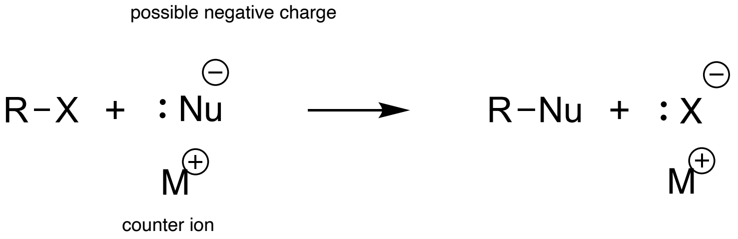
REVIEW:

Substitution Nucleophilic S_N
Nucleophile seek positive charge
Base seeks H+

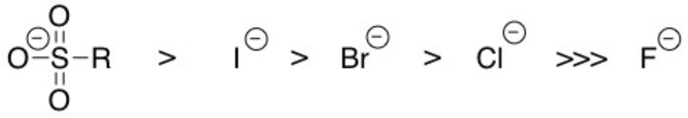


Never leaving groups: (negative charge not stabilized):

$F^{\ominus}$ $\overset{\ominus}{OH}$ $^{\ominus}OR$ $^{\ominus}NR_2$ $R:^{\ominus}$

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

Good leaving groups



$$^{\ominus}O-\overset{O}{\underset{O}{S}}-R > I^{\ominus} > Br^{\ominus} > Cl^{\ominus} >>> F^{\ominus}$$

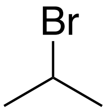
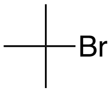
-OH or -OR can also act as leaving groups but they must first be transformed into H_2O or HOR by a strong acid

Comparison of S_N2 reactions vs S_N1 reactions

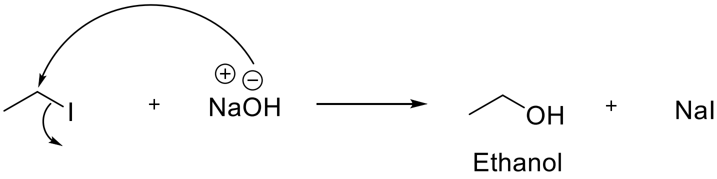
Characteristics	**S_N2 reactions**	**S_N1 Reactions**
Mechanism	Concerted (one step)	Stepwise (two steps)
Intermediate formation	No intermediate	Carbocation intermdiate
Rate dependent	Dependent on the concentration of nucleophile and substrate	Dependent on concentration of substrate
Stereochemistry	Stereospecific (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 (No substitution if X is on a multiple bond)

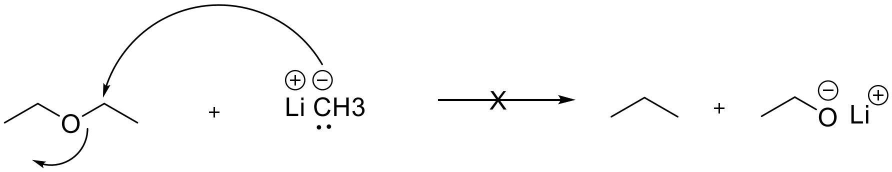
Types of alkyl halide or Haloalkane

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

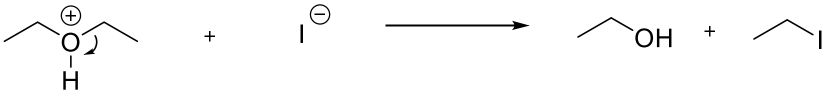
Example 1)



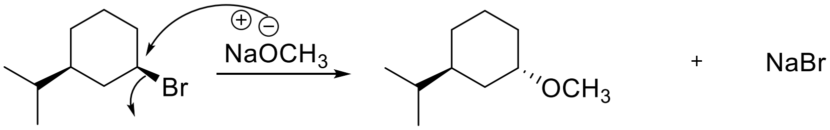
Example 2)



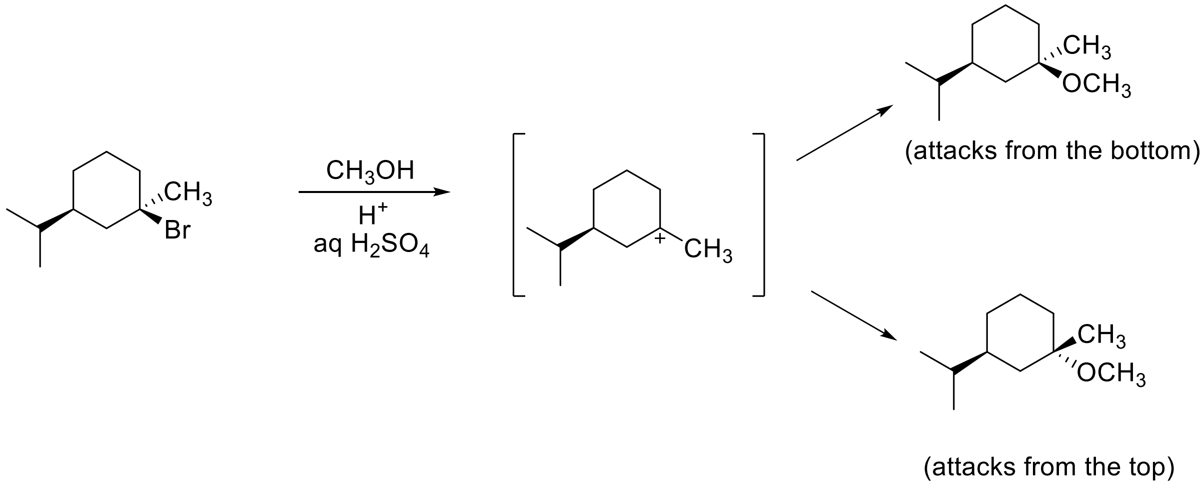
Example 3)



Example 4)

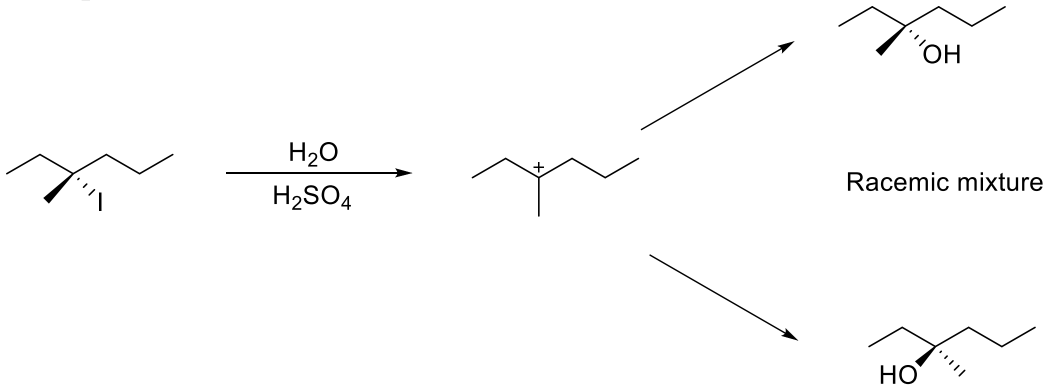


Example 5)

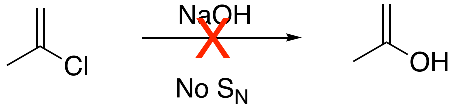


Products are diastereomers

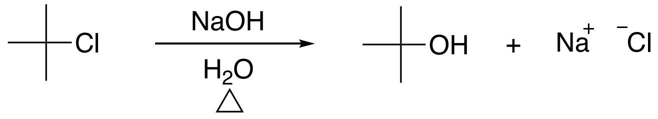
Example 6)



Example 7)

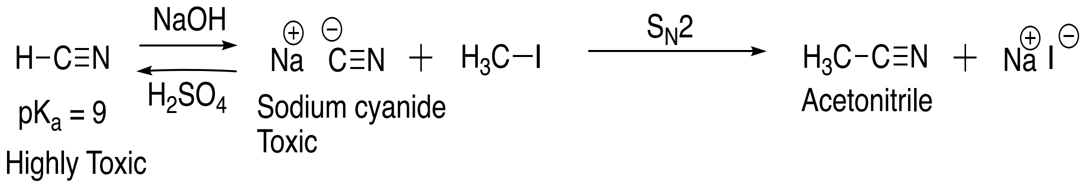


Example 8)



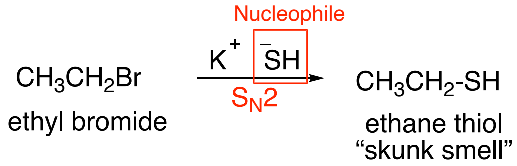
Note: in principle this reaction works but will give low yield because of side reaction (elimination reaction)

Example 9)

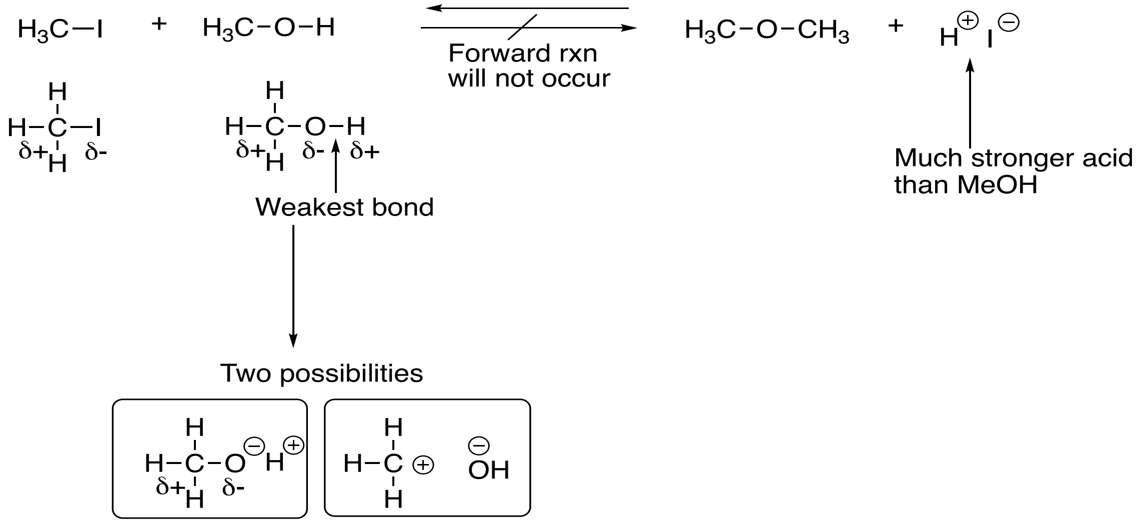


The above reaction will not occur unless hydrogen cyanide is converted into sodium cyanide using NaOH.
The product is acetonitrile, a common laboratory solvent.

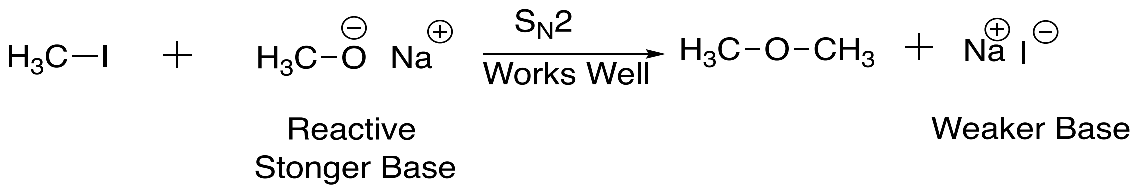
Example 10)



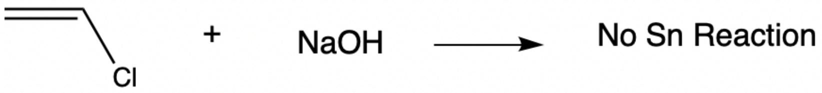
Example 11)

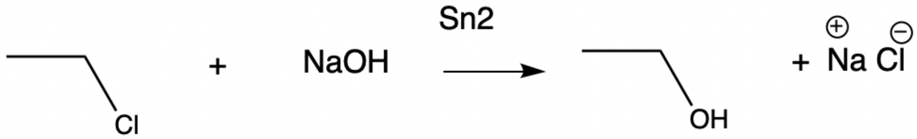


Hydrogen iodide is a strong acid and will drive the reverse reaction, meaning the forward reaction will not occur.
In order to make the above reaction occur, a stronger base (such as sodium methoxide) must be used to drive the forward reaction.



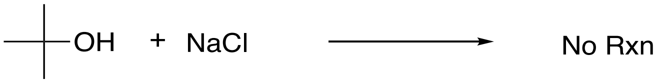
Example 12)





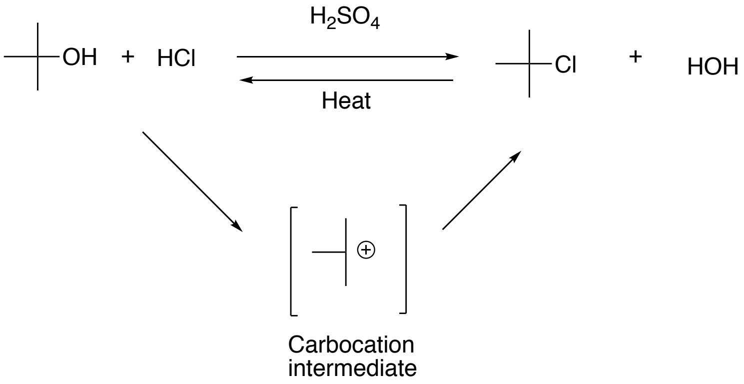
A carbon attached to a double bond cannot undergo a substitution reaction
The carbon with the leaving group must be sp^3 to undergo a substitution reaction

Example 13)

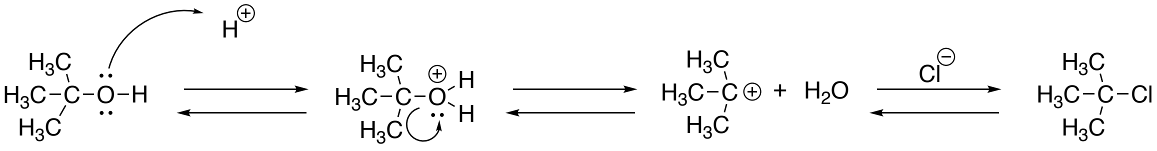


$^{\ominus}$OH is never a good leaving group

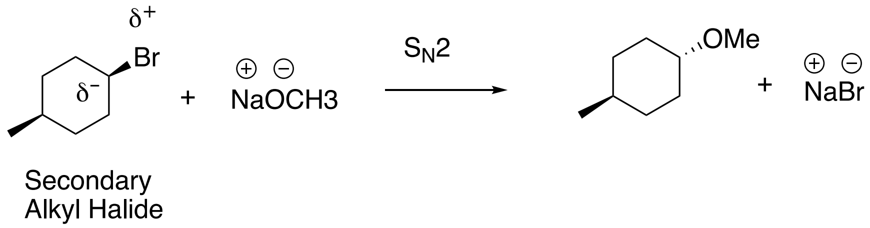
BUT Works with Acid as S_N1 Mechanism



Mechanism:

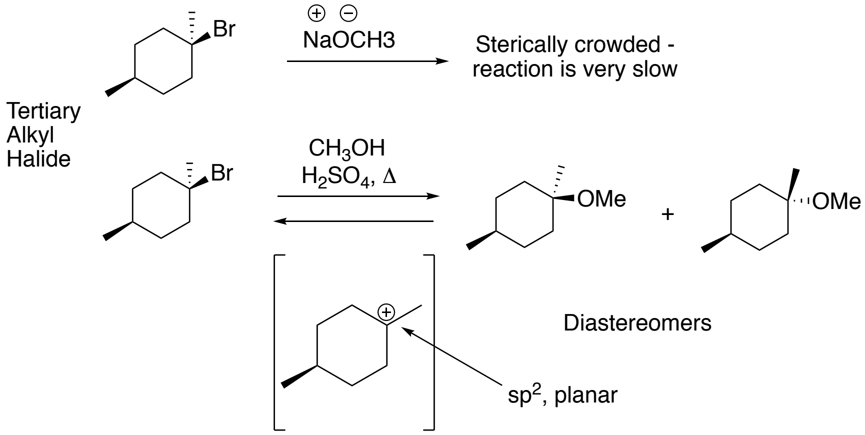


Example 14)



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

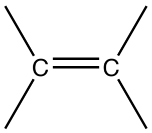
Example 15)



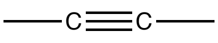
Will get a mixture of diastereomers
Note: the products are achiral

Alkenes and Alkynes Nomenclature

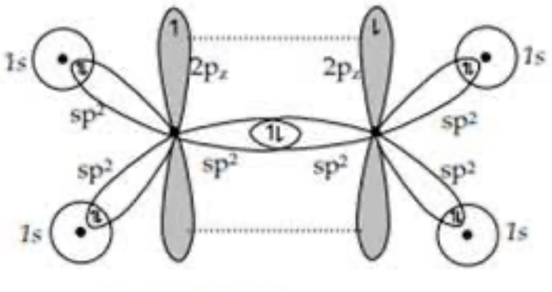
Alkene = double bond = olefin (oleum facere = to make oil)
Alkyne = triple bond = acetylene (as functional group, not compound)



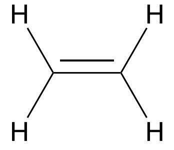
Alkene
Planar



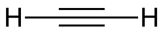
Alkyne
Linear



Orbital picture of ethylene

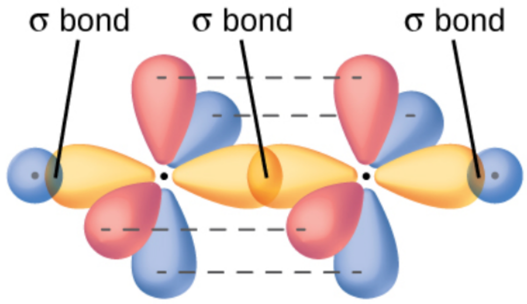


Ethylene



Acetylene

Simplest Alkene and Alkyne Possible



Orbital picture of acetylene
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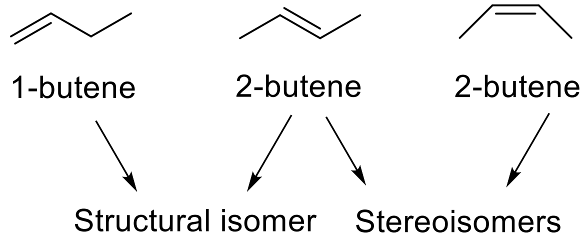
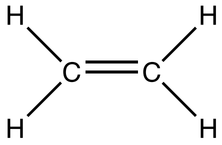
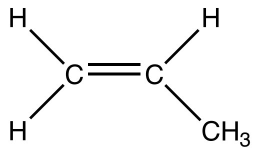
Alkene Nomenclature

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

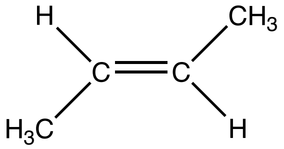


propylene OR 1-propene
prop-1-ene

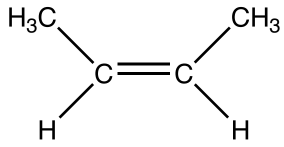
$CH_3CH_2CH=CH_2$

butylene OR 1-butene
but-1-ene

Below are two structural isomers of 1-butene



trans-2-butene

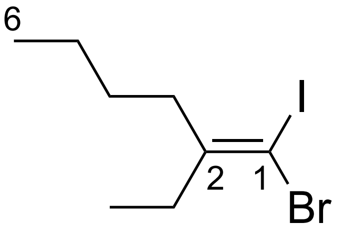


cis-2-butene

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

Nomenclature of Cycloalkenes

Cyclopropene

Cyclobutene

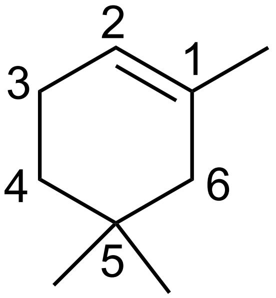
Cyclopentene

Cyclohexene

1,5,5-trimethyl-1-cyclohexene

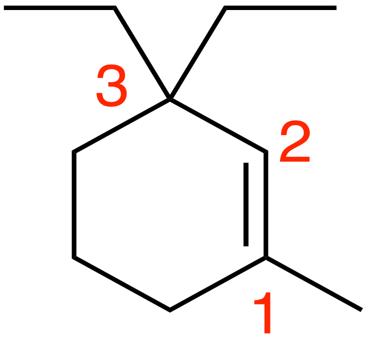
Rule: Number the cycloalkene such that the double bond is between C1 and C2 and that the first substituent has the lowest number possible.

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):

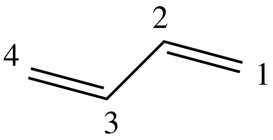
Multiple $C=C$

2 Diene

3 Triene

4 Tetraene

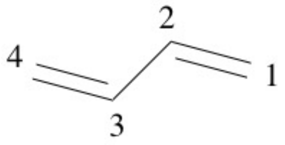
…etc



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

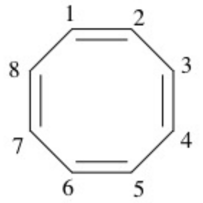
Drop -ne and add “diene”,
“triene”, etc.

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.

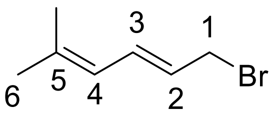


Buta-1,3-diene
1,3-Butadiene

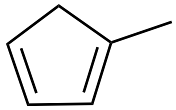
1,3-Cylcobutadiene



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

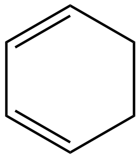


3E-1-bromo-5-methyl-2,4-hexadiene

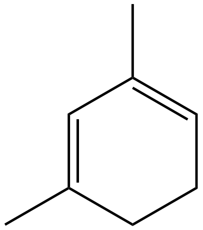


1-methyl-1,3-cyclopentadiene

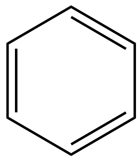
Other examples:



1,3-cyclohexadiene

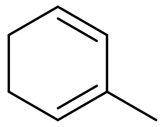


1,3-dimethyl-1,3-cyclohexadiene

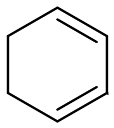


benzene
(NOT a cyclohexatriene)
(aromatic)

Abbrev:
PhH or C_6H_6 or ϕH



1-methyl-1,5-cyclohexadiene



1,3-cyclohexadiene