising agents (under normal laboratory conditions)
- Halogens (in the dark)

Candle wax and petroleum jelly (Vaseline) are common two high formula weight alkanic compounds Apart from their combustibility they are very stable and unreactive chemicals.

1. Combustion

It is an oxidation reaction involving burning of substances in air.

The combustion (burning) of alkanes produces water (steam) and CO2 and heat.

Similar equations can be written for petrol, which is being oxidised in enormous quantities daily in internal combustion engines.

Petrol consists mainly of a complex and variable (depending on its source) mixture of alkanes. While complete combustion of petrol would normally form just carbon dioxide and water, limited oxygen supplies leads to incomplete combustion and the formation of the toxic gas carbon monoxide and carbon (soot).

ii. Heating alkanes at high temp in presence of a catalyst results in alkenes. E.g.

iii. Cracking of alkanes

Cracking is the breaking up large hydrocarbon molecules into smaller molecules.

This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst.

The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum).

These fractions are obtained from the distillation process as liquids, but are re-vaporised before cracking.

The hydrocarbon molecules are broken up randomly to produce mixtures of smaller hydrocarbons, some of which have carbon-carbon double bonds.

One possible reaction involving the hydrocarbon C₁₅H₃₂ might be:

iv. Reaction with halogens

Alkanes react with halogens when heated or in the presence of visible light to form haloalkanes

E.g., methane, reacts with chlorine when heated or in the presence of visible light:

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

hight (hv) chloromethane

This reaction (and the oxidation reactions) needs the input of energy either electrical, thermal, or radiant energy.

After the first hydrogen atom has been replaced, the reaction can proceed further:

Molecular fluorine, bromine and iodine can undergo the same reaction with light but F₂ is explosively reactive and I₂ barely reacts at all.

Chlorine will also react by the same mechanism with other alkanes. For example with ethane:

CH₃-CH₃ → CH₃CH₂Cl + HCl chloroethane

All the hydrogens in ethane are identical, therefore only one product is formed, but with further reaction the hydrogens are not identical, and the product formed will depend on which hydrogen is replaced.

Therefore two products are obtained, CH3CHCl2 (1,1-dichloroethane) and ClCH2CH2Cl (1,2-dichloroethane).

These dichloroethanes are constitutional isomers.

For propane, the first halogenation step gives the possibility of two isomeric products:

Bromine is said to be **regloselective** in this reaction, preferring to replace the secondary hydrogen much more than a primary hydrogen (a regioselective reaction is a reaction in which one region of the molecule is more reactive than another, thus leading to selective product formation).

In this reaction, two different types of C-H bonds are broken and the relative amounts of product are dependent upon three factors:

- The ease with which the different kinds of hydrogens react with the halogen;
- The number of each kind of hydrogen in the molecule: the more hydrogens there are of any one type, the greater is the probability of the halogens reacting with them.

iii. The type of halogen.

Thus the chlorine atom has greater chance of colliding with a primary hydrogen than a secondary, so that more 1-chloropropane should be produced. Not only is collision between molecules of importance, but collision between certain parts of molecules can also have relevance in the course of a reaction.

An organic reaction involves:

- · breaking of bonds
- · Formation of bonds

These bonds are covalent; electron pairs are involved

It is the sequence in which bond breaking and bond formation occurs as well as how the energy of the system changes during a process which defines the mechanism of a reaction.

Uses of alkanes

- i. Heating
- ii. electricity generation
- iii. Cooking
- iv. production of polymers
- v. serve as intermediates in the synthesis of drugs and pesticides
- vi. components of gasoline (pentane and octane)
- vii. paraffin wax

Uses of Alkanes According to Number of Carbon Atom

- The first four alkanes are gases and are used for heating, cooking and electricity generation.
 - The main components of natural gas are methane and ethane.
 Propane and Butane are used as LPG (liquefied petroleum gas).
 - Propane is also used in the propane gas burner, butane in disposable cigarette lighters.
 - They are also used as propellants in Aerosol sprays.
- Alkane having carbon number 5-8 are volatile liquids.
 - They are used as fuels

- They are also used as solvents for nonpolar substances.
- 3. Alkanes from having carbon 9-16 form the major part of Diesel and aviation fuel.
- 4. Alkanes from 17 carbon upwards (solids) form the most important components of Fuel oil and lubricating oil also used as anti-corrosive agents, as their hydrophobic nature means that water cannot reach the metal surface.

Many solid alkanes find use as paraffin wax.

- Alkanes with 35 or more carbon atoms are used for road surfacing.
- Synthetic Polymers such as polyehtylene are alkanes with chains containing hundreds of thousands of carbon atoms.

Sources of alkanes: the two major sources of alkanes are natural gas and petroleum.

Natural gas consists of approximately 90 to 95% methane, 5 to 10% ethane, and a mixture of other relatively low-boiling alkanes (propane, butane and 2-methylpropane).

Petroleum is a thick, viscous, liquid mixture of thousands of compounds, most of them hydrocarbons, formed by the decomposition of marine plants and animals.

The fundamental separation process in refining petroleum is fractional distillation.

All crude petroleum that enters a refinery goes to distillation units, where it is heated to

FUNCTIONAL GROUPS

Functional group: an atom or group of atoms within a molecule that shows a characteristic set of predictable physical and chemical behaviors. They are they are centers of chemical reactivity. Functional groups are important in organic chemistry because:

- a) They are sites predictable chemical behavior. A particular functional group, in whatever compound it is found, undergo the same types of chemical reactions.
- Determine in large measure the physical properties of a molecule.
- Serve as the units by which we classify organic compounds into families.

temperatures as high as 370 to 425°C and separated into fractions.

d) Serve as a basis for naming organic compounds.

Examples

Alkene: defined by the C-C double bond

Benzene Ring: a special ring of carbons with alternating single and double bonds, has a special degree of stability

Alcohol: characterized by the hydroxy, -OH group. It is a very important group in monosaccharides (carbohydrates).

Sulfide: carbon groups bounded to a sulfur atom

Alkyne: defined by the C-C triple bond

Alkyl Halide: haloalkane, replace X in the drawing with a halogen from the periodic table; when drawing a haloalkane be sure to not forget the lone pairs on X.

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Ether: defined by an oxygen bounded to two carbons. The functional group of ethers can conform to many different functions, making it an important character in synthetic transformations

Amine: a carbon molecule bound to a nitrogen. The nitrogen typically has a lone pair of electrons.

Ketone: defined by a carbon double bound to an oxygen (different than an aldehyde because it can only be found in the inside of a molecular chain- the carbon does not have to be attached to a hydrogen). Ketones, aldehydes, and carboxylic acids contain the carbonyl functional group: C double bound to O.

Aldehyde: defined by a carbon double bound to an oxygen and single bound to hydrogen; because it is characterized by a bond to hydrogen, it can only be found at the ends of molecular chains

Carboxylic Acid: characterized by the carboxyl group; RCO2H (R being any subset of a molecule); any molecular chain bound to a carbon, this carbon has a double bond to oxygen and also attached to an alcohol group

Ester: RCO2R (R being any subset of a molecule)

Amide: contains the double bond between a carbon and an oxygen, the carbon is also bonded to a nitrogen

Imine:

Nitrile:

Acid Chlorine:

UNSATURATED HYDROCARBONS

Unsaturated Hydrocarbons — contain carbon- carbon double or triple bonds (more hydrogens can be added).

: added).

ALKENES

Alkene: an unsaturated hydrocarbon that contains one or more carbon-carbon double bonds.

The molecular formula of this group is CnH2n (n is the number of carbon atoms).

Alkenes belong to a homologus series of organic compounds in which the members differ by a constant molecular mass of 14 that is CH2.

The Suffix = -ene is added to the prefix indicating the longest carbon chain.

Alkenes have less hydrogen atoms than alkanes.

$$C_2H_4$$
, $CH_2=CH_2$, $CH_2=CH-CH_3$

In the carbon-carbon double bond, two pairs of electrons are being shared, leaving the carbon free to bond to two other atoms.

CH2CH2 ethylene, C2H4

CH2CHCH3 propylene, C3H6

IUPAC Nomenclature of Alkenes

 Step 1. Identify and name the longest continuous chain of C atoms which contains the double bond(s) (No of C +-ene).

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- Step 2. Number the longest chain so that the C's joined by the double bond have the lowest numbers possible.
- If the double bond has the same position starting from either end, use the positions of the substituents to determine beginning of the chain.
- Step 3. Locate the double bond by the lower- numbered carbon atom joined by the double bond (e.g., 1-butene).
- 5. Step 4. Locate and name attached groups.
- Step 5. Combine the names for the attached groups and the longest chain into the name.

Example 1: Provide the IUPAC names for the following compounds

- If there is more than one double bond:

 a counting prefix (di-, tri-, tetra-, etc.) is placed immediately in front of the suffix -ene to indicate the number of double bonds (diene, triene, tetraene, etc.).
- Usually, an "a" is placed before the counting prefix to make pronunciation easier (e.g., butadiene). – The starting position of each double bond is indicated by the lower number, separated by commas (e.g., 1,3-butadiene).
- 10. For cycloalkenes, the ring is named as cyclo- + no of C + -ene; one of the carbons of the double bond must be numbered "1."

Example 2: Provide the IUPAC names for the following compounds

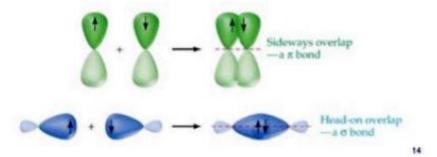
Example 3: Draw structural formulas for the following molecules:

- 2-methyl-2-butene
- · 4-methyl-1-pentene
- 2-methyl-3-pentene (what's wrong with this name?)
- · 4-ethyl-3-hexene (what's wrong with this name?)
- 2,3,4-trimethyl-1,3-pentadiene
- 1,6-dimethylcyclohexene
- 5-ethyl-1,3-cyclopentadiene

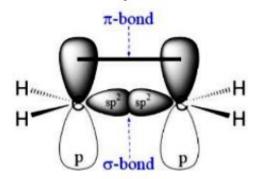
Bonding in Ethylene

When two sp²-hybridized carbons are next to each other, two kinds of orbital overlap take place:

- end-on-end overlap of the sp² orbitals to make a σ-bond (sigma bond).
- side-to-side overlap of the unhybridized p orbitals to make a π-bond (pi bond).



Because of the π -bond, free rotation is not possible around carbon-carbon double bonds.



The Shape of the Ethylene Molecule.

Since each carbon in the double bond is trigonal planar in shape, the entire ethylene molecule is a flat molecule, with the atoms separated by bond angles of 120°.

Exercise:

1. Are the following molecules geometric isomers of each other, or are they the same molecule?

Draw the two geometric isomers of the following molecule: CHClCHCH₃