CHEM 261 Oct 18, 2022

Recall the following about substitution reactions:

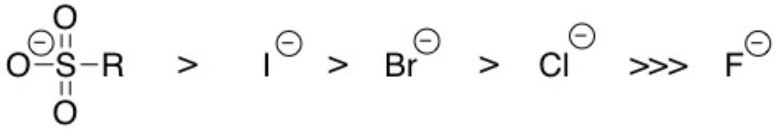
X= leaving group

Never leaving groups: (negative charge not stabilized):

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

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

Good leaving groups



$^{\ominus}O{-}S(=O)_2{-}R > I^{\ominus} > Br^{\ominus} > Cl^{\ominus} >>> F^{\ominus}$

-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:

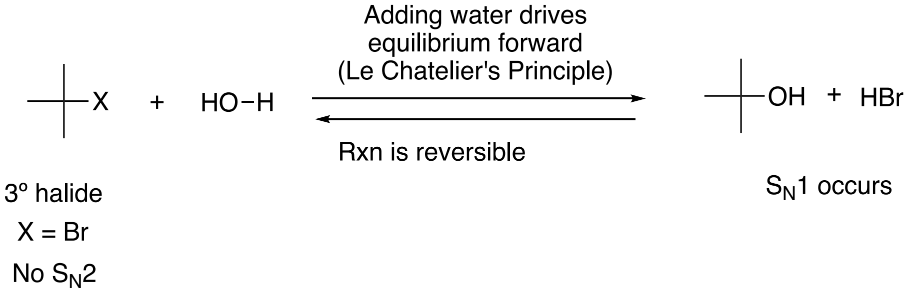
- Concerted
- Stereospeific
- Rate dependent on the concentration of nucleophile and substrate
- Works for 1° and 2° but not 3°

Characteristics of S_N1 reactions:

- Stepwise
- Carbocation intermediates
- Rate dependent on concentration of substrate
- Not stereospecific
- Favoured by heat or acid
- Works for 3° and sometimes 2° but never 1°

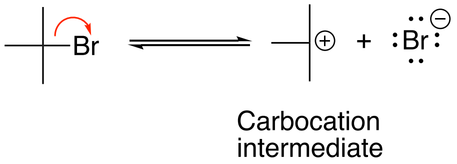
Example: Tertiary Halide

-No S_N2 possible, sterically crowded – does work by S_N1



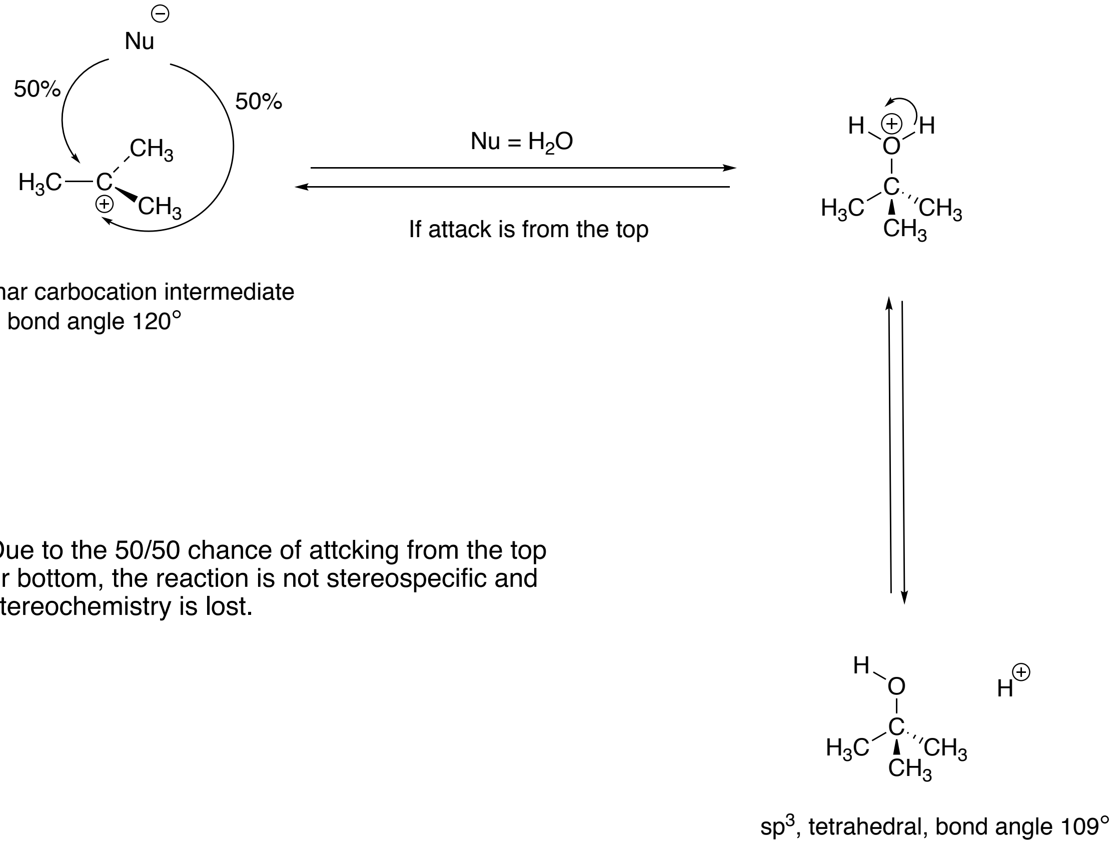
Mechanism:

The bromine group leaves with its electrons from the covalent bond, leaving behind a reactive carbocation intermediate



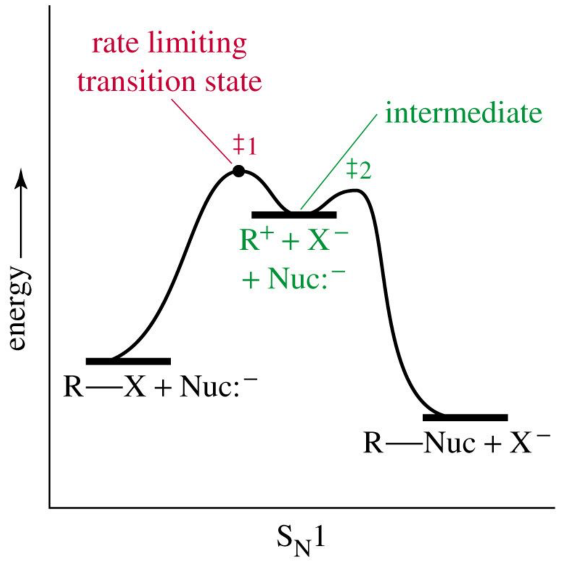
Carbocation intermediate is planar, so the nucleophile can attack from the top or bottom

Mechanism of Nucleophilic Attack on Carbocation

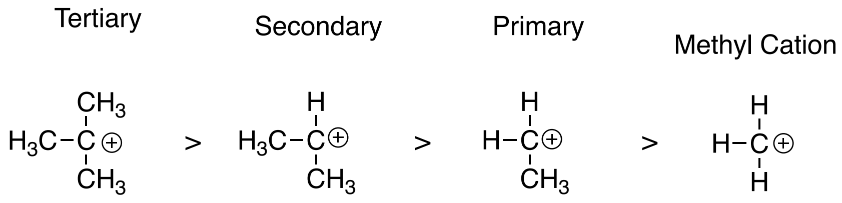


Due to the 50/50 chance of attcking from the top or bottom, the reaction is not stereospecific and stereochemistry is lost.

Energy level diagram of S_N1



Carbocation Stability:



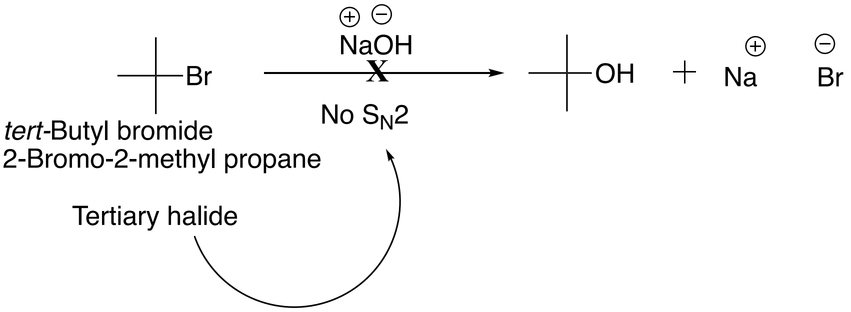
Most
stable

The 3 alkyl groups
donate e$^-$ density into
the positive charge

Least
stable
(no S_N1)

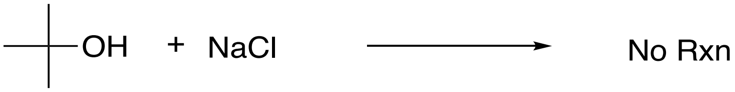
REVIEW: S_N yes or no? Examples

Ex #1) Will NOT proceed – no S_N



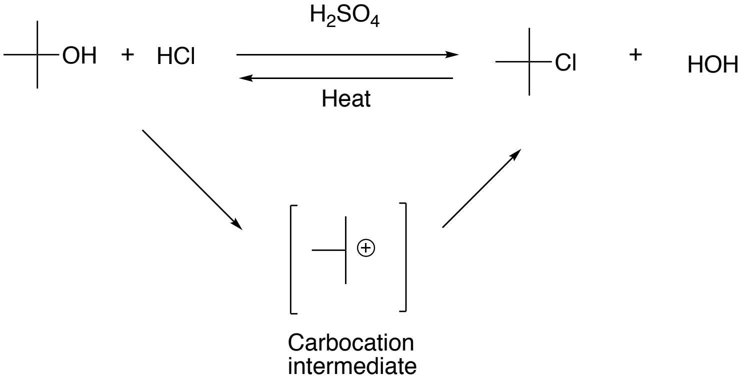
Note: alkyl groups stabilize carbocation intermediate by donating a negative charge
Note: will undergo elimination reaction (explanation of what this is comes later)

Ex #2)



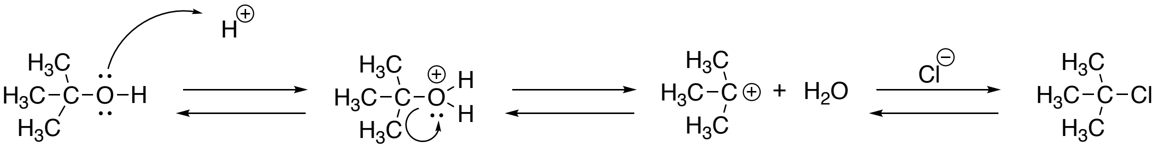
$^{\ominus}$OH is never a good leaving group

Ex #2a) Works with Acid

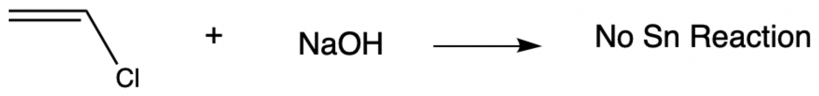


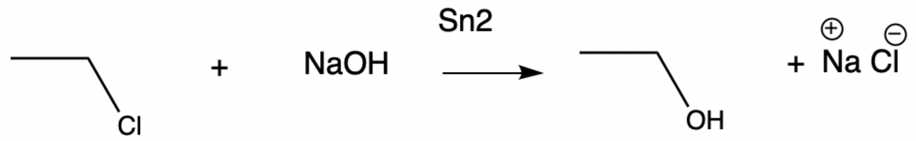
Carbocation intermediate

Mechanism:



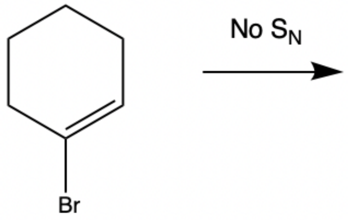
Ex #3)



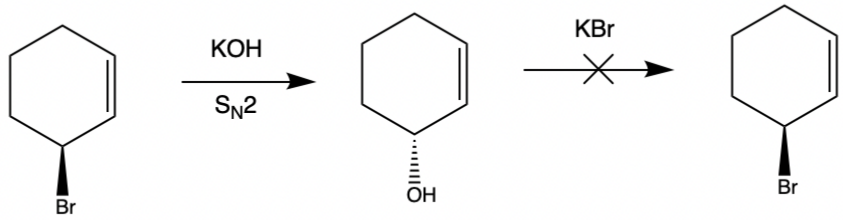


Note: a carbon attached to a double bond cannot undergo a substitution reaction

Ex #4)

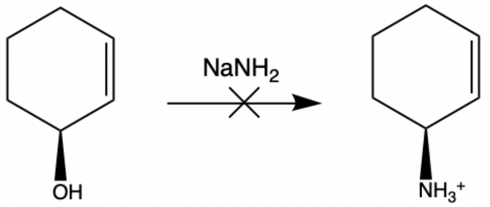


Ex #5)



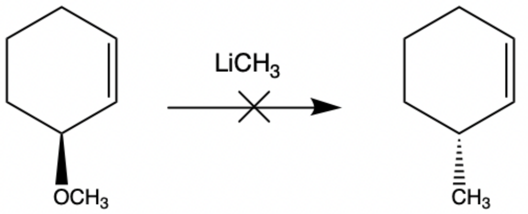
OH^- is a bad leaving group

Ex #6) Will not work



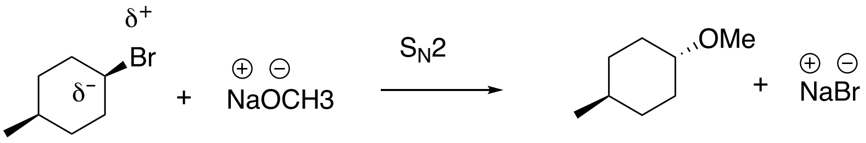
Note: these reagents will undergo an acid/base reaction rather than a substitution

Ex #7) will not work



Note: $^-OCH_3$ is a BAD leaving group

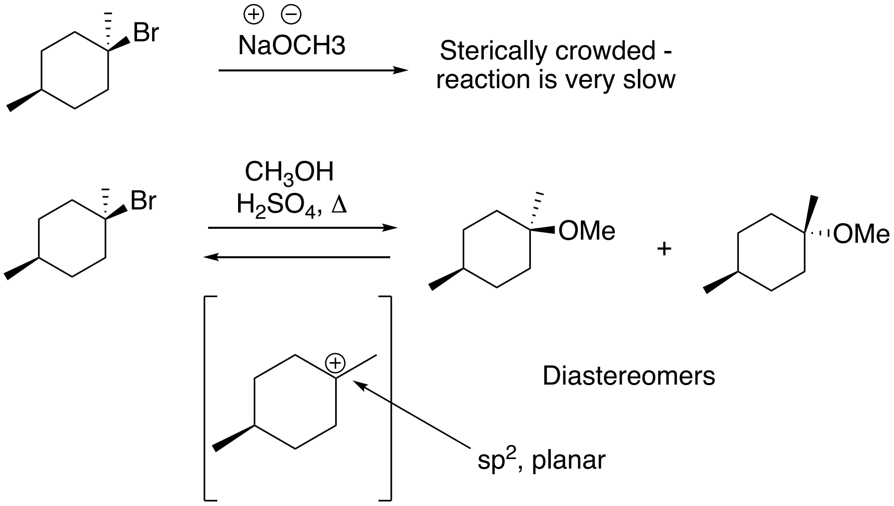
Ex #8)



Secondary
Alkyl Halide

Ex #9)

Tertiary
Alkyl
Halide



Sterically crowded -
reaction is very slow

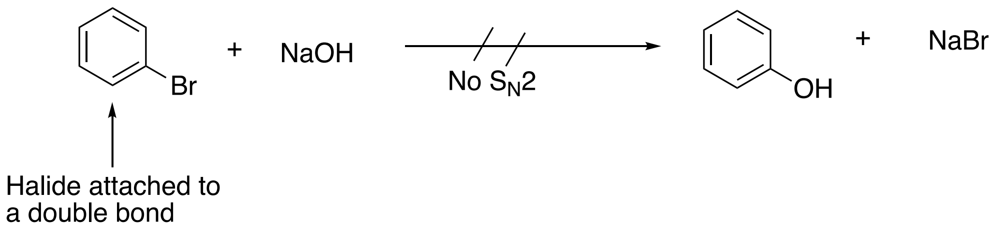
Diastereomers

sp^2, planar

Note: the products are achiral

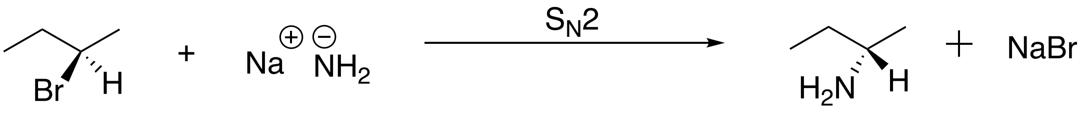
Extra examples:

Ex #1)



Halide attached to
a double bond

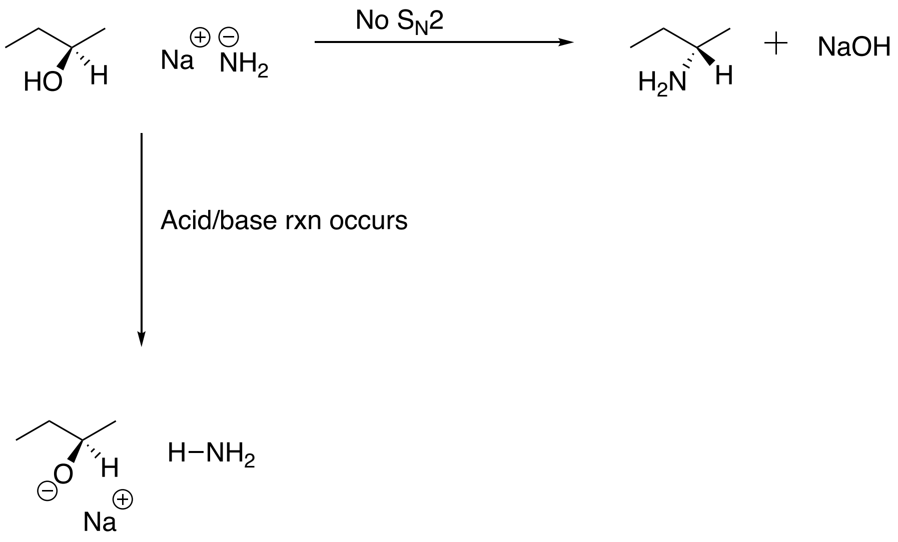
Ex #2) This one can work in principle



2-Bromobutane

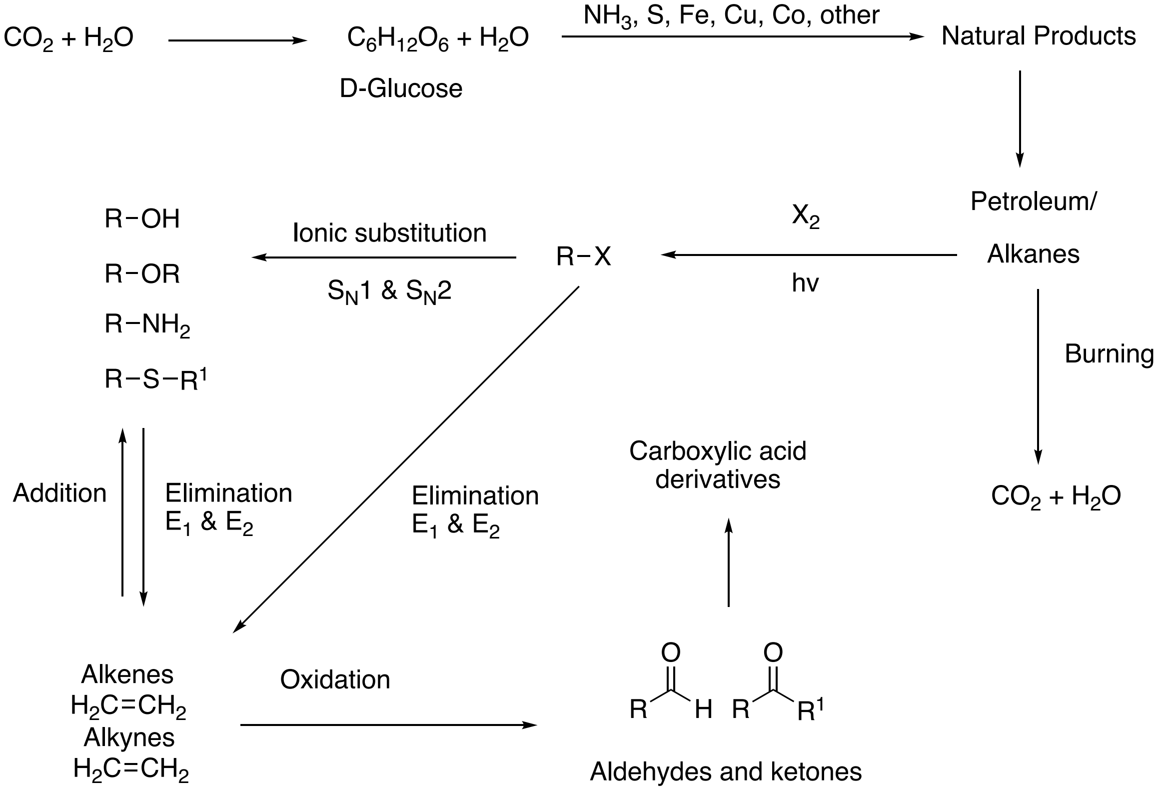
Ex #3) The one below does NOT work

$\overset{\ominus}{O}H$, $\overset{\ominus}{O}R$, $\overset{\ominus}{N}R_2$ are never good leaving groups



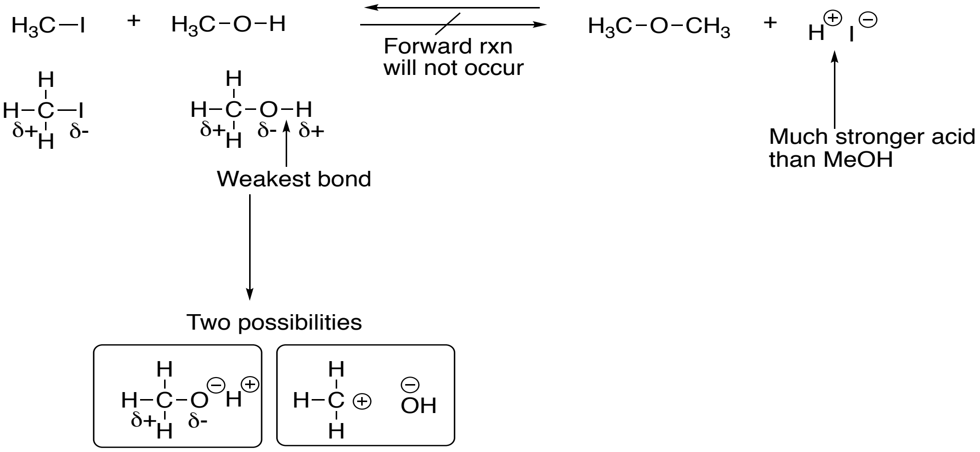
In this reaction, the NH_2 species will pull off the most acidic proton (the one on the alcohol) to from an **alkoxide** instead of undergoing an S_N2 reaction,

Photosynthesis and Related Reactions

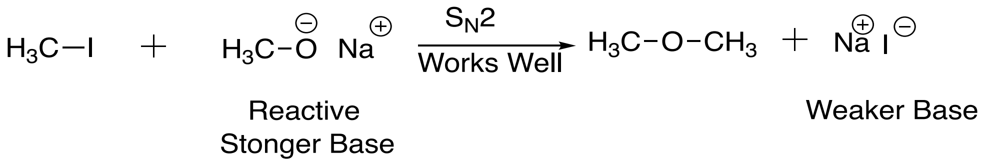


-Plants consume 4x10^{11} metric tons of CO_2 per year and convert it to D-Glucose

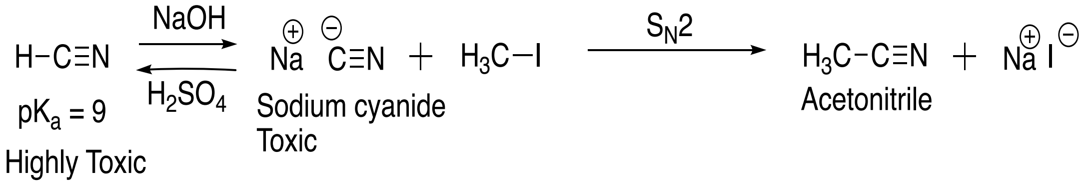
Sn Example:



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:



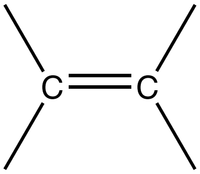
The above reaction will not occur unless hydrogen cyanide is converted into sodium cyanide using NaOH.

The product is acetonitrile, a common laboratory solvent.

Alkene and Alkyne Nomenclature

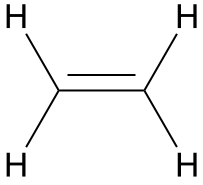
Alkene = double bond = olefin (oleum facere = to make oil)

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

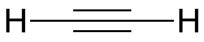


Alkene

Alkyne

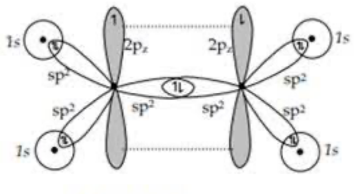


Ethylene



Acetylene

Simplest Alkene and Alkyne Possible

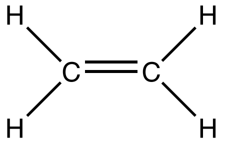


Orbital picture of ethylene

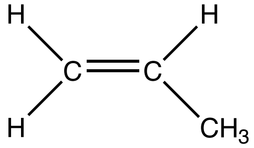
Alkene Nomenclature

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

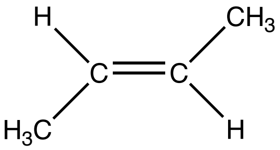


propylene OR 1-propene
prop-1-ene

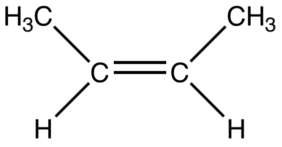
$CH_3CH_2CH=CH_2$

butylene OR 1-butene
but-1-ene

Below are two structural isomers of 1-butene



trans-2-butene



cis-2-butene

diastereomers