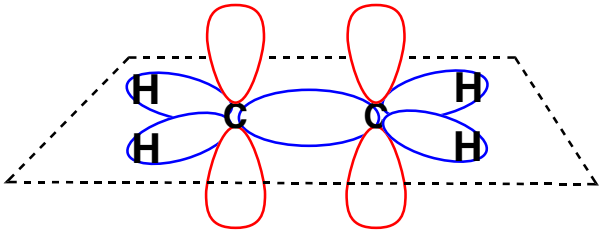
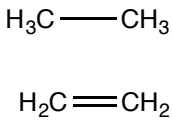
Chapter 8: Alkene Structure and Preparation via Elimination Reactions

[Sections: 8.1-8.13]

Nature of the pi bond





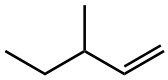
bond length

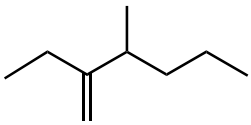
bond strength

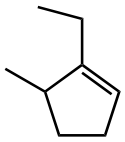
- *a C=C double bond is stronger than a C–C single bond*
- *the pi bond component, however, is generally weaker than the sigma bond component.*

Nomenclature of Alkenes

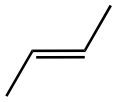
- *the longest continuous carbon chain containing **both carbons** of the C=C bond is the parent chain*
- *assign the C=C bond the lowest locant value*
- *in cyclic molecules the C=C bond is always given the 1,2-designation*

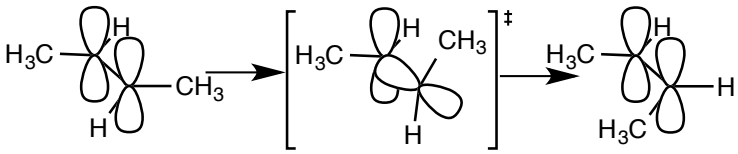






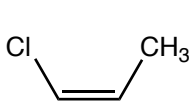
Stereochemistry of Alkenes

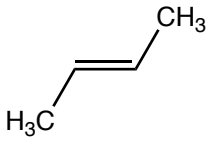


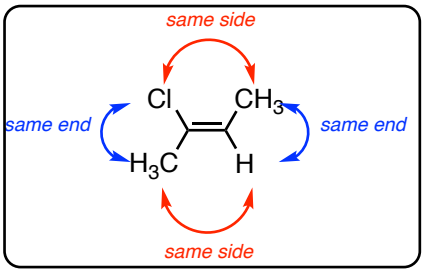


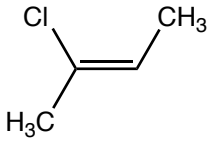
- *unlike sigma bonds where rotation takes place readily, rotation about a pi bond would require breaking the pi bond (loss of overlap of the P-orbitals) and therefore does not take place under normal condition*
- *this gives rise to two different stereoisomers. Relationship?*

Alkene Nomenclature With More Than Two Substituents on the Double Bond





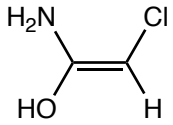


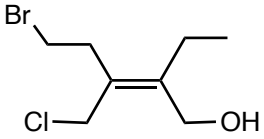


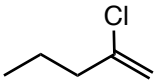
Plan of Attack *for naming alkenes*

- *assign priority for the two substituents on one "end" of the double bond*
- *repeat the process for the other end of the double bond*
- *if the two high-priority groups are on:*
  the same side of the double bond = Z isomer
  the opposite sides of the double bond = E isomer
- *cis isomers can also be called Z isomers, trans = E*

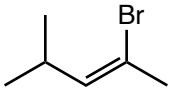
Z or E? Draw the other isomer







complete name?

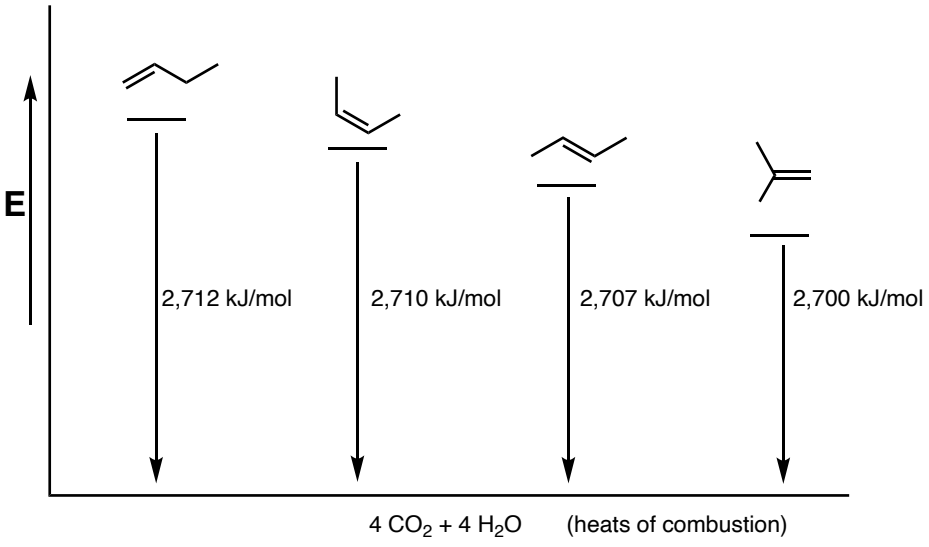


Problems: 1,2

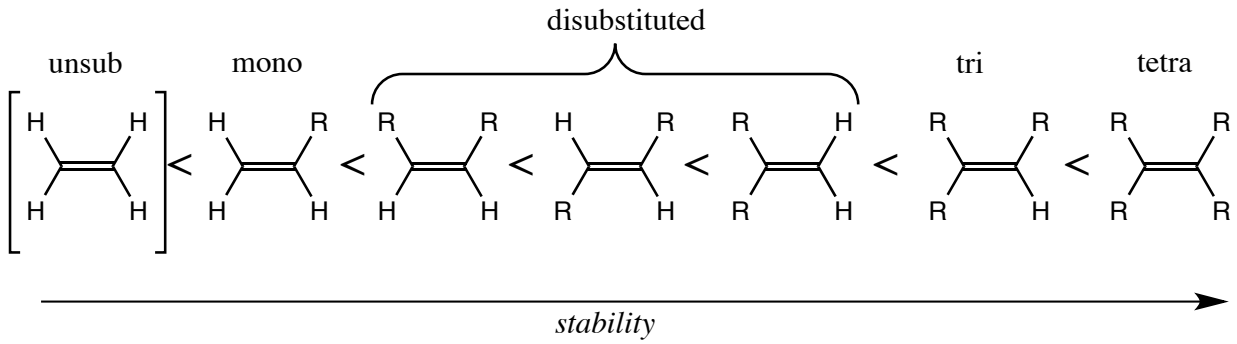
Relative Stability of Alkene Isomers

cis-2-butene $\xrightarrow{O_2}$ $CO_2 + H_2O +$ kJ/mol

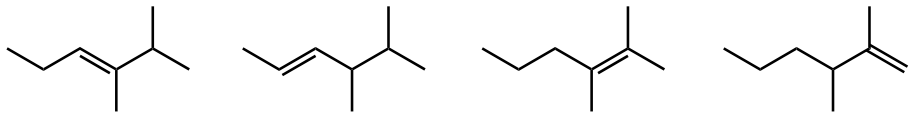
trans-2-butene $\xrightarrow{O_2}$ $CO_2 + H_2O +$ kJ/mol



Alkene Substitution Patterns



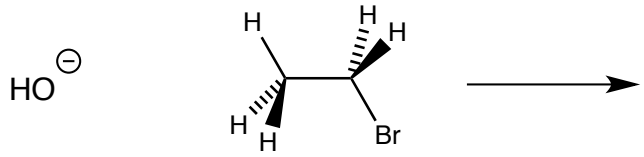
Predict the relative stabilities of the following isomeric alkenes



A **B** **C** **D**

Problems: 3, 4

Bimolecular Elimination Mechanism



- *identify starting materials and products*
- *exothermic or endothermic?*
- *multistep or concerted?*
- *RDS = unimolecular or bimolecular?*

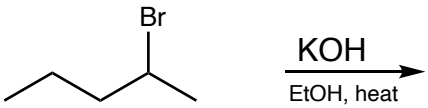
rate law:

- *dependent upon concentrations of compounds during (and prior to) the RDS*

rate = k

reaction name:

Predict the products of the following E2 reactions:

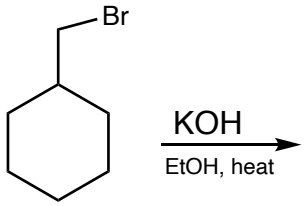


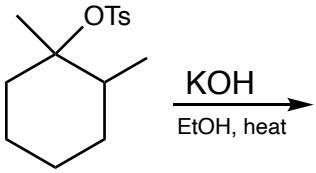
- *E2 elimination results in the formation of all possible alkene products, including stereoisomers*
- *E2 elimination using strong, small bases (such as HO^-) results in formation of the most stable alkene product (Zaitsev's rule)*
- *the most stable alkene is the most substituted*

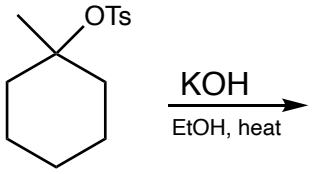
Predict all of the products of the following E2 reactions. Circle the major product:

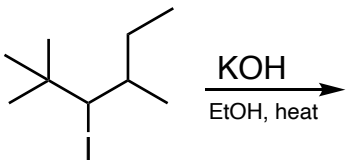
Plan of Attack *for E2 reactions*

- *identify the base*
- *identify the leaving group*
- *locate all β-hydrogens*
- *draw products from removal of a β-hydrogen and the leaving group*
- *draw stereoisomers where relevant*
- *check to make sure no products are duplicated!*





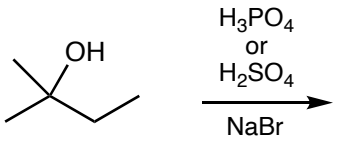




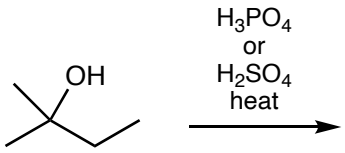
Problems: 5,6

Dehydration of Alcohols: A Unimolecular Elimination Mechanism (E1)

Substitution by the S_N1 mechanism predominates when a nucleophile is present

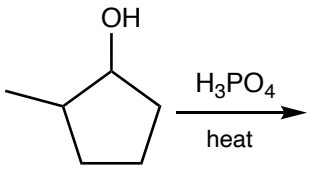


Elimination by the E1 mechanism predominates when a nucleophile is NOT present



• alcohols may react via either the S_N1 or the E1 reaction
• in both cases an acid is required to protonate the OH group to convert it to a good leaving group
• the intermediate carbocation is then either trapped by a nucleophile (S_N1) or loses a β-hydrogen (E1)
• elimination is guaranteed to occur if the acid is H_3PO_4 or H_2SO_4 since the counterions from these acids are not nucleophilic
• heat also favors the elimination process

Draw all the products expected. Circle the major product.



• because the rate determining step is formation of a cation by either the E1 or SN1 reaction mechanisms, the relative rates of reactivities for alcohols is 3° > 2° >> 1°

Chapter 8 *Essential Concepts*

1. Understand the difference in bond energies between C–C sigma and pi bonds and the impact on bond lengths
2. Be able to provide the complete IUPAC name, including stereochemistry where relevant, for alkenes
3. Know the biological significance of alkenes and alkene stereochemistry
4. Be able to determine relative stabilities of isomeric alkenes based on heat of combustion data and substitution patterns.
5. Understand the E2 reaction thoroughly. You should understand the rate law, how the rate of the reaction is affected by the nature of the base, leaving group, and solvent.
6. Be able to predict the products formed from an E2 reaction and rank them according to yields.
7. Be able to predict the products formed from an E1 reaction (including acid-catalyzed dehydration reactions) and rank them according to yields.