# Energy level diagram of S<sub>N</sub>1



Favored conditions are with stabilized carbocation - more substitution

## **Carbocation Stability:**



## Example: Tertiary Halide

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



## Mechanism of S<sub>N</sub>1:



sp<sup>3</sup>, tetrahedral, bond angle 109°

### Substitution Nucleophilic S<sub>N</sub>

Nucleophile seek positive charge Base seeks H+

possible negative charge



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

0	Θ	Θ	Θ	0
F	OH	OR	NR <sub>2</sub>	R:

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

### **Good leaving groups**

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

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

## Leaving group activation:

1) Protonation



# **Highlights:**

- $H_2SO_4$  is a proton (H<sup>+</sup>) donor.
- <sup>-</sup>OH is transformed into a better leaving group via protonation of the O atom.
- $Cl^-$  can then attack via  $S_N 2$ , kicking off  $H_2 O$  in the process.

Comparison of  $S_N 2$  reactions vs  $S_N 1$  reactions

Characteristics	S <sub>N</sub> 2 reactions	S <sub>N</sub> 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 $1^{\circ}$ and $2^{\circ}$ (but not $3^{\circ}$ )	Works for 3° (very
Material)*		occasionally 2° but never 1°)
Nucleophile	Charged/strong	Neutral/weak

**\*NOTE:** No S<sub>N</sub> will occur on C=C-X

### Types of alkyl halide or Haloalkane

Туре	Example
Primary (1°)	$CH_3CH_2Br = Br$
Secondary (2°)	Br CH <sub>3</sub> CHBrCH <sub>3</sub> =
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)

 $S_N 2$  will <u>not</u> occur on carbon sites that have multiple bonds.



# Example 1:



# Example 2:



# Example 3:



## Example 4:



# Example 5:



# Example 6:



# Example 7:



Mechanism:



### Example 8:



Example 9:

 $= Br \xrightarrow[Li \ CH_3]{\oplus} No S_N \text{ reaction}$ 

### Example 10:



Example 3)

$$\begin{array}{cccc} H-C\equiv N & \stackrel{NaOH}{\longleftarrow} & \stackrel{\oplus}{\underset{H_2}{\longrightarrow}} & \stackrel{\oplus}{\underset{Na}{\longrightarrow}} & \stackrel{\oplus}{\underset{C\equiv N}{\longrightarrow}} & H_3C-I & \stackrel{S_N2}{\longrightarrow} & H_3C-C\equiv N & + & \stackrel{\oplus}{\underset{Na}{\longrightarrow}} & \stackrel{\longrightarrow}{\underset{Na}{\longrightarrow}} & \stackrel$$

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)**

CH<sub>3</sub>CH<sub>2</sub>Br  $\xrightarrow{K^+ \ SH}$  CH<sub>3</sub>CH<sub>2</sub>-SH ethyl bromide ethane thiol "skunk smell"

Example 5)  $H_3C-O-CH_3 + H^{\oplus}_{\Lambda}I^{\odot}$ H₃C—I + H<sub>3</sub>C-O-H Forward rxn will not occur н H-C-O-H H-C  $\delta + \frac{1}{H} \delta - \frac{1}{4} \delta +$ δ-Much stronger acid than MeOH Weakest bond Two possibilities н H-¢-o⊖H⊕ Θ H−Ċ⊕ ÕН δ-Ĥ

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.

$$H_{3}C-I + H_{3}C-\overset{\bigcirc}{O} Na^{\oplus} \xrightarrow{S_{N}2}_{Works Well} H_{3}C-O-CH_{3} + Na^{\oplus} I^{\textcircled{O}}$$
Reactive Weaker Base
Example 6)
$$= \underbrace{}_{CI} + NaOH \xrightarrow{Sn2} No Sn Reaction$$

$$+ NaOH \xrightarrow{Sn2} + \underbrace{}_{OH} \overset{\textcircled{O}}{H} + \underbrace{}_{Na} \overset{\textcircled{O}}{CI}$$

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

### Example 7)

OH + NaCl → No Rxn

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

### BUT Works with Acid as S<sub>N</sub>1 Mechanism



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



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)



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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



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.