CHEM 221 section 01

LECTURE #11 Tues., Oct.11, 2005

ASSIGNED READINGS:

TODAY'S CLASS:

2.14-15	Conformations of substituted cyclohexanes
3.1	Alkenes: Formulae & degree of unsaturation
3.2	Nomenclature
3.3	Structure
3.4	E,Z system of nomenclature

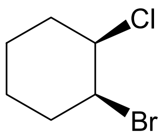
NEXT CLASS: rest of Ch.3, Ch.4…

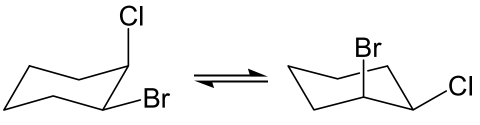
http://artsandscience.concordia.ca/facstaff/P-R/rogers

2.14 Conformations of disubstituted cyclohexanes

Naming convention: describes relative orientation of substituents to distinguish between *geometric isomers*
= isomers with same connectivity of atoms, but different spatial orientations

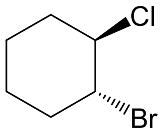
On same face of ring: "*cis*"

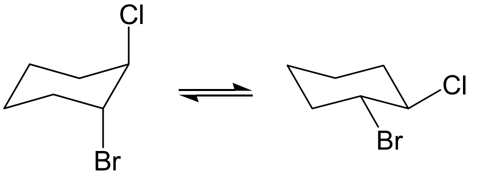




cis-1-bromo-2-chlorocyclohexane

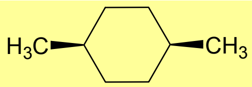
On opposite face of ring: "*trans*"

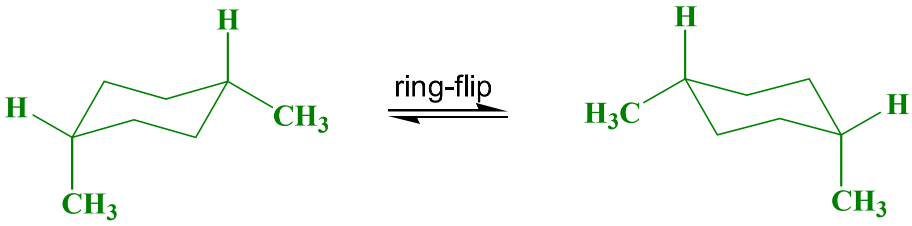




trans-1-bromo-2-chlorocyclohexane

The chair conformers of *cis*-1,4-dimethylcyclohexane

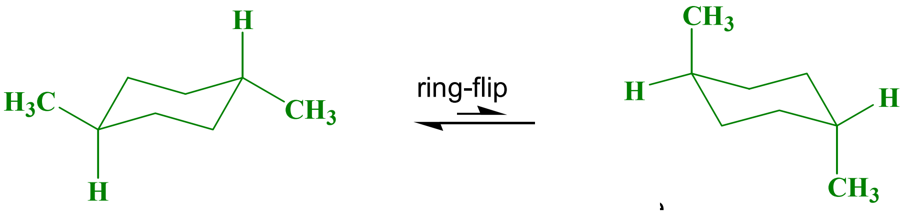




Both conformers have:
1 equatorial methyl
1 axial methyl

equally stable,
so both chair conformers
will be equally common
in a sample of molecules

The chair conformers of *trans*-1,4-dimethylcyclohexane

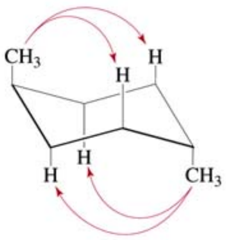


This conformer has:
2 equatorial methyls

More stable
Thus: most common
conformation in which
to find this compound

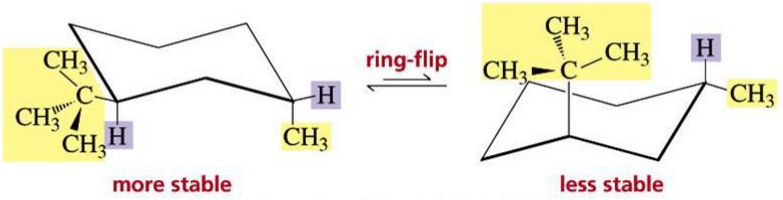
This conformer has:
2 axial methyls

Four
1,4-diaxial
interactions
→ Less stable



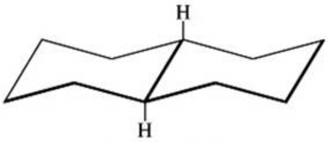
Differences between geometric isomers

trans-1-*tert*-butyl-3-methylcyclohexane



cis-1-*tert*-butyl-3-methylcyclohexane

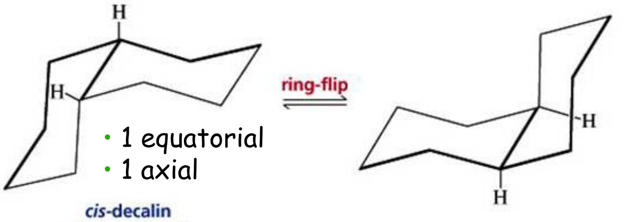
2.15 Conformations of fused rings



trans-decalin
trans-fused rings
more stable

Think of the 2nd ring as a substituent on the 1st ring:

- both substituents equatorial
- quite a stable conformation
  (ring flip would yield both axial, so compound will remain as shown)



- 1 equatorial
- 1 axial

cis-decalin
cis-fused rings
less stable

- after ring flip: still 1 eq, 1 ax
- both confo's less stable than trans-fused rings

Trans-fused cyclohexane rings are more stable than cis-fused rings
(note: would have to break C-C bonds to change geometry of ring fusion…)

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

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

$CH_3CH_2CH_2CH_2CH_3$

an alkane

C_5H_{12}

C_nH_{2n+2}

$CH_3CH_2CH_2CH{=}CH_2$

an alkene

C_5H_{10}

C_nH_{2n}

a cyclic alkane

C_5H_{10}

C_nH_{2n}

a cyclic alkene

C_5H_8

C_nH_{2n-2}

- Handy trick to help deduce a structure from a formula:

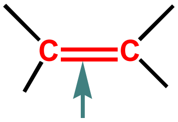
  Elements of unsaturation (degree of unsaturation)

  = total # of π-bonds & rings

  = ½ (2C + 2 – H) *where C = #C & H = #H…*

  For compounds containing heteroatoms too:
  - *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…)*

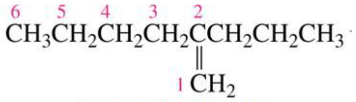
3.2 Nomenclature of Alkenes



Functional group (centre of reactivity) = C-C double bond

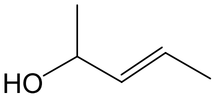
Typical IUPAC systematic naming method:

1. Find longest continuous chain containing the C=C bond
   ⇨ *use "-en-" infix to denote C=C in parent chain*
2. Number chain to give the C=C the lowest # possible *(unless…see #3)*
   ⇨ *the # given to the C=C refers to the 1st C of the C=C*
3. Specify geometry about the C=C bond: *cis/trans*, or E/Z (later…)
4. When other functional groups present (-OH, -NR$_2$…), the group that defines the name's suffix determines #ing direction
5. Typical rules about: naming substituents first, alphabetically
   no number needed if C=C between C1 & C2
   no # for cyclic monoalkenes; C=C defines C1&2
   # in direction that minimizes #s

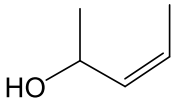


$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\underset{\overset{\|}{{}_1CH_2}}{\overset{2}{C}}CH_2CH_2CH_3$

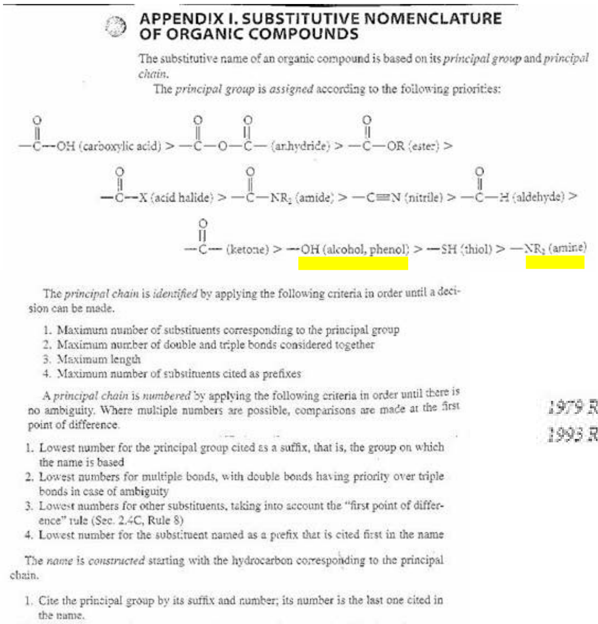
2-propyl-1-hexene



***trans*-pent-3-en-2-ol**



***cis*-pent-3-en-2-ol**



APPENDIX I. SUBSTITUTIVE NOMENCLATURE OF ORGANIC COMPOUNDS

The substitutive name of an organic compound is based on its *principal group* and *principal chain.*

The *principal group* is *assigned* according to the following priorities:

$-\overset{O}{\overset{\|}{C}}-OH$ (carboxylic acid) > $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$ (anhydride) > $-\overset{O}{\overset{\|}{C}}-OR$ (ester) >
$-\overset{O}{\overset{\|}{C}}-X$ (acid halide) > $-\overset{O}{\overset{\|}{C}}-NR_2$ (amide) > $-C\equiv N$ (nitrile) > $-\overset{O}{\overset{\|}{C}}-H$ (aldehyde) >
$-\overset{O}{\overset{\|}{C}}-$ (ketone) > $-OH$ (alcohol, phenol) > $-SH$ (thiol) > $-NR_2$ (amine)

The *principal chain* is *identified* by applying the following criteria in order until a decision can be made.

1. Maximum number of substituents corresponding to the principal group
2. Maximum number of double and triple bonds considered together
3. Maximum length
4. Maximum number of substituents cited as prefixes

A *principal chain* is *numbered* by applying the following criteria in order until there is no ambiguity. Where multiple numbers are possible, comparisons are made at the first point of difference.

1. Lowest number for the principal group cited as a suffix, that is, the group on which the name is based
2. Lowest numbers for multiple bonds, with double bonds having priority over triple bonds in case of ambiguity
3. Lowest numbers for other substituents, taking into account the "first point of difference" rule (Sec. 2.4C, Rule 8)
4. Lowest number for the substituent named as a prefix that is cited first in the name

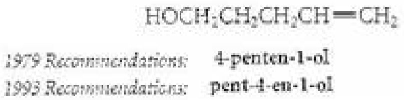
The *name* is *constructed* starting with the hydrocarbon corresponding to the principal chain.

1. Cite the principal group by its suffix and number; its number is the last one cited in the name.
2. If there is no principal group, name the compound as a substituted hydrocarbon.
3. Cite the names and numbers of the other substituents in alphabetical order at the beginning of the name.

From Loudon's *Organic Chemistry* 4th Ed.
Oxford University Press, 2002

Question from earlier:
Which has priority, alcohol *vs.* amine?
ANS: alcohol

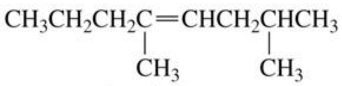
An alkene with an -OH & an -NH$_2$ would be named as "_-amino____-en-_-ol"



$HOCH_2CH_2CH_2CH{=}CH_2$

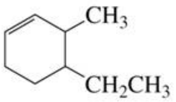
1979 Recommendations: 4-penten-1-ol
1993 Recommendations: pent-4-en-1-ol

Some examples:



$CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

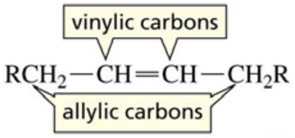
2,5-dimethyl-4-octene
not
4,7-dimethyl-4-octene
because 2 < 4



4-ethyl-3-methylcyclohexene

1,6-dichlorocyclohexene
not
2,3-dichlorocyclohexene
because 1 < 2

Special Nomenclatures: vinyl & allyl



vinylic carbons

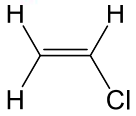
$RCH_2—CH{=}CH—CH_2R$

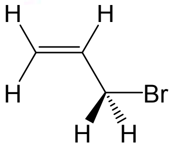
allylic carbons

$H_2C{=}CH—$
the vinyl group

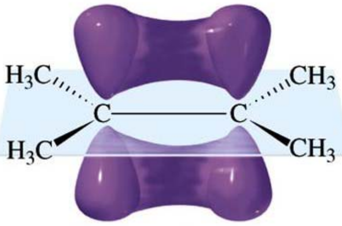
$H_2C{=}CHCH_2—$
the allyl group

	$H_2C{=}CHCl$	$H_2C{=}CHCH_2Br$
systematic name:	chloroethene	3-bromopropene
common name:	vinyl chloride	allyl bromide





3.3 Structure of alkenes: π-bond requires planarity…



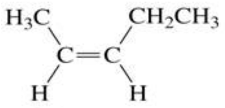
p orbitals overlap to form a π bond

- To rotate about C=C:
  E required to break p-overlap
- π-bond <u>cannot</u> rotate freely
  at T ≤ room temperature

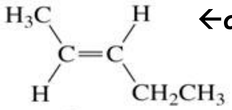
IMPLICATIONS:

- all atoms directly connected to π-bonded atoms are COPLANAR
- if sp^2 C's are asymmetrically substituted: ***geometric isomers***
  cis vs. trans

a CIS alkene→
substituents on
"same side"



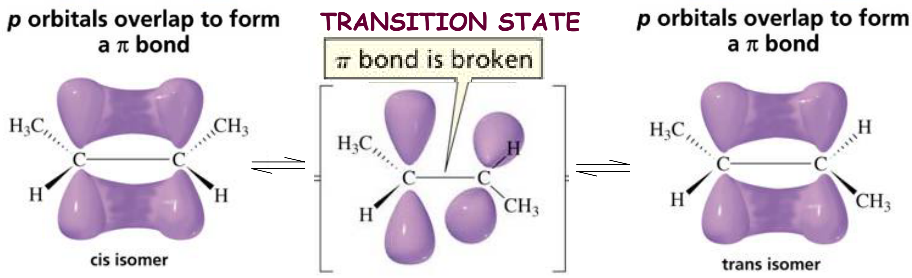
cis-2-pentene



trans-2-pentene

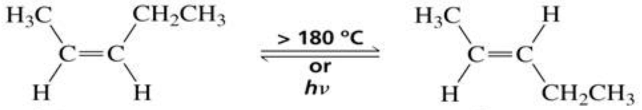
←a TRANS alkene
substituents on
"opposite sides"

3.4 Cis-trans isomerization: a rxn with a <u>large</u> E_a!



<u>Cis-trans isomerization requires large input of energy</u>:

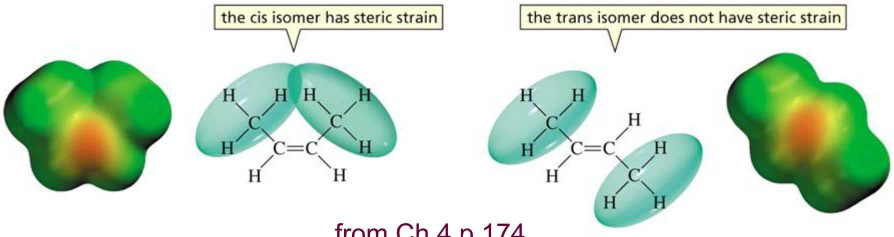
- E_a = 63 kcal/mol (~264 kJ/mol)
  compare to C-C rotation barrier 2.9 kcal/mol (12.1 kJ/mol)
- occurs at high temperature or after absorption of high E light



cis-2-pentene *trans*-2-pentene

Relative stabilities: Steric strain in alkenes

Trans isomers generally more stable than cis
→ less steric strain


the cis isomer has steric strain

the trans isomer does not have steric strain

cis-2-butene

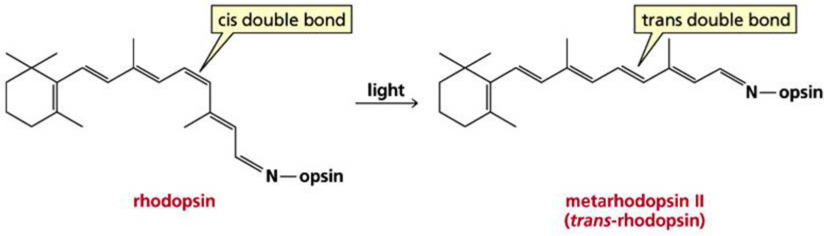
from Ch.4 p.174

trans-2-butene

This difference in stability becomes important when we consider reactions that FORM alkenes…
Which one will form preferentially?
→ depends on rxn's mechanism, & relative stabilities!

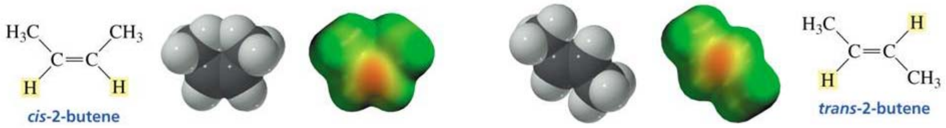
Cis-Trans interconversion plays a crucial role in vision

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:
- fatty acids (in fats) have long unsaturated alkyl chains
- *cis* geometry is typical; *trans* alkenes unusual in natural fats
- different physical properties, & processed differently by body…

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



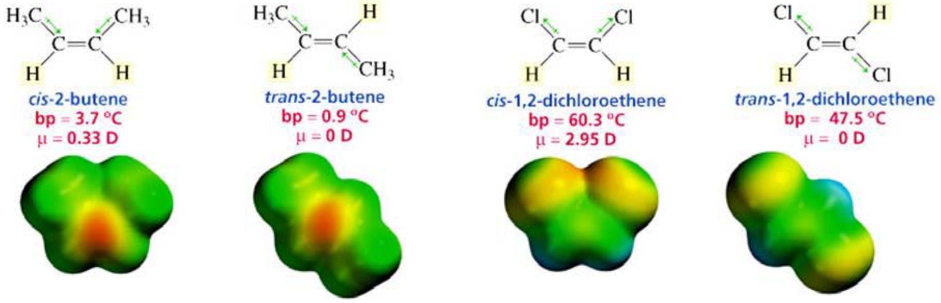
mp -139°C
bp +3.7°C

More globular shape

More rod-like
Better packing!

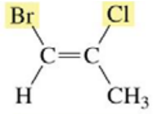
mp -105°C
bp +1°C

Polarity is affected by geometry: net dipole moment = ?



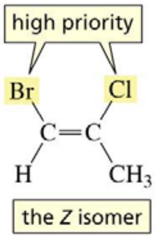
3.5 The *E,Z* system of alkene nomenclature

Cis & *trans* are helpful <u>relative</u> terms, but only useful when 'importance' of substituents is obvious. *What about…* →

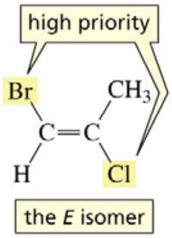


IUPAC "E/Z system" of naming is less ambiguous especially for highly substituted alkenes (many R groups on C=C)

1. Assign priorities to substituents (by atomic #) on the sp^2 Cs
2. Consider relative positions of the higher priority groups on the two different C's (*i.e.,* across the p-bond):
   - same side ⇨ "Z" from *zusammen* German for together (*"zis" ?!)*
   - opposite ⇨ "E" from *entgegen* German for opposite



(Z)-1-bromo-2-chloropropene



(E)-1-bromo-2-chloropropene

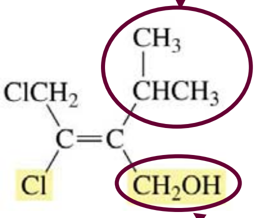
ASSIGNING PRIORITY: the Cahn-Ingold-Prelog rules

- Assign priorities based on atomic number (Z) of connecting atom:
  higher Z ⇨ higher priority
  e.g., Cl > O > N > C > H
- For isotopes (identical atomic number):
  higher priority to isotope with larger mass
  T (^3H) > D (^2H) > 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
  Similarly, triple bonds counted as 3 bonds each…

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

$$sp^2\ \mathrm{C} - \mathrm{C}\begin{array}{l}-\mathrm{H}\\-\mathrm{C}\\-\mathrm{C}\end{array}$$

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

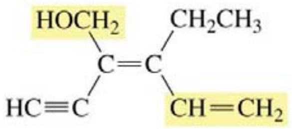
$$sp^2\ \mathrm{C} - \mathrm{C}\begin{array}{l}-\mathrm{H}\\-\mathrm{H}\\-\mathrm{O}\end{array}$$

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

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

LEFT SIDE:
O outweighs C
Hydroxymethyl higher priority

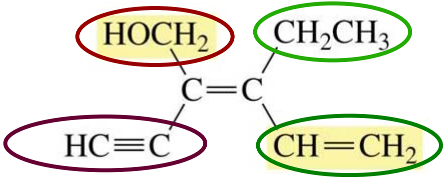
RIGHT SIDE:
Vinyl group has
higher priority



THUS:
Higher priority groups on either side of C=C are on opposite sides
→ an (E) ALKENE…

$$\begin{array}{l}\mathrm{H}-\\\mathrm{H}-\mathrm{C}-sp^2\mathrm{C}\\\mathrm{O}-\end{array}$$

$$sp^2\mathrm{C}-\mathrm{C}\begin{array}{l}-\mathrm{H}\\-\mathrm{H}\\-\mathrm{C}\end{array}$$



$$\begin{array}{l}\mathrm{C}-\\\mathrm{C}-\mathrm{C}-sp^2\mathrm{C}\\\mathrm{C}-\end{array}$$

$$sp^2\mathrm{C}-\mathrm{C}\begin{array}{l}-\mathrm{H}\\-\mathrm{C}\\-\mathrm{C}\end{array}$$

NOTE: Terminal C=C's: both substituents on one sp^2C are the same (H)
⇨ no geometric isomers possible

ASSIGNED READINGS

BEFORE NEXT LECTURE:

Read: rest of Ch.3

Practice: Naming alkenes (especially E/Z)