Elimination Reactions
1 – Alkenes: Nomenclature, Properties and Applications

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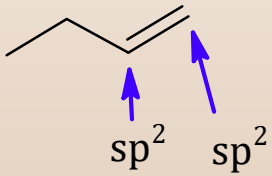
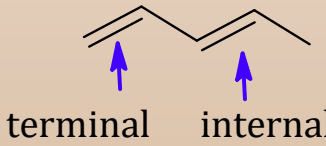
Introduction - Alkenes

Alkenes are hydrocarbons with a double bond as functional group.

- Their formula C_nH_{2n} indicates unsaturation (not enough hydrogen).
- The double bonded carbon has a hybridization of sp^2, which implies 120^o bond angle and trigonal planar structure.



- Alkenes can be found as terminal or internal double bonds. It is good to know these terms, as these alkenes are synthesized and they react differently.

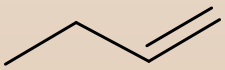


- It is also common to find double bonds in cyclic compounds.

Nomenclature - Introduction

First alkene is named ethene: $CH_2=CH_2$, next is propene $CH_3CH=CH_2$.

- Starting from butene, the double bond should have a locant. The new nomenclature is where the locant for the functional group is just before the name of the functional group. Old nomenclature is using the locant before the parent/long chain name and functional group. I have given both here. You should use the new nomenclature, but I can accept the old one also if it is correct.

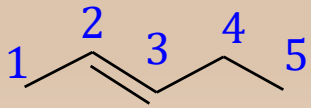
$CH_2=CHCH_2CH_3$ 

$CH_3CH=CHCH_3$ 

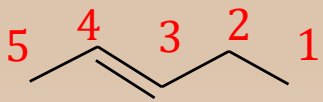
New: but-1-ene but-2-ene

Old: 1-butene 2-butene

- Double bonds should get lower locant number. The red numbering in the structure below is wrong.



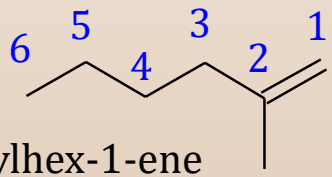
pent-2-ene



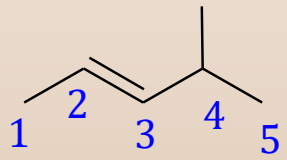
NOT: pent-3-ene or pent-4-ene

Nomenclature - Substituents

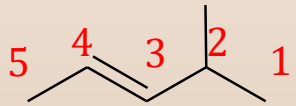
- For longer alkenes, name the longest chain hydrocarbon starting from the double bond. Include the double bond in the numbering such that it gets lower number.
- Number substituents according to their position in chain from the double bond. Name them alphabetically. Substituents have lower priority than double bonds.



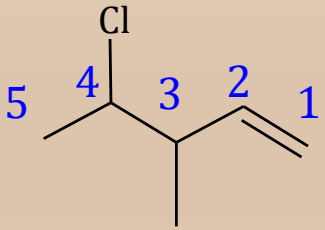
2-methylhex-1-ene
OR
2-methyl-1-hexene
NOT 2-methylhex-2-ene



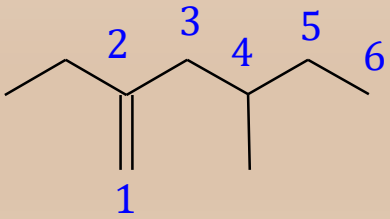
4-methylpent-2-ene



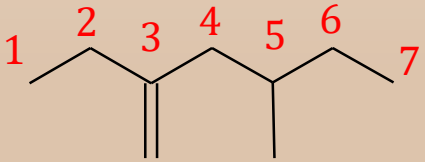
NOT:
2-methylpent-3-ene



4-chloro-3-methylpent-1-ene



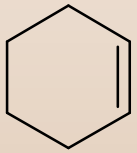
2-ethyl-4-methylhex-1-ene



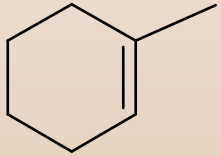
This numbering is wrong

Nomenclature – Cyclic Compounds

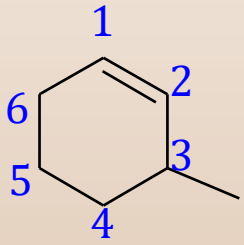
- In case of alkenes in rings, start numbering from double bond and include double bond during counting carbons.
- The double bond always gets the lower number.
- The double bond does not get a locant as it is understood that numbering starts from there.



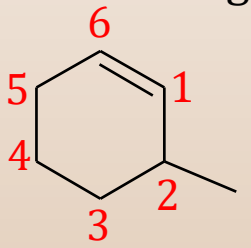
Cyclohexene
(*no numbering required*)



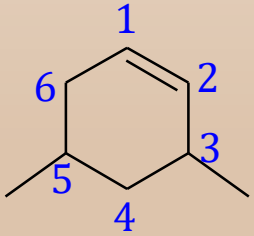
Methylcyclohexene
(*no numbering required*)



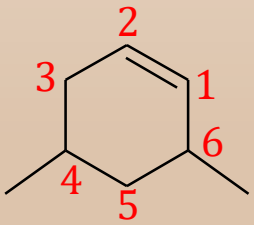
3-Methylcyclohexene
(*no locant for double bond required*)



NOT:
2-Methylcyclohexene
(*double bond should be included in numbering*)



3,5-dimethylcyclohexene
(*no locant for double bond required*)

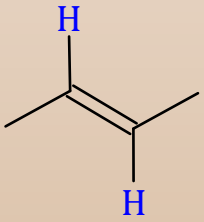


NOT: 4,5-diethylcyclohexene
(*substituents should also get lower numbers if possible*)

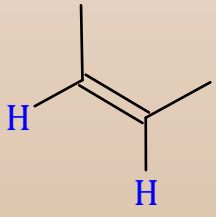
Nomenclature – Cis and Trans

Double bonds have restricted rotations, resulting in groups being stuck in their locations. Unless all the groups on the double bond are identical, alkenes show Cis and Trans isomerism. These isomers are also called **geometric isomers**.

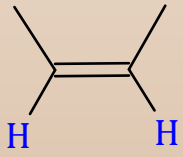
- As in cycloalkanes, **cis** isomer is when two hydrogens are on the same side and **trans** is when the two hydrogen atoms are on the opposite side.
- Cis and trans isomerism is not possible when the double bond is terminal as the atoms on the terminal carbon are the same.
- Cis and trans are written in parenthesis or in *italics*. You can use parenthesis as italics is hard to show in handwriting.



(Cis)-but-2-ene
OR
Cis-but-2-ene

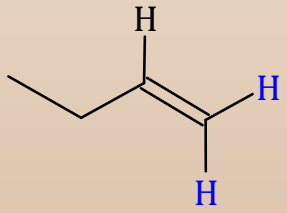


slight rotation



(Trans)-but-2-ene
OR
Trans-but-2-ene

These structures are the same, I have rotated the first one slightly to give a better visual.

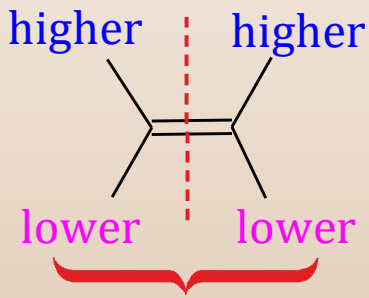


<u>Terminal double bond:</u>
cis and trans is not possible there are three hydrogens on the double bond.

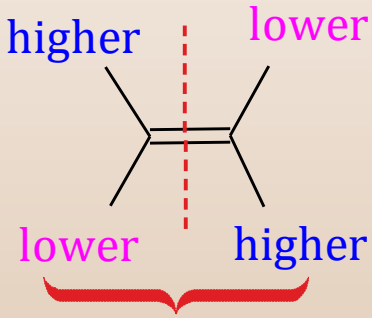
Nomenclature – E and Z

Cahn-Ingold-Prelog nomenclature of E and Z is used when two or more atoms around the double bond are not hydrogen. Priority rules are the same as in stereochemistry for R and S. (*See slides later on for a review*).

- The double bond is divided in the middle as shown by the red line on the right structures.
- Compare the priority of the atoms by atomic number, as in the Cahn-Ingold-Prelog system. Then compare if the higher groups are on same or opposite side:
  - **E -*entgegen***, *higher atomic mass atoms on* opposite sides
  - **Z - *zusammen***, *higher atomic mass atoms on* same side



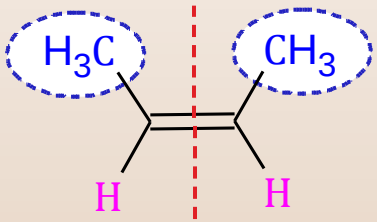
Z: higher atomic number atom on the same side



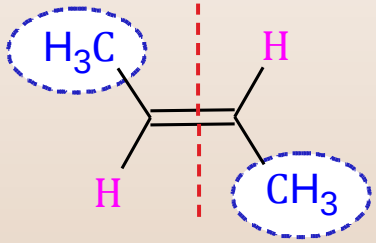
E: higher atomic number atom on the opposite side

Nomenclature – E and Z

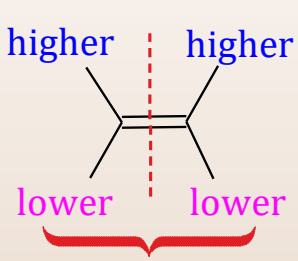
In but-2-ene shown below priority rules are used to determine that C > H in atomic number.



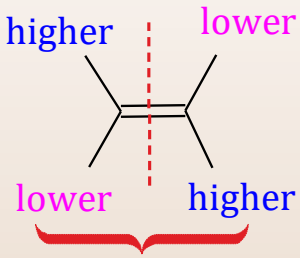
(Z)-but-2-ene



(E)-but-2-ene



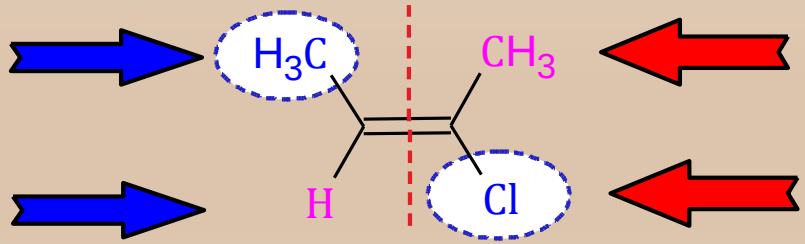
Z: higher atomic number atom on the same side



E: higher atomic number atom on the opposite side

In 2-chloro but-2-ene shown below priority rules are used to determine that C > H in atomic number on the left side but on the right side Cl > C. In this case C and Cl, the two high priority groups are on the opposite side.

The two atoms to compare are C and H and C is higher atomic weight

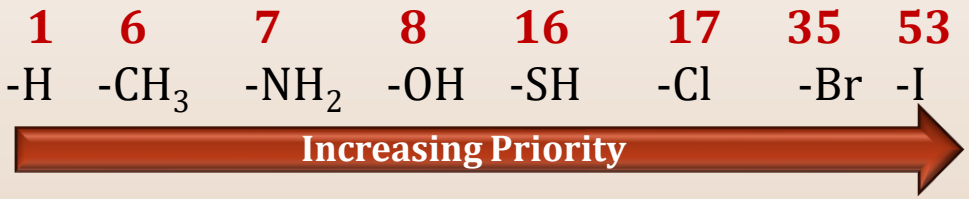


The two atoms to compare are C and Cl and Cl is higher atomic weight

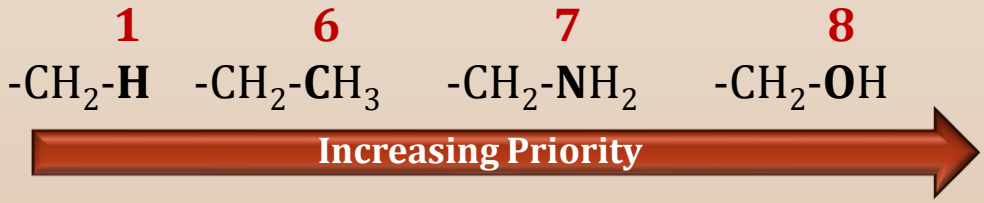
E configuration

Assigning Priority

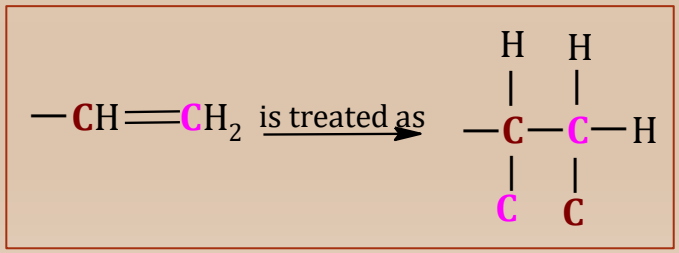
1. Look at the atom (not the group) directly attached to the carbon and arrange according to atomic number,

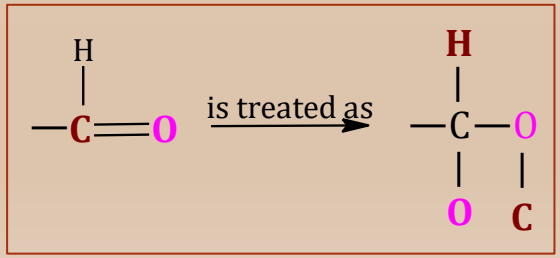


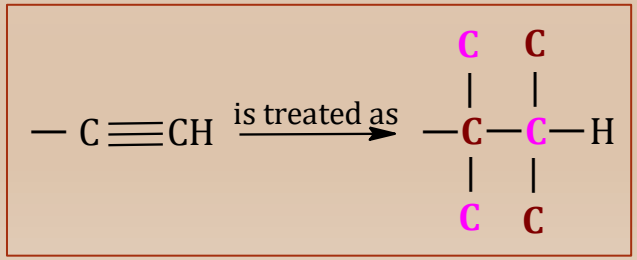
2. If priority cannot be assigned per the atoms bonded to the chiral center, look to the next set of atoms; priority is assigned at the first point of difference.



3. Groups with double or triple bonds are assigned priorities as if their atoms were duplicated or triplicated.



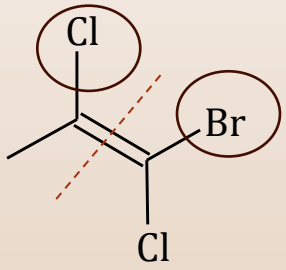




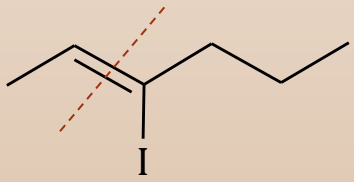
Solved Problem: Assigning E/Z configuration

Write the name of the alkenes below including the E/Z configuration. Alkenes with two hydrogens (typically assigned as cis or trans) can be named as E/E also.

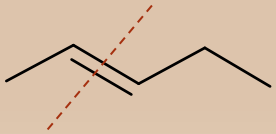
ANSWER



Cl > C on the left carbon of double bond.
Br > Cl on the right carbon of double bond.
Both higher atomic numbers are on the same side of double bond, therefore Z configuration.
***Z*-1-bromo-1,2-dichloropropene**



C > H on the left carbon of double bond.
I > C on the right carbon of double bond.
Both higher atomic numbers are on the same side of double bond, therefore Z configuration.
***Z*-3-iodohex-2-ene**



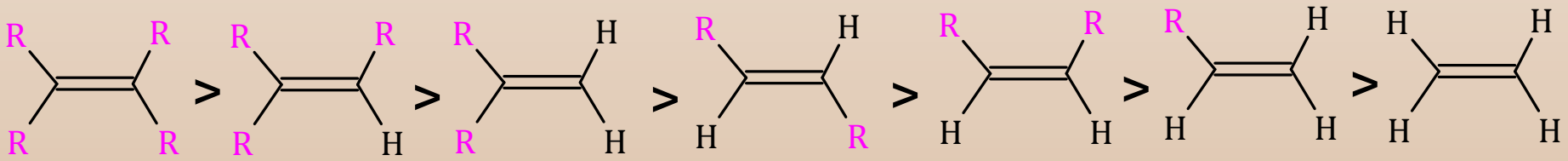
C > H on the left carbon of double bond.
C > H on the right carbon of double bond.
Both higher atomic numbers are on opposite sides of double bond, therefore E configuration.
***E*-pent-2-ene**

Stability of Alkenes

General rule for stability of alkenes is that the more substituted the double bond the more stable the alkene is.

Tetrasubstituted > Trisubstituted > Disubstituted > Monosusbtituted

- In case of cis and trans isomers: c*is* alkenes are less stable than *trans* alkenes.
- Less stable alkenes have higher energy, giving off more heat during combustion.



Degree of Unsaturation

Alkenes are considered unsaturated as they have 2 less hydrogens than alkanes. Alkanes are C_nH_{2n+2} and alkenes are C_nH_{2n} so alkenes are two less H than alkanes.

- One degree of unsaturation or Hydrogen Deficiency Index (HDI) is 2 less H in a compound than corresponding alkane of the same number of carbons.

$$\frac{\#\text{ of H in alkane} - \#\text{ of H in compound}}{2} = \text{HDI OR degree of unsaturation}$$

- 1^o of unsaturation is equivalent to either a presence of one double bond or one ring in the structure. Cycloalkanes also have the same carbon to hydrogen ratio as an alkene: C_nH_{2n}.
- 2^o of unsaturation is equivalent to:
  - one triple bond
  - OR one double bond + one ring
  - OR two rings
  - OR two double bonds

Degree of Unsaturation with Other Elements

- Halogens compounds (X: F, Cl, Br, I) Halogen replaces hydrogen one to one ratio.
  - $C_4H_6Br_2$ and C_4H_8 have one degree of unsaturation

$BrCH_2CH{=}CHCH_2CH_2Br$ = $HCH_2CH{=}CHCH_2CH_2H$

$C_4H_6Br_2$ = C_4H_8 Indicates one degree of unsaturation

($C_4H_{10} - C_4H_8 = 2 = 1^o$)

- Oxygen compounds (C,H,O) – Oxygen forms 2 bonds and don't affect the formula of equivalent hydrocarbons. They can be ignored.

$CH_2{=}CHCH{=}CHCH_2OH$ = $CH_2{=}CHCH{=}CHCH_2H$

C_5H_8O = C_5H_8 Indicates two degrees of unsaturation

($C_5H_{12} - C_5H_8 = 4 = 2^o$)

- Nitrogen compounds – subtract the N and one H. Nitrogen has two connections.

C_5H_9N = C_5H_8 Indicates two degrees of unsaturation

Solved Problem: Degree of unsaturation

Isopentyl acetate has a molecular formula of $C_7H_{14}O_2$. Calculate its HDI.

ANSWER

- Ignore the two oxygens
- New formula = C_7H_{14}
- C_nH_{2n+2} = C_7H_{16}
- (16-14)/2 = HDI of 1

Solved Problem: Degree of unsaturation

Calculate the HDI for niacin, molecular formula $C_6H_6N_2O$.

ANSWER

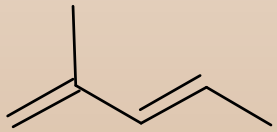
- Ignore the oxygen; for N – remove the two N and one H with each N so remove two H also
- New formula = C_6H_4
- C_nH_{2n+2} = C_6H_{14}
- (14-4)/2 = HDI of 5

Solved Problem: Degree of unsaturation and structures

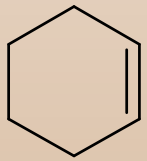
Calculate the degree of unsaturation for C_6H_{10} and propose all the structures possible.

ANSWER

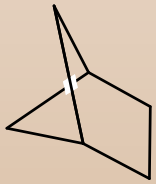
- Corresponding saturated hydrocarbon is C_6H_{14}
  - therefore 4 H's are not present ($C_6H_{14} - C_6H_{10} = 4 = 2^o$)
- This has two degrees of unsaturation
  - Two double bonds?
  - or triple bond?
  - or two rings?
  - or ring and double bond?



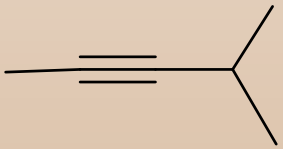
2 double bonds



1 ring
1 double bond



2 rings



1 triple bond

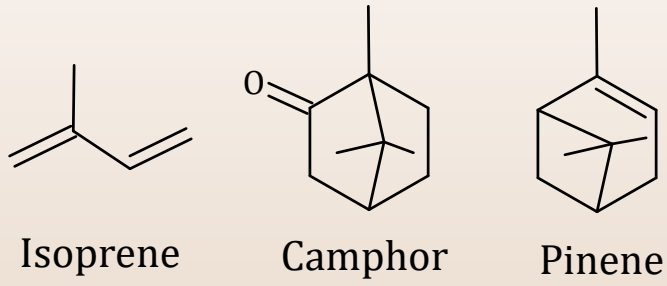
Physical Properties of Alkenes

1. Boiling points – Resemble alkanes, which is generally low boiling points; intermolecular force is primarily van der Waal's force and dispersion forces as the molecular weight increases. Boiling points increase with molecular weight.
2. Solubility in water – Insoluble in water since water is polar and alkenes are nonpolar.
3. Density –Less dense than water, just like alkanes.
4. Odor – Have unique odor, some good some bad.

Applications of Alkenes

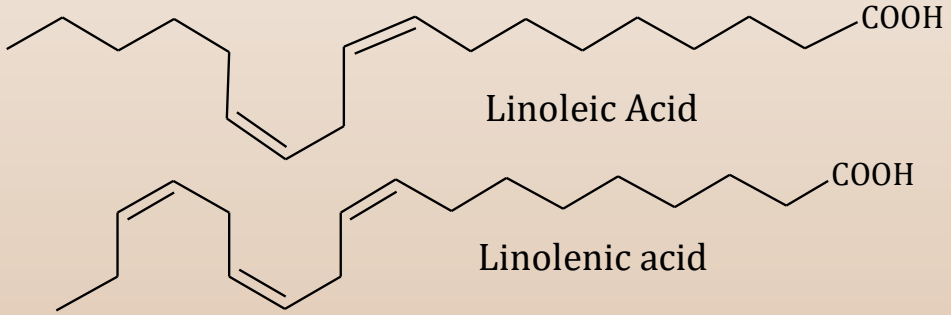
Alkenes are found in a variety of compounds:

- fragrances and flavors (***terpenes***) e.g., isoprene (the starting material for the rubber in tires); camphor, pinene



Isoprene Camphor Pinene

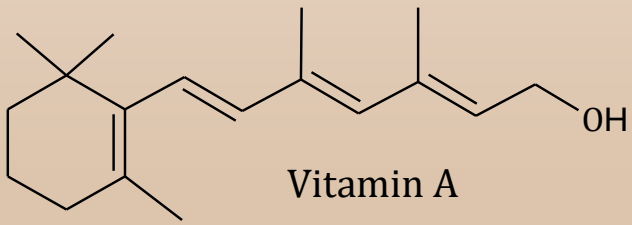
- ***fatty acids*** (oils) e.g., linoleic acid and linolenic acid.



Linoleic Acid

Linolenic acid

- Vitamins A: it is important in in the chemistry of vision (click this ***link*** to read more)



Vitamin A

We will talk more about alkenes after reactions of alkenes.

Key Words/Concepts

- Nomenclature
- Cis/trans isomerism
  - (geometric isomerism)
  - E/Z nomenclature
- Stability of alkenes
- Hydrogen deficiency index
  - (degree of unsaturation)
- Properties of alkenes