

Chapter 5: Structure and Preparation of Alkenes: Elimination Reactions

Alkenes (olefins) are hydrocarbons that contain a carbon-carbon double bond and are said to be "unsaturated."

molecular formula C_nH_{2n}

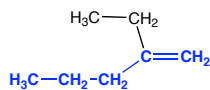
5.1: Alkene Nomenclature (please read and understand)

Prefix-Parent-Suffix

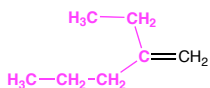
Suffix for alkenes: -ene

Many of the same rules for alkanes apply to alkenes

1. Name the parent hydrocarbon by locating the longest carbon chain that contains the double bond and name it according to the number of carbons with the suffix -ene.



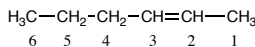
Parent = pentene



not hexene
(does not contain double bond)

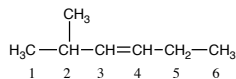
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- 2a. Number the carbons of the parent chain so the double bond carbons have the lowest possible numbers. Indicate the double bond by the number of the first alkene carbon.



2-hexene

- b. If the double bond is equidistant from each end, number so the first substituent has the lowest number.

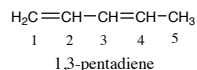
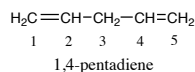


2-methyl-3-hexene

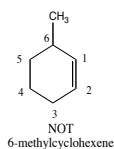
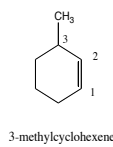
3. Write out the full name, numbering the substituents according to their position in the chain and list them in alphabetical order.

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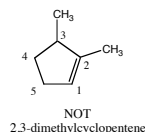
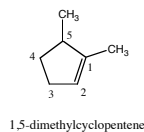
4. If more than one double bond is present, indicate their position by using the number of the first carbon of each double bond and use the suffix -diene (for 2 double bonds), -triene (for 3 double bonds), -tetraene (for 4 double bonds), etc.



- 5a. Cycloalkenes are named in a similar way. Number the cycloalkene so the double bond carbons get numbers 1 and 2, and the first substituent is the lowest possible number.

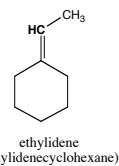
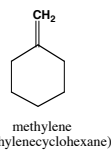
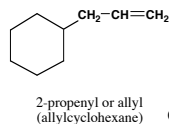
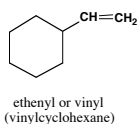


- b. If there is a substituent on one of the double bond carbons, it gets number 1.

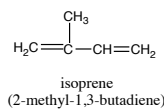
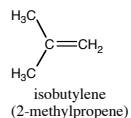
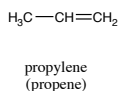


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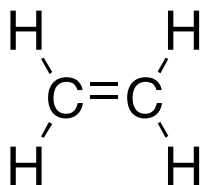
Alkenes as substituents:



Non-IUPAC Alkenes



5.2: Structure and Bonding in Alkenes



bond angles:

$$\text{H-C-H} = 117^\circ$$

$$\text{H-C-C} = 121^\circ$$

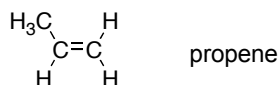
bond distances:

$$\text{C-H} = 110 \text{ pm}$$

$$\text{C=C} = 134 \text{ pm}$$

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Each carbon is sp^2 hybridized – trigonal planar geometry
 C=C bond consists of one σ -bond (sp^2 hybridized orbitals)
 and one π -bond (unhybridized p-orbitals) (see ch. 2 notes)



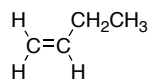
5.3: Isomerism in Alkenes

Isomers are different compounds that have the same molecular formula.

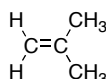
Constitutional (structural) : different connectivity

Stereoisomers: same connectivity, but different spatial arrangement of atoms or groups.

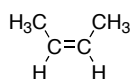
C_4H_8 : four isomeric butenes



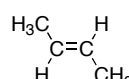
1-butene



2-methylpropene



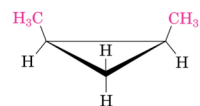
cis-2-butene



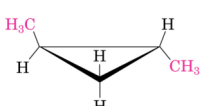
trans-2-butene

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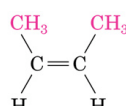
Alkenes Stereoisomers - recall cycloalkane stereoisomers: substituents are either on the same side of the ring (cis) or on opposite sides (trans).



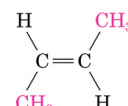
cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropane



cis-2-Butene



trans-2-Butene

Substituents on an alkene can also be either cis (on the same side of the double bond) or trans (on opposite sides of the double bond). Cis/trans isomers of alkenes are stereoisomers- they have the same connectivity but different three-dimensional arrangements of groups

Interconversion of alkene stereoisomers does not normally occur - requires breaking the π -bond.

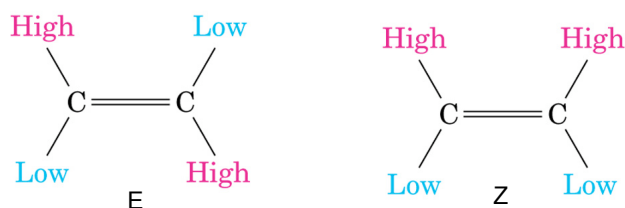
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5.4: Naming Stereoisomeric Alkenes by the E-Z Notational System. The cis and trans becomes ambiguous when there are three or four substituents on the double bond.

E/Z System: For each carbon of the double bond, the groups are Assign a priority (high or low) according to a system of rules. Thus, the high priority groups can be on the same side or on opposite Sides of the double bond.

If the high priority groups are on opposite sides then the double bond is designated as E (entgegen- across)

If the high priority groups are on the same side then the double bond is designated as Z (zusammen- together)



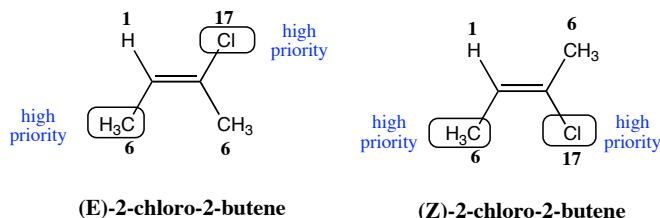
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Assigning Group Priority: The Cahn, Ingold, Prelog Rules

1. Look at the atoms directly attached to each carbon of the double bond. Rank them according to decreasing atomic number.

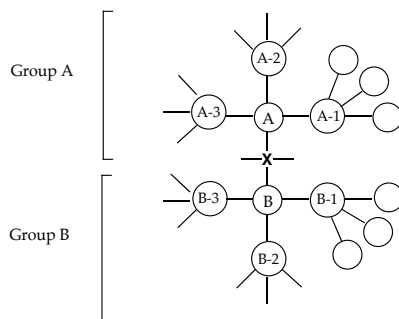
priority of common atoms: $I > Br > Cl > S > F > O > N > C > H$

If both high priority atoms are on the same side of the double bond it is designated **Z**. If the high priority atoms are on opposite sides of the double bond, it is designated as **E**.



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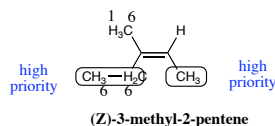
2a. If the two atoms attached to the double bond carbon are identical (designated A and B below), look at all the atoms directly attached to the identical atoms in questions (designated A-1, A-2, A-3 and B-1, B-2, B-3). Assign priorities to all these atoms based on atomic number (1 is the highest priority, 3 the lowest).



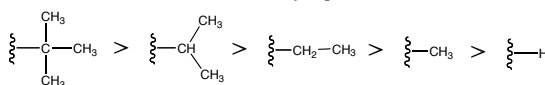
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2b. Compare the highest priority atoms, i.e. compare A-1 with B-1. If A-1 is a higher priority atom than B-1, then A is higher priority than B. If A-1 and B-1 are the same atom, then compare the second highest priority atoms directly bonded to A and B (A-2 with B-2); if A-2 is a higher priority atom than B-2, then A is higher priority than B. If A-2 and B-2 are identical atoms, compare A-3 with B-3.

2c. If a difference still can not be found, move out to the next highest priority group (A-1 and B-1 in the diagram) and repeat the process.

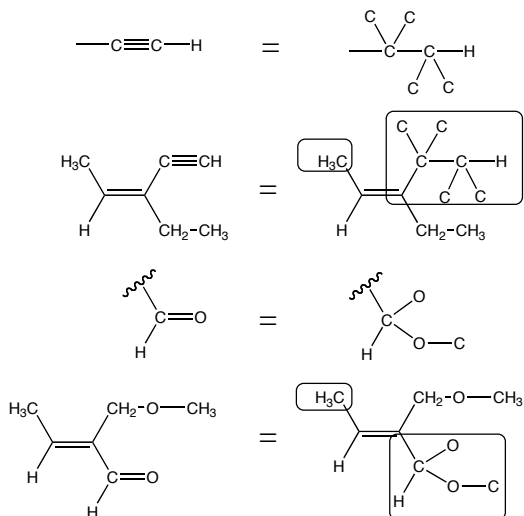


examples:



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3. Multiple bonds are considered equivalent to the same number of single bonded atoms.



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5.5: Physical Properties of Alkenes (please read)

5.6: Relative Stabilities of Alkenes

Double Bonds are classified according to the number of alkyl groups attached to C=C



monosubstituted



disubstituted

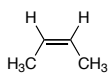


trisubstituted

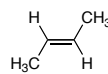


tetrasubstituted

In general, *cis*-disubstituted alkenes are *less* stable than *trans*-disubstituted



cis-2-butene

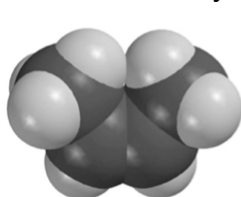


trans-2-butene

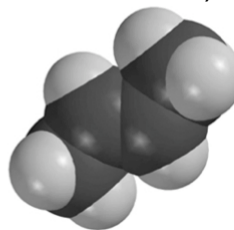
$\Delta H^\circ_{\text{combustion}}$: -2710 KJ/mol -2707 KJ/mol
trans isomer is ~3 KJ/mol more stable than the *cis*

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cis-alkenes are destabilized by steric (van der Waals) strain



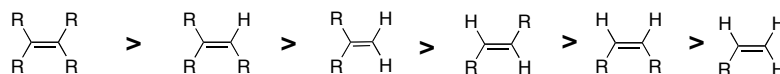
cis-2-butene



trans-2-butene

More highly substituted double bonds are generally more stable than less highly substituted ones.

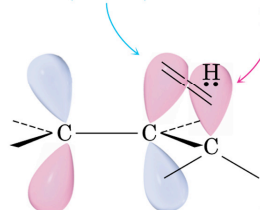
tetrasubstituted > trisubstituted > disubstituted > monosubstituted



Hyperconjugation: stabilizing effect due to “bonding” interactions between a filled C-H orbital and a vacant neighboring orbital

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Antibonding C-C π orbital (unfilled)



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Bonding C-H σ orbital (filled)

Increasing the substitution of an alkene, increases the number of possible hyperconjugation interactions

5.7: Cycloalkenes - C=C bonds can be accommodated in rings.



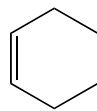
cyclopropene



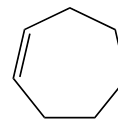
cyclobutene



cyclopentene



cyclohexene



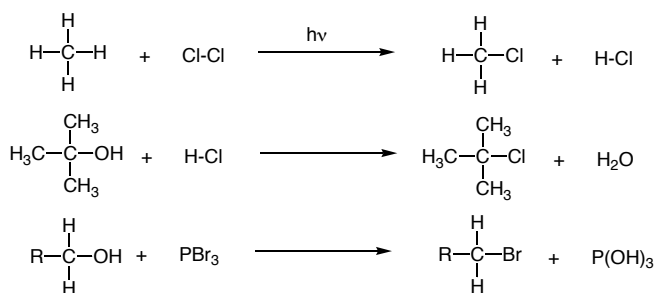
cycloheptene

- The geometry of the C=C must be *cis* for common ring sizes (3-7)
- The *cis* cycloalkene is more stable for ring size between 8-11
- *Cis*- and *trans*-cyclododecane (12) are of equal stability
- The *trans* cycloalkene is more stable for ring size over 12

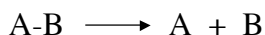
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5.8: Preparation of Alkenes: Elimination Reactions

A. Substitution Reactions: two reactants exchange parts to give new products

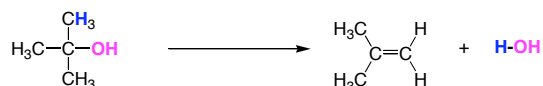


B. Elimination reaction: a single reactant is split into two (or more) products.

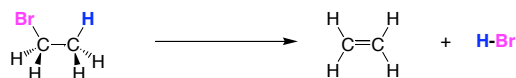


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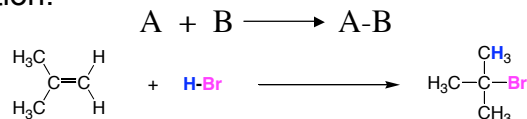
1. Dehydration: loss of H and OH (water) from adjacent carbons of an alcohol to form an alkene



2. Dehydrohalogenation: loss of H and X from adjacent carbons of an alkyl halide to form an alkene



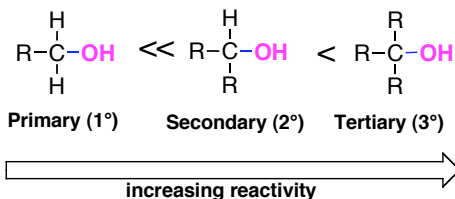
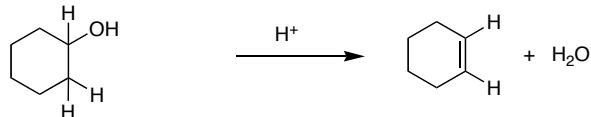
C. Addition reactions: two reactants add to form a product - no (or few) atoms are left over. Opposite of an elimination reaction.



D. Rearrangement: a reactant undergoes bond reorganization to give a product which is an isomer of the reactant

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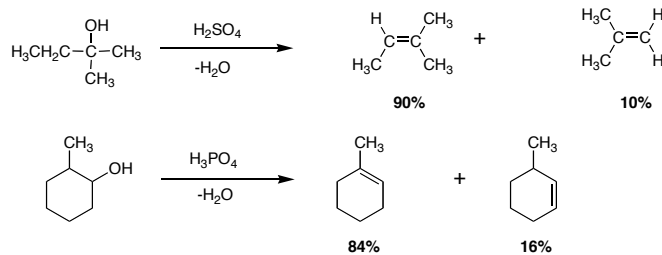
5.9: Dehydration of Alcohols - The dehydration of alcohols is acid catalyzed (H_2SO_4 , H_3PO_4)



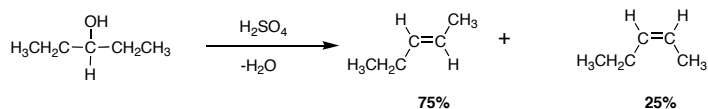
5.10: Regioselectivity in Alcohol Dehydration:

The Zaitsev Rule - When more than one alkene product is possible from an elimination reaction, the most highly substituted (most stable) alkene is usually the major product.

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5.11: Stereoselectivity in Alcohol Dehydration - the more stable double bond geometry is usually favored.



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5.12: The E1 and E2 Mechanisms of Alcohol Dehydration

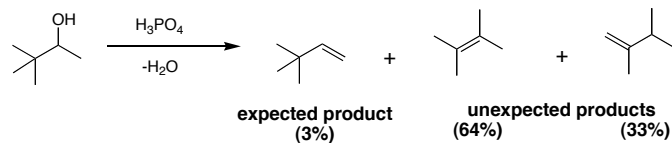
E1 mechanisms - The acid-catalyzed dehydration of 3° and 2° alcohols proceeds through a carbocation intermediate

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E2 Mechanisms - dehydration of 1° alcohols

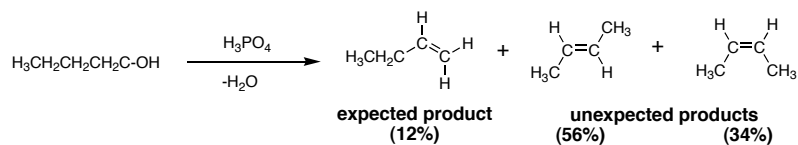
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5.13: Rearrangements in Alcohol Dehydration - less stable carbocations can rearrange to more stable carbocation



1,2-methyl shift mechanism

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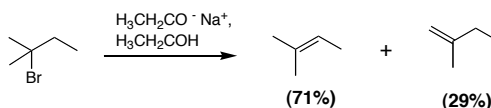


1,2-hydride shift mechanism

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5.14: Dehydrohalogenation of Alkyl Halides - loss of H and X from adjacent carbons of an alkyl halide to form an alkene.

Elimination of alkyl halides is affected by base, often the conjugate bases of alcohols (alkoxides), by an E2 mechanism. The reaction follows Zaitsev's rule in that the most stable double bond product usually predominates.

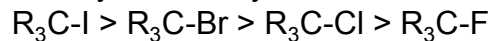


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5.15: The E2 Mechanism of Dehydrohalogenation of Alkyl Halides - rate = $k[\text{alkyl halide}][\text{base}]$

second-order (bimolecular) kinetics implies that both base and alkyl halide are involved in the rate-determining step.

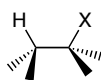
Reactivity of the alkyl halide:



Mechanism is a concerted (one-step) bimolecular process with a single transition state: C—H bond breaks, π -bond forms, and C—X bond breaks at the same time.

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5.16: Anti Elimination in E2 Reactions - The H being abstracted and the leaving group (halide) must be in the same plane



Syn periplanar:
the H and X
are eclipsed
dihedral angle = 0°

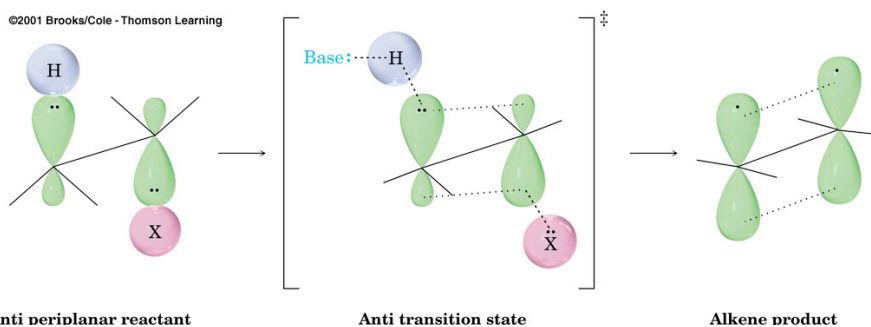
Anti periplanar:
the H and X are
anti staggered
dihedral angle = 180°

Generally, the anti periplanar geometry is energetically preferred (staggered conformation vs eclipsed)

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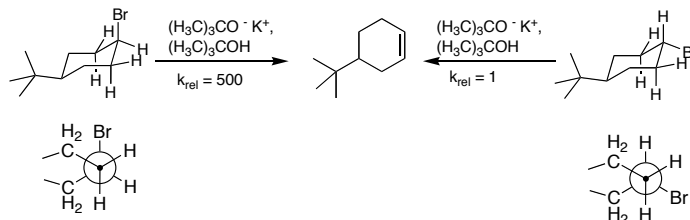
In the periplanar conformation, the orbitals are already aligned for π -bond formation

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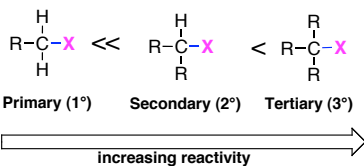
An effect on reactivity that has its origin in the spatial arrangement of orbitals or bonds is called a *stereoelectronic effect*.

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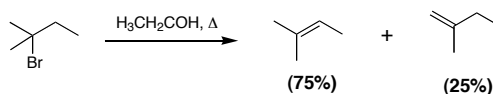
5.17: Isotopes Effects And The E2 Mechanism (please read)
5.18: The E1 Mechanism of Dehydrohalogenation of Alkyl Halides - Dehydrohalogenation of alkyl halides can also proceed by an E1 mechanism without base

Reactivity:

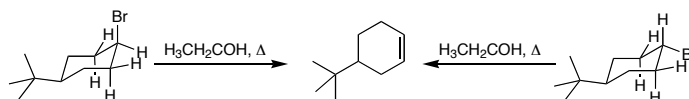


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Mechanism: rate = $k [R-X]$ (unimolecular)
 E1 elimination usually follows Zaitsev's Rule



No geometric requirements for E1 elimination.



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