Chapter 4: Alkenes and Alkynes

4.1. Review: Alkenes and Alkynes

Alkene: molecule containing C and H only with at least one C=C

Alkyne: molecule containing C and H only with at least one C≡C

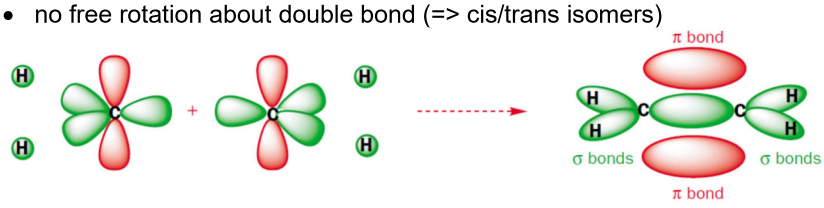
Unsaturated molecule: any molecule having fewer Hs than the corresponding alkane due to the existence of *double bonds or triple bonds*.

Arenes (Aromatic Molecules)

- Simplest arene (=aromatic molecule) is benzene
- Chemistry is quite different from alkenes (see chapter 9)
- Generally inert (=non-reactive) under conditions where alkenes react

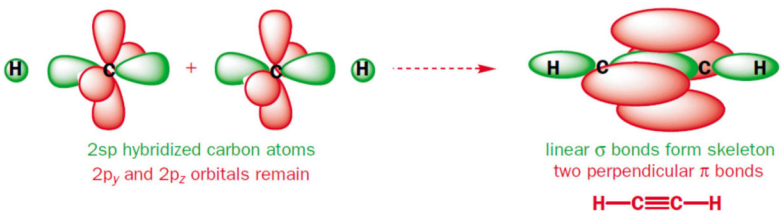
Electronic Structure of Alkenes

- sp^2-hybridized orbitals – trigonal planar
- unhybridized p orbital
- π bond made by overlapping of unhybridized orbitals
- no free rotation about double bond (=> cis/trans isomers)



Electronic Structure of Alkynes

- sp-hybridized orbitals – linear
- 2 unhybridized p orbitals
- π bond made by overlapping of unhybridized orbitals
- no free rotation



4.2 Substituted Alkenes and Their Relative Stabilities

a) Terminal alkenes

Terminal alkenes can be mono or disubstituted.

Common substituents with a terminal double bond are the vinyl, allyl and methylene groups.

Vinyl **Allyl** **Methylene**

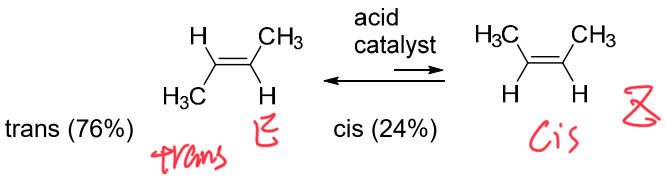
b) Cis and trans alkenes

Disubstituted ***internal alkenes*** show ***cis-trans* isomerism.**

- *Cis* and *trans* isomers a type of stereoisomers (same connectivity of atoms but different spatial arrangement)

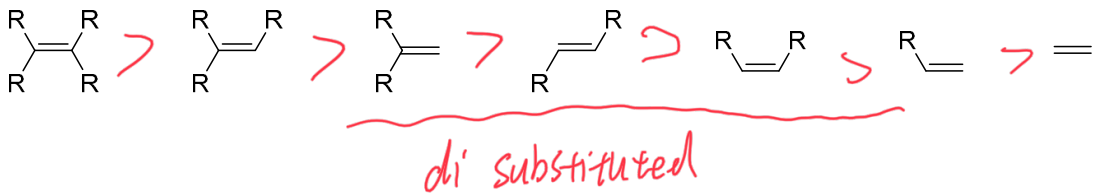
- *Cis* and *trans* isomers are different compounds and can be isolated because the double bond is rigid and rotation does not occur spontaneously.

- In the presence of an acid catalyst, cis-trans interconversion can occur and an equilibrium is established.



c) Overall Relative Stabilities of Alkenes

- The more substituted the double bond is, the lower in energy the molecule

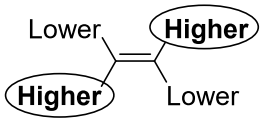


4.3 Nomenclature of Alkenes, Cycloalkenes, and Alkynes (IUPAC)

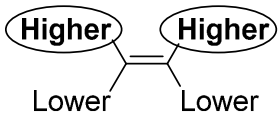
While cis/trans can be used *only* for disubstituted alkenes, the E/Z designation is applicable to all substituted alkenes

a) E,Z Designation for Di-,Tri-, and Tetrasubstituted Alkenes

- E and Z can be assigned to all unequally substituted alkenes
- The same sequence rules as for assigning R/S to stereogenic centers are used to rank the substituents of the double bond

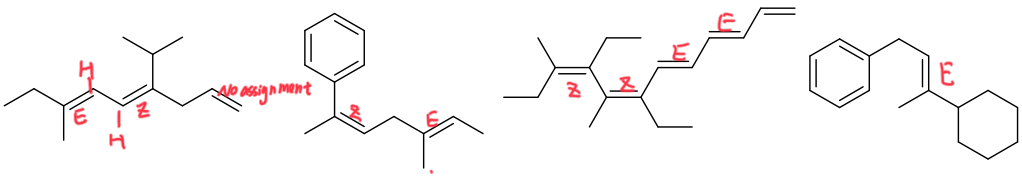


E (entgegen, opposite)



Z (zusammen, together)

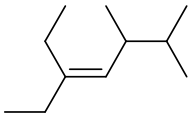
Assign E or Z to the double bonds if applicable:

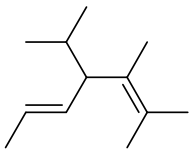


b) Nomenclature of Alkenes

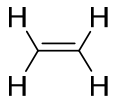
1. Name the parent hydrocarbon
   - find the longest chain containing both ends of the C=C
   - name the chain length with the –ene ending
2. Number the C atoms in the chain
   - start at the end closest to the C=C
   - if the C=C is equidistant from both ends, give the first branch the lowest number
3. Write the full name
   - number the substituents as with alkanes
   - indicate the C=C position by giving the first C number in the bond
   - if more than one C=C, give a number to each double bond and use diene, triene,…
4. Assign E or Z to the double bonds if appropriate
   - cis and trans may be used instead for disubstituted alkenes

Provide the IUPAC name for the following unsaturated molecules:

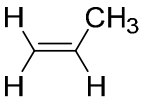




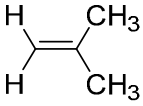
Common trivial names



ethene
ethylene



propene
propylene



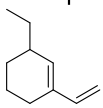
2-methylpropene
isobutylene

c) Nomenclature of Cycloalkenes

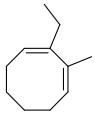
Cycloalkenes are named the same way as open-chain alkenes with the additional rules that

- C=C is given position numbers (1 and 2) so that the remaining substituents have the lowest possible locants
- There is no need to assign E and Z for smaller rings than cylcooctane: due to structural constraints only the Z (cis) form is isolable in 3-7 membered rings.

Examples:



3-ethyl-1-vinyl cyclohexene



(1Z,3Z)-2-ethyl-3 methyl cyclo^{oct}-1,3-diene

Attention: the designations cis and trans in cyclic systems is ambiguous and can be used both for relative stereochemistry of two substituents or/and for

Cis -Trans Isomerism in Cycloalkenes

Cyclooctene is the smallest ring that can contain a *trans* double bond\

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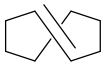
E



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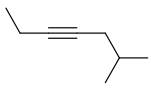
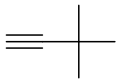
d) Nomenclature of Alkynes

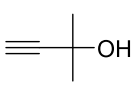
- Follow the general rules for alkanes and alkenes
- -yne ending for the parent chain
- C≡C position is indicated by the first number in the chain
- Numbering of the chain begins at the end closest to the C≡C
- Triple bonds take priority over double bonds when assigning numbers.



6-methyl-hept-3-yne



3,3-dimethyl but-1-yne



2-methyl but-3-yn-2-ol

4.4 Acidity of Terminal Alkynes

Acidity of Alkanes, Alkenes, and Alkynes:

Water	$pK_a = 15.7$	
Alkyne	$pK_a = 25$	sp (50% s-character)
Alkene	$pK_a = 44$	sp^2 (33% s-character)
Alkane	$pK_a = 51$	sp^3 (25% s-character)

Example: Deprotonation of terminal alkyne by amide base:

pK_a 25 pK_a 38