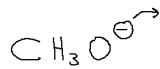
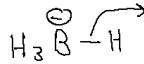
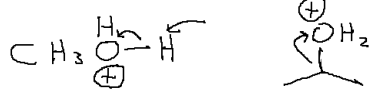



## roles that atoms can play in reactions

NUCLEOPHILES AND BASES	
nucleophile: donates electrons to join an electrophile base: donates electrons to receive a proton from an acid So a nucleophile or base goes at the tail of an electron pushing arrow.	
First, look for: negative formal charge Otherwise, look for: $\delta^-$ or lone pair, or a carbon-carbon pi bond Neutral atoms with lone pairs are generally not nucleophilic unless they are bonded to at least one hydrogen.	
ELECTROPHILES AND ACIDS	
electrophile: receives electrons to join a nucleophile acid: receives electrons to donate a proton to a base So an electrophile or acid goes at the head of an electron pushing arrow.	
First, look for: positive formal charge Otherwise, look for: $\delta^+$	
LEAVING GROUPS	
leaving group: receives electrons to leave something So a leaving group goes at the head of an electron pushing arrow.	
First, look for: positive formal charge Otherwise, look for: a neutral halogen (Cl, Br, or I); or, a neutral atom whose negative charge after leaving will be resonance stabilized	

## effect of formal charges on atoms' roles

	rule	exception
<b>negative formal charge</b>	The atom with the negative charge is the nucleophile or base. 	If the negative charge is on a metal or semimetal (e.g., Al, B, or Fe), then the <i>attached</i> atom is the nucleophile or base, and it donates the electrons from its bond. 
<b>positive formal charge</b>	The atom with the positive charge is the leaving group. The <i>attached</i> atom may act as an electrophile. 	If the positive charge is on a carbon, then the carbon is the electrophile. No leaving group is necessary.  If the positive charge is on a hydrogen, then the hydrogen is an acidic proton. If the positive charge is on a metal, then the metal is an unreactive spectator ion.

the rules for using electron-pushing arrows to draw the products of a step

1. Redraw the starting materials. Number all the carbons in both your “before” and “after” drawings.
2. For each electron-pushing arrow: If the arrow is breaking a bond, erase that bond. If the arrow is forming a bond, draw that bond. If the arrow is <i>both</i> breaking a bond <i>and</i> forming a bond, erase the bond that breaks and draw the new bond that forms.
3. Change two charges. Make the atom that is losing electrons at the <i>start</i> of the chain of arrows one step less negative. Make the atom that is gaining electrons at the <i>end</i> of the chain of arrows one step more negative. Ask (a) what formal charge did the atom start with, and (b) is the atom gaining or losing electrons? (For this step focus only on formal charges; ignore $\delta^-$ and $\delta^+$ charges.)

the rules for whether to break a bond, form a bond, or both

<b>break a bond</b>	when the tail of the electron-pushing arrow is on a bond
<b>form a <math>\sigma</math> bond</b>	when the arrow head is pointing to an atom which was not already sharing the electrons represented by the arrow
<b>form a <math>\pi</math> bond</b>	when the arrow head is pointing to a bond

acids and bases

	<b>acids</b>	<b>bases</b>
<b>Examples to help you remember acid/base properties</b>	$H^+$ or $H_3O^+$	$HO^-$
<b>Bronsted-Lowry definition</b>	$H^+$ donor	$H^+$ acceptor
<b>Lewis definition</b>	$e^-$ acceptor	$e^-$ donor
<b>Makes things it reacts with...</b>	positive	negative
<b>So all intermediates and products should be...</b>	neutral or positive <sup>1</sup>	neutral or negative <sup>2</sup>
<b>Aids reactions by making things into better...</b>	electrophiles leaving groups	nucleophiles

<sup>1</sup>Except for the conjugate base of the acid.

<sup>2</sup>Except for the spectator ion from the base.

how to assign  $\delta$  charges

Do not assign $\delta$ charges to a molecule which has a formal charge.
If the molecule has no formal charges, then:
1. When two identical atoms are covalently bonded, neither has a delta charge.
2. When a carbon is bonded to a hydrogen, neither has a delta charge.
3. Otherwise, in ochem, when two different atoms are covalently bonded, the atom to the left in the periodic table has a $\delta^+$ and the atom to the right in the periodic table has a $\delta^-$ .

## reaction types

<b>Substitution:</b> substituting one group for another group.
<b>Elimination:</b> eliminating two groups to form a pi bond.
<b>Addition:</b> adding two groups to remove a pi bond

## stereochemistry of reactions

You need to use wedges and dashes: (1) around a stereocenter, or (2) when there are cis/trans relationships around a ring.
Otherwise, you don't need wedges and dashes.
When you attack an atom that is tetrahedral, you get one product.
When you attack an atom that is trigonal planar, you get two stereoisomer products, if possible.

## the rule for determining hybridization

number of hybridized orbitals = number of attached atoms + number of lone pairs
Radicals are $sp^2$ hybridized.

## molecular geometry

An atom that is $sp^3$ hybridized with no lone pairs is tetrahedral.
An atom that is $sp^2$ hybridized with no lone pairs is trigonal planar.

## single-swap rule

If you make a single swap, while maintaining the same bond orientation, at a stereocenter, you invert the configuration at that stereocenter.
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## common patterns for reactions with one nucleophile-electrophile step

N/E	1. N/E 2. A/B	1. A/B 2. N/E	1. A/B 2. N/E 3. A/B
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Moral: For reactions with a single N/E step, you alternate between N/E and A/B. You generally stop when the “main molecule” has no charge.

N/E = nucleophile/electrophile step

A/B = acid/base step

common patterns for reactions with two nucleophile-electrophile steps  
(these reactions generally don't occur until the second semester)

1. A/B 2. N/E <b>3. A/B</b> <b>4. A/B</b> 5. N/E 6. A/B	1. A/B 2. N/E <b>3. A/B</b> <b>4. A/B</b> 5. N/E	1. N/E <b>2. A/B</b> <b>3. A/B</b> 4. N/E 5. A/B
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Moral: For reactions with two N/E steps, you do two A/B reactions in a row between the two N/E steps.

(However, as a “shortcut”, these two A/B reactions are sometimes combined into a single step.)

## start with N/E or A/B?

## STRONG ACID

**In the presence of strong acid**, start with an A/B step.

The strong acids are: molecules with positive formal charges, HCl, HBr, HI, H<sub>2</sub>SO<sub>4</sub>.

## STRONG BASE

**In the presence of H<sup>-</sup> or N<sup>-</sup>**, start with A/B.

**In the presence of LiAlH<sub>4</sub>, Grignard reagents, or alkyl lithiums**, start with A/B if there is a strong or weak acid present; otherwise, start with N/E.

You should generally avoid using strong or weak acids in the presence of these reagents, since they are generally *intended* for use as nucleophiles, not as bases.

**In the presence of O<sup>-</sup>**, you have to learn whether to start with A/B or N/E by studying the details of particular reactions.

## NO STRONG ACID OR STRONG BASE

**In the absence of a strong acid or strong base**, start with N/E.