

A 12-Step Program for Arrow Pushers

Adapted from Prof. K. A. Woerpel and Prof. C. J. Douglas

1. Electrons flow from sites of high electron density (filled orbitals, HOMO's) to sites of low electron density (unfilled orbitals, LUMO's). Arrows represent this electron flow.
2. Balance the equation. It really helps.
3. Don't violate the basic rules of physics.
 - a. Conservation of mass and energy (a corollary to step 2)
 - b. Conservation of charge (a more common error than you might think)
4. Three-Arrow Rule: Don't push more than 3 arrows at one time.
 - a. Some rules were made to be broken — this one gets broken a fair amount, but do follow it as you are starting out.
5. Draw out all intermediates.
 - a. Take your time here: a common mistake is to improperly draw an intermediate.
 - b. Draw out the lone pairs and H's on reacting atoms.
 - c. A 3-D depiction can be useful. Use models if necessary.
 - d. Consider the reaction conditions when drawing intermediates: Do not draw carbocations under basic conditions or anionic leaving groups under acidic conditions.
6. Use your lone pairs.
7. All steps are, in principle, reversible.
8. Contemplate your options and carry each to its conclusion before discarding.
 - a. It can be helpful to star (*) the intermediates where you made a choice to follow one pathway over another.
9. The correct mechanism gives the observed product.
10. Use connectivity to tell you how the puzzle fits together.
 - a. A logical numbering system works wonders.
 - b. "Principle of least action."
11. Always identify the nucleophiles and electrophiles at every step.
 - a. At times it may be useful to substitute oxidants & reductants for nucleophiles and electrophiles.
12. Work backwards from the product to likely precursors.

Learning how to push arrows will help develop your 'chemical intuition.' These "12-steps" have been very helpful to me.