REVIEW:

Substitution Nucleophilic S_N

Nucleophile seek positive charge Base seeks H+

possible negative charge

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

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$$O_{-S}^{\bigcirc ||} - R > I^{\bigcirc} > Br^{\bigcirc} > CI^{\bigcirc} > P^{\bigcirc}$$

-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 $S_N 2$ reactions vs $S_N 1$ reactions

Characteristics	S _N 2 reactions	S _N 1 Reactions
Mechanism	Concerted (one step)	Stepwise (two steps)
Intermediate formation	No intermediate	Carbocation intermdiate
Rate dependent	Dependent on the concentration	Dependent on concentration
	of nucleophile and substrate	of substrate
Stereochemistry	Stereospecific (with inversion of	Not stereospecific (forms
	configuration)	racemic mixture)
Substrate (Starting	Works for 1° and 2° (but not 3°)	Works for 3° (very
Material)*		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

Туре	Example
Primary (1°)	$CH_{3}CH_{2}Br = Br$
Secondary (2°)	CH ₃ CHBrCH ₃ =
Tertiary (3°)	$(CH_3)_3CBr =$ Br

Example 1)



Example 2)



Note: in principle this reaction 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)





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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.

$$H_{3}C-I + H_{3}C-\overset{\ominus}{O} \overset{\oplus}{Na} \xrightarrow{S_{N}2} H_{3}C-O-CH_{3} + \overset{\oplus}{Na}I^{\textcircled{\ominus}}$$
Reactive Weaker Base Stonger Base Example 6)



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

Example 7)



NaCl ------ No Rxn

 $\overset{\bigcirc}{\operatorname{OH}}$ OH is never a good leaving group

BUT Works with Acid as S_N1 Mechanism



Mechanism:



Example 8)



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



Alkenes and Alkynes Nomenclature

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



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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 ₃ CH ₂ CH=CH ₂	butylene	OR	1-butene but-1-ene

Below are two structural isomers of 1-butene



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.

Compare the left side of the C=C bond

Compare the right side of the C=C bond

larger















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