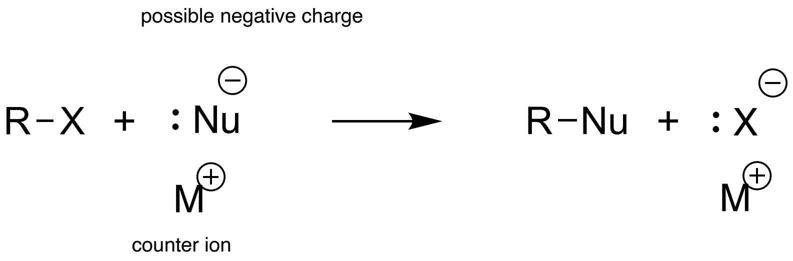
REVIEW:

Substitution Nucleophilic S_N

Nucleophile seek positive charge
Base seeks H+

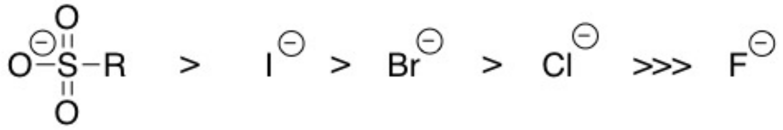


Never leaving groups: (negative charge not stabilized enough):

$F^{\ominus}$ $\quad$ $\overset{\ominus}{O}H$ $\quad$ $^{\ominus}OR$ $\quad$ $^{\ominus}NR_2$ $\quad$ $R:^{\ominus}$

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

Good leaving groups



-OH or -OR can also act as leaving groups but they must first be transformed into H_2O or HOR by a strong acid

Characteristics of S_N2 reactions:

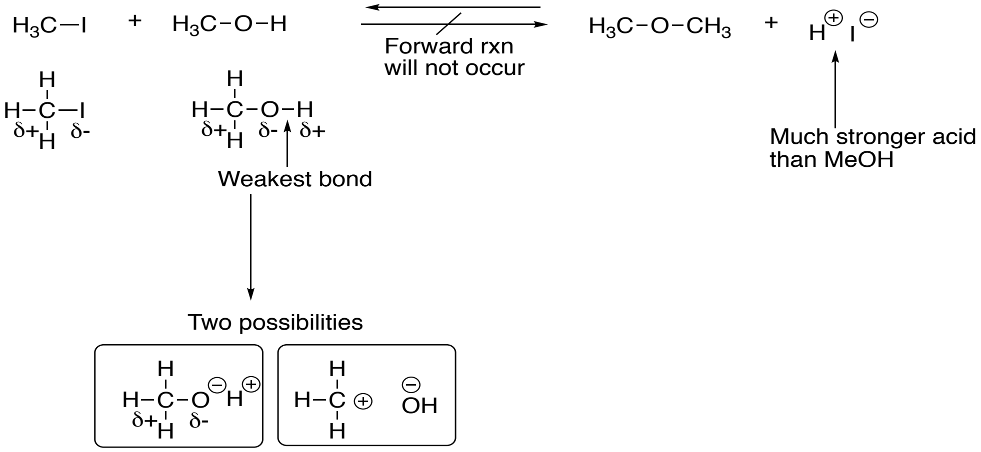
- Concerted (one step)
- Stereospecific
- No intermediate
- Rate dependent on the concentration of nucleophile and substrate
- Works for 1° and 2° (but not 3°)

Characteristics of S_N1 reactions:

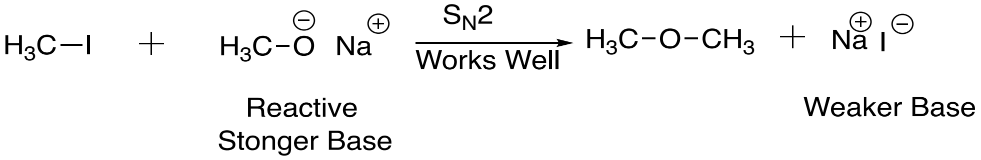
- Stepwise (2 steps)
- Carbocation intermediates
- Rate dependent on concentration of substrate
- Not stereospecific

- Favored by heat or acid
- Works for 3° (very occasionally 2° but never 1°)

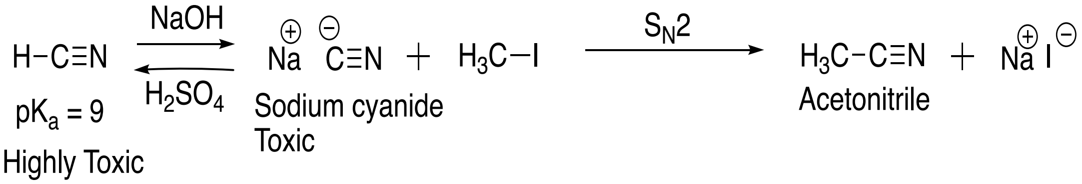
Example 1)



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.



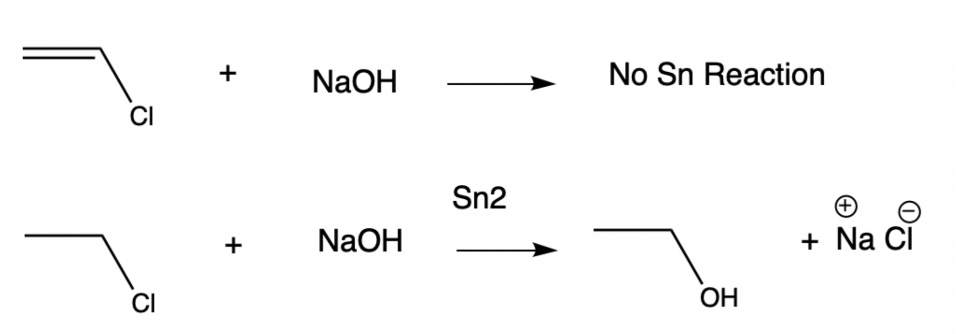
Example 2)



The above reaction will not occur unless hydrogen cyanide is converted into sodium cyanide using NaOH.

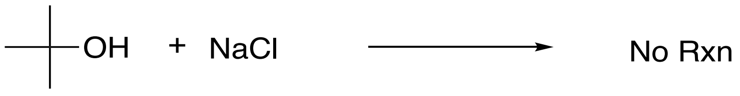
The product is acetonitrile, a common laboratory solvent.

Example 3)



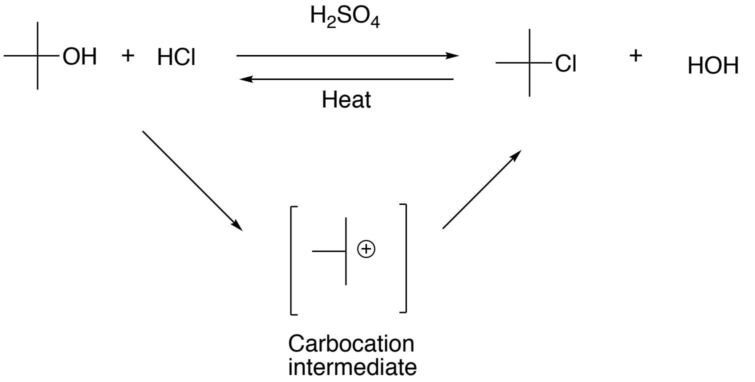
A carbon attached to a double bond cannot undergo a substitution reaction
The carbon with the leaving group must be sp^3 to undergo a substitution reaction

Example 4)

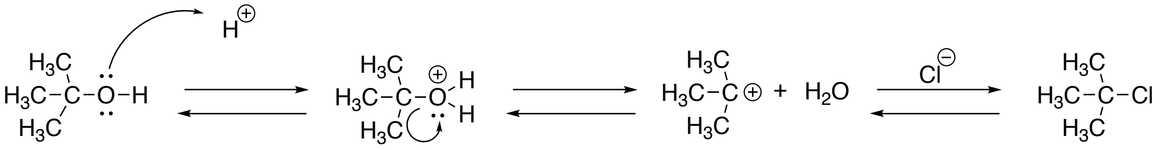


$^{\ominus}$OH is never a good leaving group

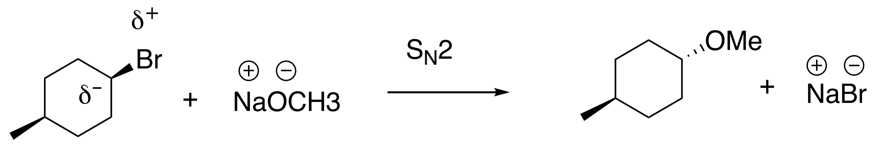
BUT Works with Acid as S$_N$1 Mechanism



Mechanism:



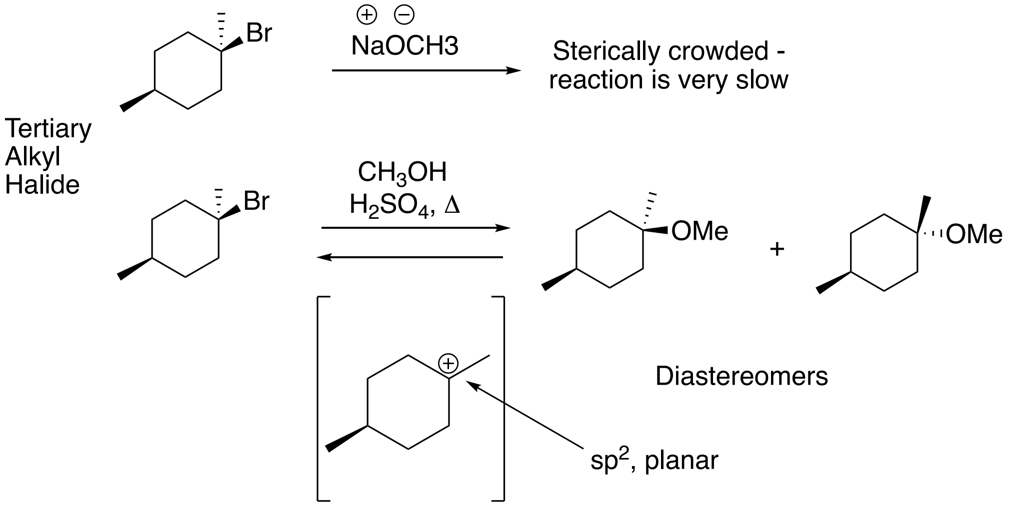
Example 5)



Secondary
Alkyl Halide

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

Example 6)

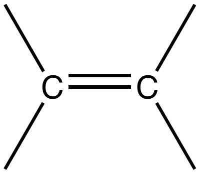


Will get a mixture of diastereomers
Note: the products are achiral

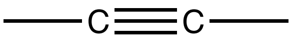
Alkene and Alkyne Nomenclature

Alkene = double bond = olefin (oleum facere = to make oil)

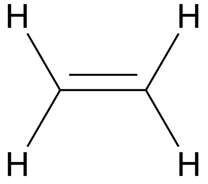
Alkyne = triple bond = acetylene (as functional group, not compound)



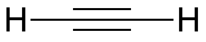
Alkene



Alkyne

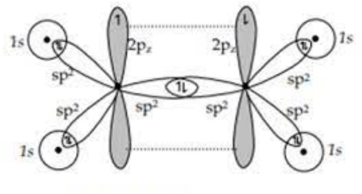


Ethylene



Acetylene

Simplest Alkene and Alkyne Possible

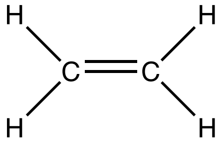


Orbital picture of ethylene

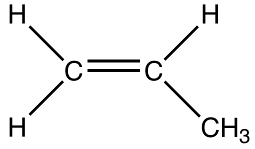
Alkene Nomenclature

Find longest chain, number from end to contain both ends of C=C and give lowest number to 1st C of C=C

Change “ane” to “ene” precede with number to indicate first double bond position



ethylene OR ethene

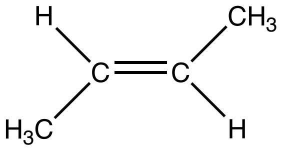


propylene OR 1-propene
prop-1-ene

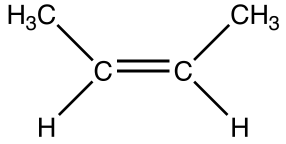
$CH_3CH_2CH{=}CH_2$

butylene OR 1-butene
but-1-ene

Below are two structural isomers of 1-butene



trans-2-butene

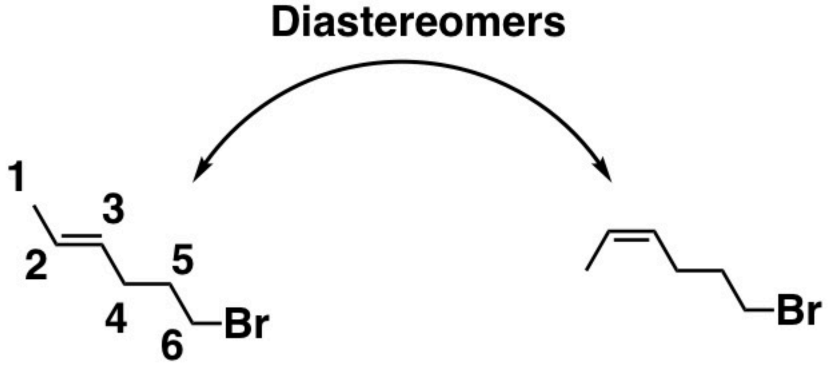


cis-2-butene

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

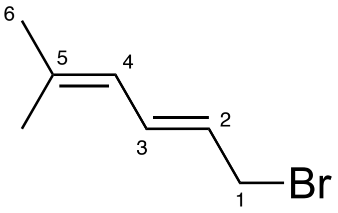


trans-6-Bromo-2-hexene **cis-6-Bromo-2-hexene**

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

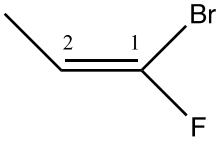
Rule – if you have more than one double bond, then you add a prefix
2 di- , 3 tri- , 4 tetra-

Example 2: (two double bonds)

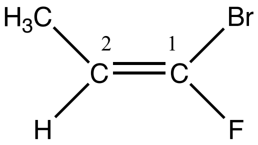


trans-1-bromo-5-methyl-2,4-hexadiene
trans-1-bromo-5-methylhexa-2,4-diene

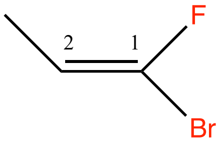
Example 3: 1-Bromo-1-fluoro-1-propene



means



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

<u>E, Z - Nomenclature</u>

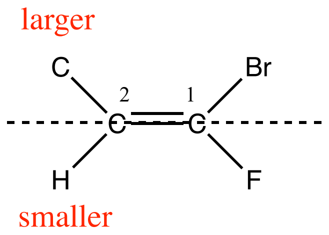
E - Entegegen - Opposite
Z - Zusammen - Together

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

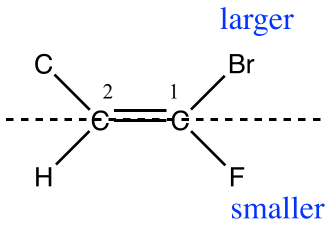
Example 1: 1-bromo-1-fluoro-1-propene

- compare the atomic no. of the adjacent atoms.

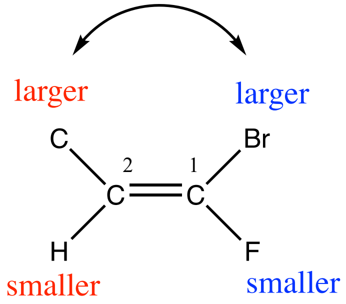
Compare the left side of the C=C bond



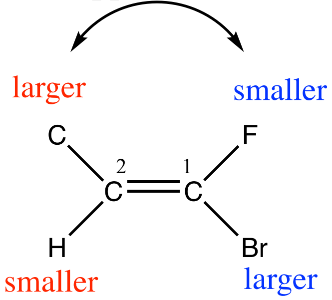
Compare the right side of the C=C bond



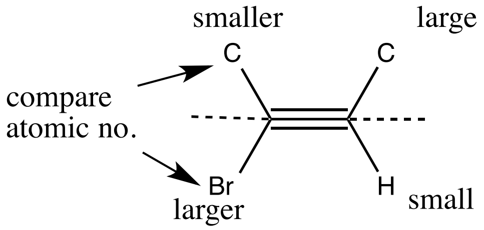
same side = Z



opposite = E

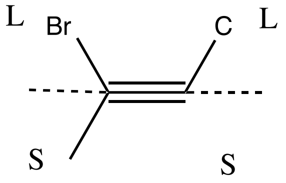


Example 2: 2-bromo-2-butene



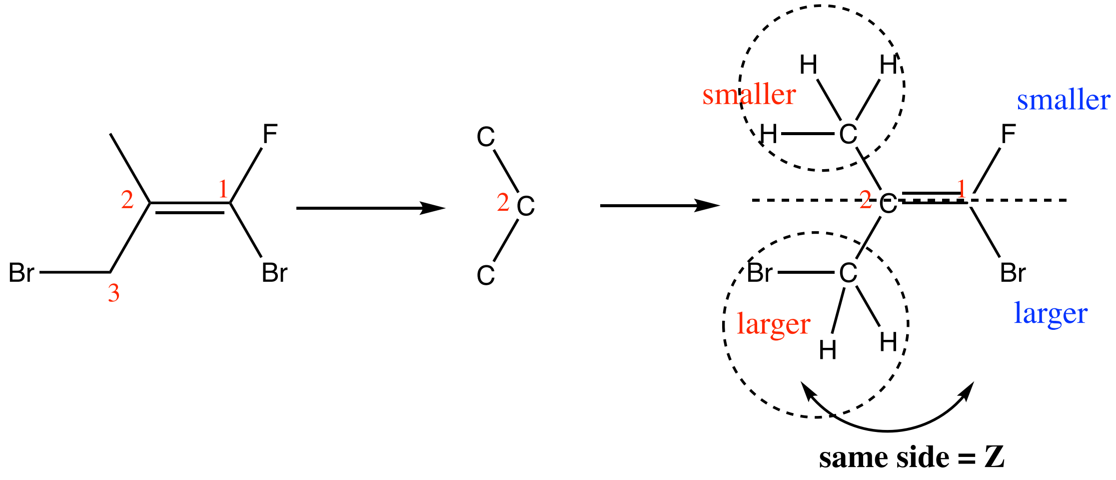
Large groups are on opposite sides on the C=C --> E

E-2-bromo-2-butene



Z-2-bromo-2-butene

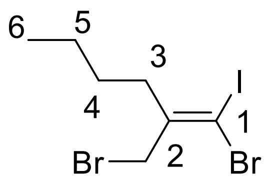
Example 3: 1,3-dibromo-1-fluoro-2-methyl-1-propene



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.