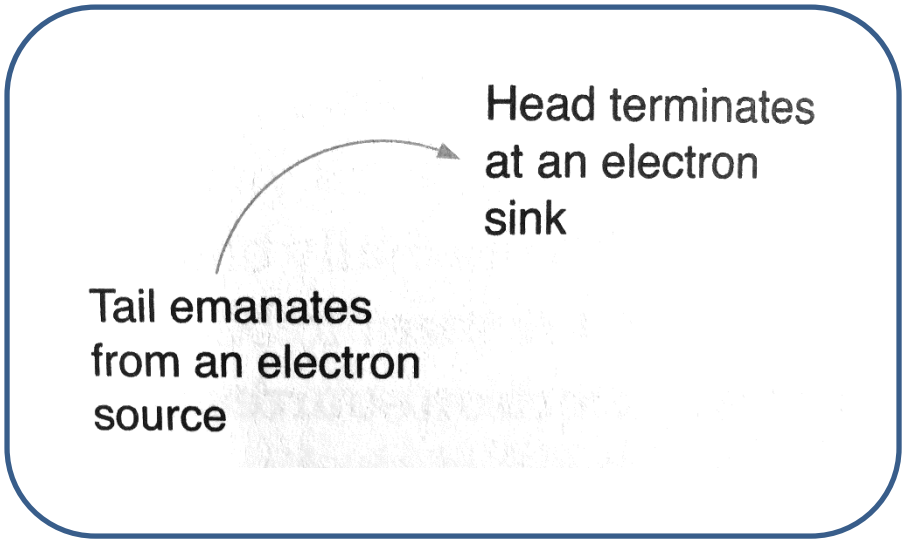
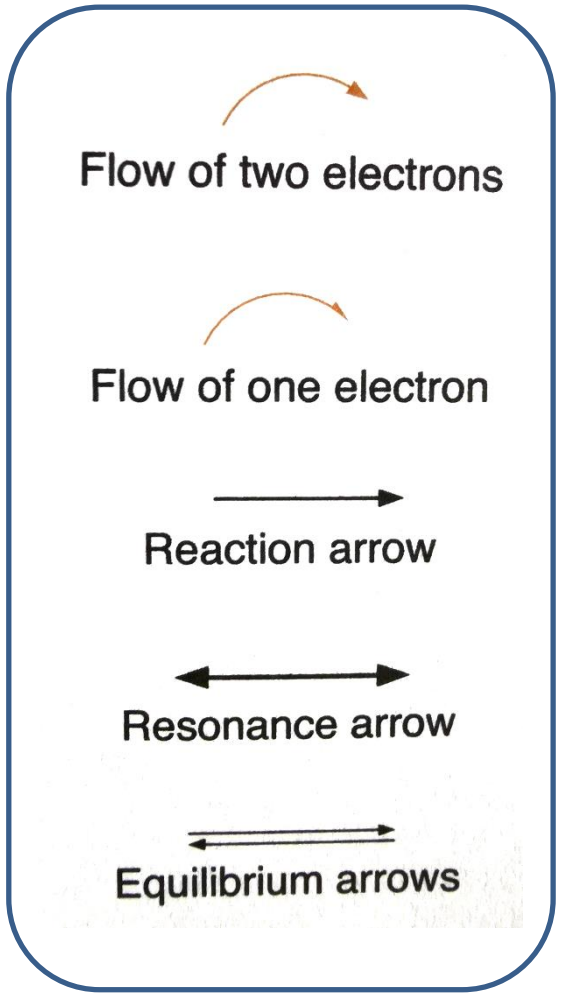
Basics in pushing electrons





Common electron sources

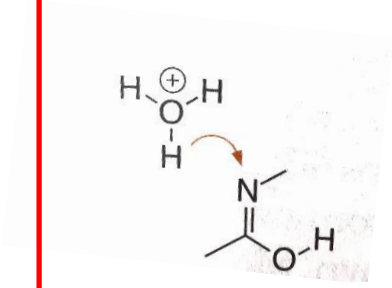
I. Sources (R = H, alkyl, aryl)
Nonbonding Electrons
A. The lone pairs on the heteroatoms on the following structures: X^-, RO^-, R_2O, NR_3, NR_2^-, RCO_2^-, RCO_2R, R(CO)R, $R(CO)NR_2$, R_2S, RS^-, CN^-, N_3^-, R_3P, R_2Se, and RSe^-
Electron Rich or Strained σ Bonds
A. Organometallics: RMgX, RLi, R_2CuLi, and R_2Zn B. Hydride reagents: $LiAlH_4$, $NaBH_4$, NaH, and BH_3 C. Cyclopropropyl or cyclobutyl
π Bonds
Alkenes, dienes, alkynes, allenes, and arenes
Electron Rich π Bonds
Enols, enamines, enolates, anilines, and phenols

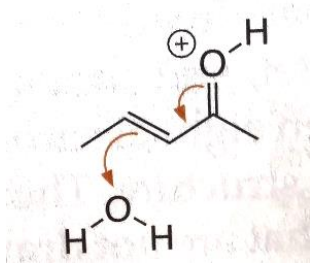
Common electron sinks

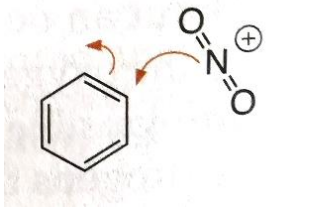
II. Sinks (R = H, alkyl, aryl)
Species with Empty Orbitals
Carbocations, aluminum and boron containing Lewis acids, and transition metal (mercury, cadmium, and zinc) reagents
Acidic Hydrogens
Mineral acids, carboxylic acids, water, alcohols, amines, and terminal acetylenes
Weak Single Bonds
Peroxides (ROOR), molecular halogens (X_2), bleach (HOX), and disulfides (RSSR)
The Carbons in Polarized σ Bonds
Alkyl halides, alkyl tosylates, protonated alcohols (ROH_2^+), and protonated amines (RNH_3^+)
The Carbons in Polarized Multiple Bonds
$R_2C{=}O$, nitriles, α,β-unsaturated carbonyl compounds, acyl halides, anhydrides, esters, and amides

Common Electron-pushing Errors

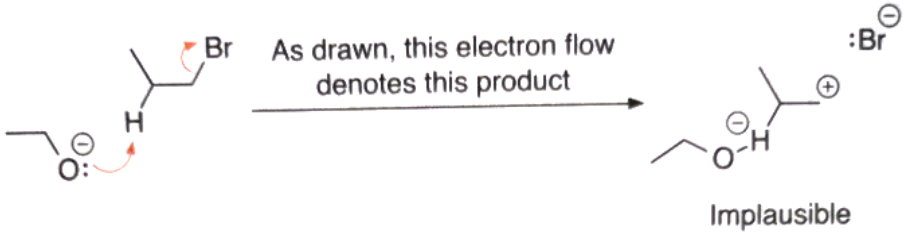
Backwards Arrow Pushing



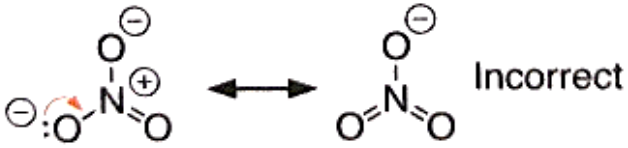


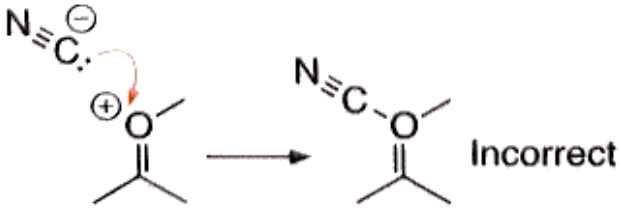


Not enough Arrows

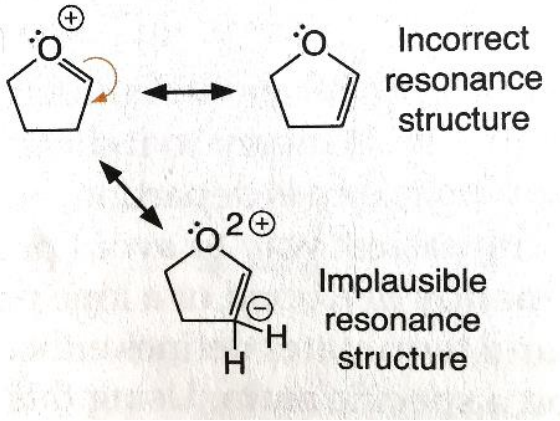


Losing track of the octet rule



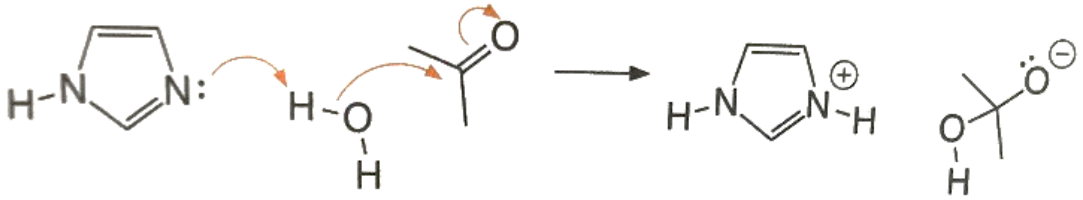


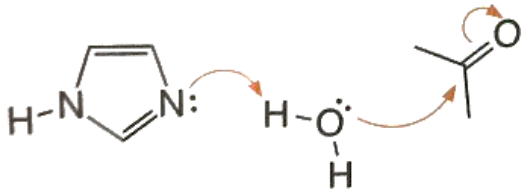
Losing track of hydrogens and lone pairs

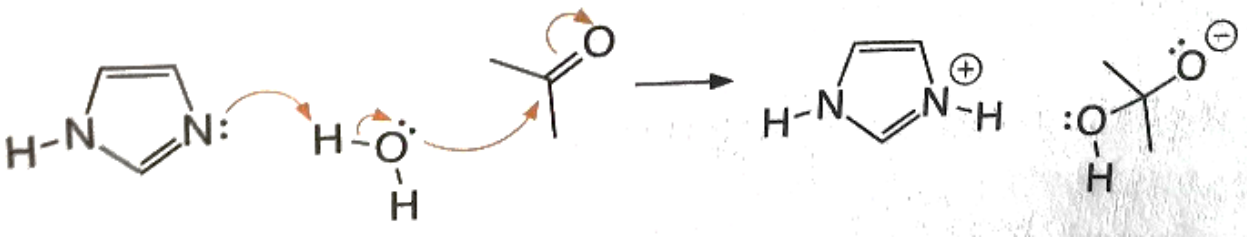


Common Electron-pushing Errors

Not using the proper source

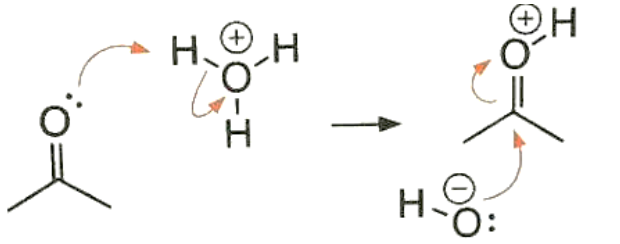


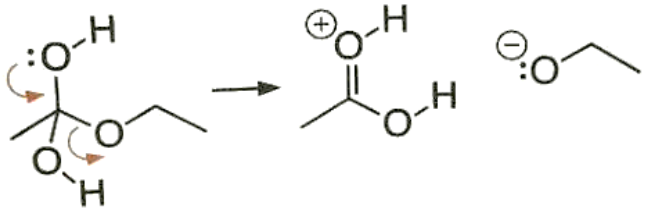




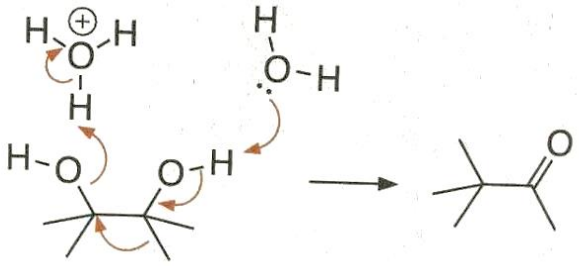
Common Electron-pushing Errors

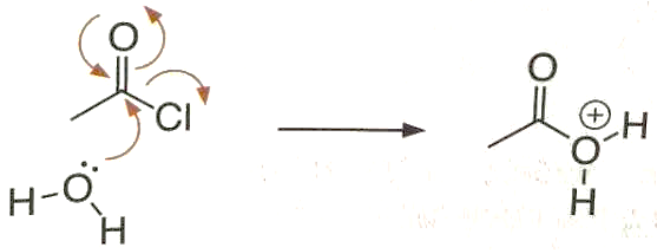
Mixed media mistakes





Too many arrows — Short cuts



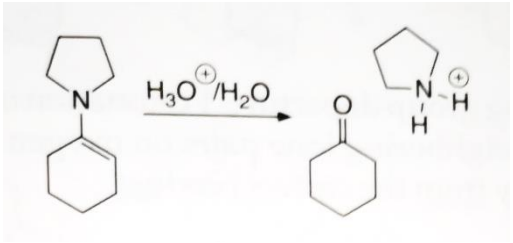


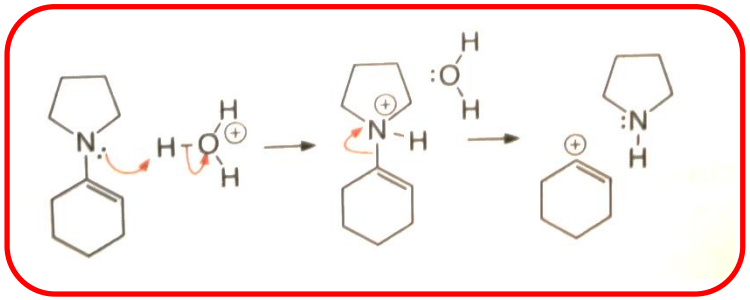
Drawing a chemically reasonable mechanism

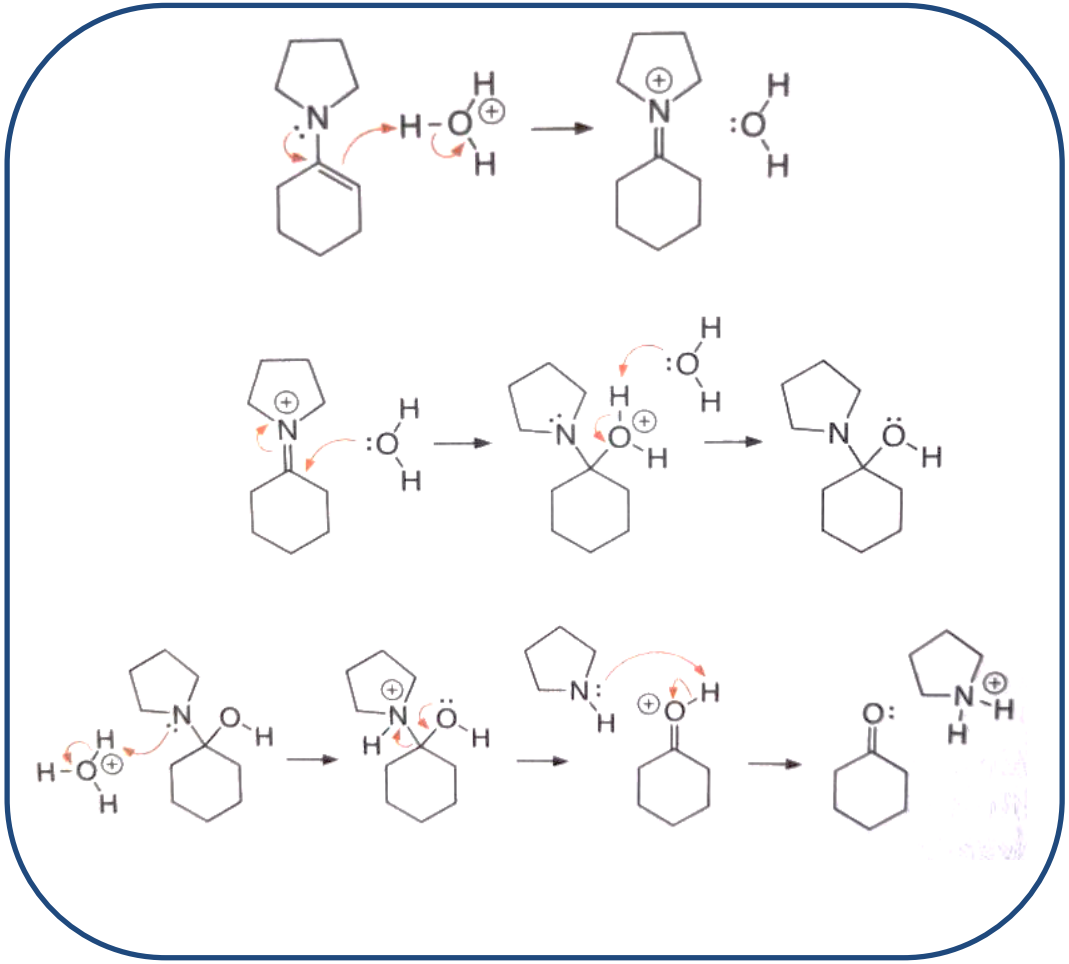
A few simple rules:

- Find a 1:1 correspondence between all atoms in the reactants and the products.
- Look for a path that will lead to the product. Note which groups have added to or left from the reactant. Make sure such steps are included in the mechanism.
- Note any rearrangement of atoms within the chemical structure and make sure appropriate steps are included.
- Do not push too many arrows as a way to create a short cut to the product.
- Avoid the common electron-pushing mistakes.
- Do not form intermediates with unreasonably high energy

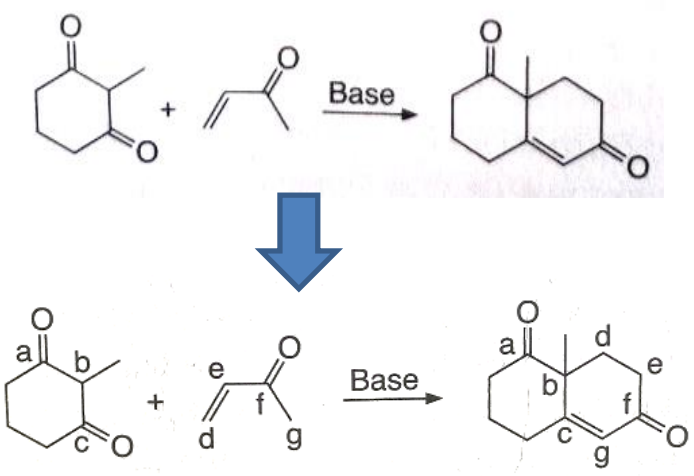
Case study — 1

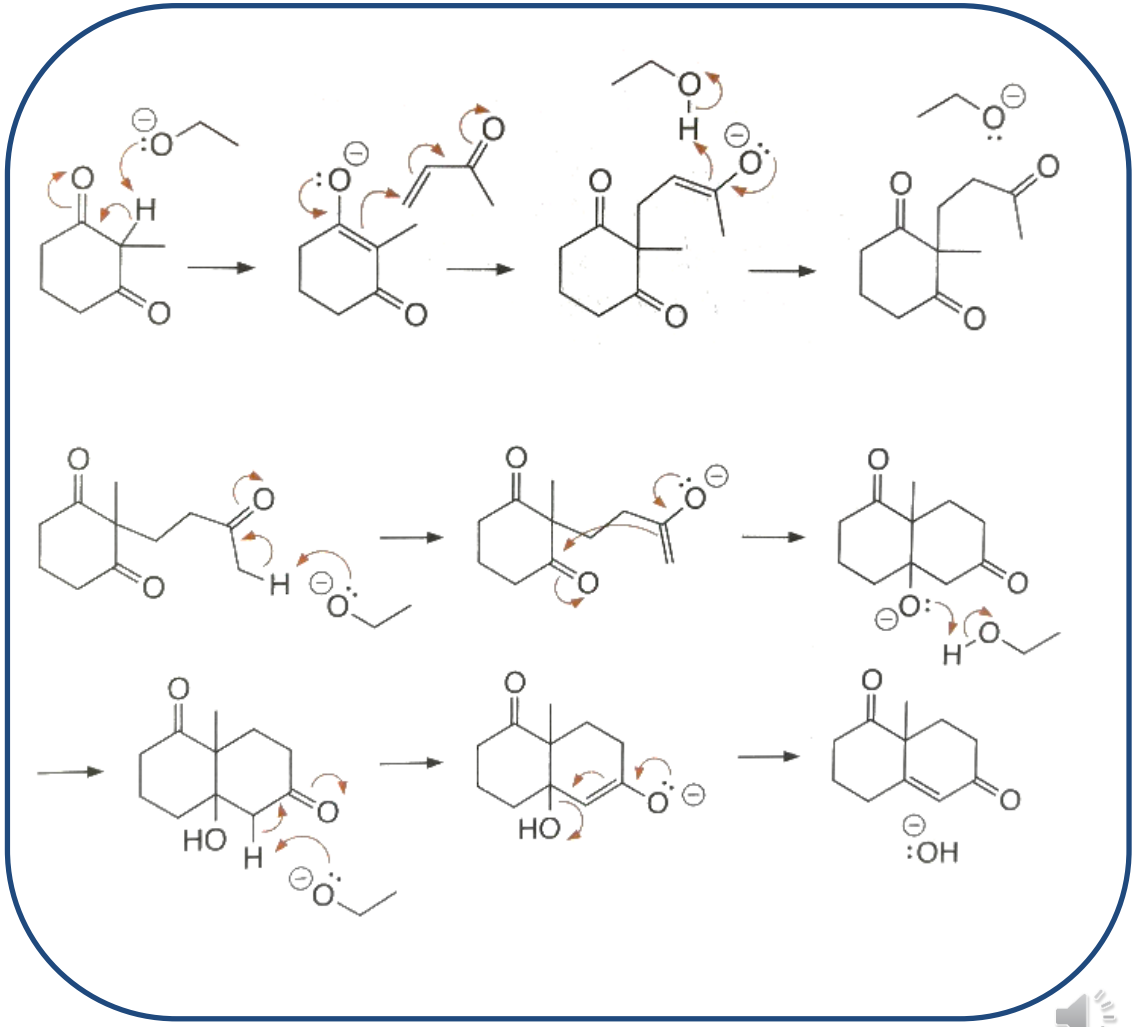






Case study — 2





Case study — 3