CHEM 221 section 01

LECTURE #16 Thurs., Oct.27, 2005

ASSIGNED READINGS:

TODAY'S CLASS: Rest of Ch.4, start Ch.5

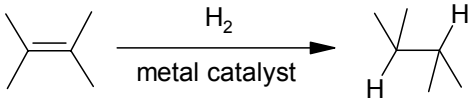
NEXT LECTURE: continue with Ch.5

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

4.11 Relative stabilities of alkenes → determined from rates of rxn with H_2

"HYDROGENATION":

Common catalysts:
nickel (Ni), Pt/C, Pd/C



= platinum or palladium-impregnated graphite
"platinum on carbon", "palladium on carbon"

Exact **Mechanism of hydrogenation** is not known, but is roughly like this:

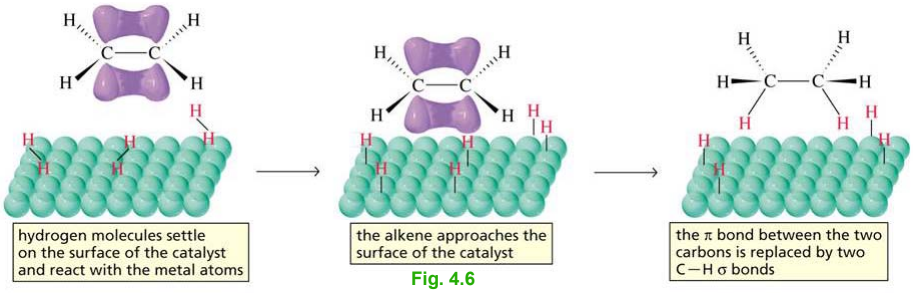


Fig. 4.6

Heats of hydrogenation (ΔH_{rxn} for alkene + H_2 / cat) provide a measure of relative E of alkene isomers

e.g., three isomers:
3-methylbutene
2-methylbutene
2-methyl-2-butene

H_2 / Pt/C →

All yield same product:

2-methylbutane + HEAT

More heat released MUST mean original alkene was less stable…

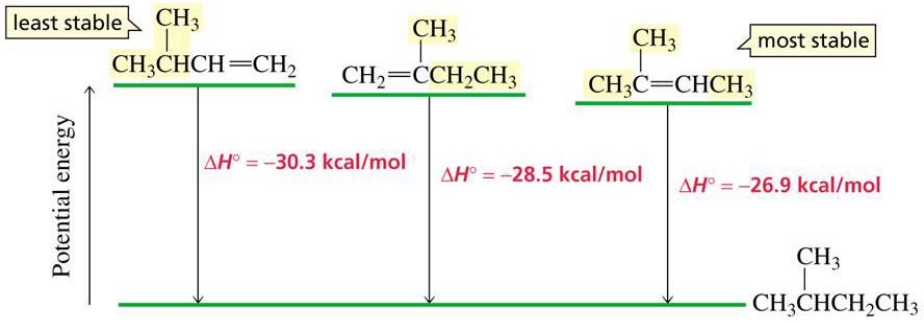


Fig. 4.7

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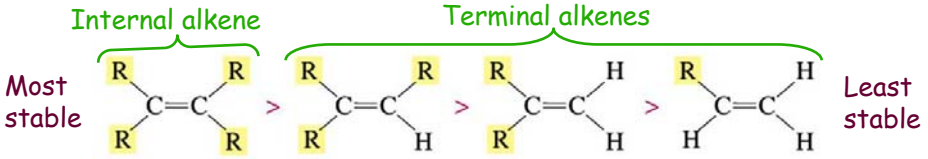
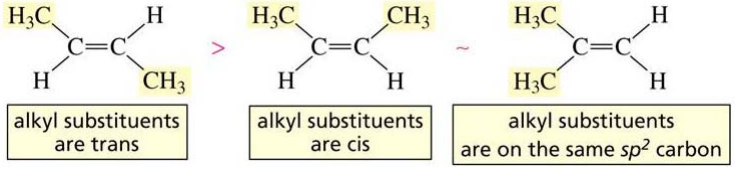
Relative stabilities of alkenes:
Correlates with steric strain (less strain → more stable)



- Terminal alkenes (C=C at end of chain) are ***less stable*** than isomeric internal alkenes (C=C midchain) → *steric effects shown below*



- More highly substituted alkenes are generally more stable
- Other factor to consider: extended π-systems are REALLY stable

Relevance? *Predicting regiochemistry of rxns that form alkenes: Ch.11*
→ major product is usually the more-stable alkene

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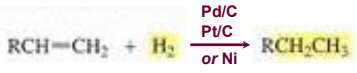
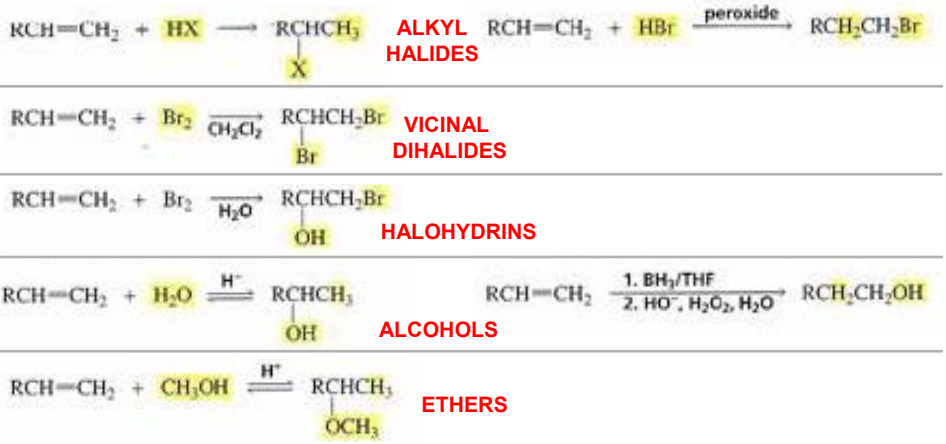
4.12 Reactions and synthesis

Summary of alkene rxns: what can we make starting from here?

STARTING WITH AN ALKENE
- **Can add electrophiles**



MARKOVNIKOV ADDITIONS **ANTI-MARKOVNIKOV ADDITIONS**



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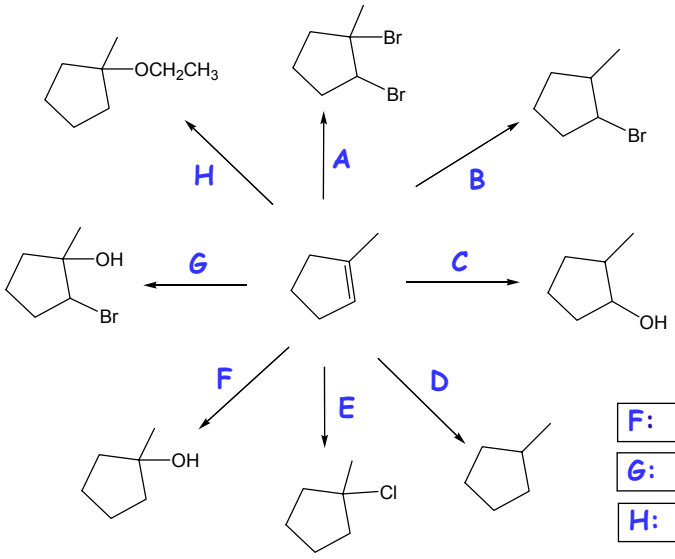
What reagents should we use to perform the following synthetic transformations?



A: Br_2 / non-Nu solvent

B: HBr, ROOR (anti-Markovnikov)

C: hydroboration (anti-Markovnikov)
1. BH_3 / THF
2. H_2O_2 / OH^-

D: H_2 / Pd cat.

E: HCl / non-Nu solvent

F: H_2O, H^+ cat.

G: Br_2 / H_2O

H: CH_3CH_2OH, H^+ cat.

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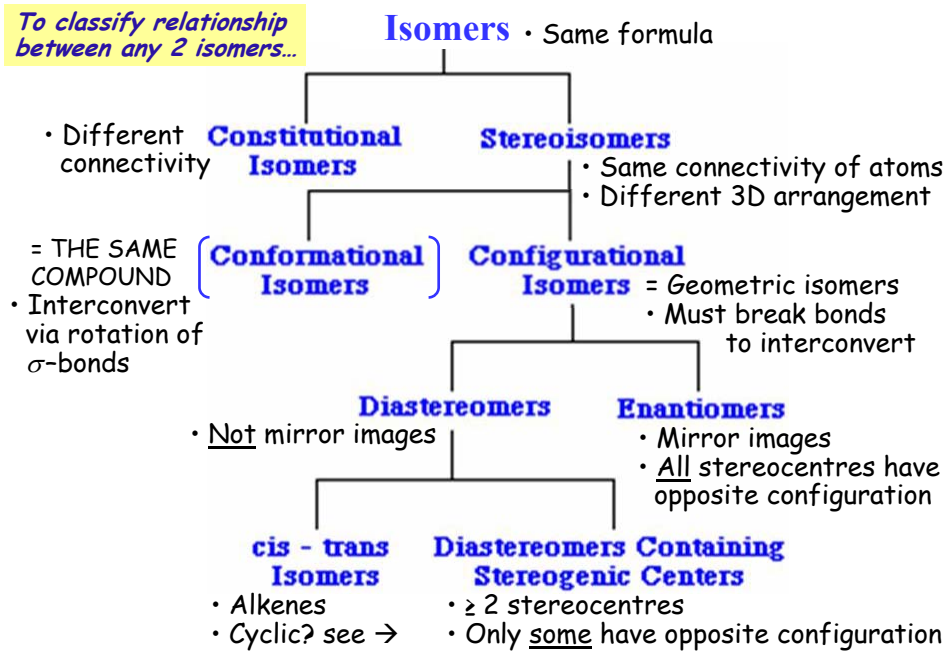
Chapter 5: Stereochemistry

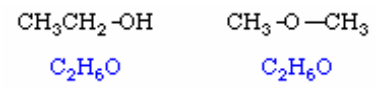
Chapter Goals: *To understand the importance of permanent differences in the spatial arrangement of atoms in molecules.*

- Learn to identify different types of isomers.
- Understand symmetry and chirality, and their implications.
- Understand stereochemistry of reactions.

5.1	Cis-trans isomers
5.2	Chirality
5.3	Asymmetric carbons, chirality centres, and stereocentres
5.4	Isomers with one asymmetric carbon
5.5-5.6	Drawing & naming enantiomers
5.7-5.8	Optical activity, optical purity & enantiomeric excess
5.9-5.11	Isomers with more than on asymmetric carbon
5.12	Rxns of compounds that contain an asymmetric carbon
5.13	Absolute configuration
5.14-5.15	Separating enantiomers: in the lab, & biologically
5.16-5.18	*covered in more advanced courses*
5.19	Stereochemistry of electrophilic addition rxns of alkenes
5.20	Stereochemistry of enzyme-catalyzed reactions



Classification of Isomers



1. Constitutional isomers: different connectivity

e.g. 1-butane and methylpropane (*i.e.* isobutane)

SUBTYPES:

(a) Positional isomers: different position of functional groups
e.g. 1,2-dichlorobenzene (mp 183 °C)
1,3-dichlorobenzene (mp 172 °C)

(b) Functional isomers: different functional groups
same bulk formulas but very different properties
e.g. C_2H_6O = ethanol, methoxymethane, *etc…*

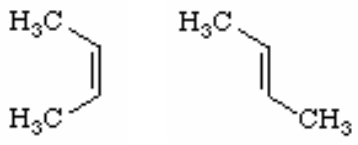
2. Stereoisomers: same connectivity, but different arrangement of atoms in space
(permanently different 3D orientation)

"Configurational isomers"

- actually different compounds (definitely isolable)
- to interconvert them: must BREAK covalent bonds

a) *cis/trans* isomers: arrangement around C=C of alkenes

cis- and *trans*-2-butene



Must break π-bond to interconvert them
(very LARGE E_a! not thermally accessible at RT; requires UV)

b) Isomers that contain CHIRAL centres: next…

we'll see that class (b) includes cyclic *cis-trans* isomers

Isomers are NON-identical…

TECHNICALLY SPEAKING: conformers are isomers

IN PRACTICE: Usually non-isolable (cannot isolate them)…

THEREFORE: conformers not usually considered isomers:
treat them as IDENTICAL

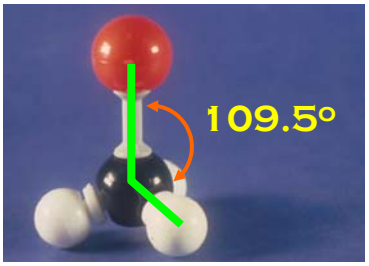
To be isomers, molecules must not be identical.
- check: are they just different conformations?

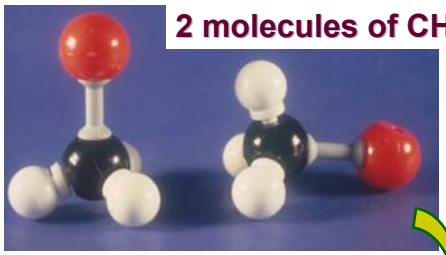
The test for "identicality": can they be superimposed??

Carbon is tetrahedral: Consequences…

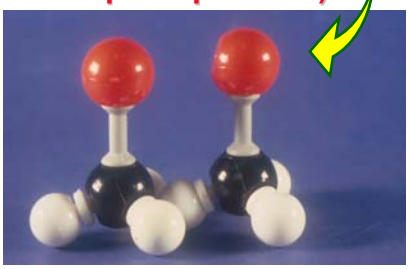
EXAMPLE #1:

Td C with one substituent (CH_3X)





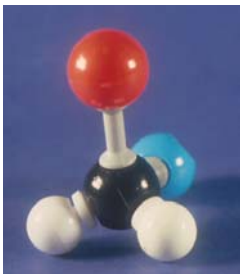
Identical molecules!
(can be superimposed…)



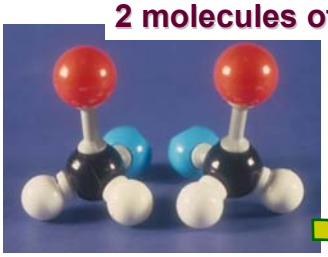
Carbons with two different substituents still have two substituents that are the same… ∴ symmetric

EXAMPLE #2:

Td C with TWO substituents (CH_2XY)



2 molecules of CH_2XY



Identical molecules! (can be superimposed…)

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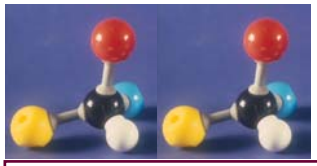
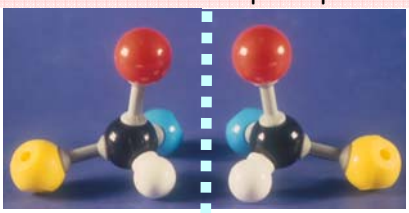
Carbons with 4 different groups are "asymmetric"

Sometimes 2 CHXYs ARE superimposable (∴ identical)



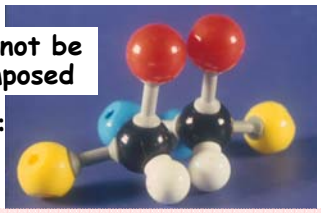
Td C with THREE substituents (CHXYZ)

NOT all CHXYs are identical (non-identical if non-superimposable)



They are mirror images

AND cannot be superimposed



THEREFORE: different compounds

If two molecules are **non-superimposable mirror-images** of each other:

they have **opposite "configuration"**

The two molecules are called **"ENANTIOMERS"**

(Greek *enantion* = opposite)

These molecules are described as being **"handed"** or **"CHIRAL"**

(Greek *cheir* = hand)

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5.2 Chirality: "Chiral" things are asymmetric

Why does your right hand not fit properly in your left glove?

ANS: because hands are chiral.

- Right and left hands are mirror images.
- They are not superimposable

} they have **opposite configuration**!

- To convert your right hand into your left hand, you would need to:
  remove your thumb & move it to other side of palm
  (and your fingers too actually)

Anything with a non-superimposable mirror image is CHIRAL.

- HINT: all chiral objects are inherently asymmetric
  e.g., hands, feet

Anything with a superimposable mirror image is ACHIRAL.

- HINT: look for internal planes of symmetry
  - any object (or molecule) with a mirror plane within it can be superimposed onto its own mirror image
    ⇨is symmetric, ∴ achiral
    e.g., human body (as viewed from the outside)

Key stereochemical terms: CHIRALITY

"Chiral" describes objects that are not superposable on their mirror image, *i.e.,* objects that have "handedness"

Achiral is thus used to described the lack of chirality

A plane of symmetry is an imaginary plane passing trough an object, dividing it so that one half is the mirror image of the other one

A centre of symmetry is a point so situated that identical components of an object are located on opposite sides and equidistant from that point along any axis passing through it

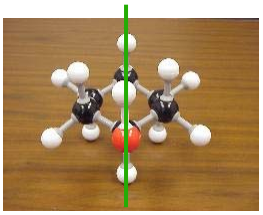
Two ways to evaluate a molecule, or any object, as being ACHIRAL

…if it's not achiral, it's chiral…

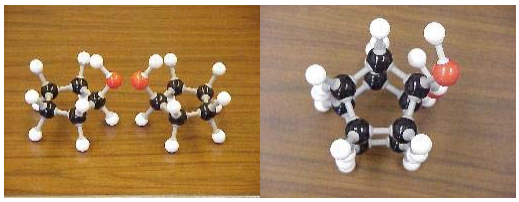
1.) Does it have a plane of symmetry? If YES ⇨ achiral

2.) Does it have a superimposable mirror image? If YES ⇨ achiral

Cyclohexanol



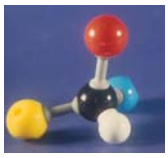
Plane of symmetry



Superimposable mirror image

5.3 Stereocenters go by many names

- An atom with 4 different substituents is called a **stereocenter**
- also called: stereogenic center (gives rise to stereoisomers)
  chirality center, chiral center, asymmetric atom…



A compound with n stereocenters can have a maximum of 2^n "stereoisomers"

- a pair of molecules where ALL stereocentres have opposite configuration = enantiomers
- if NOT ALL stereocentres are opposite: molecules being compared called diastereomers

NEXT UP: learning to draw enantiomers & diastereomers
perspective drawings *(dashes & wedges)*
Fisher projections

ASSIGNED READINGS

BEFORE NEXT LECTURE:

Read: Ch.5 up to 5.5

Practice: Ch.4 writing mechanisms & predicting products