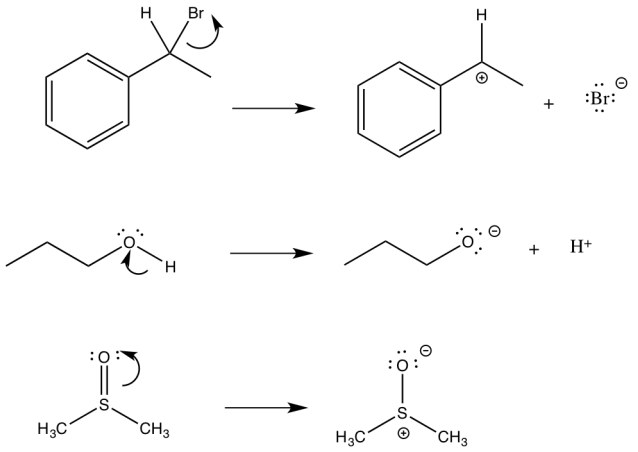
Use of Electron Pushing Arrows in Organic Chemistry

The use of electron pushing arrows in organic chemistry is vital for understanding chemical reactions. When used in resonance structures electron pushing arrows help us keep track of formal charges and bonding. In chemical reactions we are able to understand bond breaking and bond forming.

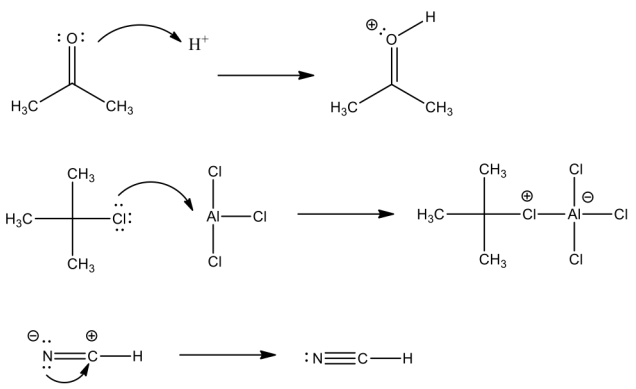
Let us consider bond breaking and bond formation and how electron pushing arrows are used:

Bond breakage



Arrows always start at a bonding pair of electrons and move to an atom. In this process an electron deficient atom (without an octet) is left behind and an atom with an extra lone pair of electrons.

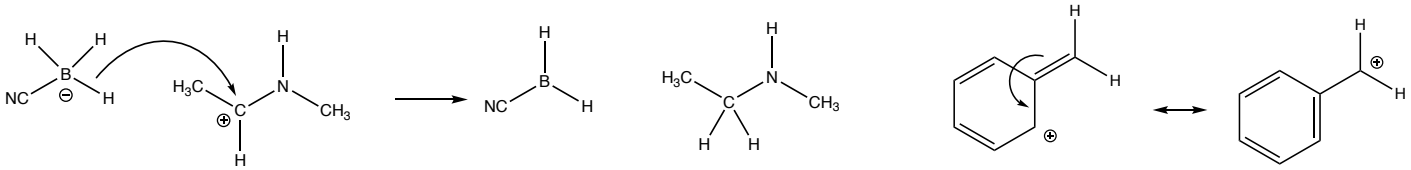
Bond forming



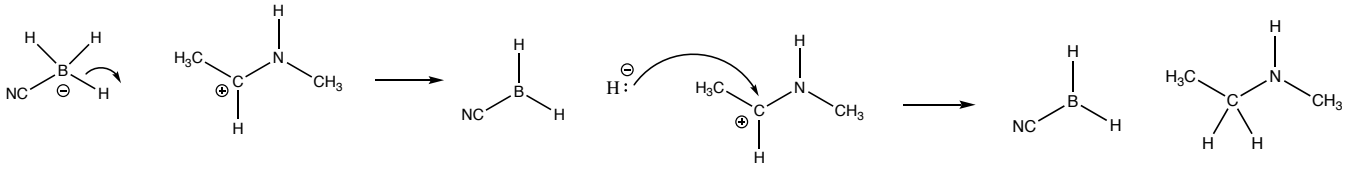
Arrows always start at a lone pair of electrons and move to make a new bond whether single, double or triple.

In each of the cases just seen electron movement makes the starting atom increase one formal charge unit and the other atom increase in one negative charge.

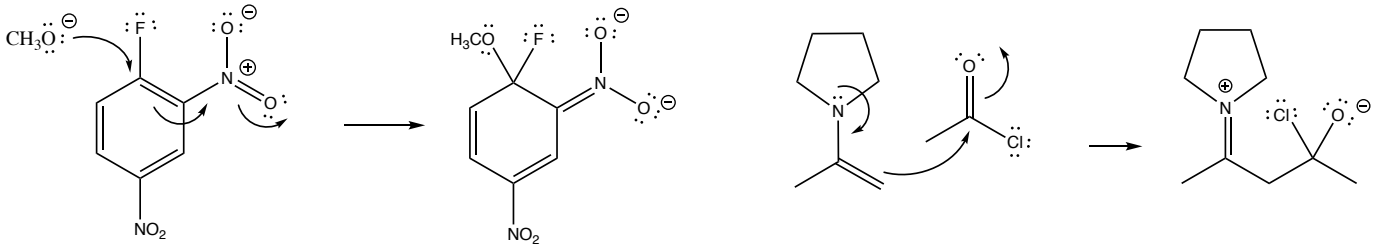
Sometimes we shorten a reaction process by showing one bond formation.



When in reality it may be the reaction occurs as a two-stage process of bond breakage and bond forming.

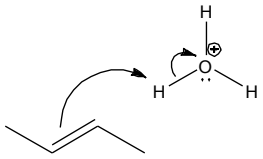


It is important to keep track of the bond breakage and bond forming processes because a pair of electrons may end up on an atom that already has a complete octet. If the process cannot rearrange electrons to regain their full octet then the process is not logical. On the other hand, if a series of electron movements can be strung together then only the first and last atoms of the series will change their number of bonds (see below).

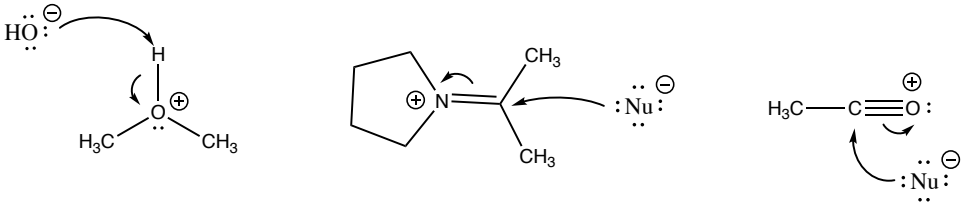


Things to watch for when writing electron pushing

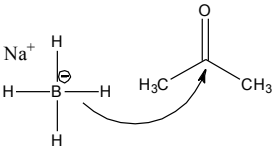
- Draw all the atoms attached to the atom undergoing the transformation. (Check for any violations of the Octet Rule.)
- Always draw arrows in the right direction, that is, from electron donor to electron acceptor. Therefore, in this scenario the double bond attacks the hydrogen atom (or better H attached to solvent, etc).



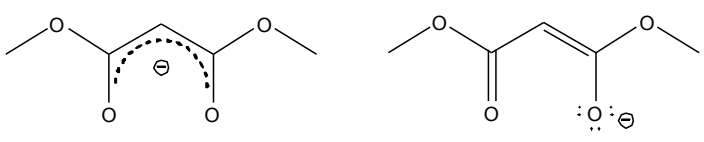
- Electron deficiency and positive charge should be clearly distinguished. For example, an ammonium ion which, has a positive charge is not electrophilic at the nitrogen atom. In each of the ions shown below the positively charged oxygen and nitrogen atoms are not the electrophilic species. The less electronegative is the most electrophilic of the pair.



- Conversely, check for formal negative charges and lone pairs of electrons. In the example shown below the pair of electrons to make a bond comes from the sigma bond, σ, attached to the atom that has the formal negative charge.



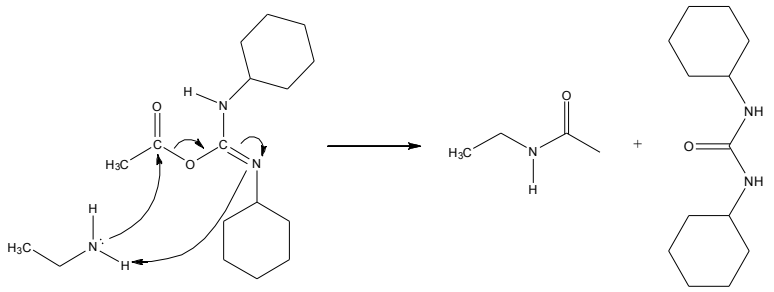
- For structures that exhibit resonance do not use the "hybrid" form. Usually these do not show electron pairs or bonds.



wrong right

- Mechanisms written with a continuous series of arrows is discouraged. It is often that a mechanism of a chemical reaction contains an intermediate. You should be able to include the intermediate in your mechanism.

Incorrect:



The actual mechanism involves several steps:
a) Nucleophilic attack on the carbonyl.
b) Collapse of the alkoxide to an sp^2-carbon and release of DCC.
c) Acid-base reaction.

Correct: