

SECTION 5 – STRUCTURE AND REACTIVITY OF ALKENES

5-1 -- Alkenes (“Olefins”)

- Strength of a Double Bond (d.b) Relative to a Single Bond (s.b)

5-1 -- Stereoisomerism of Alkenes (Cis/Trans)

5-1 -- Nomenclature of Alkenes

- 6 Rules for Naming Alkenes
- Numbering the Principal Chain (Main Chain)
- Identifying Locator #'s for Double Bonds
- Endings / Suffixes (-ene, -diene, -triene, and -tetraene)

5-3 -- Naming Branched Alkenes

- Alkenyl Substituents (Alkenes as Branches)

5-4 -- Naming Alkenes that Exhibit Stereoisomerism

- E-Configurations and Z-Configurations (E/Z Stereochemistry)
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5-7 -- Relative Stabilities of Alkenes

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- Alkyl Group Substitution (Branches) Stabilize Alkenes

5-8 -- Electrophilic Addition Reactions

- Electrophilic Addition of HX (X = -Cl, -Br, -I)
- Regiospecific Reactions

5-9 -- Markovnikov's Rule

- Carbocation Stability
- Hyperconjugation and Electron Delocalization
- Resonance Picture of Carbocations

5-11 -- The Hammond Postulate

5-12 -- Rearrangement of Carbocations

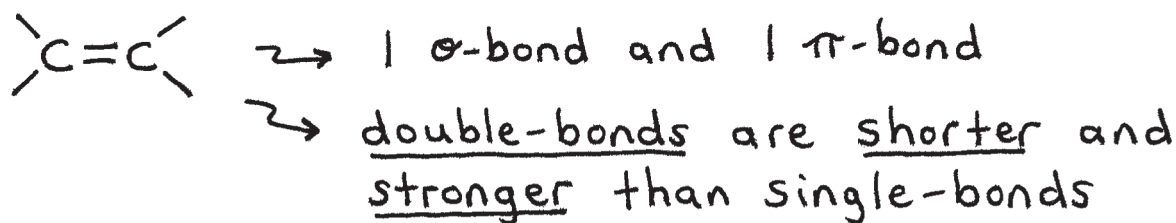
- 1,2-Hydride Shifts (:H^-)
- 1,2-Alkyl Shifts (:R^-)

5-13 -- Degree of Unsaturation

- Calculating the Degree of Unsaturation
- General Formula for Degree of Unsaturation

Section 5 = Structure and Reactivity of Alkenes. 5-1

- Alkenes ("olefins") = hydrocarbons with one or more double-bonds (d.b.'s).

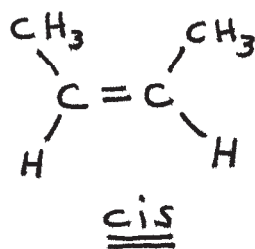
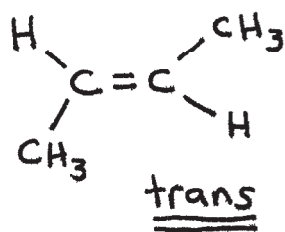


\rightarrow lengths:

d.b. = 1.33 Å
s.b. = 1.54 Å
(1 Å = 1×10^{-10} m)

- Strength of a C=C d.b. \Rightarrow 145-150 kcal/mol
(σ and π combined) vs. 80-85 kcal/mol (C-C σ -bond).

* Stereoisomerism:



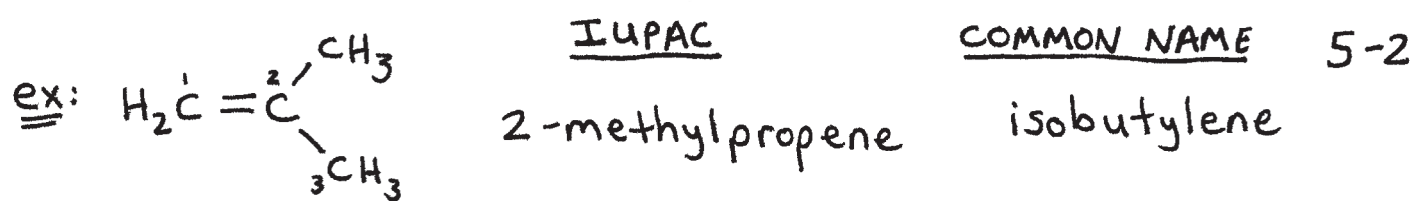
} the energy-barrier (E_a) is too high at room temp. to rotate 1 end by 180° .

* Nomenclature of Alkenes.

\rightarrow name of principal (main) chains or rings contain "-ene" endings.

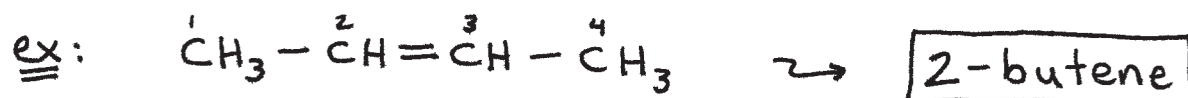
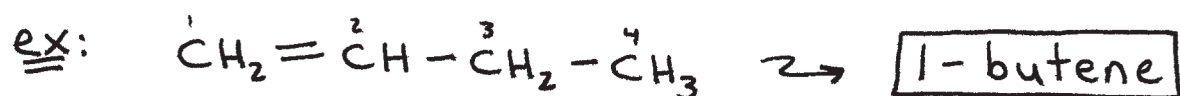
	<u>IUPAC</u>	<u>COMMON NAME</u>
<u>ex</u> : $\text{H}_2\text{C}=\text{CH}_2$	ethene	ethylene

<u>ex</u> : $\text{H}_2\text{C}=\text{CH}-\text{CH}_3$	propene	propylene
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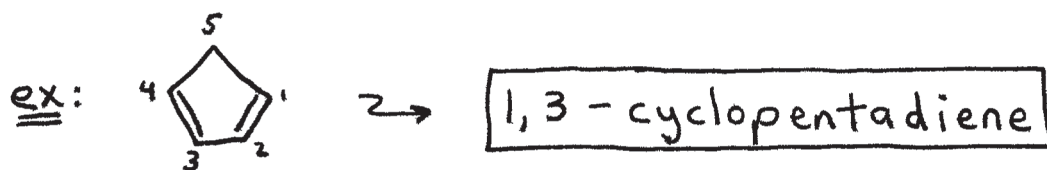
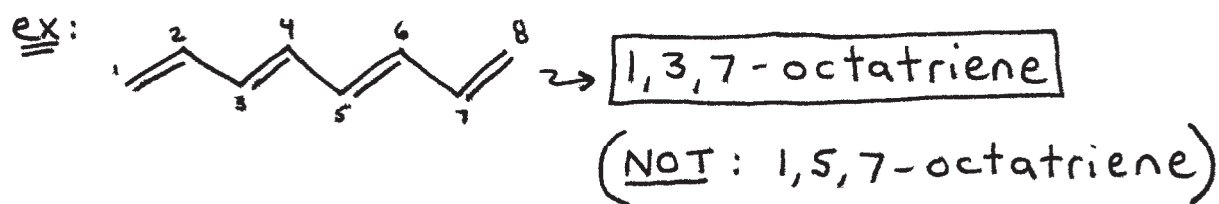
* 6 Rules for Naming Alkenes. ***

① Chains numbered from an end such that the d.b. gets the lowest locator number, specifying the first carbon of the d.b.



② If 2 or more d.b.'s are present, number the main chain so that the d.b.'s get the lowest #'s overall.

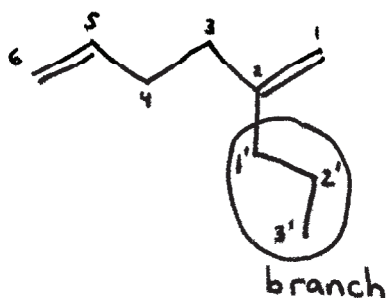
* endings (suffixes) \Rightarrow -diene, -triene, and -tetraene



③ Branched Alkenes.

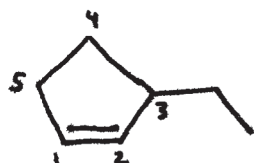
- 1st priority: principal (main) chain is the one with the most d.b.'s. It's not simply the longest chain!
- Tiebreaker: if 2 or more chains have the same # of d.b.'s, choose the longest chain.

ex:



→ 2-propyl-1,5-hexadiene

ex:



→ 3-ethylcyclopentene

↳ no need to specify "1" for the alkene location. It's implied.

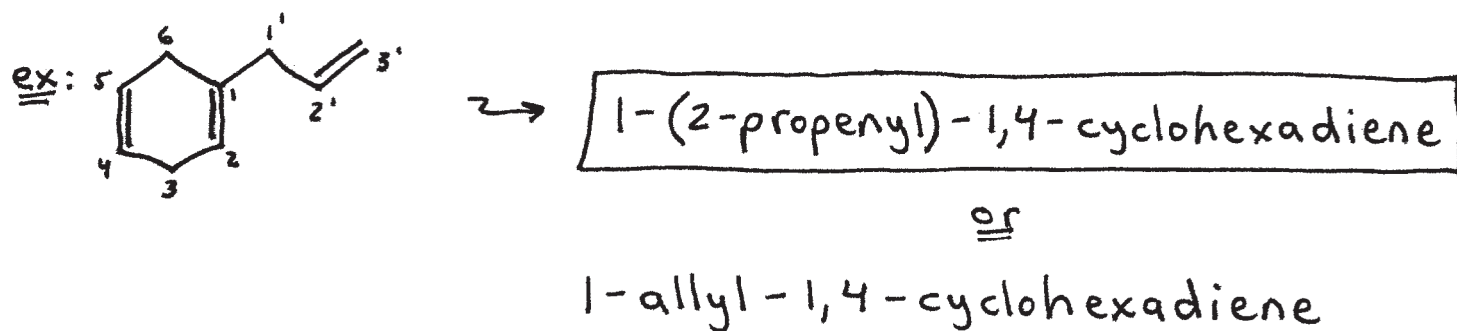
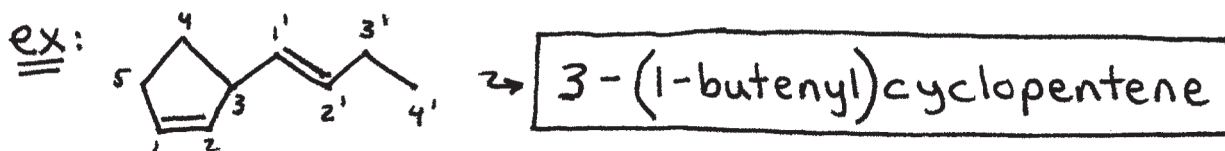
④ Alkenal Substituents (Branches).

- ↳ "alkenes as branches"
- ↳ change "ene" ending to "enyl" ending

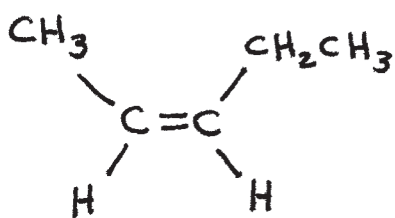
- a) number the branch from its point of attachment to the main chain.
- b) specify branch #'s with a locator #.

* examples on the next page...

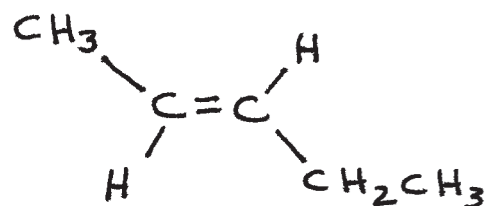
$-\text{CH}=\text{CH}_2$	<u>IUPAC</u> -ethenyl	<u>COMMON NAME</u> -vinyl	5-4
$-\text{CH}_2-\text{CH}=\text{CH}_2$	-2-propenyl	-allyl	
$-\text{CH}=\text{CH}-\text{CH}_3$	-1-propenyl	(none)	



⑤ Stereoisomerism = possible if and only if each of the d.b. C's has 2 different things attached.



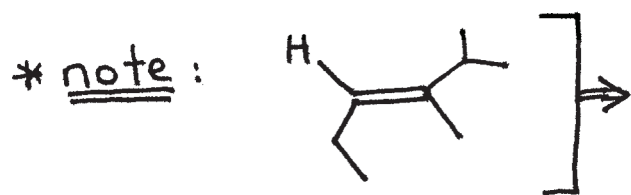
cis-2-pentene



trans-2-pentene

cis = "similar groups" on the same side.

trans = "similar groups" on the opposite side.

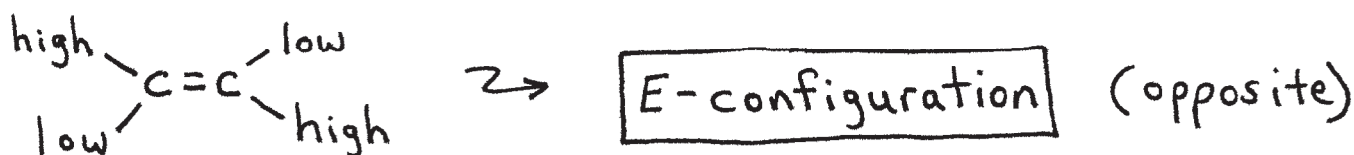
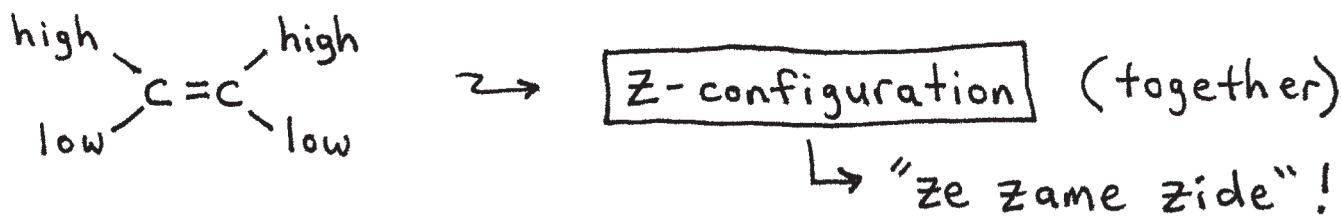


cis/trans unclear here,
so see rule ⑥ on the
next page...

⑥ Priority System within Nomenclature.

5-5

→ assign high and low priorities to groups or atoms attached to each double-bond (d.b.).



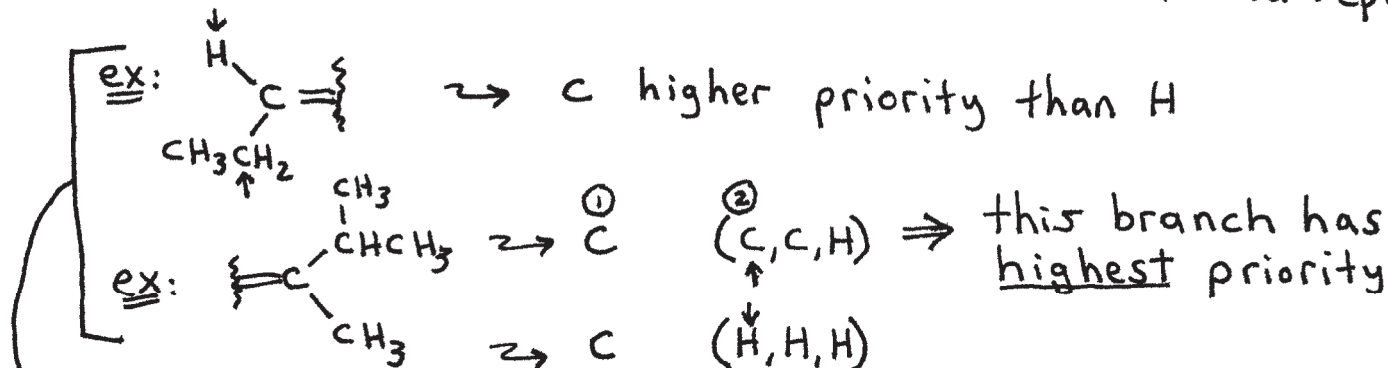
* unimportant, but: $\left. \begin{array}{l} \rightarrow \text{Z} = \text{Zusammen} \\ \rightarrow \text{E} = \text{entgegen} \end{array} \right\} \rightarrow \text{German words}$

- highest priority substituents \Rightarrow atom with the highest atomic #

↳ (1) compare the atoms directly attached to the d.b. carbons.

^{1st} tiebreaker \rightsquigarrow (2) list atoms attached to the atoms in (1) above in order of decreasing atomic #, and compare until first point of difference

^{2nd} tiebreaker \rightsquigarrow (3) move to first atom of the list and repeat.



→ zipped together on the next page...

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