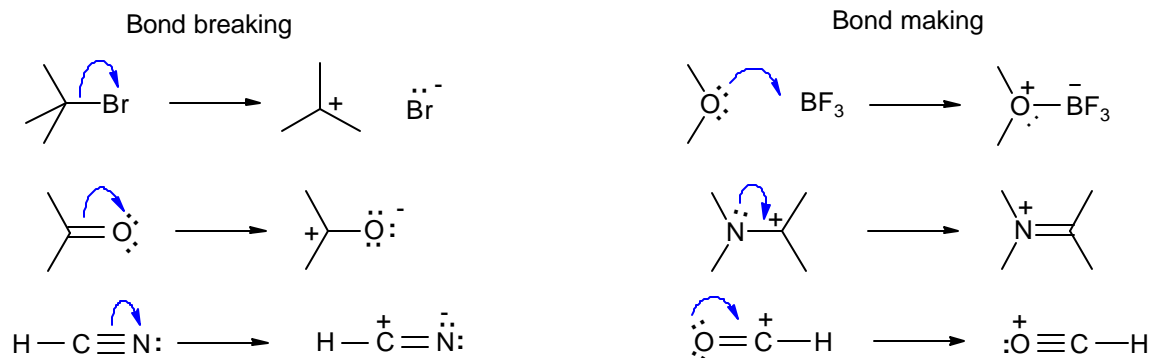


Electron Pushing in Organic Chemistry

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This handout deals with electron pushing arrows: the movement of a pair of electrons from an electron rich site (a lone pair of electrons or a bond) to an electron poor site. Electron pushing arrows are used as a "bookkeeping" device to easily keep track of bonding and formal charges when interconverting resonance structures or depicting reactions. Used properly, they have tremendous value not just for understanding reactions, but also for predicting chemical reactivity

There are two fundamental types of electron pushing processes:

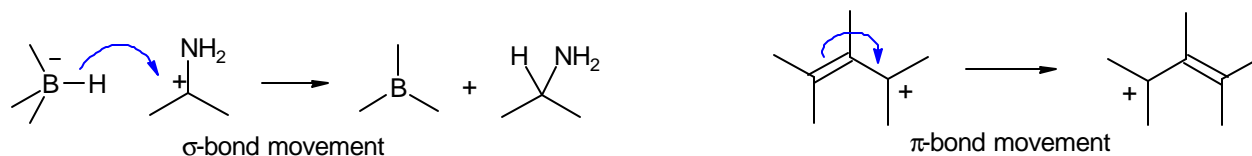


Arrow starts at a bonding pair of electrons and ends at an atom, creating a sextet atom (or H⁺) at the originating atom and new lone pair of electrons at the terminal end.

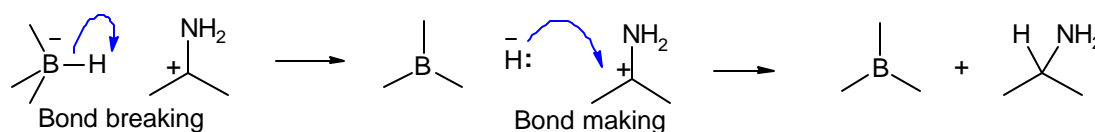
Arrow starts at a lone pair of electrons and ends at a sextet atom (or H⁺), creating a new single bond, or converting a single bond to a double bond.

In each case, the formal charge becomes one unit more positive at the starting atom and one unit more negative at the terminal atom.

A third very commonly used type, Bond Movement, is used to depict synchronous processes. A Bond Movement arrow starts at a σ or π bond, and ends at a sextet atom, forming a new σ or π bond:



It is really shorthand for consecutive or simultaneous bond breaking and bond making processes:



For Bond Movement processes, neither the charge nor the total number of bonds change at the central atom, the initial and final atoms behave as for bond breaking and bond making processes.

When a Bond Making or Bond Movement arrow ends at an octet atom, then a Bond Breaking or a second Bond Movement processes has to "clear out" the extra pair of electron. If this cannot be done in an electronically reasonable fashion, then the process is not feasible. In this way a series of electron movements can be strung together. Again, all of the central carbons have no change in their charges or number of bonds, the first and last atoms change as for Bond Making and Bond Breaking processes.



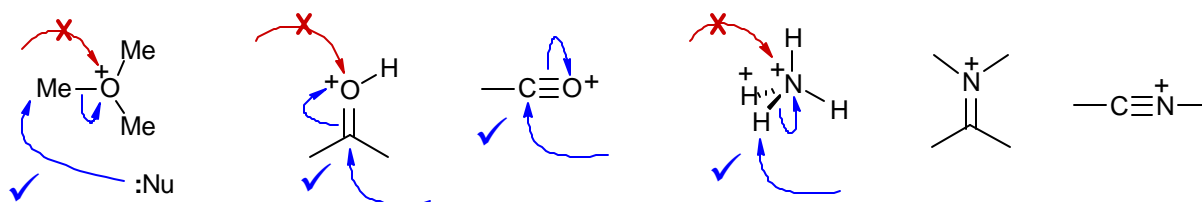
Common problems with electron pushing

- Watch for violations of the octet rule - always specifically draw in all of the atoms (including hydrogens and lone pairs) at any atom undergoing a transformation
- Draw arrows in the right direction (from donor to acceptor). We may think of a proton as attacking a double bond, but in electron-pushing terms, it is the double bond that is attacking the proton.

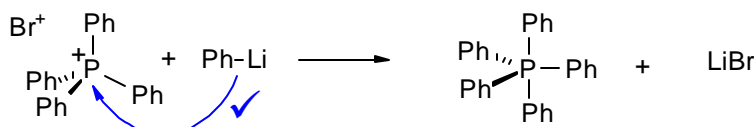


Note: free protons don't actually exist in solution - they are always bonded to something (usually an O or N)

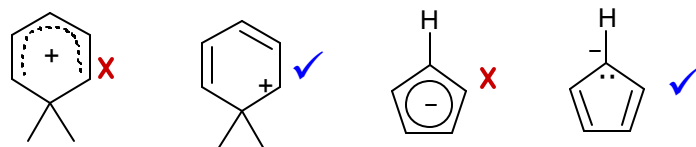
- Clearly distinguish positive charge, and electron deficiency (a sextet atom). Cationic species like oxonium ions, ammonium ions and the like are usually NOT electrophilic at the atom bearing the formal positive charge. Each of the species below has electrophilic properties, but the positively charged O and N atoms are not electrophilic - it is the atoms attached to O and N that are electrophilic and thus subject to attack by bases and nucleophiles.



However, this stricture has to be relaxed for heavier elements like P and S which are capable of forming compounds that formally violate the octet rule

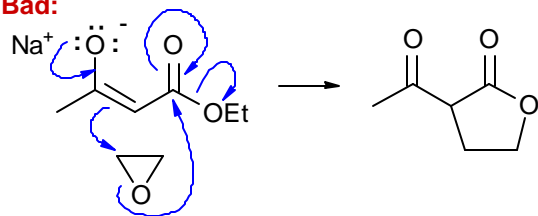


- Similarly, make a clear distinction between formal negative charges and lone pairs of electrons - they are not always synonymous. For boron and aluminum ate complexes, there are no lone pairs. Any donor character arises from the sigma bonds attached to the negative charged atom.
- For delocalized structures, you must pick a specific resonance structure to do any electron pushing - the "dotted line" formulas and circle structures for aromatic systems do not work, since bonds and electron pairs are not shown.



- Do not combine multiple steps into one long series of arrows. An experienced chemist may be able to get away with this sort of behavior, but such mechanisms are confusing and can contain fatal errors. If a reaction involves a true intermediate, your mechanism should reflect that.

Bad:



The real mechanism probably involves three discrete steps:

1. Nucleophilic attack on the epoxide
2. Nucleophilic attack of the alkoxide on the ester carbonyl
3. Loss of the ethoxy group.

Good:

