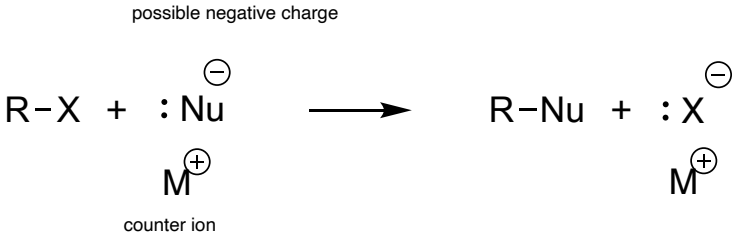
REVIEW:

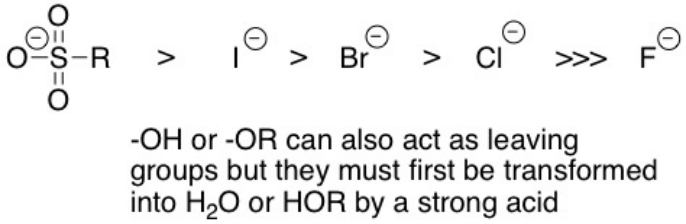
Substitution Nucleophilic S_N
Nucleophile seek positive charge
Base seeks H+



Never leaving groups: (negative charge not stabilized):

Fluorine, though electronegative, is a bad leaving groups as it is small and poorly solvated.

Good leaving groups

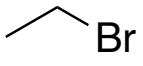
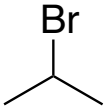
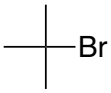


Comparison of S_N2 reactions vs S_N1 reactions

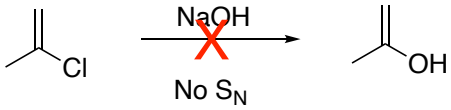
Characteristics	**S_N2 reactions**	**S_N1 Reactions**
Mechanism	Concerted (one step)	Stepwise (two steps)
Intermediate formation	No intermediate	Carbocation intermdiate
Rate dependent	Dependent on the concentration of nucleophile and substrate	Dependent on concentration of substrate
Stereochemistry	Stereospecific (with inversion of configuration)	Not stereospecific (forms racemic mixture)
Substrate (Starting Material)*	Works for 1° and 2° (but not 3°)	Works for 3° (very occasionally 2° but never 1°)
Nucleophile	Charged/strong	Neutral/weak

***NOTE:** No S_N will occur on C=C-X

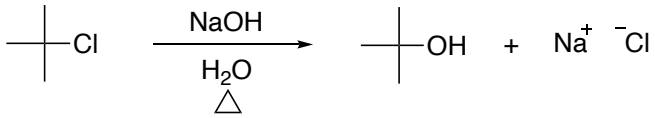
Types of alkyl halide or Haloalkane

Type	Example
Primary (1°)	CH_3CH_2Br = 
Secondary (2°)	$CH_3CHBrCH_3$ = 
Tertiary (3°)	$(CH_3)_3CBr$ = 

Example 1)

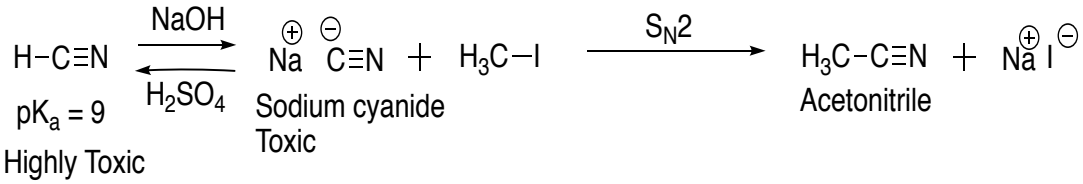


Example 2)



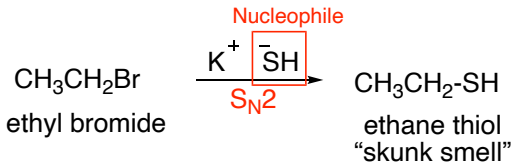
Note: in principle this reaction (Sn1) works but will give low yield because of side reaction (elimination reaction)

Example 3)

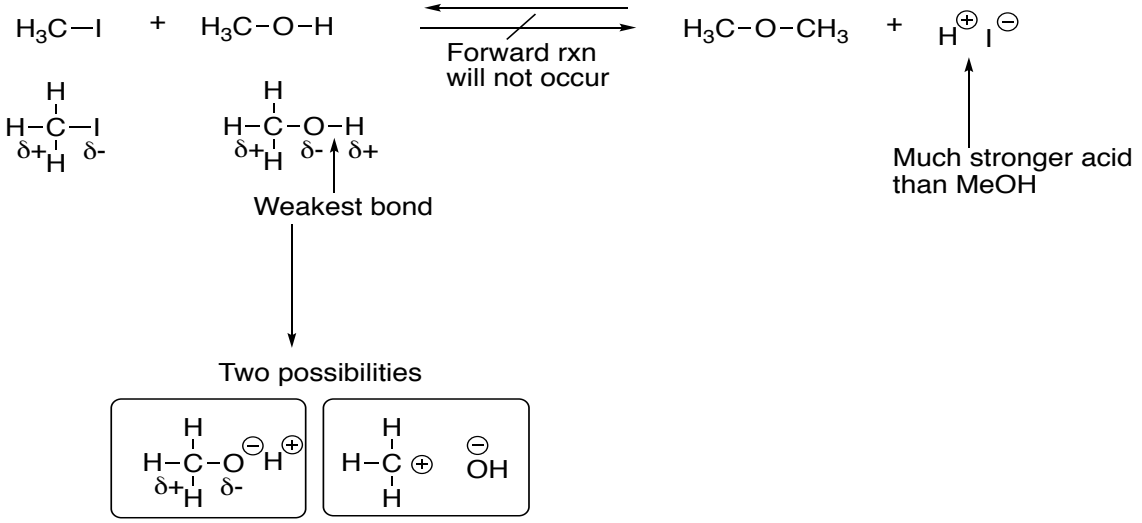


The above reaction will not occur unless hydrogen cyanide is converted into sodium cyanide using NaOH.
The product is acetonitrile, a common laboratory solvent.

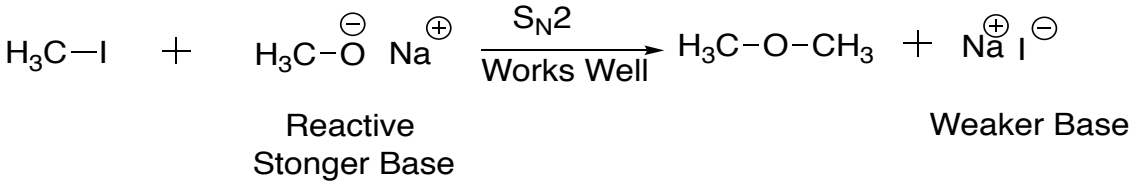
Example 4)



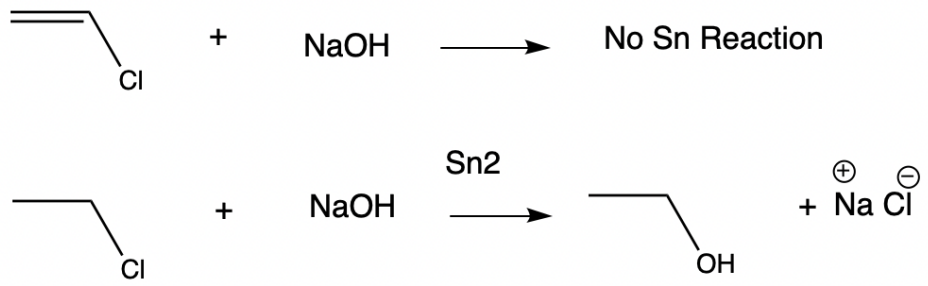
Example 5)



Hydrogen iodide is a strong acid and will drive the reverse reaction, meaning the forward reaction will not occur.
In order to make the above reaction occur, a stronger base (such as sodium methoxide) must be used to drive the forward reaction.

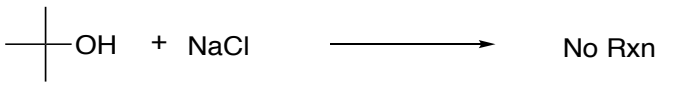


Example 6)



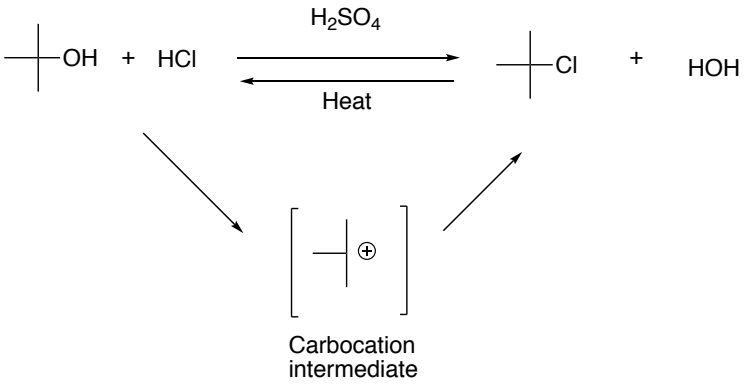
A carbon attached to a double bond cannot undergo a substitution reaction
The carbon with the leaving group must be sp^3 to undergo a substitution reaction

Example 7)

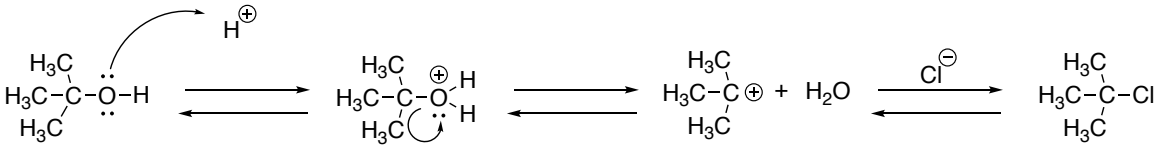


⊖OH is never a good leaving group

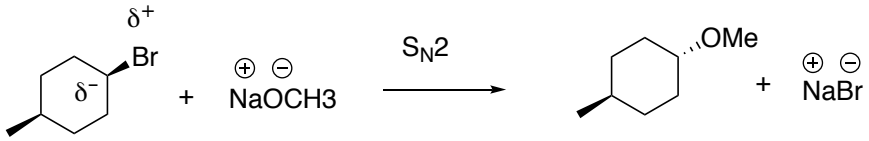
BUT Works with Acid as S_N1 Mechanism



Mechanism:



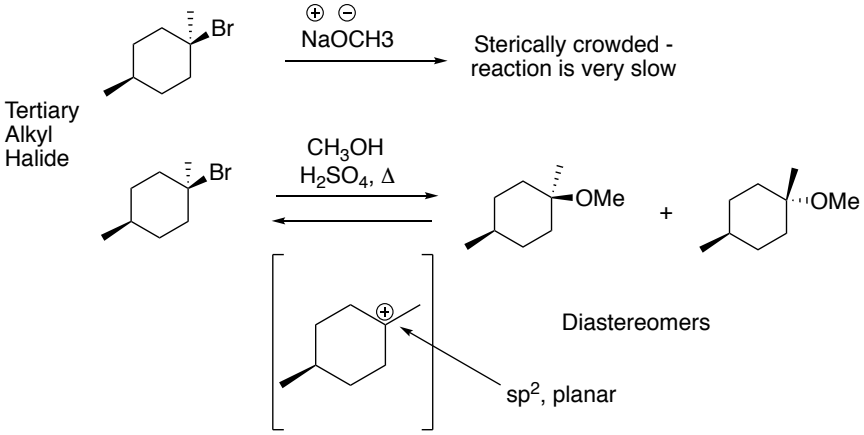
Example 8)



Secondary
Alkyl Halide

$-OCH_3$ is a strong, negatively charged nucleophile, so it favors a S_N2 mechanism (inversion of stereochemistry)

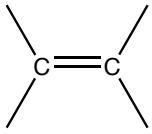
Example 9)



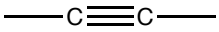
Will get a mixture of diastereomers
Note: the products are achiral

Alkenes and Alkynes Nomenclature

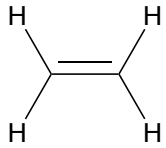
Alkene = double bond = olefin (oleum facere = to make oil)
Alkyne = triple bond = acetylene (as functional group, not compound)



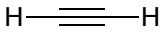
Alkene
Planar



Alkyne
Linear

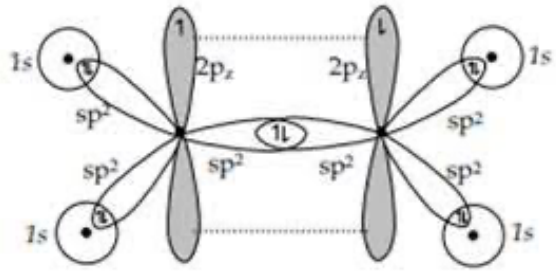


Ethylene

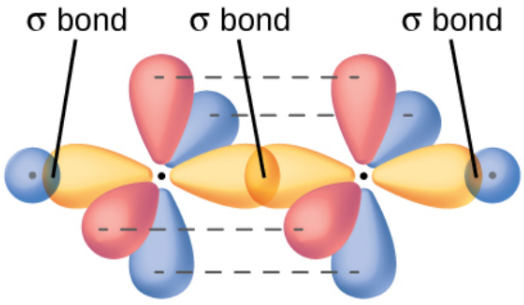


Acetylene

Simplest Alkene and Alkyne Possible



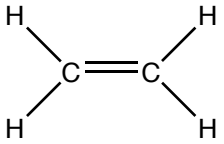
Orbital picture of ethylene



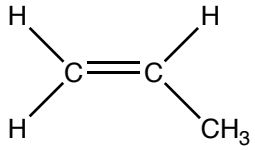
Orbital picture of acetylene

Alkene Nomenclature

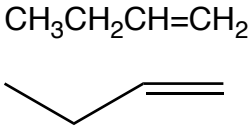
1. Find longest chain
2. Number from end to contain both ends of C=C and give lowest number to 1st C of C=C
3. Change "ane" to "ene" precede with number to indicate first double bond position



ethylene OR ethene

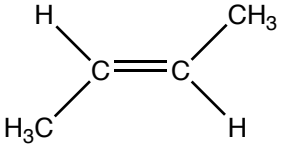


propylene OR 1-propene
prop-1-ene

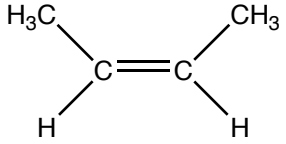


butylene OR 1-butene
but-1-ene

Below are two structural isomers of 1-butene



trans-2-butene

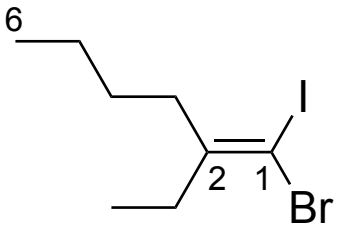


cis-2-butene

} diastereomers

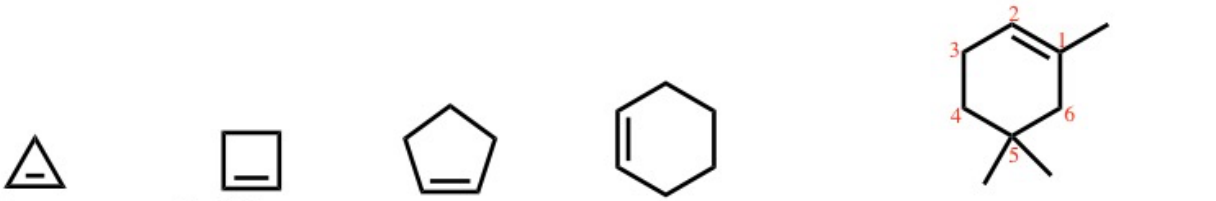
Note: no free rotation around the double bond. No way to interconvert between the *cis* and *trans* isomer without a chemical reaction.

Example:



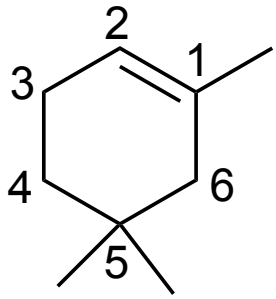
1-bromo-2-ethyl-1-iodo-1-hexene

Nomenclature of Cycloalkenes



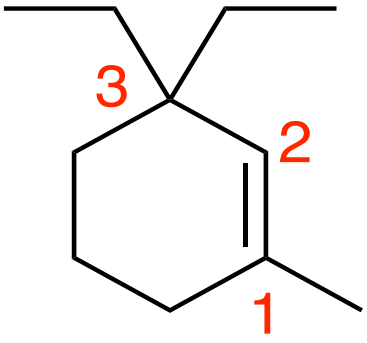
Rule: Number the cycloalkene such that the double bond is between C1 and C2 and that the first substituent has the lowest number possible.

Example:



1,5,5-trimethyl-1-cyclohexene

Example:



3,3-diethyl-1methyl-1-cyclohexene or
3,3-diethyl-1methylcyclohex-1-ene

Nomenclature of alkenes with multiple carbon-carbon double bonds (poly-enes):

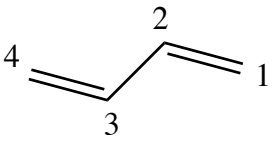
Multiple C=C

2 Diene

3 Triene

4 Tetraene

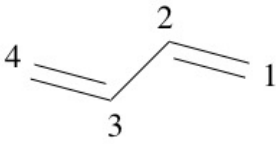
…etc



Buta-1,3-Diene
1,3-Butadiene

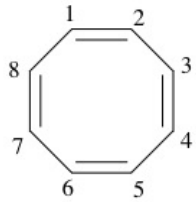
Drop -ne and add "diene", "triene", etc.

1) Find the longest chain containing the maximum number of double bonds.
2) Start numbering such that the first doubly bonded position would have the lowest number possible
3) Write out the full name. Number the substituents according to their position in the chain and list them alphabetically.

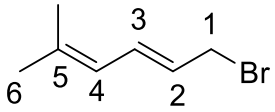


Buta-1,3-diene
1,3-Butadiene

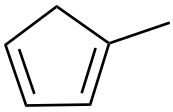
1,3-Cylcobutadiene



1,3,5,7-Cyclooctatetraene (All *Z*)
COT

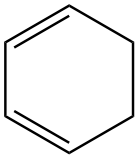


3E-1-bromo-5-methyl-2,4-hexadiene

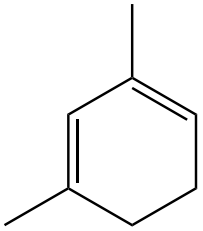


1-methyl-1,3-cyclopentadiene

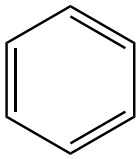
Other examples:



1,3-cyclohexadiene

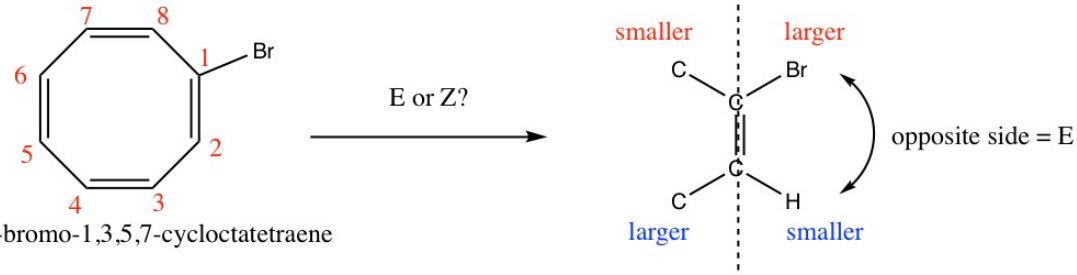


1,3-dimethyl-1,3-cyclohexadiene



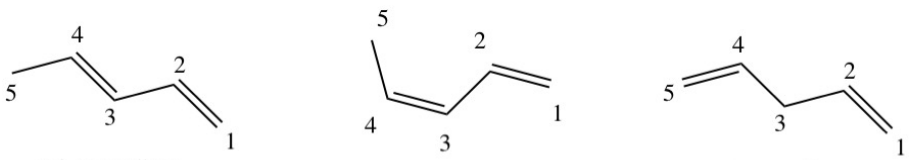
benzene
(NOT a cyclohexatriene)
(aromatic)

Abbrev:
PhH or C_6H_6 or ϕH



1-bromo-1,3,5,7-cycloctatetraene

It is therefore (E)-1-bromo-1,3,5,7-cyclooctatetraene



1,3-pentadiene (trans/ 3E)

1,3-pentadiene (cis/ 3Z)

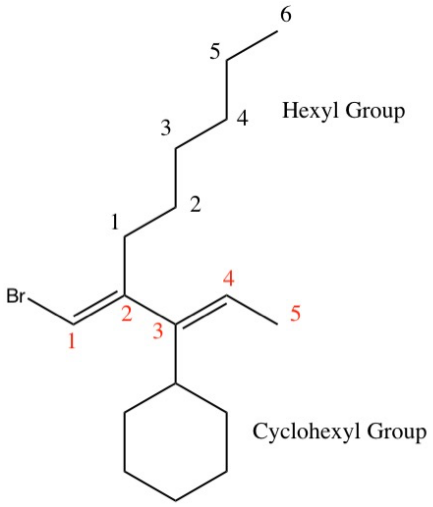
1,4-pentadiene

Diastereomers

Structural isomer

1,3-pentadiene (trans) = (E)-1,3-pentadiene

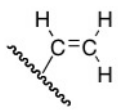
1,3-pentadiene (cis) = (Z)-1,3-pentadiene



1E,3E-1-Bromo-3-cyclohexyl-2-hexyl-1,3-pentadiene

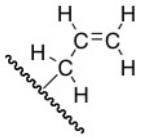
Note: Carbons attached to double and triple bonds are depicted as additional carbon-carbon bonds in the representations above.

Special Nomenclature of Common Groups:

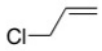


Vinyl group

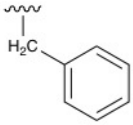
Vinyl chloride
1-chloroethene



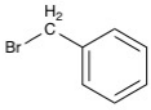
Allyl group



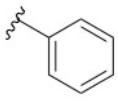
Allyl chloride
3-chloropropene



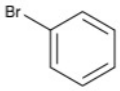
Benzyl group



Benzyl bromide



Phenyl group



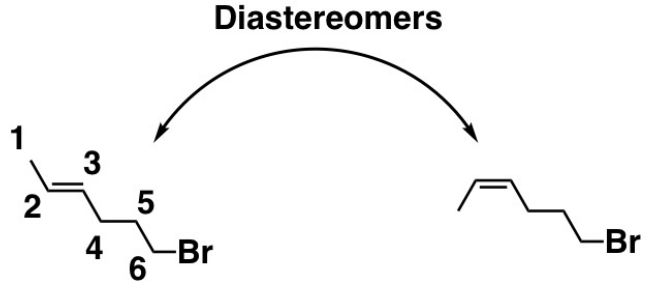
Phenyl bromide

Note: phenyl bromide is commonly called bromobenzene

Nomenclature of Alkynes (also known as acetylenes)
Rules:

- Find longest chain with max number of multiple bonds
- Number from end to give 1st multiply bonded position the lowest number
- Drop "ane" and add "yne"
- For multiple triple bonds, drop "ne" and add "diyne"," triyne", etc.
- Halides and alkyl substituents take lower priority than double or triple bon

Example 1: 6-Bromo-2-hexene (or 6-Bromohex-2-ene)



trans-6-Bromo-2-hexene cis-6-Bromo-2-hexene

In the cis isomer, the two higher priority groups on either side of the carbon-carbon double bond are pointing in the same direction.

Rule – if you have more than one double bond, then you add a prefix
2 di- , 3 tri- , 4 tetra-

E, Z - Nomenclature

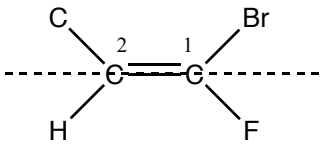
E - Entegegen - Opposite
Z - Zusammen - Together

Naming based on atomic number, similar process to identifying S/R stereochemistry

Example 1: 1-bromo-1-fluoro-1-propene
- compare the atomic no. of the adjacent atoms.

Compare the left side of the C=C bond

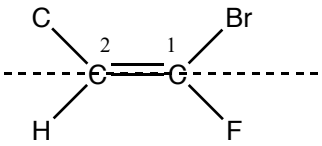
larger



smaller

Compare the right side of the C=C bond

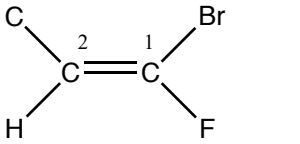
larger



smaller

same side = Z

larger larger

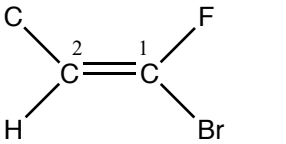


smaller smaller

(Z)-1-bromo-1-fluoro-1-propene

opposite = E

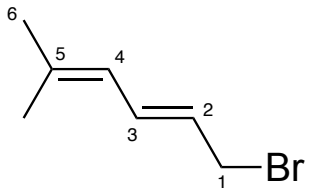
larger smaller



smaller larger

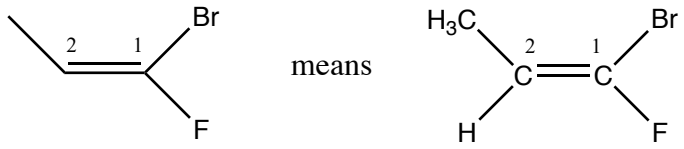
(E)-1-bromo-1-fluoro-1-propene

Example 2: (two double bonds)

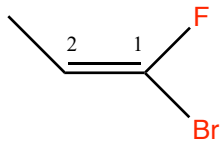


trans-1-bromo-5-methyl-2,4-hexadiene
trans-1-bromo-5-methylhexa-2,4-diene

Example 3: 1-Bromo-1-fluoro-1-propene



1-bromo-1-fluoropropene

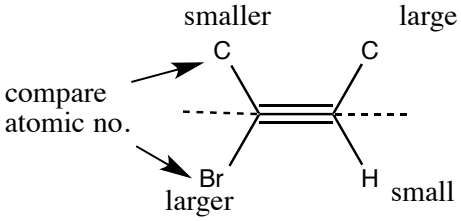


1-bromo-1-fluoropropene

Question: Are the compounds above the same?

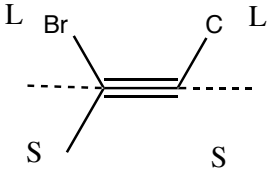
Answer: No, they are diastereomers and we can differentiate them by using the E and Z nomenclature

Example 2: 2-bromo-2-butene



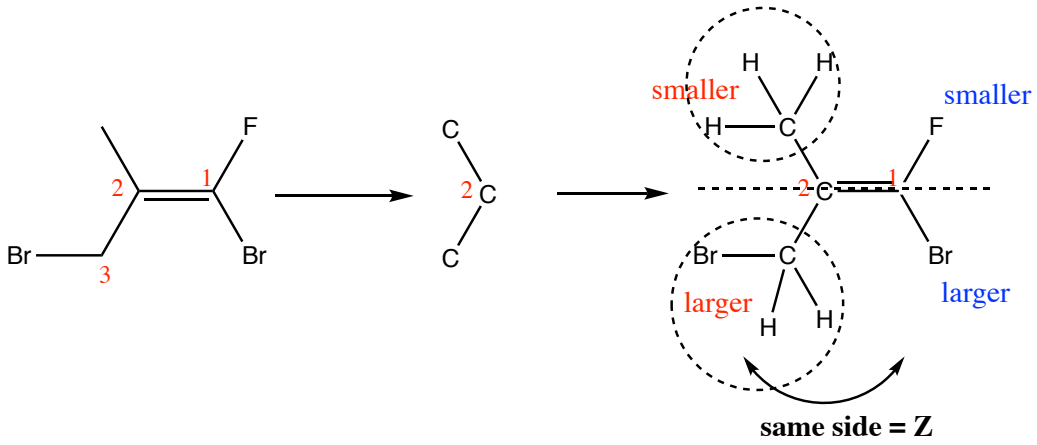
Large groups are on opposite sides on the C=C --> E

E-2-bromo-2-butene



Z-2-bromo-2-butene

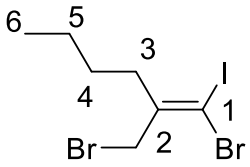
Example 3: 1,3-dibromo-1-fluoro-2-methyl-1-propene



Therefore the name is: (Z)-1,3-dibromo-1-fluoro-2-methyl-1-propene

Note: If you cannot decide on basis of atomic number of atoms directly attached to double bond, go to the next set of atoms until a higher atomic number is found

Example 4:



1-E-1-bromo-1-iodo-2-(bromomethyl)-1-hexene

Iodine is on the opposite side to the bromomethyl (highest priority groups on either side of the alkene) and so the stereochemistry is deemed E