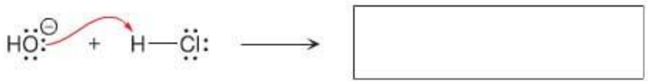
***Chapter 7 Worksheets*** *Organic Chemistry*

**7.1 YOUR TURN**

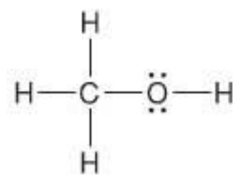
In the following proton transfer step, identify the electron-rich and electron-poor sites, and label the curved arrow that connects the two as "electron rich to electron poor." Which reactant is the Lewis acid and which is the Lewis base?

**7.2 YOUR TURN**

Use the box provided to draw the product suggested by the faulty curved arrow notation in the following chemical equation. What is unacceptable about the product you drew?



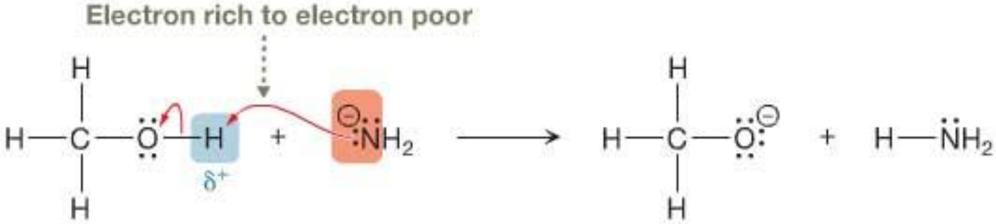
**SOLVED problem 7.1** Identify the electron-poor H atom in methanol. Draw the mechanism by which methanol acts as an acid in a proton transfer reaction with $H_2N^-$.



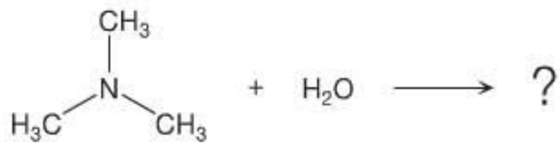
**Methanol**

**Think** What kinds of charges characterize an electron-poor atom? Are there any formal charges present? Any strong partial charges? When $H_2N^-$ and $CH_3OH$ are combined, what curved arrow can we draw to depict the flow of electrons from an electron-rich site to an electron-poor site?

**Solve** $CH_3OH$ does not bear any full charges, but the highly electronegative O places a strong partial positive charge on the H to which it is bonded. That H is therefore electron poor, and a blue screen is placed behind it as a reminder. $H_2N^-$ bears a full negative charge and is therefore electron rich. As a reminder, a red screen is placed behind N. To represent the flow of electrons from the electron-rich site ($H_2N^-$) to the electron-poor site ($CH_3OH$), draw a curved arrow from a lone pair on N to the H atom on O. A second curved arrow is needed to make sure H has only one bond, not two.



**problem 7.2** Identify the electron-rich and electron-poor sites in each of the following reactant molecules:

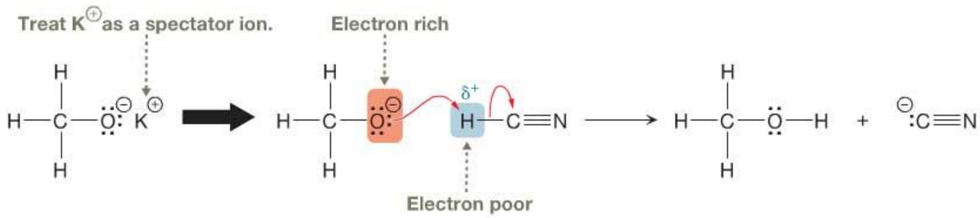


Draw the curved arrows and the products for the proton transfer between these two molecules and label the curved arrow that represents the flow of electrons from an electron-rich site to an electron-poor site.

**SOLVED problem 7.3** Draw the necessary curved arrows for the proton transfer between $KOCH_3$ and HCN in solution.

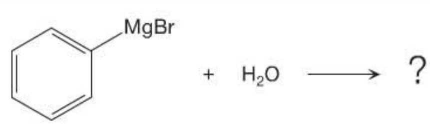
**Think** What are the electron-rich and electron-poor sites in each compound? Are there any simplifying assumptions we can make?

**Solve** $KOCH_3$ is an ionic compound that dissolves in solution as $K^+$ and $CH_3O^-$. We can therefore treat $K^+$ as a spectator ion and $CH_3O^-$ as an electron-rich Lewis base. HCN has an electron-poor H atom due to the high effective electronegativity of the *sp*-hybridized C and N atoms. Thus, HCN acts as a Lewis acid. A curved arrow is drawn from the electron-rich O to the electron-poor H to initiate the proton transfer. A second curved arrow is drawn to break the H—C bond to avoid two bonds to H.



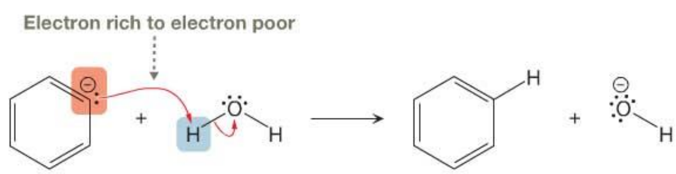

**problem 7.4** Use curved arrow notation to indicate the proton transfer between NaSH and $CH_3CO_2H$.

**SOLVED problem 7.5** What are the products of the proton transfer step between $C_6H_5MgBr$ and $H_2O$?



**Think** What are the electron-rich sites? What are the electron-poor sites? What can be disregarded?

**Solve** In $H_2O$, O is electron rich, and both H atoms are electron poor. In $C_6H_5MgBr$, we can disregard the MgBr portion because it contains the metal, and treat the reactive species as $C_6H_5^-$. Hence, the proton transfer is initiated by drawing a curved arrow from the electron-rich C on $C_6H_5^-$ to an electron-poor H on $H_2O$.



**problem 7.6** Use curved arrow notation to show the proton transfer step that occurs between $CH_3Li$ and $CH_3OH$. Predict the products of this reaction.

**problem 7.7** Use curved arrow notation to show the proton transfer step that takes place between $LiAlH_4$ and water. Predict the products of the reaction. Do the same for the proton transfer step between $NaBH_4$ and phenol ($C_6H_5OH$).

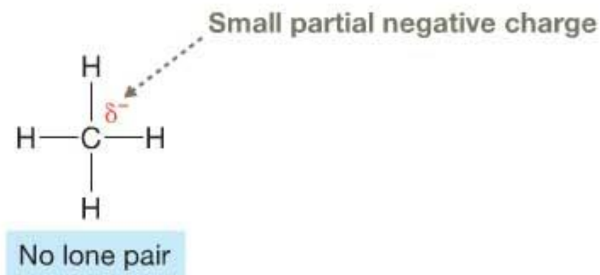
**YOUR TURN 7.3**

Draw the complete Lewis structures for three of the *negatively charged* nucleophiles listed on the previous page (other than $HO^-$) and for three of the uncharged nucleophiles (other than $H_3N$). Include all lone pairs. For each of the uncharged nucleophiles, write "$\delta^-$" next to the atom bearing a partial negative charge.

**SOLVED problem 7.8** Should $CH_4$ act as a nucleophile? Why or why not?

**Think** Does $CH_4$ have an atom that carries a partial or full negative charge? Does that atom have a pair of electrons that can be used to form a bond to another atom?

**Solve** The complete Lewis structure for $CH_4$ is as follows:




The C atom has a small partial negative charge (because C is slightly more electronegative than H), but it does not possess a lone pair of electrons that can be used to form a bond with another atom. Thus, $CH_4$ should not act as a nucleophile.

**problem 7.9** Which of the following species can behave as a nucleophile? Explain.

**(a)** $SiH_4$ **(b)** NaSCN **(c)** $NH_4^+$ **(d)** $CH_3Li$

**7.4 YOUR TURN**

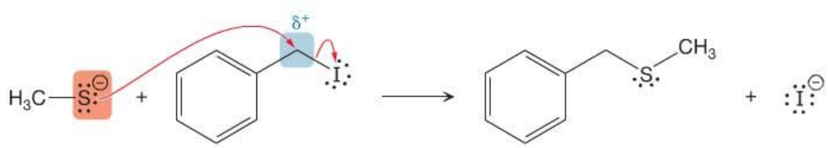
The following $S_N2$ step is similar to the one in Equation 7-4b:

Label the appropriate reacting species as "electron rich" or "electron poor" and draw in the correct curved arrows.

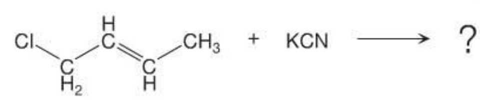
**SOLVED problem 7.10** Draw the $S_N2$ step that would occur between $C_6H_5CH_2I$ and $CH_3SNa$.

**Think** Which species is the nucleophile? Which is the substrate? What do we do with the metal atom? Which species is electron rich? Electron poor?

**Solve** $C_6H_5CH_2I$ will behave as the substrate because it possesses as I, a good leaving group that departs as $I^-$. The conjugate acid of $I^-$, HI, is a very strong acid. $CH_3SNa$ has a metal atom that can be treated as a spectator ion and thus ignored. The nucleophile is therefore $CH_3S^-$. In an $S_N2$ step, a curved arrow is drawn from the lone pair of electrons on the electron-rich S atom to the electron-poor C atom bonded to I. A second curved arrow must be drawn to indicate that the C—I bond is broken (otherwise that C would have five bonds).



**problem 7.11** Draw the $S_N2$ step that would occur between the two compounds at the right.



**YOUR TURN 7.5**

In Equations 7-5 through 7-8, identify all atoms lacking an octet.

**YOUR TURN 7.6**

Label each reactant in Equation 7-6 as either a Lewis acid or a Lewis base.

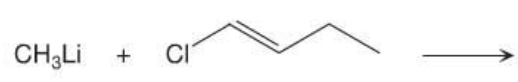
## problem 7.12

**(a)** Draw the appropriate curved arrows for the coordination step between $FeCl_3$ and $Cl^-$. Draw the reaction products. Identify which species acts as the Lewis acid and which acts as the Lewis base.

**(b)** Use curved arrow notation to show the product from part (a) undergoing heterolysis to regenerate $FeCl_3$ and $Cl^-$.

**problem 7.13** Supply the appropriate curved arrows and the products for each of the following E2 steps.

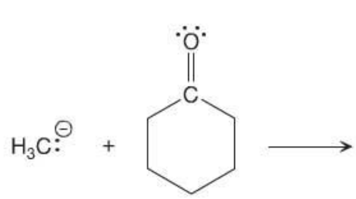

**(a)**




**(b)**

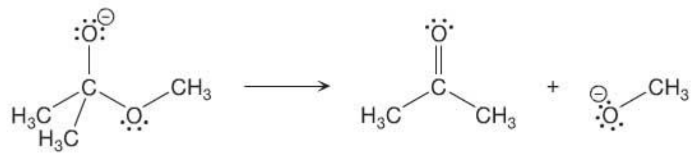
**YOUR TURN 7.7**

For the following nucleophilic addition step, label the pertinent electron-rich and electron-poor sites. Add the appropriate curved arrows and draw the product. Identify the curved arrow that is drawn from the electron-rich site to the electron-poor site.

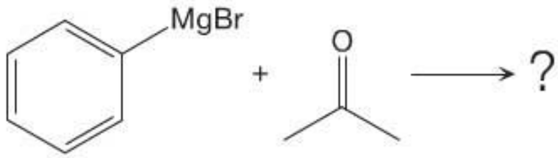


**YOUR TURN 7.8**

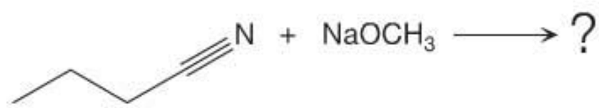
For the following nucleophile elimination step, label the pertinent electron-rich and electron-poor sites. Add the appropriate curved arrows and identify the curved arrow that is drawn from the electron-rich site to the electron-poor site.



**problem 7.14** Draw the appropriate curved arrows and the products for each of the following nucleophilic addition steps.

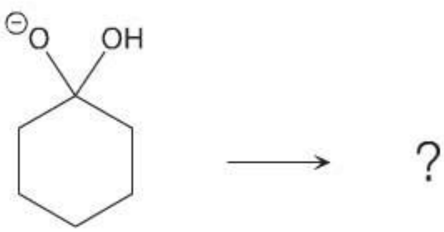


(a)

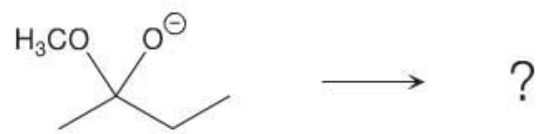


(b)

**problem 7.15** Draw the appropriate curved arrows necessary for each of the following nucleophile elimination steps to produce a ketone, and draw the resulting ketone.



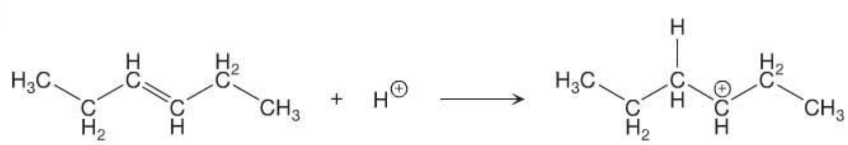
(a)



(b)

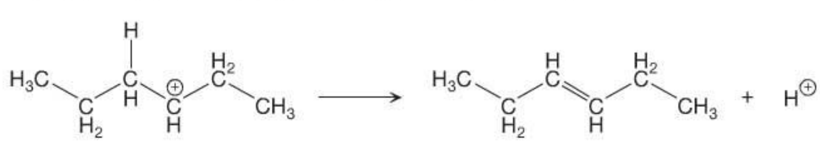
**YOUR TURN 7.9**

Add the appropriate curved arrows for the following electrophilic addition step.



**YOUR TURN 7.10**

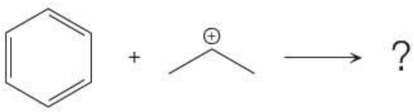
Add the appropriate curved arrow(s) to the following electrophile elimination step, which is the reverse of the addition step in Your Turn 7.9.



In both Your Turn 7.9 and 7.10, label the pertinent *electron-rich* and *electron-poor* sites.

**7.11 YOUR TURN**

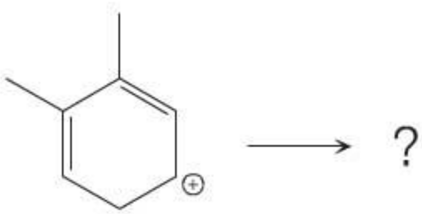
**problem 7.16** Supply the appropriate curved arrows and draw the product of each of the following electrophilic addition steps.



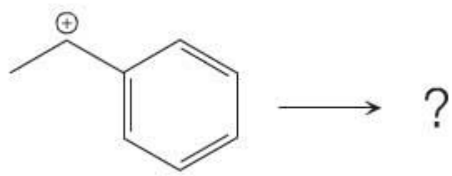
(a)

(b)

**problem 7.17** Supply the appropriate curved arrows and draw the product of each of the following electrophile elimination steps.

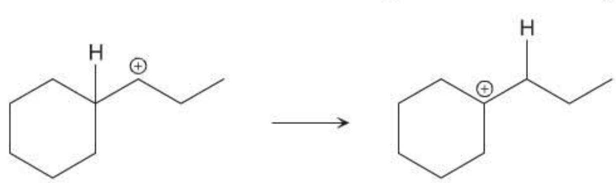


(a)



(b)

Supply the curved arrow notation for the following carbocation rearrangement.



**7.12 YOUR TURN**

**problem 7.18** Supply the appropriate curved arrows and draw the product for the following carbocation undergoing **(a)** a 1,2-hydride shift and **(b)** a 1,2-methyl shift.

**7.13 YOUR TURN**

Consult Table 6-1 to verify that HCl is a stronger acid than HF. Write the $pK_a$ values of the two acids below. With those $pK_a$'s, use Equation 6-11 to compute the value of $K_{eq}$ for the proton transfer reaction in Equation 7-29.

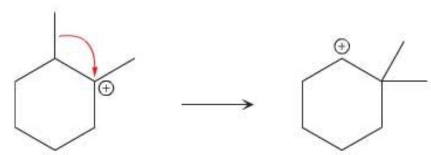
$pK_a$ of HCl: $pK_a$ of HF:

**7.14 YOUR TURN**

Consult Table 6-1 to verify that HCl is a stronger acid than $NH_3$. Write the $pK_a$ values of the two acids below. With those $pK_a$'s, use Equation 6-11 to compute the value of $K_{eq}$ for the proton transfer reaction in Equation 7-31.

$pK_a$ of HCl: ________________ $pK_a$ of $NH_3$: ________________

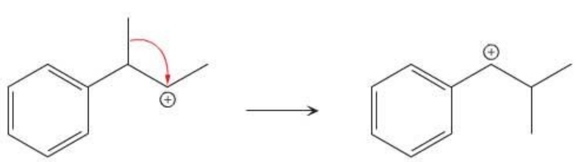
**SOLVED problem 7.19** Determine which side of this carbocation rearrangement is favored.



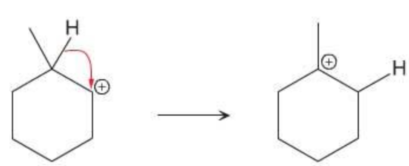
**Think** On the two sides of the reaction, is there a difference in charge stability? Is there a difference in total bond energy?

**Solve** The positive charge is on a tertiary carbon in the reactant and is on a secondary carbon in the product. Because a tertiary carbocation is more stable (Section 6.6e), charge stability favors the reactant side. Total bond energy is not a significant factor in this reaction because a C—C σ bond is broken in the reactant and another one is formed in the product. Overall, then, this reaction will favor the reactant side.

**problem 7.20** Determine which side of each of the following carbocation rearrangements is favored.



(a)




(b)

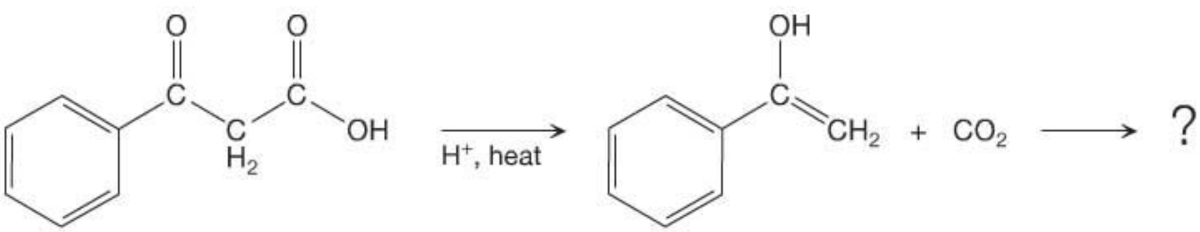
**7.15 YOUR TURN**

In Figure 7-4, there is a similar bond in red in the keto form for each bond in blue in the enol form. Therefore, we can pair these bonds as follows:

| Bond in Keto Form | Bond in Enol Form | Difference in Bond Energy |
|---|---|---|
| C=O | C=C | |
| C—C | C—O | |
| C—H | O—H | |

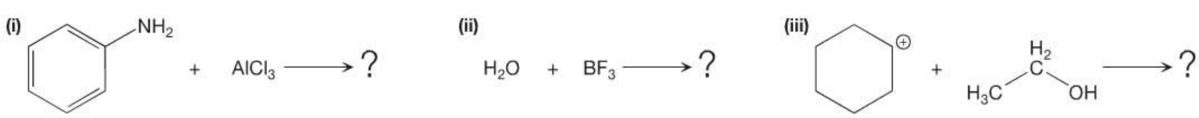
For each pair, compute the *difference* in bond energy and enter it into the table. Based on these data, which bond is most responsible for the additional stability of the keto form? _______________

**problem 7.21** Decarboxylation (i.e., elimination of $CO_2$) occurs when a β-ketoacid is heated under acidic conditions.




The immediate product of decarboxylation is an enol, which quickly rearranges. Draw the overall product of the rearrangement.

**7.22** **(a)** Draw the appropriate curved arrows and products for each set of reactants undergoing a coordination step. Identify each reactant species as either a Lewis acid or Lewis base.
**(b)** Use curved arrow notation to show each product undergoing heterolysis to regenerate reactants.

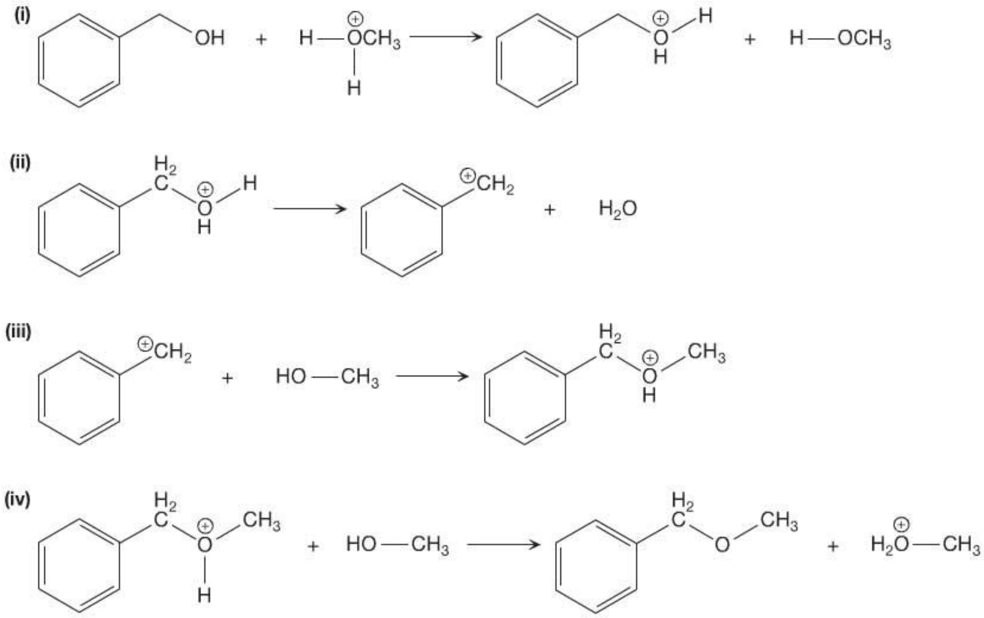


**7.23** The following reaction, which is discussed in Chapter 8, is an example of a unimolecular nucleophilic substitution ($S_N1$) reaction. It consists of the four elementary steps shown here. For each step (i–iv),

**(a)** identify all electron-rich sites and all electron-poor sites,

**(b)** draw in the appropriate curved arrows to show the bond formation and bond breaking that occur, and

**(c)** name the elementary step.



**7.24** The following reaction, which is discussed in Chapter 8, is an example of a unimolecular elimination (E1) reaction and consists of the three elementary steps shown. For each step (i–iii),

**(a)** identify all electron-rich sites and all electron-poor sites,

**(b)** draw in the appropriate curved arrows to show the bond formation and bond breaking that occur, and

**(c)** name the elementary step.