Tikrit University
College of Science
Dep. Of Chemistry
Graduate studies

Advanced Organic Chemistry

"Writing Reaction Mechanisms In Organic Chemistry"

By

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Aims :

- Explain the importance of reaction mechanisms in organic chemistry
- Understand the difference between elementary and stepwise reactions, and the role played by transition states and intermediates
- Know the main types of bond-breaking and bond-making processes
- Identify the bonds made and broken in a reaction, given the starting materials and products , thereby allowing a number of possible reaction mechanisms to be written.

Writing Reaction Mechanisms In Organic Chemistry

The ability to write an organic reaction mechanism properly is key to success in organic chemistry classes. Organic chemists use a technique called **arrow pushing** to depict the flow or movement of electrons during chemical reactions. Arrow pushing helps chemists keep track of the way in which electrons and their associated atoms redistribute as bonds are made and broken. The essential rules to keep in mind are the following:

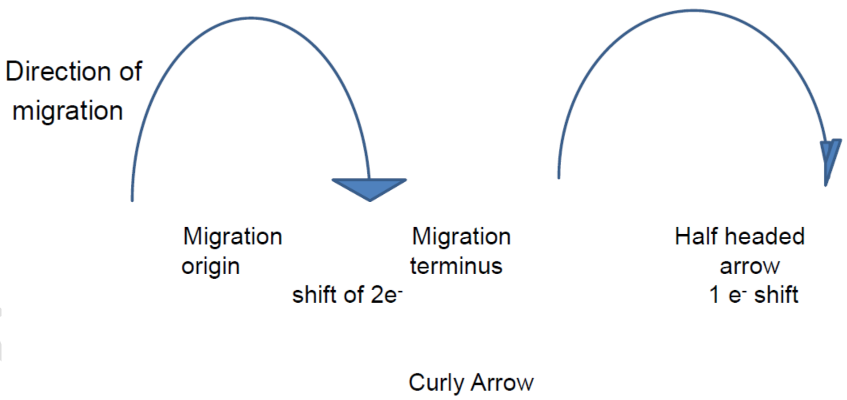
1- Draw the curved arrow so that it points from the source of an electron pair to the atom receiving the pair.
2- Always show the flow of electrons from a site of higher electron density to a site of lower electron density.
3- **Never** use curved arrows to show the movement of atoms. Atoms are assumed to follow the flow of the electrons.
4- Make sure that the movement of electrons shown by the curved arrow does not violate the octet rule for elements in the second row of the periodic table.

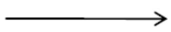
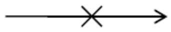
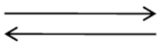
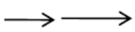
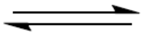
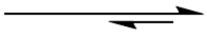
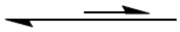
Indicating Steps in Mechanisms

- Curved arrows indicate breaking and forming of bonds

- Arrowhead with a "half" head ("fish-hook") indicates homolytic and homogenic steps (called 'radical processes')

- Arrowhead with a complete head indicates heterolytic and heterogenic steps (called 'polar processes')

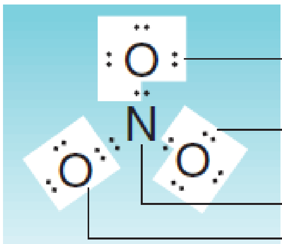


	Irreversible reaction to product
	Reaction which does not processd
	Forward & Backward reaction
	Reaction with more than one step
	Reversible reaction
	Reversible reaction ; Equilibrium favours products
	Reversible reaction ; Equilibrium favours reactant
	Reaction with inversion of cofiguration
	Indication of resonance

Examination of a molecule with respect to its electronic structure

Formal charge

Formal charge = number of valence electrons - 1/2 number of shared electrons - number of unshared electrons



Formal charge $= 6 - (^1/_2)2 - 6 = -1$

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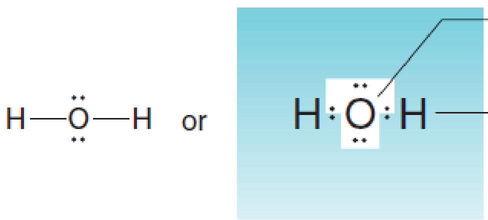
Formal charge $= 5 - (^1/_2)8 = +1$

Formal charge $= 6 - (^1/_2)4 - 4 = 0$

Charge on ion $= 2(-1) + 1 + 0 = -1$

Water

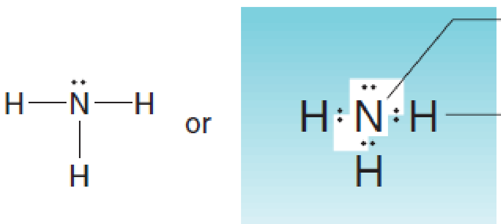


Formal charge $= 6 - (^1/_2)4 - 4 = 0$

Formal charge $= 1 - (^1/_2)2 = 0$

Charge on molecule $= 0 + 2(0) = 0$

Ammonia

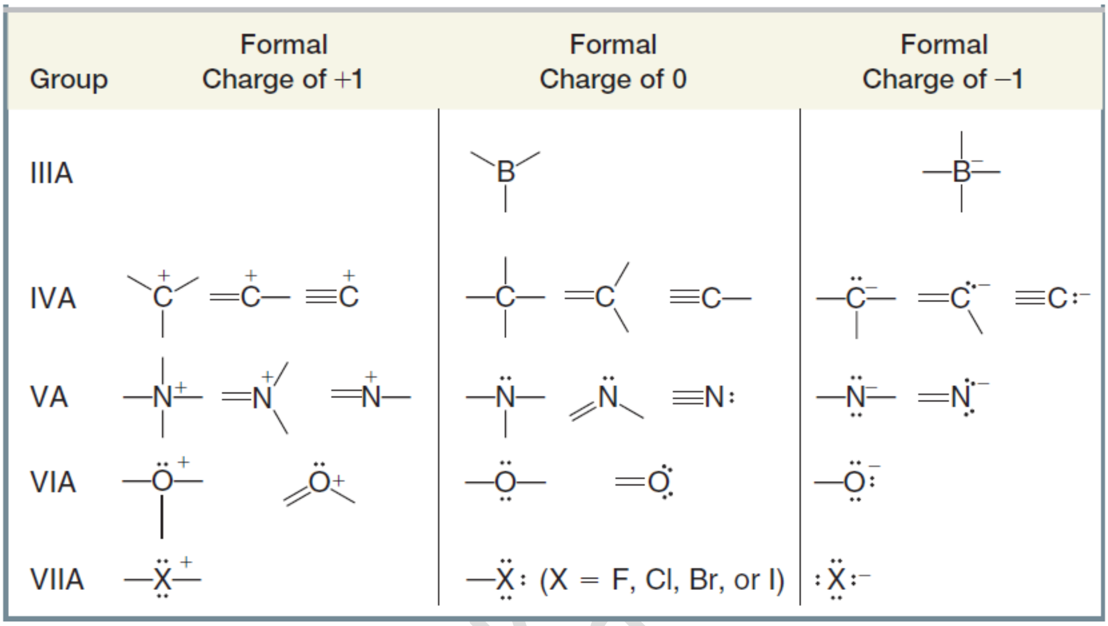


Formal charge $= 5 - (^1/_2)6 - 2 = 0$

Formal charge $= 1 - (^1/_2)2 = 0$

Charge on molecule $= 0 + 3(0) = 0$

A Summary of Formal Charges

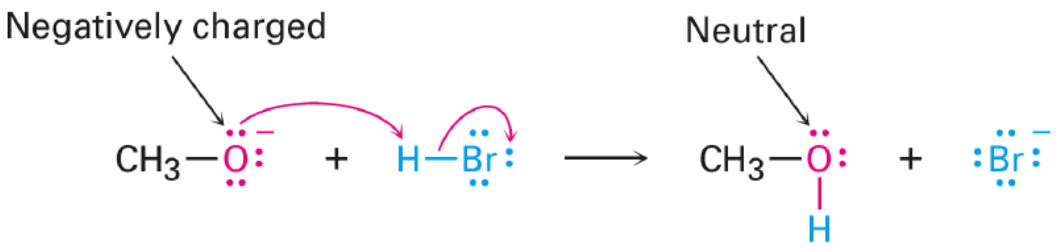


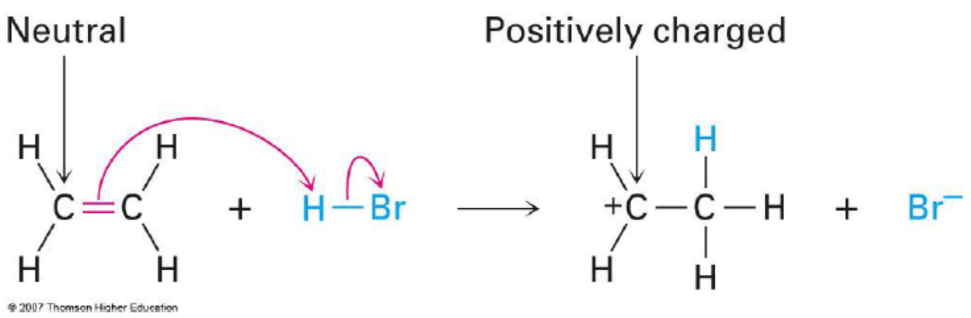
Using Curved Arrows in Polar Reaction Mechanisms

- Curved arrows are a way to keep track of changes in bonding in polar reaction
- The arrows track "electron movement"
- Electrons always move in pairs
- Charges change during the reaction
- One curved arrow corresponds to one step in a reaction mechanism
- The arrow goes from the nucleophilic reaction site to the electrophilic reaction site

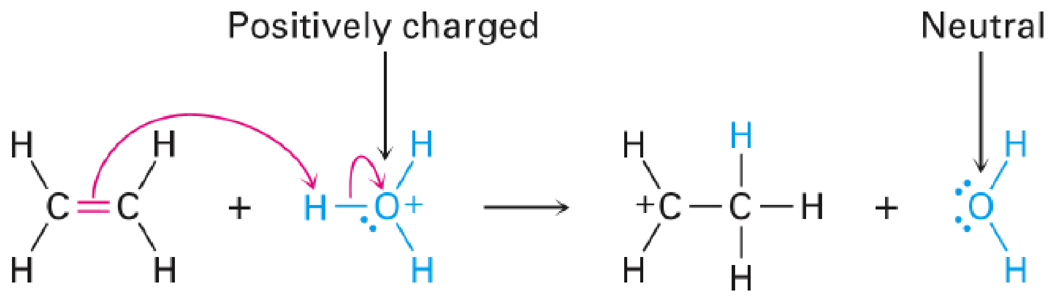
Rules for Using Curved Arrows

- The nucleophilic site can be neutral or negatively charged

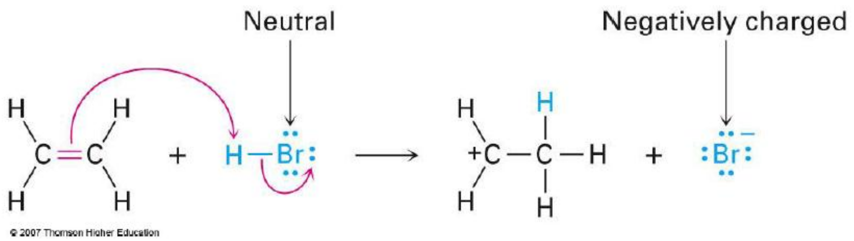


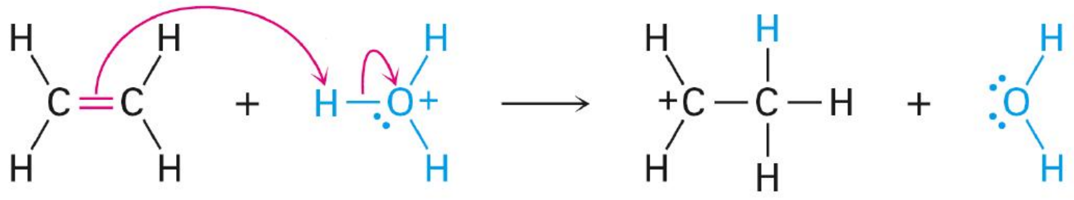


- The electrophilic site can be neutral or positively charged



- Don't exceed the octet rule (or duet)

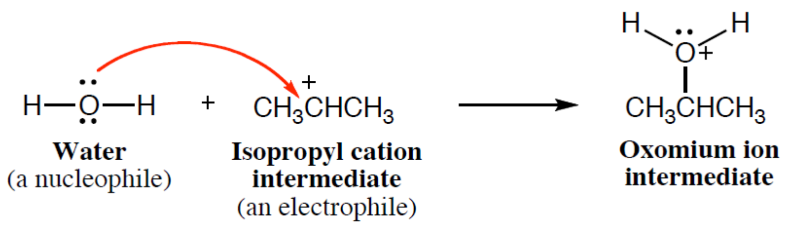




There are a surprisingly small number of different types of characteristic mechanism elements (patterns of arrows) to be considered when trying to predict individual steps of even complex chemical reactions. For this reason, you should view the prediction of each step in an organic mechanism as essentially a *multiple choice* situation in which your most common choices are the following:

1- Make a new bond between a nucleophile (source for an arrow) and an electrophile (sink for an arrow).

Use this element when there is a nucleophile present in the solution as well as an electrophile suitable for reaction to occur

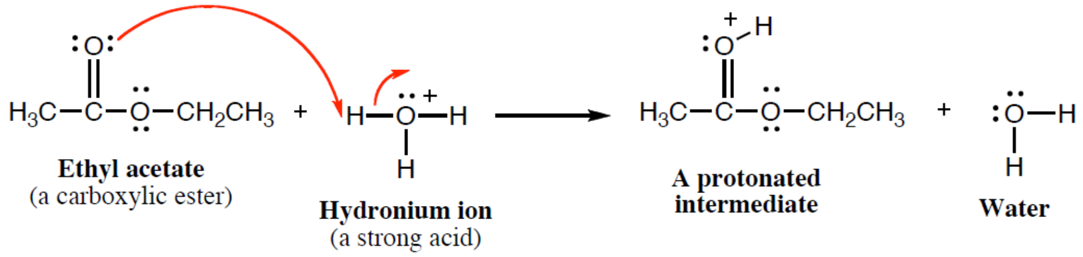


2- Break a bond so that relatively stable molecules or ions are created

Use this element when there is no suitable nucleophile-electrophile or proton transfer reaction, but breaking a bond can create neutral molecules or relatively stable ions, or both.

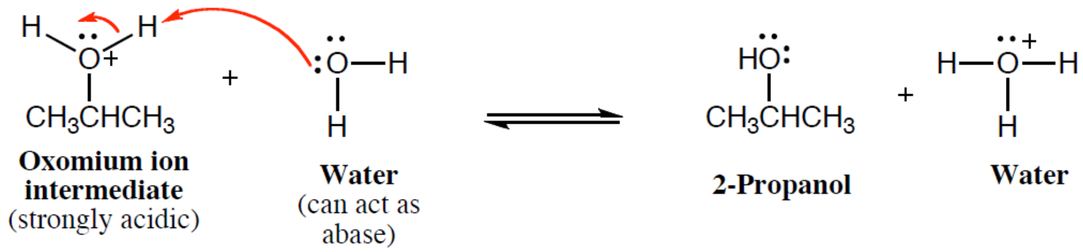
3- Add a proton

Use this element when there is no suitable nucleophile-electrophile reaction, but the molecule has a strongly basic functional group or there is a strong acid present.



4- Take a proton away

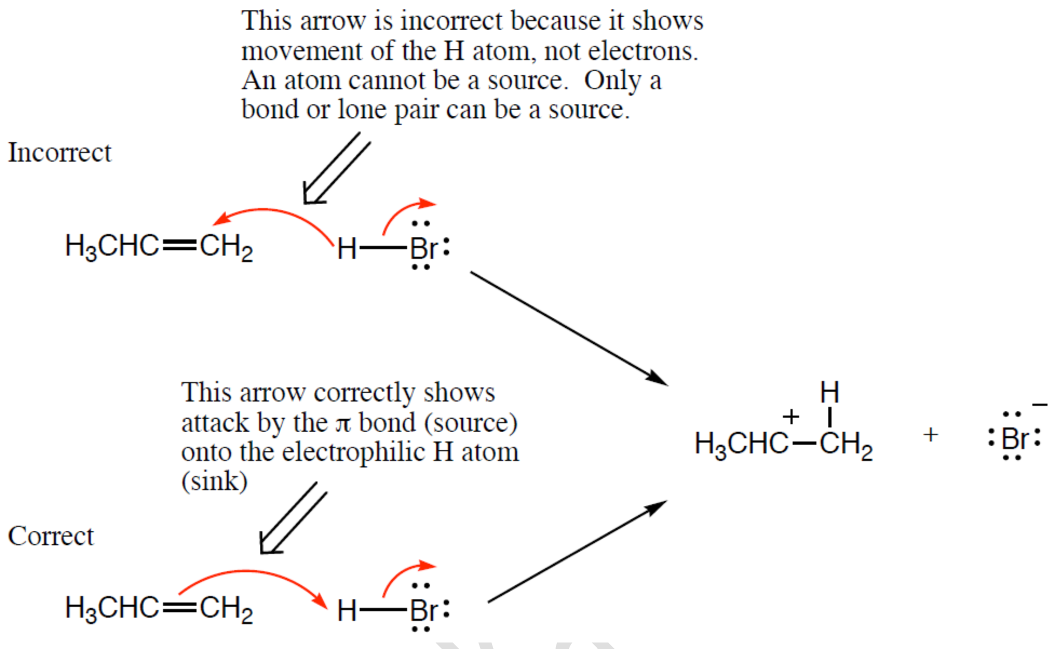
Use this element when there is no suitable nucleophile-electrophile reaction, but the molecule has a strongly acidic proton or there is a strong base present.



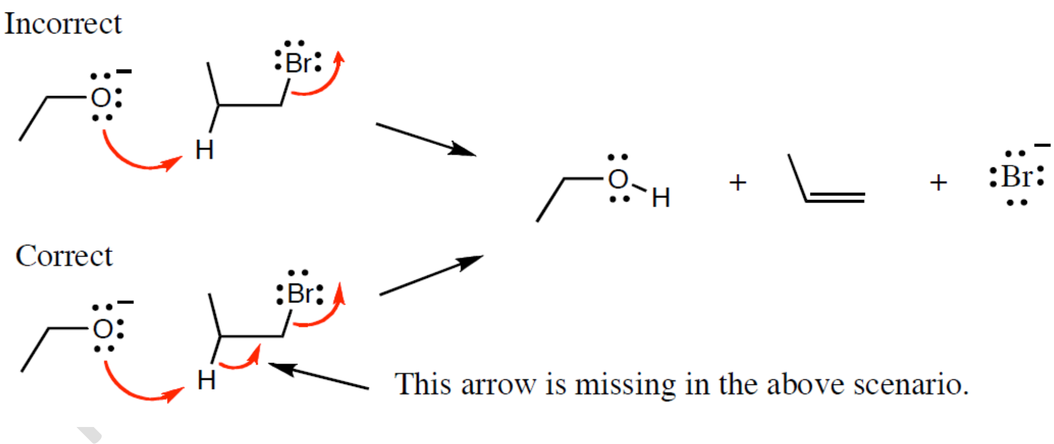
Many times, more than one of the four choices occurs simultaneously in the same mechanism step and there are some special situations in which unique or different processes such as electrophilic addition or 1,2 shifts occur.

Common Mistakes in Arrow Pushing

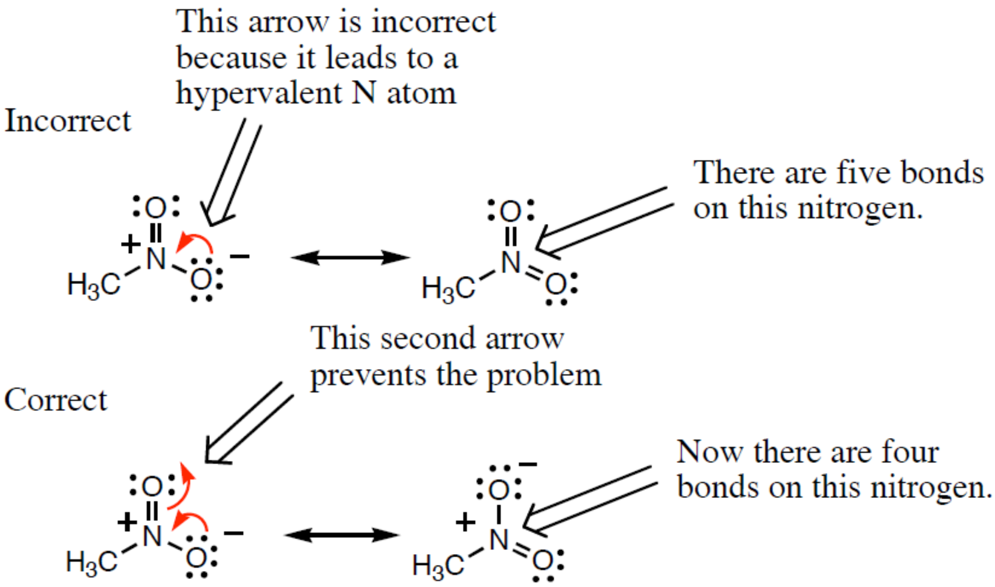
1- Backwards Arrows



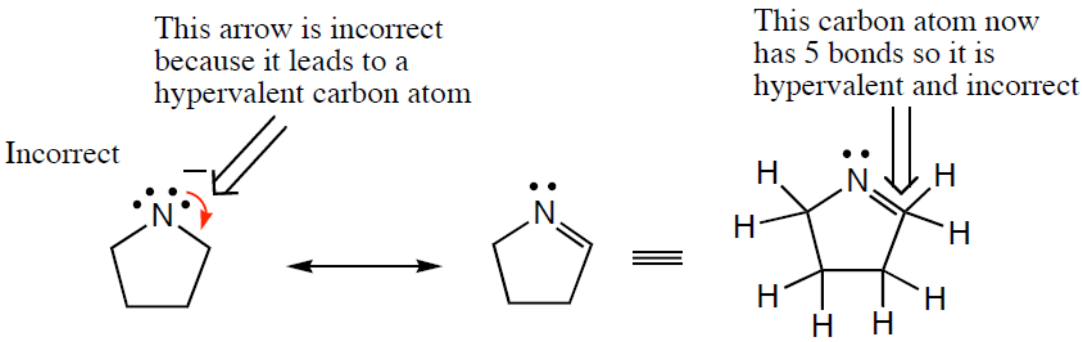
2- Not Enough Arrows



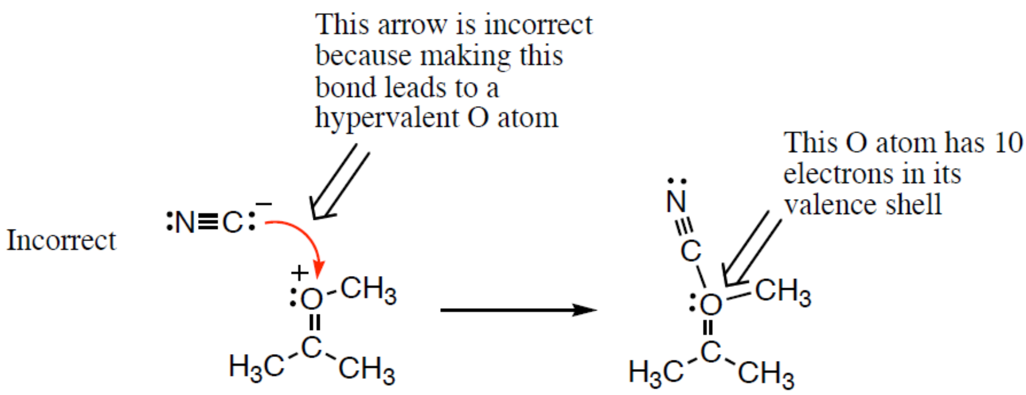
3- Hypervalency



Another common way students mistakenly end up with a hypervalent atom is to forget the presence of hydrogens that are not explicitly written.



Another common way to make a hypervalency mistake is by forgetting to count all lone pairs of electrons.



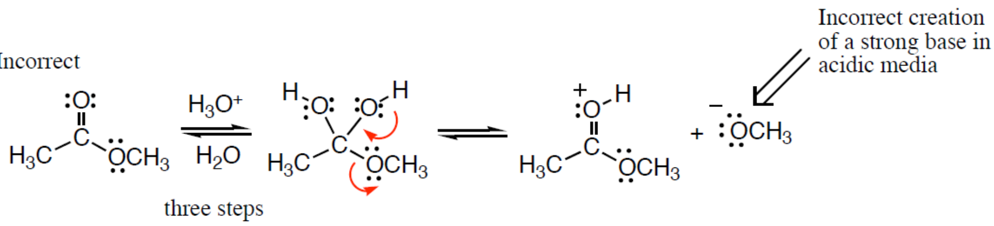
4- Mixed Media Errors

Acids and bases are catalysts, reactants, products, and intermediates in many organic chemistry transformations. When writing mechanisms for reactions involving acids and bases, there are three general rules that will help guide you in depicting the correct mechanism.

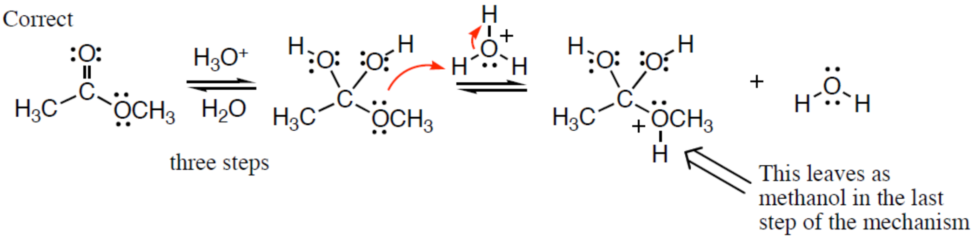
- Do not show the creation of a strong acid for a mechanism of a reaction that is performed in strongly basic media.
- Do not show the creation of a strong base for a mechanism of a reaction that is performed in strongly acidic media.
- In strongly acidic media, all the intermediates and products will be either neutral or positively charged, while in strongly basic media, all the products and intermediates will be neutral or negatively charged.

The reason for these rules is that significant extents of strong acids and bases cannot coexist simultaneously in the same medium because they would rapidly undergo a proton transfer reaction before anything else would happen in the solution.

Incorrect

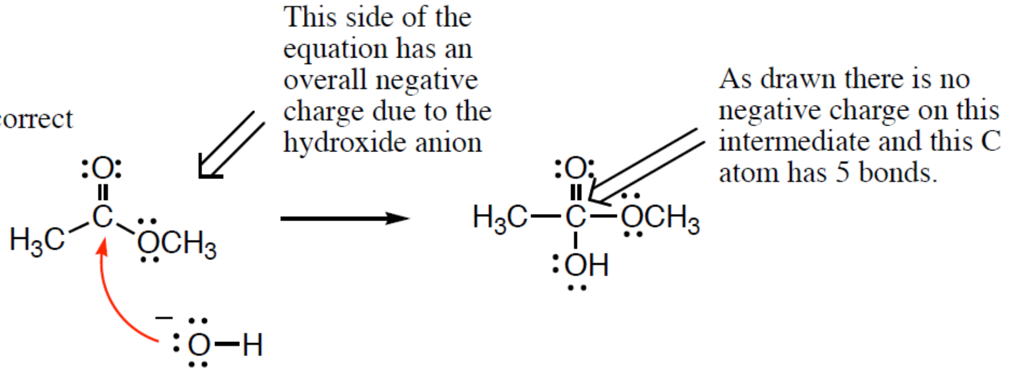


Correct

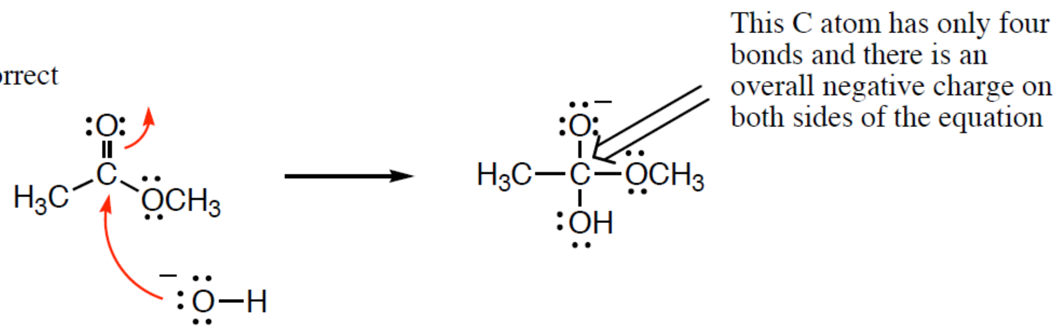


5- Failing to conserve charge

Incorrect



Correct



References:

1- Audrey Miller, Philippa H. Solomon. Writing reaction mechanism in organic chemistry 2ed 1999.
2- Daniel E.Levey. Arrow pushing in organic chemistry an easy approach to understanding reaction mechanisms 2008.
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