Recall

R–H + X_2 → R–X + XH
Reactivity: $F_2 > Cl_2 > Br_2 >> I_2$ (unreactive)
Selectivity: more reactive → less selective (mixture of products)
Less reactive → more selective (single products)
Hammond's postulate:
Chlorination → RDS is exothermic → early TS → small ΔEa
Bromination → RDS is endothermic → late TS → large ΔEa

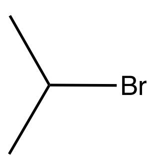
Naming of Alkyl Halides = Haloalkanes

CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Methyl chloride Chloromethane	Methylene chloride Dichloromethane	Chloroform Trichloromethane	Carbon tetrachloride Tetrachloromethane

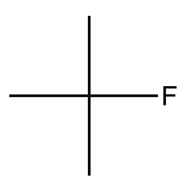
Structure and Nomenclature

1) Find longest chain with largest number of branches
2) Number from end so as to give 1st halogen the lowest number
3) Name prefix with "halo" (chloro, bromo, iodo, fluoro) OR name alkyl and add halide (chloride, bromide, iodide, fluoride) as the suffix

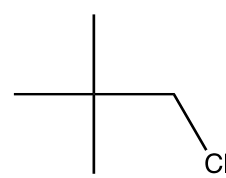
Examples:



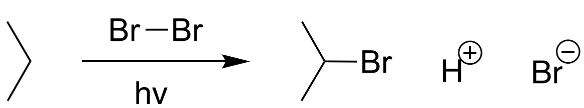
Isopropyl Bromide
2-Bromopropane



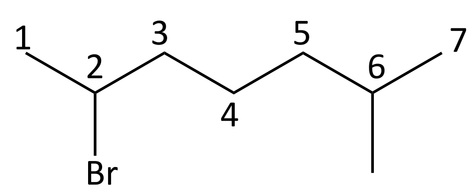
tert-Butyl fluoride
2-Fluoro-2-methylpropane



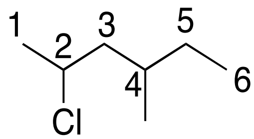
Neopentyl chloride
1-Chloro-2,2-dimethylpropane



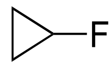
propane



2-bromo-6-methylheptane

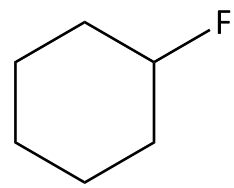


2 -chloro -4-methylhexane

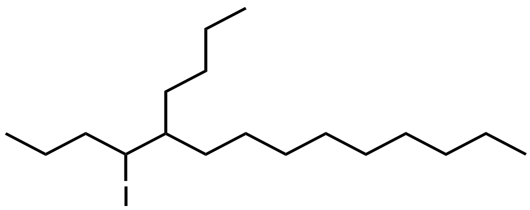


Fluorocyclopropane

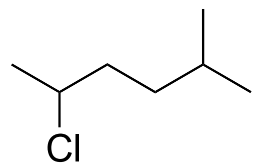
Cyclopropyl fluoride



cyclohexyl fluoride
1-fluorocyclohexane



5-Butyl-4-iodotetradecane

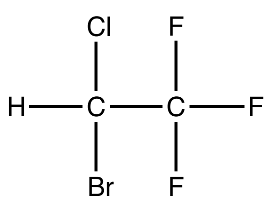


2-chloro-5-methylhexane

Note: Tert-Butyl = t-Butyl = tertiary Butyl

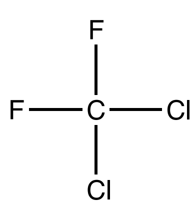
Applications of Haloalkanes

1.) Halothane (anesthetic)

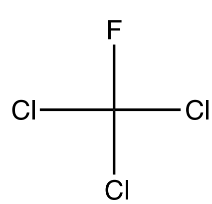


1,1,1-trifluoro-2-bromo-2-chloroethane

2.) Freon = refrigerants/coolants

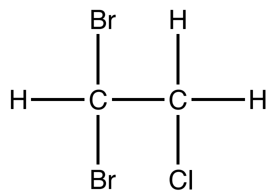


Freon 12



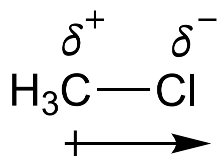
Freon 11

3.) 1,1-dibromo-2-chloroethane = male contraceptive (sperm count drops down to zero from 100 million/mL)



Physical Properties of Alkyl Halides:

- Governed primarily by dipole-dipole interactions, more polar than hydrocarbons/alkanes.
- High MP and BP relative to hydrocarbons of similar molecular weight
- Good solvents for organic compounds e.g. methylene chloride (CH_2Cl_2) and chloroform ($CHCl_3$) are very common.
- If % composition ≥ 65% halogen by weight, then more dense than water ($\rho > 1.0$ g/cm^3)
- Immiscible (insoluble) in H_2O, which floats on top of the halide

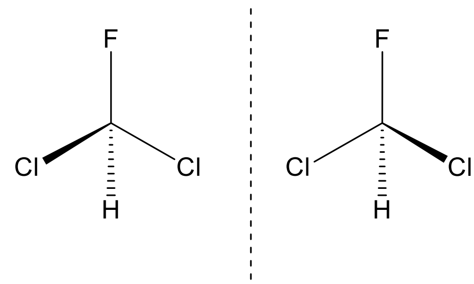


NEXT SECTION: Lecture Outline 3: Stereochemistry and Chirality

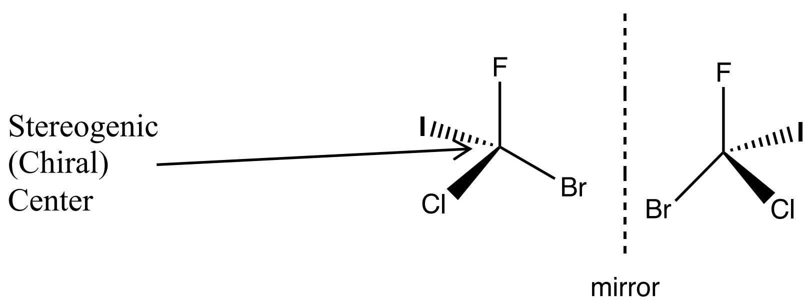
Introduction to Stereochemistry and Chirality (terminologies)

Chiral object or molecule: has a non-superimposable mirror image
Achiral object: not chiral, has a superimposable mirror image

Tetrahedral carbon with 4 different groups are said to be **CHIRAL** and are said to contain a **STEREOGENIC (CHIRAL) CENTER**



Achiral, identical – have a plane of symmetry



Non-superimposable

1850 - Louis Pasteur separated the "right-handed" and "left-handed" forms of tartaric acid crystals (from wine)

1876 - J. van't Hoff and Le Bel proposed that differences are due to tetrahedral geometry of carbon
- Kolbe did not receive van't Hoff's idea very well

1901 - J. van't Hoff was the first recipient of the Nobel Prize in Chemistry

Resolution – separation of enantiomers

Enantiomers: molecules that are stereoisomers and are non-superimposable mirror images of each other. Opposite stereochemistry at every chiral center. Physical properties of enantiomers are the same, as far as they are measured in an achiral environment. A chiral agent of molecule is necessary to distinguish them.

Diastereomers: all stereoisomers that are not enantiomers

Enantiomers

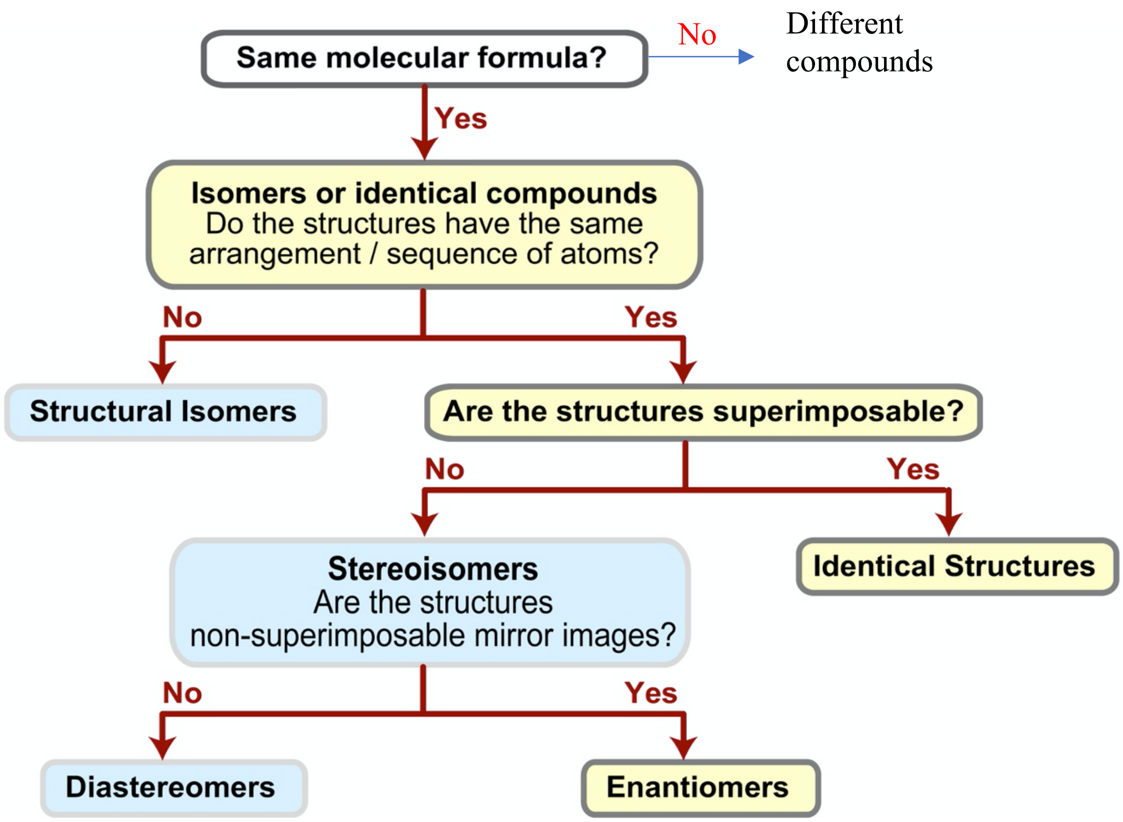
Same physical properties (i.e., m.p, b.p, etc.)
Bend polarized light differently
Hard to separate
Mirror images
Non-superimposable

Diastereomers

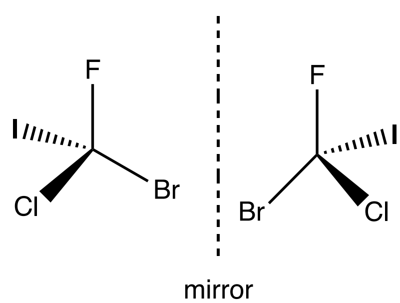
Different chemical properties

Easier to separate
Not mirror images
Non-superimposable

How to Determine Relationships Among Structures



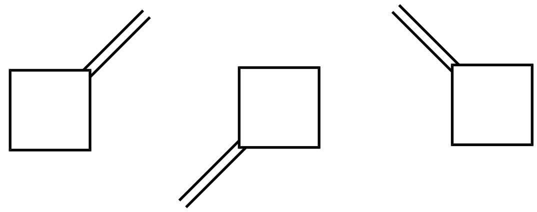
Example 1:



1) Same molecular formula? Yes
2) Same arrangement of atoms? Yes
3) Superimposable? No
4) Non-superimposable mirror images? Yes

NON-SUPERIMPOSABLE → Enantiomers

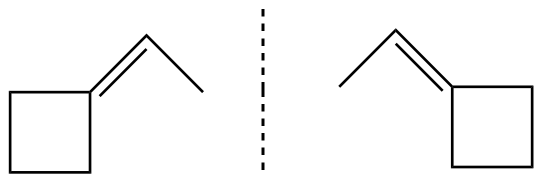
Example 2:



Identical structures, superimposable, achiral

1. Same molecular formula? Yes
2. Same arrangement of atoms? Yes
3. Superimposable? Yes

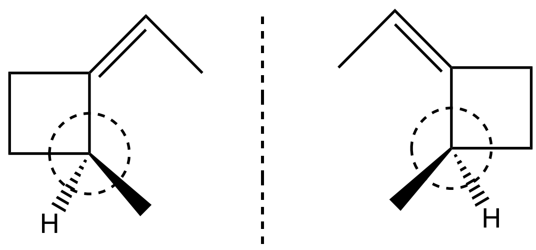
Example 3:



- achiral
- no stereogenic center

Same, identical compound

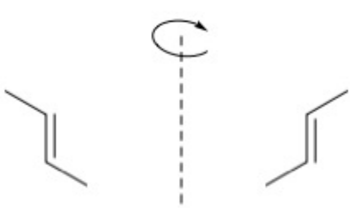
1. Same molecular formula? Yes
2. Same arrangement of atoms? Yes
3. Superimposable? Yes



- enantiomers
- dashed circle is stereogenic center carbon atom

1. Same molecular formula? Yes
2. Same arrangement of atoms? Yes
3. Superimposable? No
4. Non-superimposable mirror images? Yes

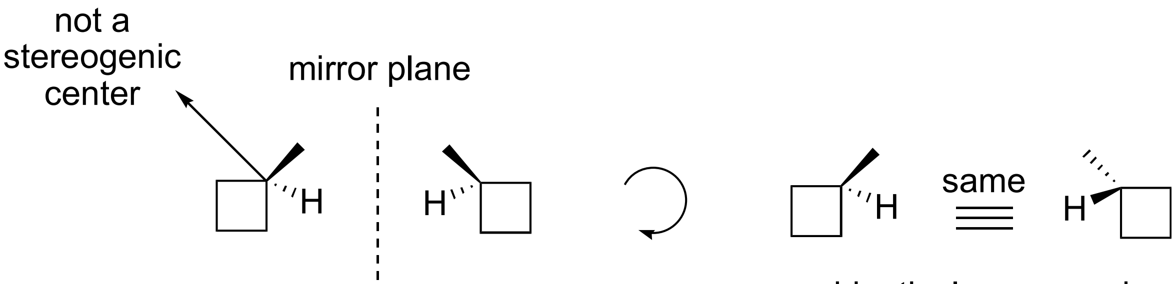
Example 4:



These two mirror images are superimposable as seen by a simple rotation

trans-2-butene is achiral

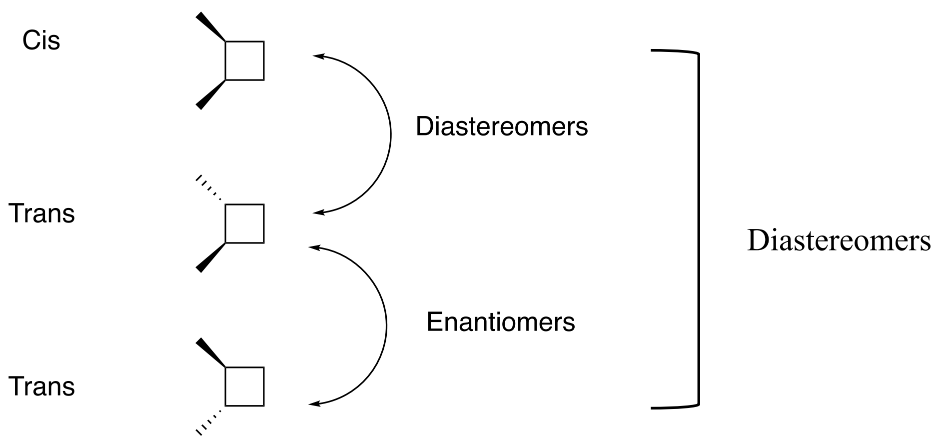
Examples of determining chirality within molecules



- identical compounds

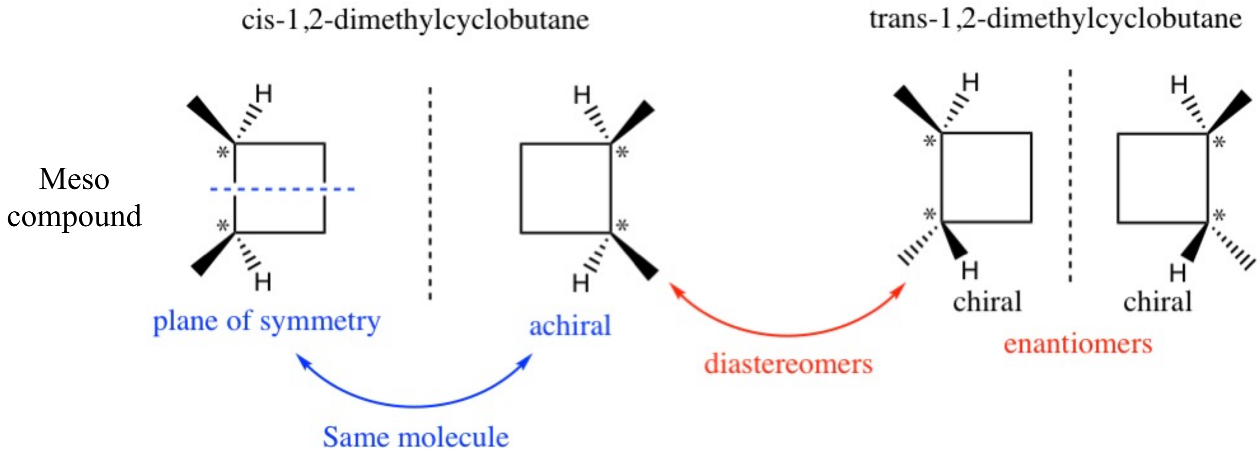
chiral?
No, both structures are achiral (not chiral) and different drawings of same molecule

Example:

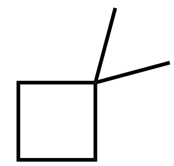


Enantiomers have opposite stereochemistry at **every** stereocenter (chiral center)

Diastereomers are all stereoisomers that are not enantiomers



** indicates a chiral center*



Diastereomers have different physical properties (e.g. mp, bp, etc), and can be separated. Stereogenic centers can exist in a molecule but if there is a plane of symmetry, it renders the whole molecule achiral.

Note: a chiral center (or stereogenic center) exists if *4 different groups* are attached to the carbon in question

If there is plane of symmetry within a molecule, then the molecule is **achiral** (not chiral)

Meso compounds – molecules containing chiral (stereogenic) centers but has a plane of symmetry, therefore they are achiral

Labelling Stereocentres

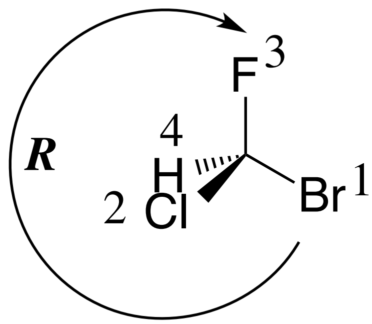
R/S Nomenclature:

R and S designation of stereoisomers
- R = Rectus (right, clockwise)
- S = Sinister (left, counterclockwise)

Labeling a stereogenic center as R or S:
- Identify all stereogenic centers (i.e. 4 different substituents)
- Look at atomic number of atoms attached to the stereogenic center
- Assign priority based on atomic number. If you cannot decide, go to the next set of atoms.
- Number from highest to lowest priority, then with the lowest priority group pointing back, count 1, 2, 3:
  - Clockwise → R configuration
  - Counterclockwise → S configuration

Each stereogenic center in a molecule is analyzed separately

Example:

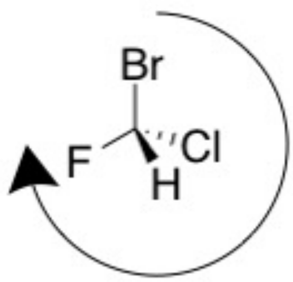


Place lowest priority to the back

1,2,3 --> clockwise = "R"
1,2,3 --> counterclockwise = "S"

Bromine has the highest atomic number (35), followed by chlorine (17), then fluorine (9), and lastly hydrogen (1).

<u>What if the lowest priority group is pointing forward?</u>



Counting 1, 2, 3 gives clockwise, BUT the smallest group is pointing forward, so the configuration is opposite of what you get if the smallest group is back

In this case, the configuration of the stereogenic center is "***S***"