REVIEW:

Substitution Nucleophilic S_N

Nucleophile seek positive charge on C (or other atom that is not H) Base seeks H+

possible negative charge



Never leaving groups: (negative charge not stabilized): H minus, alkyl (R) minus



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

Good leaving groups

 $O_{=S-R}^{\ominus \parallel} > I^{\ominus} > Br^{\ominus} > CI^{\ominus} > > F^{\ominus}$

-OH or -OR can also act as leaving groups but they must first be transformed into H₂O or HOR by a strong acid

Characteristics of S_N2 reactions:

- Concerted (one step)
- Stereospecific (with inversion of configuration)
- 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)

$$\begin{array}{c} H-C\equiv N & \stackrel{NaOH}{\longrightarrow} & \stackrel{\oplus}{\underset{H_2SO_4}{\longrightarrow}} & \stackrel{\oplus}{\underset{Na}{\longrightarrow}} & \stackrel{\oplus}{\underset{C\equiv N}{\longrightarrow}} & H_3C-I & \stackrel{S_N2}{\longrightarrow} & H_3C-C\equiv N & + & \stackrel{\oplus}{\underset{Na}{\longrightarrow}} I^{\bigoplus} \\ \text{Sodium cyanide} & \text{Acetonitrile} \\ \text{Highly Toxic} \end{array}$$

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

The product is acetonitrile, a common laboratory solvent.





A carbon attached to a double bond cannot undergo a substitution reaction The carbon with the leaving group must be sp³ to undergo a substitution reaction







This Works with Acid as S_N1 Mechanism





Example 5)



 $-OCH_3$ 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 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





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



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

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.



Example 2: 2-bromo-2-butene





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

E-2-bromo-2-butene







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.

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.

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



- 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





1,3,5,7-Cyclooctatetraene COT





1,3-Cylcobutadiene

1-methyl-1,3-cyclopentadiene

Other examples:



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



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:



Note: phenyl bromide is commonly called bromobenzene