CHEM 221 section 52

LECTURE #05 Thurs., Jan.31, 2008

ASSIGNED READINGS:

TODAY'S CLASS:

3.1-3.5 Alkenes
nomenclature
properties: stability, isomerism

NEXT CLASS: finish Ch.3 (review kinetics & thermo!)
start Ch.4: reactions of alkenes

(1)

Chapter 3: Alkenes, Thermodynamics & Kinetics

Chapter Goals

Learn details about alkenes, plus fundamental principles governing rxns

- Learn to draw & name alkenes – *structure & nomenclature*
- Review principles of energetics & rxn rates – *thermodynamics, kinetics*

Chapter Outline:

3.1-3.5 Structure, properties & nomenclature of alkenes

3.6 How alkenes react – using curved arrows to show mechanisms

3.7 Thermodynamics & kinetics

(2)

3.1 Molecular formula & degree of unsaturation

- a "**saturated**" hydrocarbon = C_nH_{2n+2} ⇨ no rings, no C=C's
- "**unsaturated**" hydrocarbons: do not have max. # H's per C
  - ⇨ missing 2H for every 1 π-bond or ring
  - ⇨ an "**element of unsaturation**" = a π-bond or a ring

- To help deduce structure from formula: degree of unsaturation

  Elements of unsaturation = total # of π-bonds & rings
  = $\frac{1}{2}$ (2C + 2 – H) *C = #C & H = #H...*

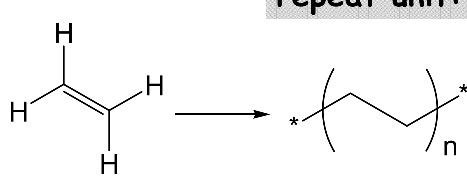
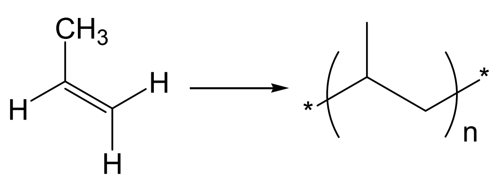
For compounds also containing heteroatoms:
- count halogens as hydrogens (use up 1 bond to C)
- ignore oxygen (can add O to chain without changing # C/H)
- count N as half a C (midchain: $-CH_2-$ units, vs. -NH- units...)

(3)

Useful for drawing all isomers of a given formula...

Industrial importance of alkenes (*aka* olefins)

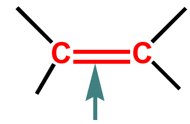
- Starting materials for **POLYMERS** = chains of repeating units
  - alkene polymers = plastics
  - polyethylene: 50 million tonnes/year made worldwide
  - big business: designing new catalysts for polymer synthesis

Monomer:		Polymer repeat unit:	Polymer name:
Ethylene: ETHENE			Polyethylene (PE) HDPE LDPE
Propylene: PROPENE			Polypropylene (PP) PP

(4)

Facts/images from Wikipedia – but that's not a real scientific reference!

3.2 Nomenclature of Alkenes

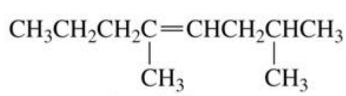


Functional group (centre of reactivity): **C=C π-bond**

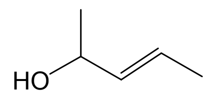
Typical IUPAC systematic naming method:

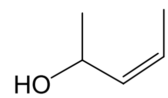
1. Find longest continuous chain containing C=C bond: **"-en-" infix**
2. # chain to give C=C lowest # possible *(if no principal funct gp present)*
   ⇨ **# given to "ene" unit refers to 1st C of C=C**
3. Specify geometry about the C=C bond: ***cis/trans*, or E/Z** (later…)

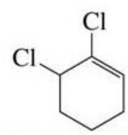
+ rest of rules: use principal function gp SUFFIX
choose # direction to bump into substituents early in chain



2,5-dimethyl-4-octene

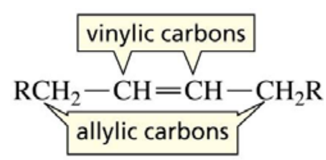






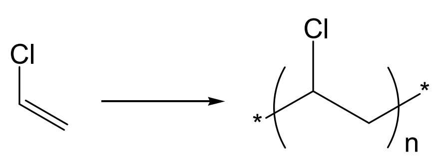
(5)

Terms for specific groups & positions: vinyl *vs.* allyl



$H_2C{=}CH-$
the vinyl group

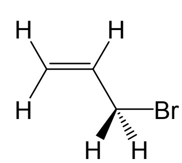
$H_2C{=}CHCl$
chloroethene
vinyl chloride



Polyvinylchoride (PVC)
aka vinyl

$H_2C{=}CHCH_2-$
the allyl group

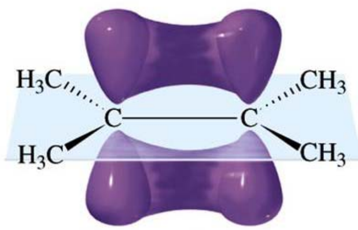
$H_2C{=}CHCH_2Br$
3-bromopropene
allyl bromide



An alkylating agent
= reagent for attaching "R" gp

(6)

3.3 Structure of alkenes: π-bond requires planarity…



p orbitals overlap to form a π bond

- To rotate about C=C: break p-overlap
- π-bond cannot rotate freely at T ≤ RT

IMPLICATIONS:

⇨ all atoms directly connected to π-bonded atoms are COPLANAR

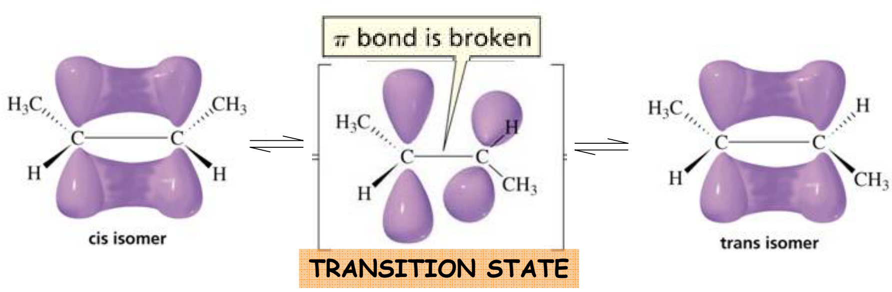
⇨ if sp^2 C's are asymmetrically substituted: ***geometric isomers***
cis vs. trans

(7)

a CIS alkene
substituents on "same side"

a TRANS alkene
substituents on "opposite sides"

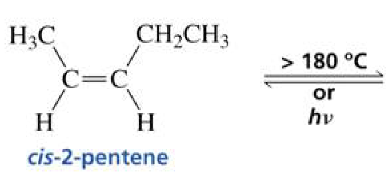
3.4 Cis-trans isomerization: a rxn with a large E_a!



Cis-trans isomerization requires large input of energy:

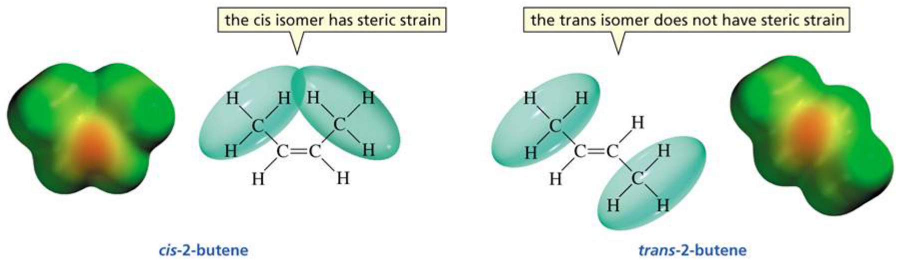
- E_a = 63 kcal/mol (~264 kJ/mol) *vs* 2.9 kcal/mol (12.1 kJ/mol) for C—C σ-bond rotation
- occurs at high temperature or after absorption of high E light

(8)



Relative stabilities: Steric strain in alkenes

Trans isomers generally more stable than cis: **less steric strain**



Difference in stability important when consider rxns that FORM alkenes…

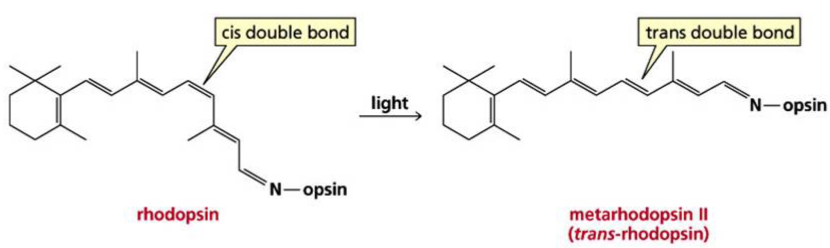
Which one will form preferentially?
⇨ depends on rxn's mechanism,
& relative stabilities!

(9) Fig. from Ch.4 p.174

Cis-Trans interconversion plays a crucial role in vision

Doesn't follow simple stability rules

- *cis* isomer is stabilized in specific environment within opsin protein
- isomerizing to *trans* results in changes in protein's conformation
- causes a signal to be sent…

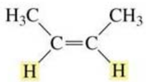


Another aspect of alkene chemistry in our lives:

- unsaturated fatty acids: have long alkyl chains with a few C=C bonds
- *cis* geometry is typical
- *trans* alkenes unusual in natural fats
- different physical properties, & processed differently by body…

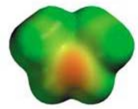
(10)

Alkene isomers have different properties
- **Geometry influences: packing, polarity, sterics…**

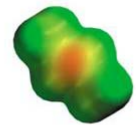


cis-2-butene

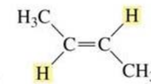
mp -139°C
bp +3.7°C

More globular shape

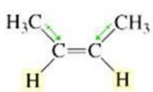
More rod-like
Better packing!



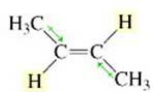
trans-2-butene

mp -105°C
bp +1°C

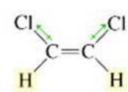
Polarity is affected by geometry: net dipole moment = ?



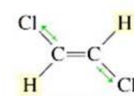
cis-2-butene
bp = 3.7 °C
μ = 0.33 D



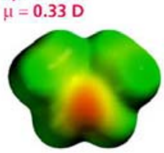
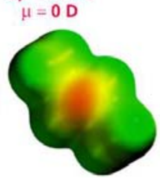
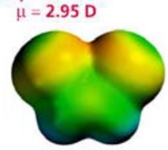
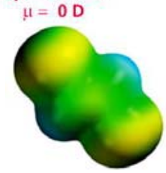
trans-2-butene
bp = 0.9 °C
μ = 0 D



cis-1,2-dichloroethene
bp = 60.3 °C
μ = 2.95 D

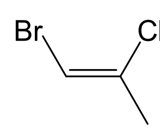


trans-1,2-dichloroethene
bp = 47.5 °C
μ = 0 D

(11)

3.5 *E,Z* system of alkene nomenclature



Cis & *trans* = <u>relative</u> terms, but only useful when 'importance' of substituents is obvious.

IUPAC "E/Z system" of naming is less ambiguous
especially for highly substituted alkenes (many R groups on C=C)

1. Assign priorities to substituents (by atomic #) on sp^2 Cs
2. Consider relative positions of higher priority gps on two sp^2 Cs (*i.e.*, across the π-bond):
   - same side ⇨ "Z" *zusammen* German for together ***(sounds like "zis" ?)***
   - opposite ⇨ "E" *entgegen* German for opposite

Z-isomer **E-isomer**

(Z)-1-bromo-2-chloropropene (E)-1-bromo-2-chloropropene

(12)

ASSIGNING PRIORITY: the Cahn-Ingold-Prelog rules

- Assign priorities based on atomic # (Z) of connecting atom:
  higher Z ⇨ higher priority
  e.g., Cl > O > N > C > H

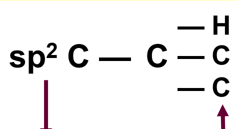
- For isotopes (same Z): higher priority to heavier isotope
  T (^{3}H) > D (^{2}H) > H

- If two identical atoms are attached to the sp^2 carbon:
  compare next atom in each chain until tie is broken
  $-CH_2CH_2Br$ > $-CH_2CH_3$ > $-CH_3$

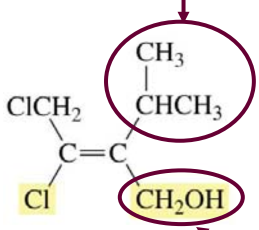
- A double bond counts as 2 bonds for both atoms involved
  triple bonds counted as 3 bonds each…

(13)

If there is a tie in priorities at 1st atoms, compare the next atoms…



NOTE: do NOT add atomic #s…

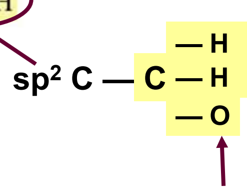


CH_2OH higher priority than *i*-Pr ⇨ a Z alkene

(Z)-3,4-dichloro-2-(1-methylethyl)-but-2-en-1-ol

OR, somewhat less systematically,

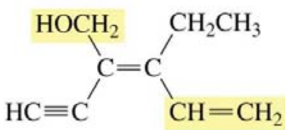
(Z)-3,4-dichloro-2-isopropylbut-2-enol



O has highest atomic # of H, C & O…
Thus: breaks the tie.

(14)

Multiple bonds treated as 2 or 3 bonds to same atom type



LEFT SIDE:
O outweighs C
Hydroxymethyl higher priority

RIGHT SIDE:
Vinyl group has
higher priority

THUS:
Higher priority gps
on opposite sides
⇨ an (E) ALKENE…

Note: **Terminal C=C's:** both substituents on one sp^{2}C are same
⇨ *no geometric isomers possible*

(15)

ASSIGNED READINGS

BEFORE NEXT LECTURE:

Read: rest of Ch.3

Review: kinetics, thermodynamics & equilibrium concepts from Gen.Chem.II (206)

Practice: drawing & naming alkenes (+ E/Z)

identifying relative stabilities

(16)