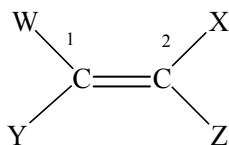


I. DEFINITION & STRUCTURE OF ALKENES (Section 3.3)

- Alkenes (also called olefins or unsaturated hydrocarbons) are hydrocarbons that contain a C=C.
- The two carbon atoms which make up the carbon-carbon double bond are sp^2 hybridized.
- More highly substituted alkenes are more stable than less substituted alkenes.
- Trans alkenes are more stable than cis alkenes.



W, X, Y, Z = substituents on C₁ or C₂

Alkene Type	C ₁ Substitution	C ₂ Substitution
Unsubstituted	Two H atoms	Two H atoms
Monosubstituted (two possibilities)	One H atom, one other than H	Two hydrogen atoms
Disubstituted (three possibilities)	Two H atoms	One H; one other than H
	Two other than H atoms	Two H atoms
	One H, one other than H	One H, one other than H
Trisubstituted (two possibilities)	Two other than H	One H, one other than H
	One H, one other than H	Two other than H
Tetrasubstituted	Two other than H	Two other than H

II. NOMENCLATURE OF ALKENES (IUPAC) (Section 3.2)

- The suffix "ene" is used for alkenes.
- Name the parent by finding the longest, continuous carbon chain that contains the alkene functional group. Name according to the number of carbon atoms in that chain.
- Number the parent chain so as to give the lowest possible numbers to the carbon atoms of the double bond, then the lowest possible numbers to any substituents.
- If there is more than one double bond in the molecule the following suffixes are used in place of "ene":
 - Two double bonds: "diene"
 - Three double bonds: "triene"
 - Four double bonds: "tetraene"
- Only the lower number of one of the alkene carbons is used to indicate the alkene position in the name.
- CYCLOALKENES
 - Cycloalkenes are named just as cycloalkanes except the "ene" suffixes used in place of "ane".
 - For substituted cycloalkenes or for cycloalkenes that contain more than one double bond, the ring must be numbered to indicate the position of the double bond(s) relative to the substituent(s).
- ALKENES AS SUBSTITUENTS
 - When an alkene is a substituent on a larger molecule the "e" is dropped and replaced by a "yl" suffix.
 - There are some common names for alkenyl substituents.
 - Two carbon: vinyl
 - Three carbon: allyl

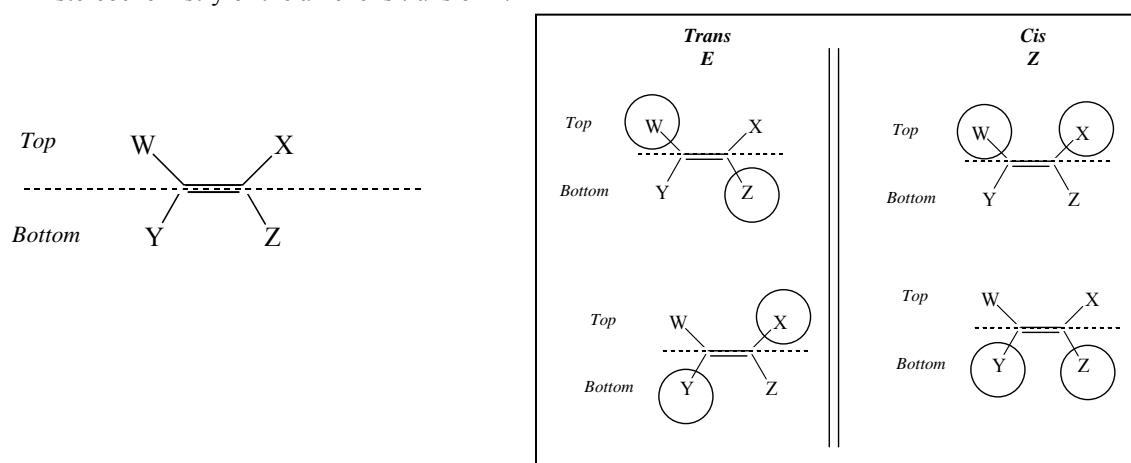
III. STEREOCHEMISTRY OF ALKENES (Section 3.4-3.6)

A. DEFINITIONS

1. A "cis" stereoisomer (also called a Z isomer) is one in which the substituents of highest priority are on the same side of the double bond.
2. A "trans" stereoisomer (also called an E isomer) is one in which the substituents of highest priority are on opposite sides of the double bond.
3. PRIORITY RULES: Priority (or sequence) rules are used to assign order of priority to substituents.
 - a. Highest priority is assigned to substituents of highest atomic number.
 - b. If priority cannot be established from atoms directly bonded to the carbon atoms of the alkene, move out along each substituent until a distinction can be made.
 - c. A carbon-carbon double bond is equivalent to a carbon atom bonded to two other carbon atoms. A carbon oxygen double bond is equivalent to a carbon bonded to two oxygen atoms.

B. DETERMINING STEREOCHEMISTRY OF ALKENES

1. Draw a dotted line along the axis of the double bond.
2. Label one side 'top' and the other side "bottom".
3. Number the two carbon atoms of the double bond as "1" and "2".
4. Prioritize the two substituents bonded to C₁. Circle the substituent of highest priority bonded to C₁.
5. Prioritize the two substituents bonded to C₂. Circle the substituent of highest priority bonded to C₂.
6. If both circled substituents are either on the top side or the bottom side, the stereochemistry of the alkene is cis or Z.
7. If one circled substituent is on the top and the other circled substituent is on the bottom, then the stereochemistry of the alkene is trans or E.



IV. DEFINITION & STRUCTURE OF ALKYNES (Section 6.4)

- A. Alkynes are hydrocarbons which contain a carbon-carbon triple bond.
- B. The carbon atoms associated with the triple bond are sp hybridized.
- C. Alkynes are classified as terminal or internal alkynes.
 1. Terminal Alkynes: One of the C atoms of the triple bond is bonded to at least one H atom
 2. Internal Alkynes: Neither C atom of the triple bond is bonded to a H atom

V. NOMENCLATURE OF ALKYNES (IUPAC rules) (Section 6.1)

- A. The suffix "yne" is used.
- B. The parent name is based on the longest carbon chain that contains the triple bond.
- C. The parent chain is numbered so as to give the alkyne carbon atoms the lowest possible numbers.
- D. Compounds which contain more than one triple bond are named in the following ways.
 1. Two triple bonds: Suffix "diyne" is used.
 2. Three triple bonds: Suffix "triyne" is used.
 3. Four triple bonds: Suffix "tetrayne" is used.
- E. Compounds which contain both a double bond and a triple bond are called "enynes".

1. The suffix "enyne" is used with numbers inserted to indicate the relative positions of the double and triple bonds (eg., 1-en-3-yne).
 2. Numbering of the parent always starts at the end nearer the multiple bond (either the double or the triple bond) to insure the lowest possible numbers for BOTH multiple bonds. Double bonds take precedent when the chain can be numbered equally in either direction.
- F. Hydrocarbon substituents derived from alkynes are called "alkynyl" groups.

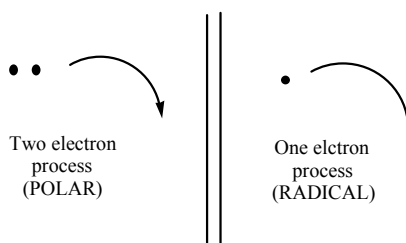
VI. REACTION MECHANISMS: DEFINITIONS

- | | | |
|------------------------|---------------------------|----------------------|
| A. Reaction Scheme | E. Electrophiles | I. Transition States |
| B. Reaction Mechanisms | F. Leaving Groups | |
| C. Reaction Conditions | G. Radical | |
| D. Nucleophiles | H. Reaction Intermediates | |

Nucleophiles	Electrophiles	Leaving Groups
Amines (N atom lone pairs)	Alkyl halide (C bonded to halogen)	Water
Alcohols (O atom lone pairs)	Proton	Halogen
Alkoxides (- on oxygen atom)	Carbocation	Tosylate
Carbanions (derived from Grignard or alkyl lithiums, alkynes)		Alcohol
Thiols, Thiolates	Aldehydes, Ketones,	Carboxylate
	Acid halides, Anhydrides	

VII. USING THE CURVED ARROW CONVENTION (Section 3.6)

- A. Arrows are used to show breaking and formation of bonds in reaction mechanisms.
- B. Double headed arrows are used to show movement of two electrons during chemical reactions.
- C. Single-headed arrows are used to show movement of one electron in a chemical reaction.



- D. The head of the arrow indicates where the electron(s) is (are) going to, and the tail indicates where the electron is coming from. The head shows where the bond is forming and the tail shows where the bond is breaking.

VIII. REACTION MECHANISMS: RADICAL & POLAR REACTIONS

- A. RADICAL REACTIONS (HOMOLYTIC PROCESS)
 1. Radical mechanisms involve the symmetrical breaking of a bond into radical intermediates. A radical reaction is a one electron process.
 2. There are two general types of radical mechanisms.
 - a. RADICAL SUBSTITUTION REACTION
 - b. RADICAL ADDITION REACTION
 3. All radical reactions proceed according to a three-step process.
 - a. INITIATION STEP: Formation of the first radical intermediate.
 - b. PROPAGATION STEP: Reaction of the radical intermediate with a second neutral molecule to give a new radical intermediate and a new neutral molecule.
 - c. TERMINATION STEP: Coupling of two radicals to give a neutral product.
- B. POLAR REACTIONS (HETEROLYTIC PROCESS)
 1. Polar reactions involve unsymmetrical breaking of bonds. A polar reaction is a two electron process.
 2. After bond cleavage, a nucleophile (e⁻ rich species) and an electrophile (e⁻ poor species) are generated.
 3. There are four types of polar reactions (i.e., additions, eliminations, substitutions and rearrangements).

IX. TYPES OF ORGANIC REACTIONS

A. ADDITION REACTIONS

Addition reactions occur when two compounds "add" together to give a single product.

Example: Electrophilic Addition

Electrophilic addition reactions are the most important reactions that alkenes undergo. Electrophilic addition is the reaction of an alkene with an electrophile. *All electrophilic addition reactions of alkenes involve a carbocation intermediate.* Reaction of hydrohalic acids with *alkenes* results in formation of Markovnikov *alkyl halides*

B. ELIMINATION REACTIONS

Elimination reactions occur when a single reactant splits apart to form two new products.

Example: E₁ and E₂ eliminations.

C. SUBSTITUTION REACTIONS

Substitution reactions occur when two reactants exchange parts to give two new products.

Example: Nucleophilic Substitutions

There are two basic types of nucleophilic substitutions of sp³ hybridized carbons bonded to a leaving group; SN₁ and SN₂ substitutions

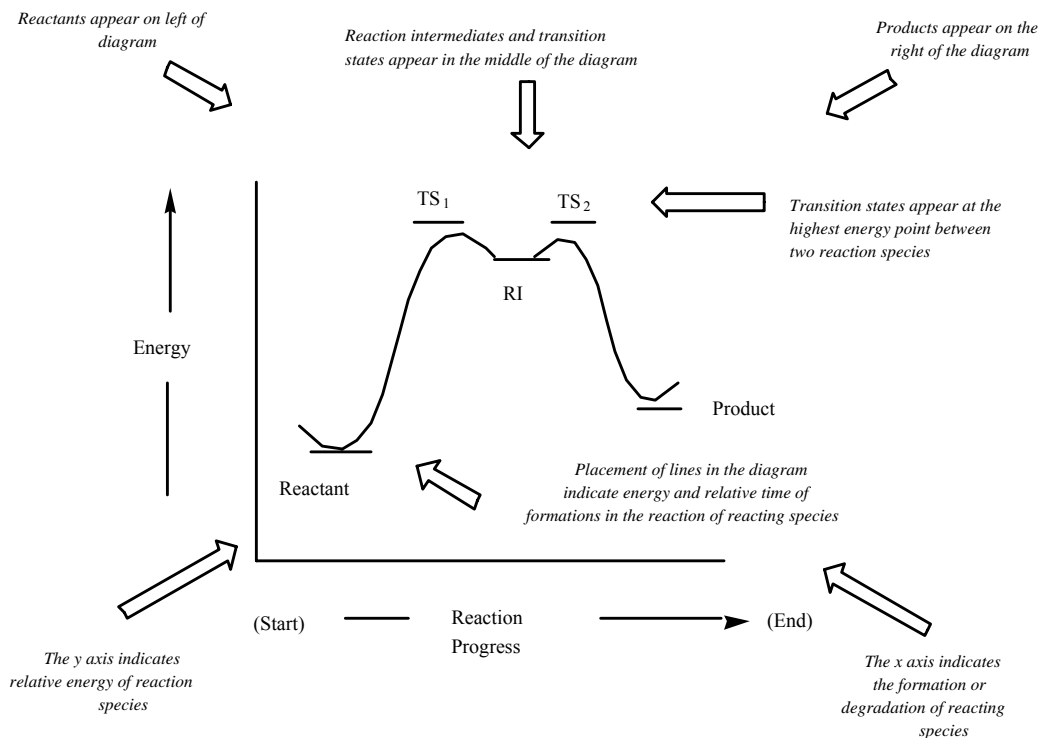
D. REARRANGEMENT REACTIONS

Rearrangement reactions occur when a single reactant reorganizes its bonds to give a new product.

Example: Rearrangements of Carbocations in an Electrophilic Addition

X. REACTION ENERGY DIAGRAMS (Section 3.8)

A reaction energy diagram describes the relative energies of all species involved in a reaction and how that reaction proceeds.



XI. EQUILIBRIA IN ORGANIC REACTIONS (THERMODYNAMICS) (Section 3.7)

The equilibrium of a reaction describes how much reactant will be converted to product during the course of the reaction.

A. EQUILIBRIUM CONSTANT

The equilibrium constant (K_{eq}) is the molar ratio of products over reactants

$$K_{eq} = P/R$$

B. THE GIBBS FREE-ENERGY EQUATION

The Gibbs Free Energy equation relates the equilibrium constant to the energy required for the reaction to occur.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{or} \quad \Delta G^\circ = -RT \ln K_{eq}$$

1. (ΔH°): The bond dissociation energy is the total energy required to homolytically break a bond into two radicals at 25°C in the gas phase.
2. (ΔS°): The entropy factor is the total disorder caused by a given reaction.
3. The free-energy (ΔG°) is the energy difference between reactants and products.
 - a. A negative ΔG° indicates the products are more stable than the reactants (EXOTHERMIC)
 - b. A positive ΔG° indicates the reactants are more stable than the product (ENDOTHERMIC)

XII. RATES OF ORGANIC REACTIONS (KINETICS) (Section 3.7)

The rate of an organic reaction describes how fast a particular reactant will be converted to a particular product.

A. REVIEW OF RATE LAWS

1. The overall rate of a reaction is measured by the rate of the slowest step of the reaction, or the rate-determining step.
2. First Order Reactions
The rate of first order reactions depends on the concentration of only 1 reacting species. The rate expression of a first order reaction is:

$$\text{Rate} = k [c]$$

Rate is expressed as the change in concentration of product in mols/L/sec. The rate constant has the units sec^{-1} . The rate constant corresponds to a rate at a specific temperature. Thus, the higher the concentration of the reacting species, the faster the rate.

3. Second Order Reactions
The rate of a second order reaction depends on the concentration of two reacting species.

$$\text{Rate} = k[a][b]$$

B. REACTION RATE AND TRANSITION STATE ENERGIES

1. A transition state is a structure representing the highest energy point along the reaction pathway.
2. The activation energy (ΔG^\ddagger) is the energy difference between the reactants and the transition state.
3. The rate of a given reaction is determined by the activation energy of the rate determining step of the reaction.
 - a. A large activation energy results in a slow reaction.
 - b. A small activation energy results in a fast reaction.

XIII. EQUILIBRIA AND REACTION RATES: THE HAMMOND POSTULATE

There is no absolute relationship between rate and equilibrium of a reaction however the Hammond Postulate relates these two quantities.

The HAMMOND POSTULATE states that the structure of the transition state can be inferred from the structure of a relatively stable species (reaction intermediate, reactant, product) nearest in energy to the transition state along the reaction pathway.