Learning Guide for Chapter 7 - Organic Reactions I

I. Introduction to Reactions
II. Principles of Kinetics
III. Principles of Thermodynamics
IV. Nucleophiles and Electrophiles
V. Acids and Bases

I. Introduction to Chemical Reactions

What a chemical reaction is

What always happens during a chemical reaction?

How to Represent Chemical Reactions

How can a reaction be represented without showing specific compounds?

Energy Diagrams for Chemical Reactions

What do energy diagrams tell us?

What is on each axis?

What basic pattern does the energy of all reactions follow?

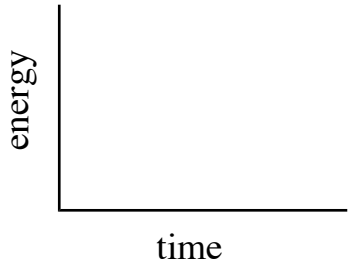
Where is the transition state? Why is it higher in energy than either products or reactants?

What is the activation energy of a reaction??

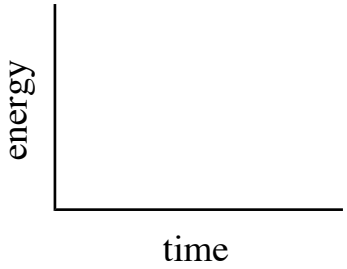
What is the difference between an exothermic and endothermic reaction?

Draw the energy diagrams for an exothermic and an endothermic reaction.

exothermic



endothermic



What is the difference between the energy at the beginning and at the end?

When is it positive, and when is it negative?

What determines the enthalpy of the reactants and products?

If a reaction has stronger bonds at the beginning than at the end, is it exothermic or endothermic?

II. Kinetics of Reactions

What does understanding the kinetics of a reaction tell you? Why do we care?

What must happen in order for two molecules to react?

How will the following factors affect the rate of a reaction, and why?

activation energy (E_a):

probability factor (A):

concentration of the reactants [ ]:

temperature (T):

Which are always the same for a certain reaction?

Which of these are within our control?

What does the rate law for a reaction look like?

If a reaction has a large rate, what does that tell you?

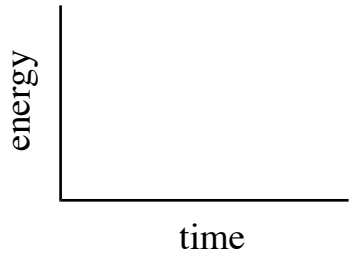
What do the exponents tell you?

How do we find out what the exponents are?

What is a mechanism?

What would happen with a one step reaction?

$A + B \longrightarrow C + D$



What would happen tot he rate of the reaction if we doubled the concentration of A? of B?

What would happen to the rate of the reaction if we doubled the concentration of C or D?

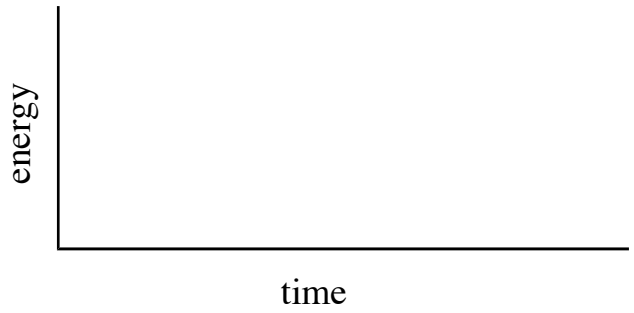
What if the reaction is reversible?

What happens if a reaction requires multiple steps?

overall reaction: $A + B + C \longrightarrow E + F + G$

mechanism:

Which step controls the rate of the reaction?



What would happen to the rate of the reaction if we doubled the concentration of each reagent?

III. Thermodynamics of Reactions

What does studying the thermodynamics of a reaction tell us? Why is this important?

How do you show that a reaction is reversible?

When a reaction has reached equilibrium, what will be happening?

What is the equilibrium constant?

If the $K_{eq} = 10^{18}$, what does that tell us?

If $K_{eq} = 10^{-25}$, what does that tell us?

The rate of a reaction and the equilibrium constant are independent. What would happen if:

K_{eq} is large, rate is large

K_{eq} is large, rate is small

K_{eq} is small, rate is large

K_{eq} is small, rate is small

Where does the equilibrium constant come from?

If the free energy of the reactants is higher than the free energy of the products, what would you predict about the reaction?

If the free energy of the reactants is lower than the free energy of the products, what would you predict about the reaction?

How are ΔG and K_{eq} related mathematically?

How is ΔG different from ΔH?

When would ΔS be important?

What would cause a significant change in ΔS?

How does a reaction get to equilibrium and stay there?

If the $K_{eq} = 1$ and you add 20 moles of A and 20 moles of B together, what will happen in order for equilibrium to be reached?

What happens to the rates of reaction during this process?

What would happen if, after the reaction has reached equilibrium, you add 10 more moles of A to the reaction?

What would happen if C or D were removed?

How could a reagent be removed from a reaction?

What would happen if there was a large excess of A, say 1000 moles?

What would happen if the K_{eq} were very large?

What would happen if there were two steps in a reaction, and the first had a small K_{eq} and the second had a large K_{eq}?

$$A + B \longrightarrow C \quad K_{eq} = 10^{-12}$$

$$C + D \longrightarrow E \quad K_{eq} = 10^{8}$$

What if the first was large and the second small?

When $K_{eq} = 1$, why are the rates equal when the reaction is at equilibrium?

How can the rates be equal in an exothermic reaction?

How can the reaction rates be equal in an endothermic reaction?

III. Electrophiles and Nucleophiles

Write the definitions of the following terms:

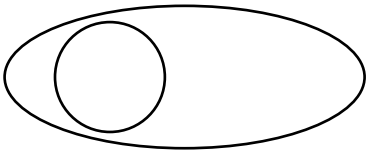
Bronsted-Lowry acid:

Bronsted-Lowry base:

Lewis acid:

Lewis base:

What is the relationship between these definitions?



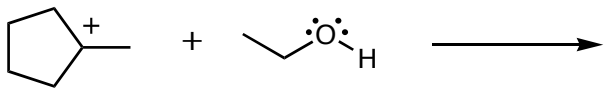
There are three basic types of Lewis acid/base reactions. What do each of these words mean in ordinary English? What do they remind you of?

displacement:

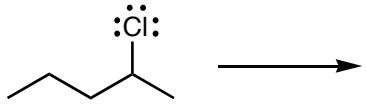
association:

dissociation:

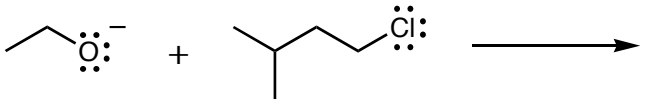
Below are some a Lewis acid/base reactions. Watch how the electron movement causes the reaction to occur. What description fits best?



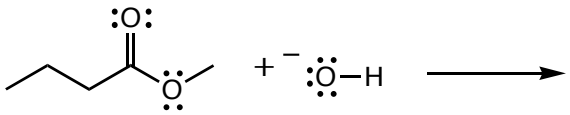
What happens in an association reaction?

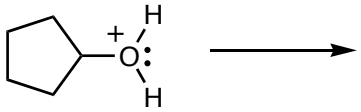


What happens in a dissociation reaction?



What happens in a displacement reaction?



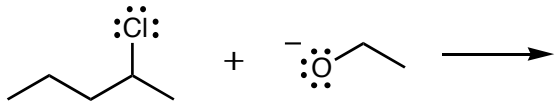


When a bond is broken, which atom gets the electron pair?

What do all of the nucleophiles in the examples have in common?

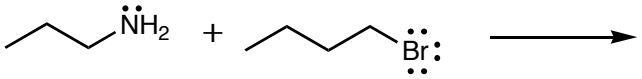
How is the electrophile in an association reaction different from an electrophile in a displacement reaction?

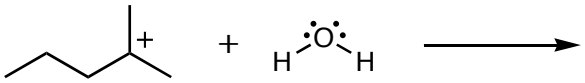
What would happen if you tried to do an association reaction on the following compound?

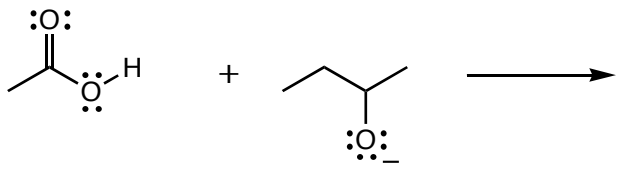


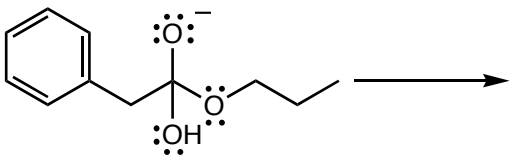
What makes reactions happen?

What products would result from the following reactions? Identify the nucleophile and electrophile, and classify the reaction as an association, dissociation, or displacement.







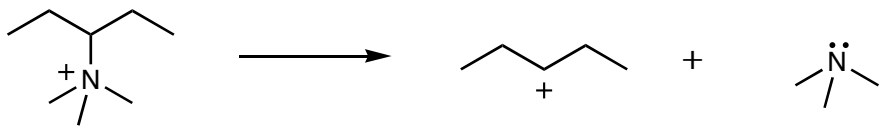


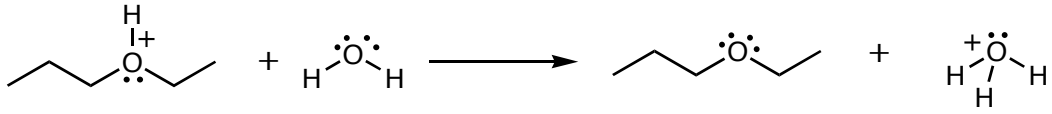
Look for patterns of what electrons do:

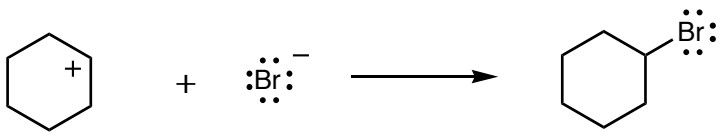
What can lone electron pairs do?

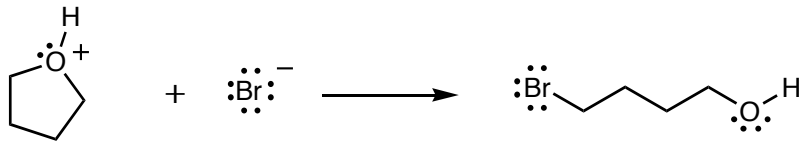
What can electron pairs in bonds do?

Draw arrows to show how the following took place. Identify the nucleophile and electrophile (if any). Classify them as association, dissociation, or displacement reactions.





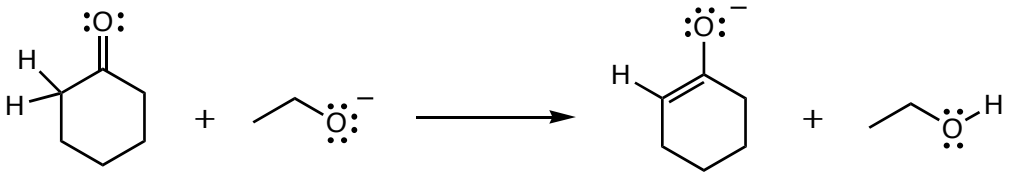




Some complex displacements involve more than two arrows. When dealing with these kinds of electron movements, it can be helpful to number the carbons, so that you can keep track of where they went. Then look at exactly what happened:

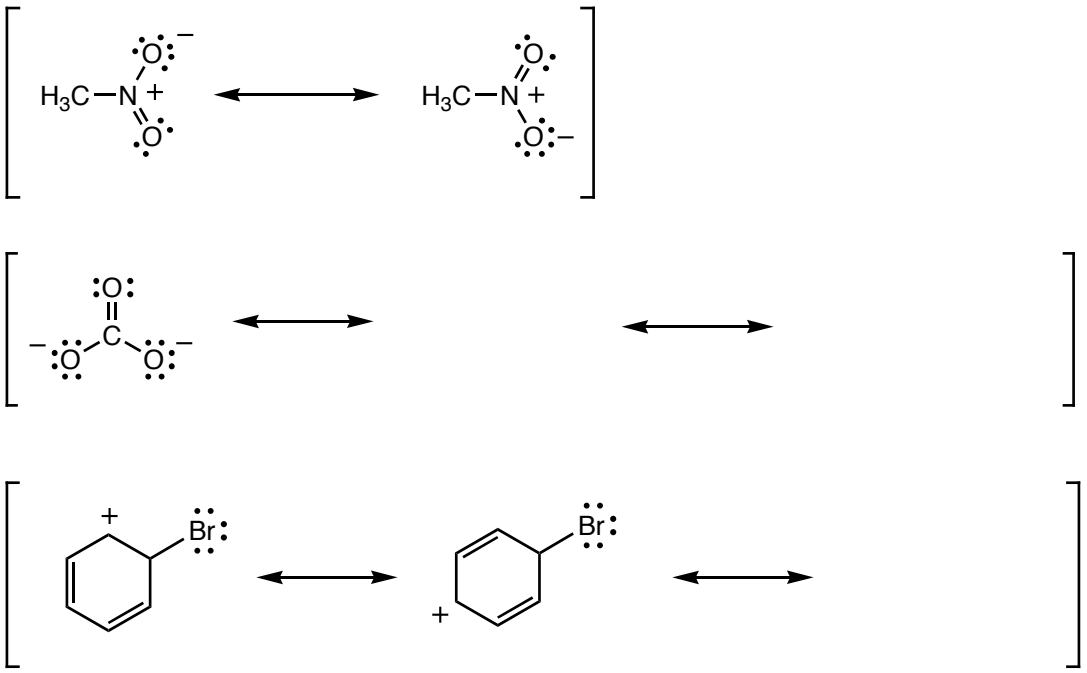
When you have established this, you must then figure out how the bonds that were broken and electron pairs that disappeared could move (without flying through the air) to create the bonds that were formed and electron pairs that appeared.

What arrows would be needed to show how the following reaction occurs?



Resonance structures

The electron arrows used in Lewis acid/base reactions can also be used to convert one resonance structure to another.



Remember, with resonance structures, the electrons are not actually moving. This is just a convention to represent electrons occupying orbitals that cover more than two atoms.

Strengths of nucleophiles and electrophiles

What makes nucleophiles strong?

1) negative charge vs. neutral atom of the same element

H_2O NaOH

why?

2) less electronegative atom vs. more electronegative atom in the same period

NaOH $HC{\equiv}CNa$

why?

3) larger atoms vs. smaller atoms in the same family

NaOH NaSH

why?

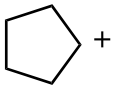
4) less hindered vs. more hindered atoms of the same element

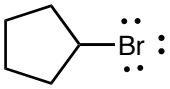
$(CH_3)_3COK$ CH_3CH_2ONa

why?

What makes electrophiles strong?

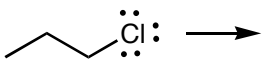
1. having an empty orbital

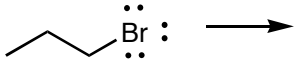




why?

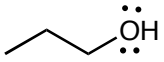
2. Having a weak bond between the carbon and leaving group

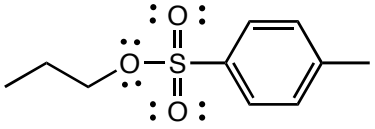




why?

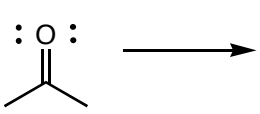
3. Having a leaving group that is low in energy

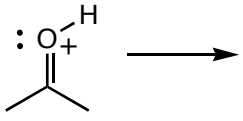




why?

4. Having a positively charged atom next door



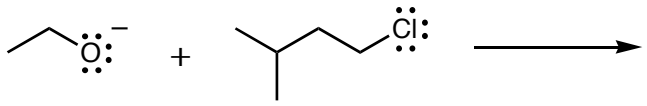


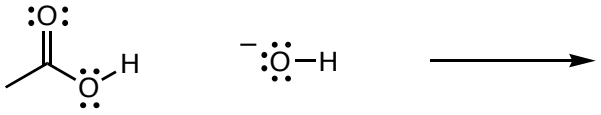
why?

V. Bronsted-Lowry acids and bases

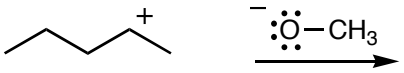
Introduction to acids and bases

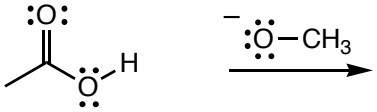
What makes Bronsted-Lowry acids and bases different from Lewis acids and bases?





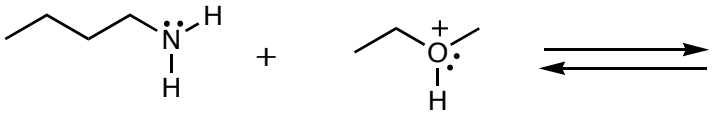
Could the same reactant be a nucleophile or base? If so, how do we know which?





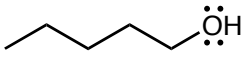
Are acid/base reactions usually reversible?

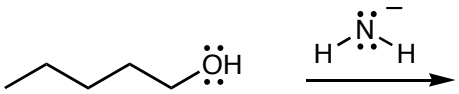
How are the products related to the reactants?

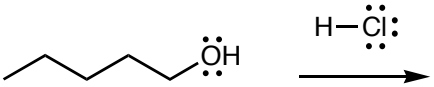


Some compounds are amphoteric - what does this mean?

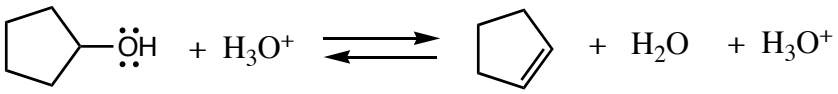
What must they have in order to do this?



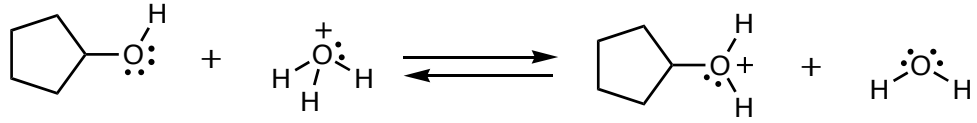


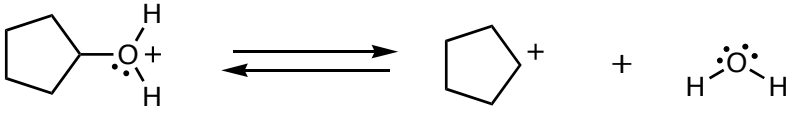


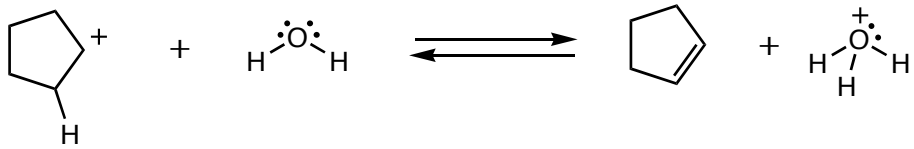
How is a reaction related to its mechanism?

overall reaction: 

mechanism:

step 1: 

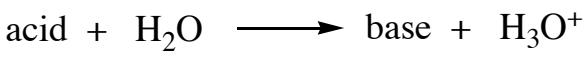
step 2: 

step 3: 

easier way to write the steps:

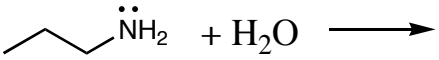
Using pKa's to determine acid and base strength

What is the equilibrium constant for the reaction of an acid with water?

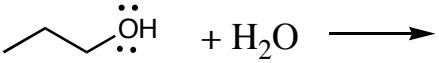


K_a =

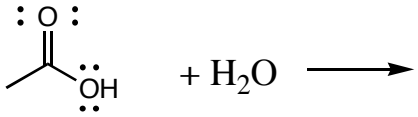
How does K_a show how strong an acid is?



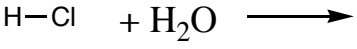
K_a =



K_a =



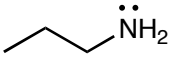
K_a =



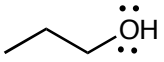
K_a =

How does strong of a base is water?

How does pKa relate to the Ka of an acid?



K_a =



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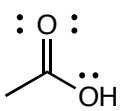

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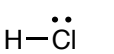


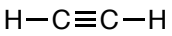
K_a =

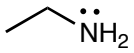
Get a pKa chart in class or on the course website.

Where are the strongest acids?

Where are the weakest acids?

Which compound is the stronger acid in each pair?

HCl H_3O^+ 

H_2SO_4 HF 

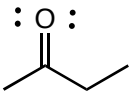
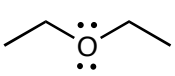
How can you determine the strength of a base?

How strong of a base is HSO_4^-?

How strong of a base is NH_2^-?

Where are the strongest bases on the pKa chart? Where are the weakest bases?

Which compound is the stronger base in each pair?

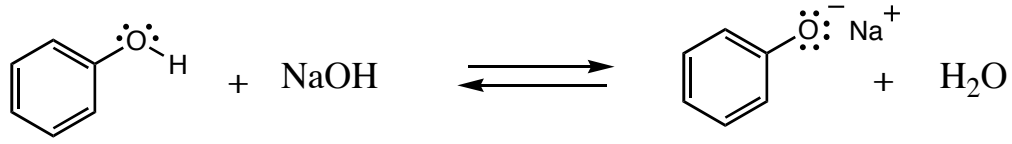
 

NaH NaOH

Using pKa's to predict whether an acid/base reaction will be favorable

How can you use pKa's to get the equilibrium constant for an acid/base reaction?

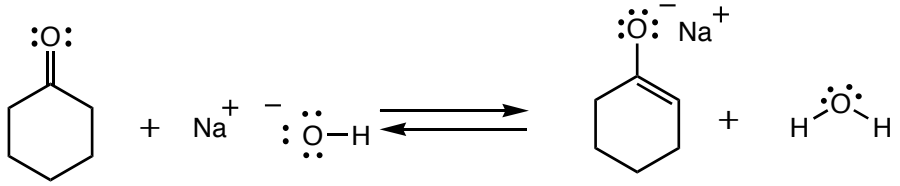
1. Locate the acid on each side
2. Use their pKa's and determine which acid is stronger.
3. Subtract the pKa of the product acid from the pKa of the reactant acid, and take 10 to that power.



Will the stronger acid be in the reactants or products?

Will the stronger base be in the reactants or products?

Is NaOH a strong enough base to take the H from phenol?



Is NaOH a strong enough base to take the H from a ketone?

If you need a base to take the H from an amide, where should you look on the chart?

If you need an acid to protonate a carboxylate, where should you look on the chart?

Which of the following will be favorable? acid above the base acid below the base

Predicting relative acid and base strength

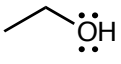
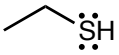
What causes some acids to be stronger than others?

1. Electronegativity of the element the H is attached to:

CH_4 NH_3 H_2O HF

why?

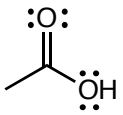
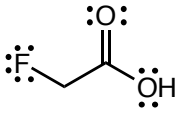
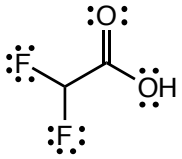
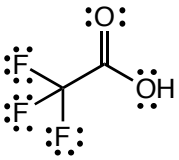
2. Size of the atoms the H is attached to:

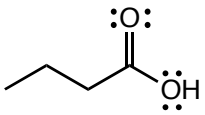
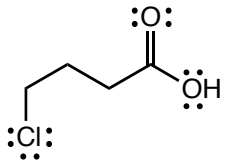
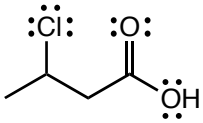
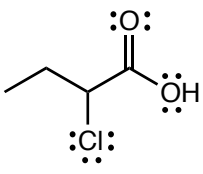
$pK_a = 16$ $pK_a = 10.5$

why?

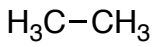
3. The presence of electronegative groups nearby:

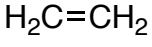





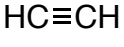
why?

4. Hybridization of the atom the H is attached to:

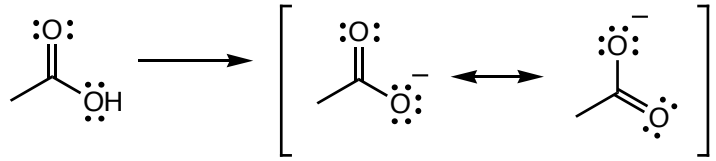


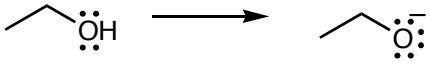




why?

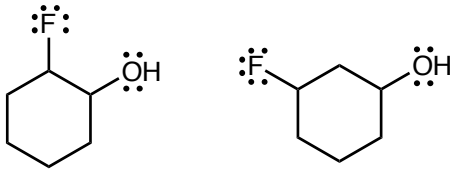
5. Resonance of the conjugate base:

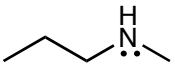


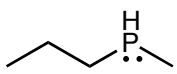


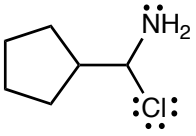
why?

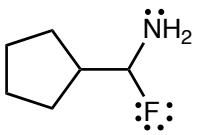
Circle the more acidic compound and explain your reasoning.

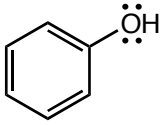
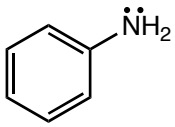
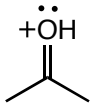
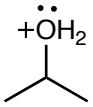
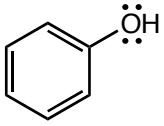
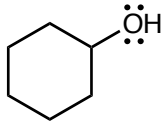










How can you use these rules to predict the stability of bases?

Circle the more basic compound and explain your reasoning.