

Study Guide Chapters 19-20
Alkanes, Alkenes and Alkynes

- 1) Carbon-Carbon Bonding in Alkanes (C-C), Alkenes (C=C) and Alkynes (C≡C). Understand the hybridization of atomic orbitals (ground state → promotion → hybridization) and the formation of sp³, sp², and sp bonds. Understand the difference between sigma (σ) and pi (π) bonding and the formation of C=C and C≡C. Understand the molecular geometry (bond angles, flexible or rigid). See previous hand out for more details.
- 2) Functional Groups: First 4 lines of Table 19.1 p 501 (Alkanes, Alkenes, Alkynes, Alkyl Halides). In addition be familiar with Cyclic and Aromatic molecules.
- 3) Isomers: Molecules with the same formula but different structure. Recognize isomers. Draw all isomers for a given formula.
- 4) Naming Alkanes: Numerous examples have been provided in your notes, homework and extra credit assignments to illustrate naming of organic molecules. Study them well. Below is a rough summary of the IUPAC rules for naming alkanes. Names for the first 10 straight-chain Alkanes are found in Table 19.2 p504. Memorize the names as they are the base for all organic compounds.
 - a. Identify longest chain and branch/side-chains.
 - b. Number the carbon atoms from one end of the parent chain such that the side chains begin with the lowest possible number.
 - c. Name each branch/side-chain and designate its position on the parent carbon chain by number. Names for side chains between 1 and 10 carbons long and selected special groups are found in Table 19.3 p 511. It is strongly recommended that you memorize this table. Ignore the special groups (on the right side of the table).
 - d. Side-chains occurring multiple times should be indicated by the prefix (di, tri, tetra etc.) written in front of the side-chain.
 - e. Order side chains in alphabetical order.
 - f. Use the prefix “cyclo” when naming the parent chain of cyclic alkanes.
- 5) Chemistry of Alkanes: Recognize the reaction conditions and be able to identify reactants or product for typical reactions that alkanes undergo.
 - a. Substitution: one atom of a molecule is exchanged by another atom or group of atoms.
 - i. Halogenation: Alkane + Halogen → Alkyl halide + Acid

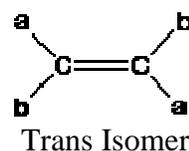
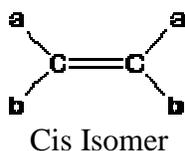
Ex: $\text{RH} + \text{X}_2 \rightarrow \text{RX} + \text{HX}$ (X= halogen F, Cl, Br, I)
Ex: $\text{CH}_4 + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{HBr}$
 - b. Elimination: a single reactant is split into two products and one of the products is eliminated
 - i. Dehydrogenation: Alkane → Alkene + something (generally H₂)

Ex: $\text{C}_n\text{H}_{2n+2} \rightarrow \text{C}_n\text{H}_{2n} + \text{H}_2$
Ex: $\text{CH}_3\text{CH}_3 \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2$
 - ii. Loss of Acid: Alkyl Halide → Alkene + Acid

Ex: $\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{CH}_2=\text{CH}_2 + \text{HCl}$
 - c. Addition: Adding two reactants together to form a single product (opposite of elimination)



- 6) Cycloalkanes: General formula C_nH_{2n} . Naming (see #4 above). Conformations (chair and boat), Equatorial and Axial hydrogens
- 7) Naming Alkenes and Alkynes: Use the above rules and the additional rules below.
- Follow the above rules, but the main chain should contain the (C=C or C≡C).
 - When naming the parent chain for C=C change the “ane” ending to “ene”. When naming the parent chain for C≡C change the “ane” ending to “yne”.
 - Place a number in front of the parent name indicating where the double bond occurs. Numbering should be such that the C=C has the lowest possible number.
- 8) Geometric Isomerism in Alkenes (Cis/Trans):
- Same formula, same structure, different geometry.
 - Compound containing C=C have a restricted rotation about the double bond. This restriction gives rise to geometric isomerism, where the molecules don't differ by the order of atoms but by their geometry of the atoms.

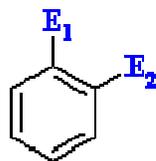


- 9) Aromatics:
- Be familiar with the bonding in the Benzene molecule (p563)
 - Naming
 - Monosubstituted Benzenes: memorize the 6 molecules below. They take precedence when naming a molecule over the benzene ring. Always start numbering, or determining ortho, meta, para (see below) from the functional group in the table.

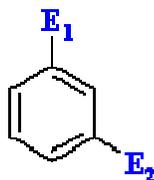
 Nitrobenzene	 Aniline	 Phenol
 Benzaldehyde	 Benzoic Acid	 Toluene

ii. Disubstituted Benzenes: Use when neither substituent is one with a special name (see table above) or when only two side chains are present.

1. ortho (o) – side chains are adjacent
2. meta (m) – side chains are one apart (an empty carbon between them)
3. para (p) – side chains are on opposite sides of the benzene ring



ortho-



meta-



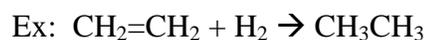
para-

iii. Polysubstituted Benzenes: When there are 3 or more substituents number the rings to give the lowest numbering, if tied, then alphabetically). If the compound is one of the special ones (see figure in section i) then the special group is considered to be on carbon 1. (See p 563 for more details)

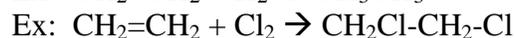
10) Chemistry of Alkenes and Alkynes:

a. Addition:

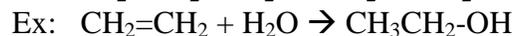
i. Alkene + Hydrogen \rightarrow Alkane



ii. Alkene + Halogen \rightarrow Haloalkane



iii. Alkene + $\text{H}_2\text{O} \rightarrow$ Alcohol

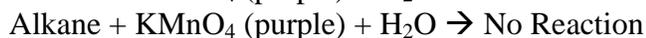
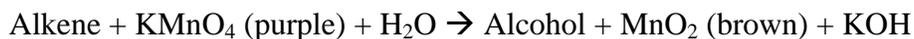


b. Markovnikov's Rule for Addition reactions (p555) When an unsymmetrical molecule (HX) adds to a C=C, the hydrogen from HX goes to the carbon atom that has the greater number of hydrogen atoms.



c. Carbocation Stability: Tertiary (3°). > Secondary (2°) > Primary (1°) > CH_3^+ (p 538)

d. Oxidation (Baeyer Test p. 557): This test is a standard way to differentiate between Alkanes (no reaction) and Alkenes (color changes from purple \rightarrow brown).



11) Chemistry of Aromatics

a. Aromatic Substitutions: (see p. 569 for more details)

Halogenation	<chem>c1ccccc1.ClCl>>c1ccccc1Cl.Cl</chem>
Nitration	<chem>c1ccccc1.O=[N+]([O-])O>>c1ccccc1[N+](=O)[O-].O</chem>
Alkylation	<chem>c1ccccc1.CC(Cl)C>>c1ccccc1C.Cl</chem>

b. Aromatic/Side-Chain Oxidation: (see p. 571)

Side Chain Oxidation	<chem>CCCC1=CC=CC=C1.O=O>>OC(=O)C1=CC=CC=C1.CC(=O)O</chem>
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12) Physical Properties of Alkanes, Alkenes, Alkynes, Aromatics

Property	Alkanes	Alkene	Alkynes	Aromatics
Bonding	C-C only	at least one C=C	at least one C≡C	Benzene Ring
Hydrogen bonding	No	No	No	No
B _p and M _p	Low	< Alkanes	< Alkanes	
Polarity	Non-polar	Non-polar	Non-polar	Non-polar
Solubility (in H ₂ O)	Insoluble	Insoluble	Insoluble	Insoluble

12) Bonding in Alkanes, Alkenes, and Alkynes.

Property	Alkanes	Alkenes	Alkynes
Bond Type	Single bond C-C	Double bond C=C	Triple bond C≡C
Bond Angle	109.5° - flexible	120° - rigid	180° - rigid
Bonding Orbitals			
Orbitals used for Carbon-Carbon bond	4 - sp^3	3 - sp^2 1 - p	2 - sp 2 - p
Sigma (σ) and Pi (π) Bonds	1 - sp^3	1 - sp^2 1 - p	1 - sp 2 - p
Hybridization	1 - σ	1 - σ 1 - π	1 - σ 2 - π
Shape of Orbitals	Tetrahedral	Trigonal Planar	Linear
Illustrations	Figure 1 below Hein Figure 19. (p505)	Figure 2 below Hein Figure 20.2 (p539)	Figure 3 below Hein Figure 20.4 (p540)

Figure 1: Hybridization of orbitals in Ethane (C-C single bond)

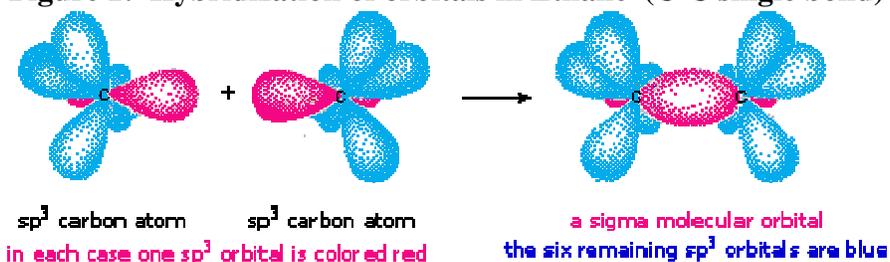


Figure 2: Hybridization of orbitals in Ethene (C=C double bond)

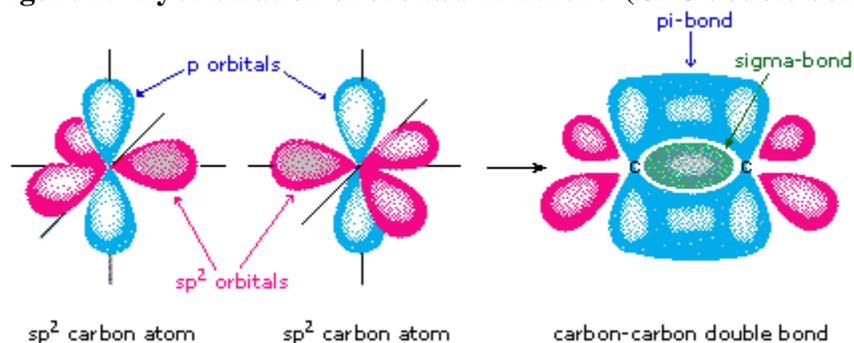


Figure 3: Hybridization of orbitals in Ethyne (C≡C triple bond)

