# Chapter 2

**2.1** Which element in each of the following pairs is more electronegative?

(a) Li or H

(b) B or Br

(c) Cl or I

(d) C or H

Solution:

(a) H

(b) Br

(c) Cl

(d) C

**2.2** Use the δ+/δ- convention to indicate the direction of expected polarity for each of the bonds indicated.

(a) $H_3C$—Br

(b) $H_3C$—$NH_2$

(c) $H_3C$—Li

(d) $H_2N$—H

(e) $H_3C$—OH

(f) $H_3C$—MgBr

(g) $H_3C$—F

Solution:

(a) δ+ δ-
$H_3C$—Br

(b) δ+ δ-
$H_3C$—$NH_2$

(c) δ- δ+
$H_3C$—Li

(d) δ- δ+
$H_2N$—H

(e) δ+ δ-
$H_3C$—OH

(f) δ- δ+
$H_3C$—MgBr

(g) δ+ δ-
$H_3C$—F

**2.3** Use the electronegativity values shown in Figure 2.2 to rank the following bonds from least polar to most polar:

Solutions

$H_3C$—Li 1.5

$H_3C$—K 1.7

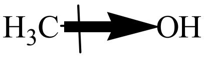
$H_3C$—F 1.5

$H_3C$—MgBr 1.3

$H_3C$—OH 1.0

so it's $H_3C$—MgBr, $H_3C$—OH, $H_3C$—Li $H_3C$—F, $H_3C$—K

**2.4** Tell the direction of polarization of the C-O bond:



**2.5** Carbon dioxide, $CO_2$, has zero dipole moment even though carbon-oxygen bonds are strongly polarized. Explain.

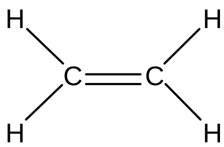
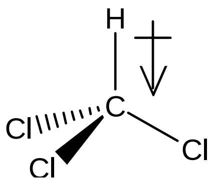
Solution:

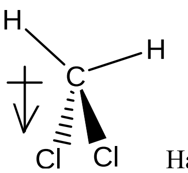
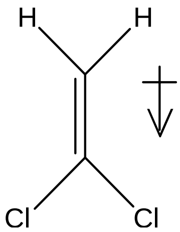
Because the two carbon-oxygen bonds have the same diple moments, and they are in the same line, but in the opposite directions.---The net polarity of the $CO_2$ is zero.

**2.6** Make three-dimensional drawings of the following molecules, and predict whether each has a dipole moment. If you expect a dipole moment, show its direction.

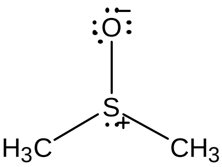
(a) $H_2C{=}CH_2$ (b) CHCl3 (c) CH2Cl2 (d) $H_2C{=}CCl_2$

Solution:

(a)  Hasn't a dipole moment (b)  Has a dipole moment

(c)  Has a dipole moment (d) 

**2.7** Dimethyl sulfoxide, a common solvent, has the structure indicated. Show why dimethyl sulfoxide must have formal charges on S and O.

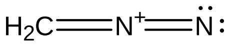


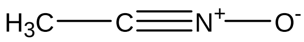
Solution:

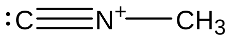
For S: Valence electrons = 6
Bonding electrons = 6
Nonbonding electrons = 2
Formal charge = 6 – 6/2 – 2 = +1

For O: Valence electrons = 6
Bonding electrons = 2
Nonbonding electrons = 6
Formal charge = 6 – 2/2 – 6 = –1

**2.8** Calculate formal charges for the nonhydrogen atoms in the following molecules:

(a) Diazomethane, 

(b) Acetonitrile oxide, 

(c) Methyl isocyanide, 

Solutin:

(a) For the middle N: formal charge = 5 – 8/2 – 0 = +1

For the end N: formal charge = 5 – 4/2 – 4 = –1

(b) For C: formal charge = 4 – 8/2 – 0 = 0

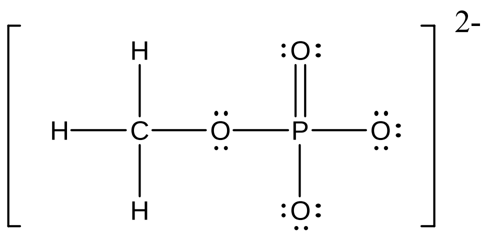
For N: formal charge = 5 – 8/2 – 0 = +1

For O: formal charge = 6 – 2/2 – 6 = –1

(d) For C: formal charge = 4 – 6/2 – 2 = –1

For N: formal charge = 5 – 8/2 – 0 = +1

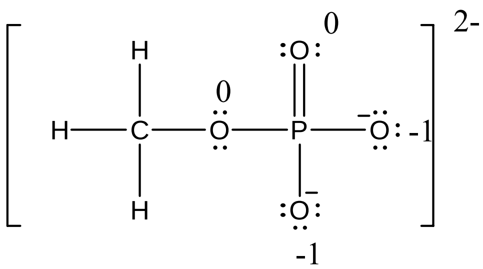
**2.9** Organic phosphates occur commonly among biological molecules. Calculate formal charges on the four O atoms in the methyl phosphate ion.



Methyl phosphate

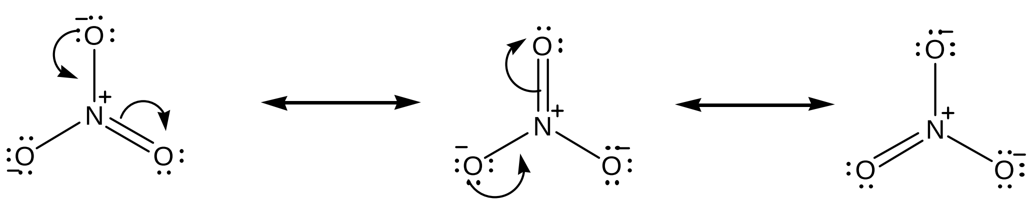
Solution:

The formal charges have been assigned as follows:

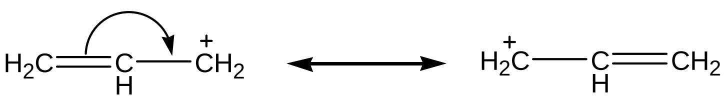


**2.10** Draw the indicated number of resonance structures for each of the following species:

(a) The nitrate ion, $NO_3^-$ (3)

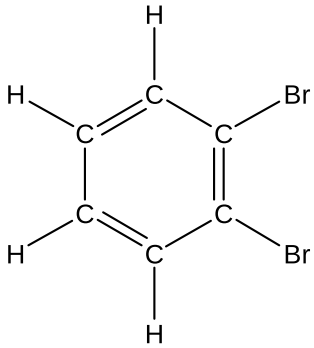


(b) The allyl cation, $H_2C{=}CH{-}CH_2^+$ (2)

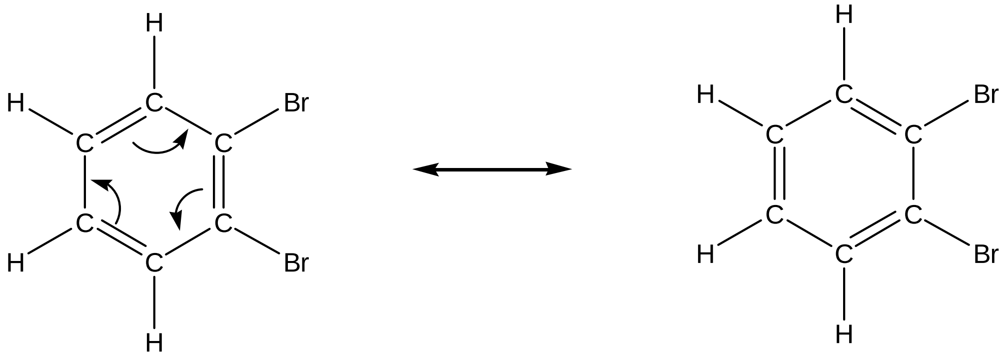


(c) Hydrazoic acid, (2)

(d) (2)



ortho-Dibromobenzene



**2.11** Nitric acid reacts with ammonia to yield ammonium nitrate. Write the reaction, and identify the acid, the base, the conjugate acid product, the conjugate base product.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Answer: | HNO3 | + | NH3 | = | $^{+}$NH4 | + | $^{-}$NO3 |
| | acid | | base | | conjugate acid | | conjugate base |

**2.12** Formic acid, HCO2H, has pKa=3.75, and picric acid, C6H3N3O7, has pKa=0.38. which is the stronger acid?

Answer: picric acid is stronger.

**2.13** Amide ion, $H_2N^-$, is a much stronger base than hydroxide ion, $HO^-$. Which would you expect to be a stronger acid, $NH_3$ or $H_2O$? Explain.

Solution: $H_2O$ is the stronger acid. Because a strong base yields a weak acid, a weak base yields a strong base. $HO^-$ is a weaker base so the conjugate acid $H_2O$ is a stronger acid.

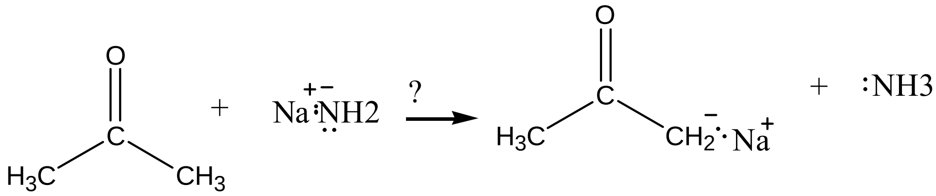
**2.14** Will either of the following reactions take place as written, according to the pKa data in Table 2.3?

(a) $HCN + CH_3CO_2^-Na^+ \xrightarrow{?} Na^+\text{-}CN + CH_3CO_2H$

(b) $CH_3CH_2OH + Na^+\text{-}CN \xrightarrow{?} CH_3CH_2O^-Na^+ + HCN$

Solution: Both the two reactions can't take place. The product acid must be weaker and less reactive than the starting acid, but HCN's pKa is 9.31, $CH_3CO_2H$'s pKa is 4.76, that is $CH_3CO_2H$ is a stronger acid; $CH_3CH_2OH$'s pKa is 16.00, HCN's pKa is 9,31, that is HCN is a stronger acid, so both reactions can't occur.

**2.15** Ammonia, $NH_3$, has pKa= 36 and acetone has pKa=19. Will the following reaction take place?



Solution:

Because acetone is a stronger acid (pKa=19) than ammonia (pKa=36), this reaction will take place.

**2.16** What is the Ka of HCN is its pKa=9.31?

Solution:

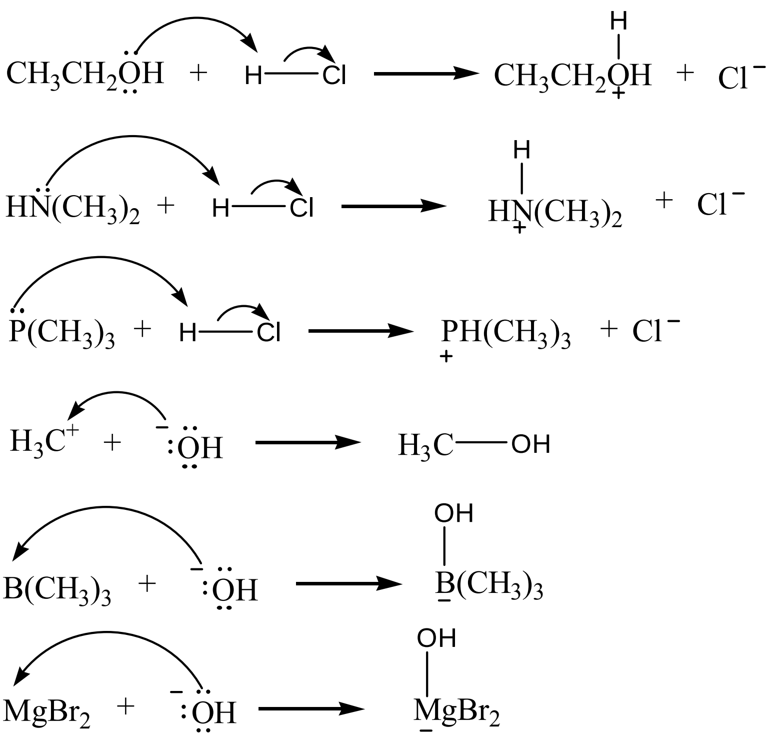
$-lgKa = pKa, Ka=10^{-Pka}=10^{-9.31}=4.90*10^{-10}$

**2.17** Using curved arrows, show how the species in part (a) can act as Lewis bases in their reactions with HCl, and show how the species in part (b) can act as Lewis acids in their reaction with OH-.

(a) $CH_3CH_2OH$, $HN(CH_3)_2$, $P(CH_3)_3$

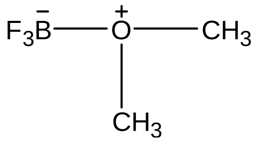
(b) $H_3C^+$, $B(CH_3)_3$, $MgBr_2$

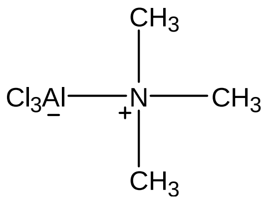
Solution: (a)



(b)

**2.18** Explain by calculating formal charges why the following acid-base reaction products have the charges indicated:

(a) 

(b) 

Solution: (a) For boron: FC= 3 – 8/2 – 0 = –1

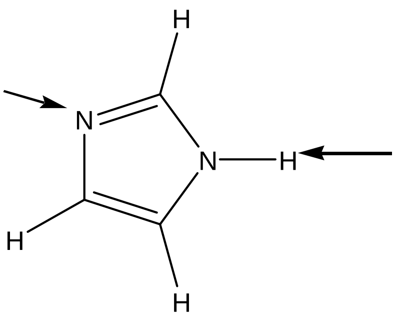
For oxygen: FC= 6 – 6/2 – 2 = +1

(b) For aluminum: FC= 3 – 8/2 – 0 = –1

For nitrogen: FC= 5 – 8/2 – 0 = +1

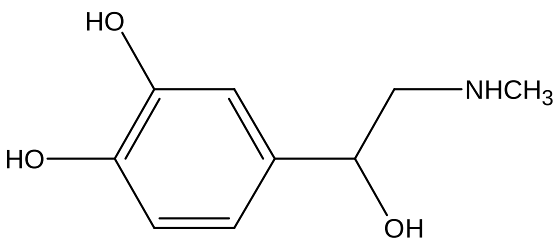
**2.19** The organic compound imidazole act as both a acid and a base. Look at the following electrostatic potential map, and identify the most acidic hydrogen atom and the most basic nitrogen atom in imidzole.

Solution:



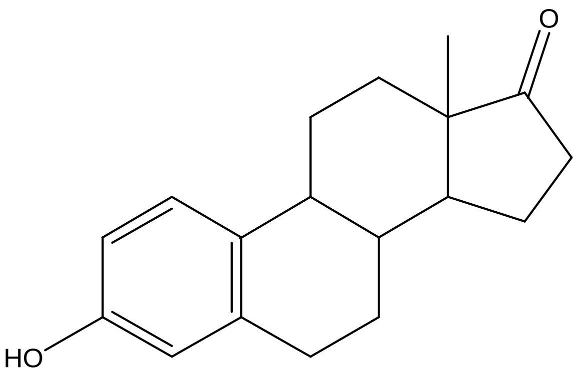

**2.20** Tell how many hydrogens are bonded to each carbon in the following compounds, and give the molecular formula of each substance:

(a)



Adrenaline

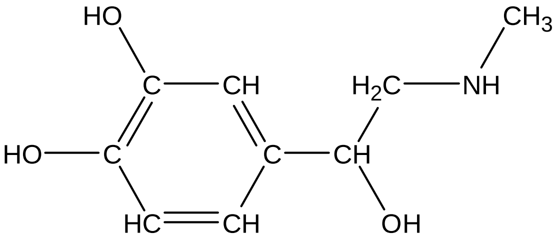
(b)



Estrone(a hormone)

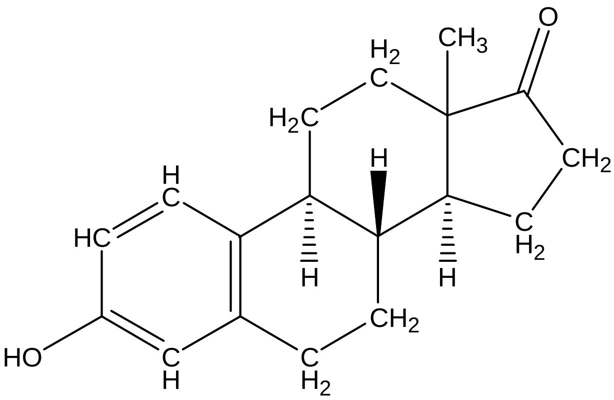
Solution:

(a)




adrenaline $C_9H_{13}NO_3$

(b)

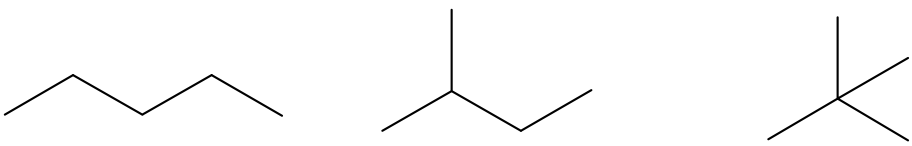



estrone $C_{18}H_{22}O_2$

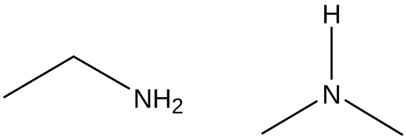
**2.21** Propose skeletal structures for compounds that satisfy the following molecular formulas(there is more than one possibility in each case):

(a) C5H12 (b) C2H7N (c) C3H6O (d) C4H9Cl

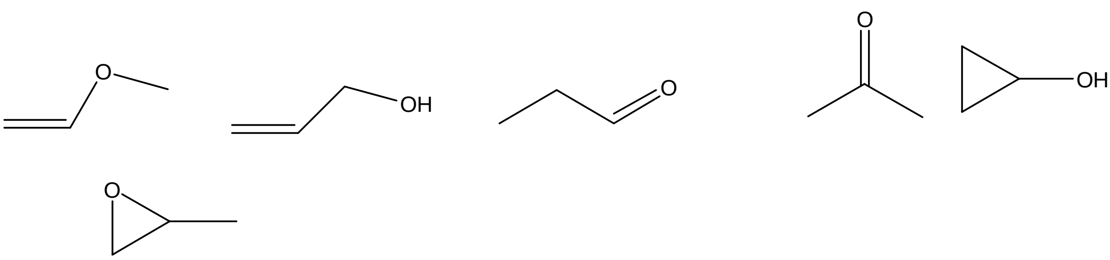
Solution: (a)



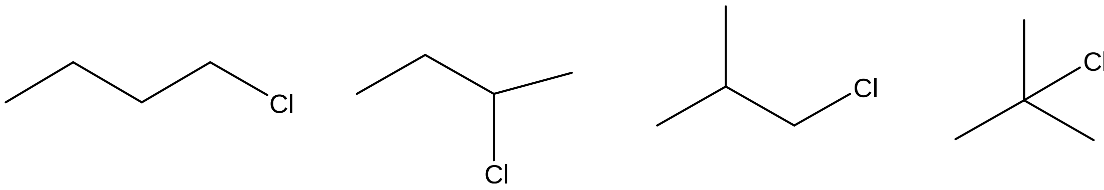
(b)



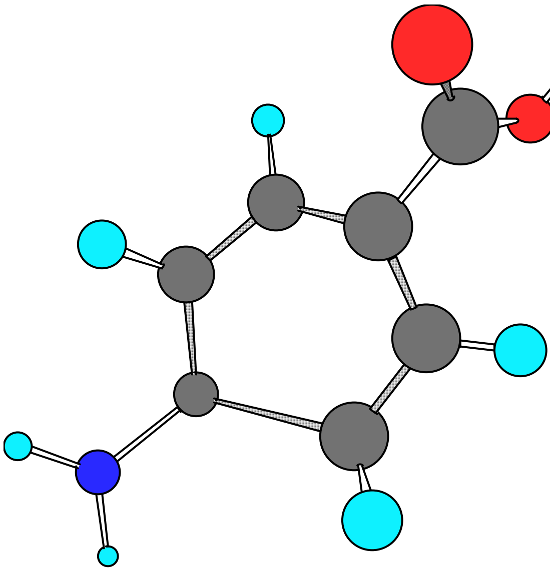

(c)



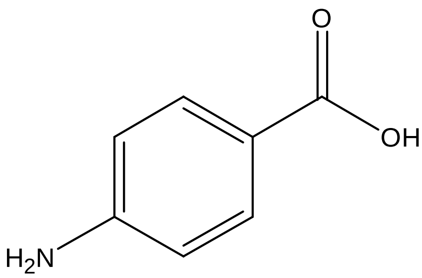
(d)



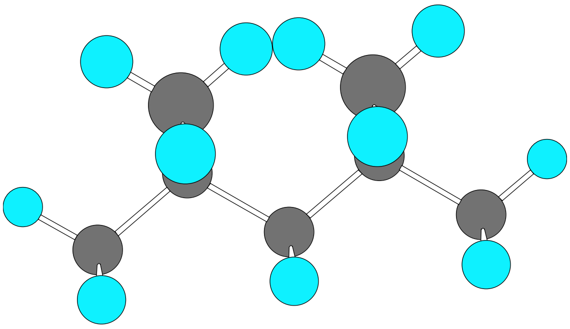

**2.22** The following molecular model is a representation of Para-aminobenzoic acid (PABA), the active ingredient in many sunscreens. Indicate the positions of the multiple bonds, and draw a skeletal structure.



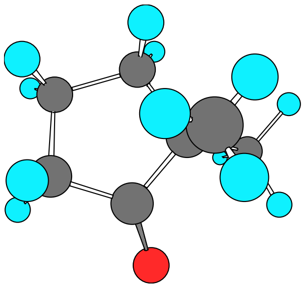
Solution:



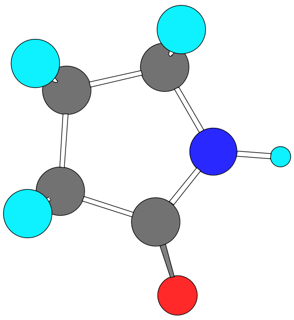

**2.23** Convert each of the following models into a skeletal structure. Only the connections between atoms are shown; multiple bonds are not indicated.



**(a)**

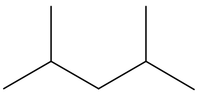


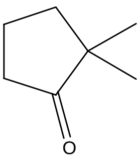
**(b)**

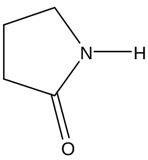


**(c)**

Solution:

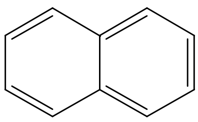
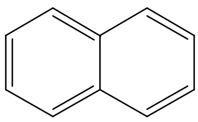
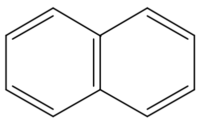
a) 

b) 


c) 

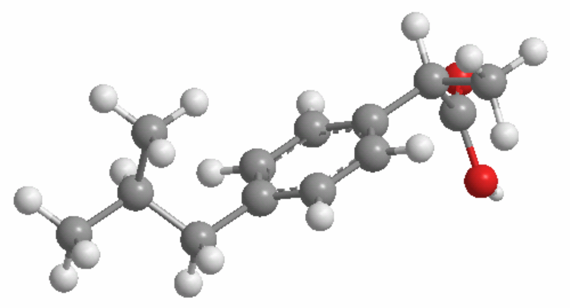

**2.24** Fill in the multiple bonds in the following model if naphthalene, C10H8. How many resonance structures does naphthalene have?

Solution:

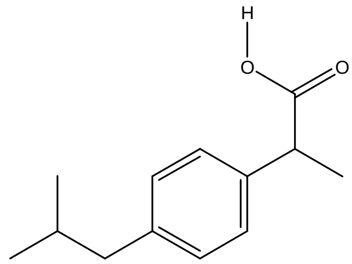
There are 3 resonance structures.   and 

**2.25** The following model is a representation of ibuprofen, a common over-the-counter pain reliever.

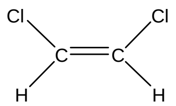
Indicate the positions of the multiple bonds, and draw a skeletal structure (gray=C, red=O, ivory=H).



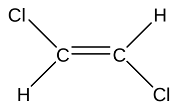
Solution:




**2.26** *cis*-1,2-Dichloroethylene and *trans*-1,2-dichloroethylene are *isomers*, compounds with the same formula but different chemical structures. Look at the following electrostatic potential maps, and tell whether either compound has a dipole moment.



1,2-Dichloro-ethene



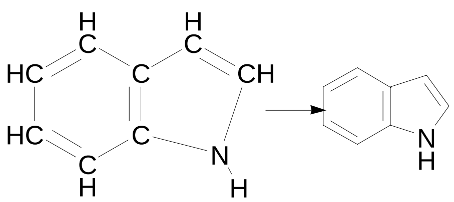
1,2-Dichloro-ethene

Solution:

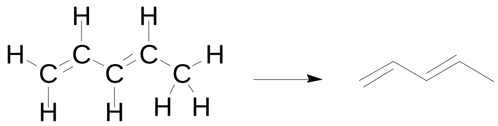
*cis*-1,2-Dichloroethylene has a dipole moment while *trans*-1,2-dichloroethylene has no dipole moment.

**2.27** Convert the following structure into skeletal drawings:

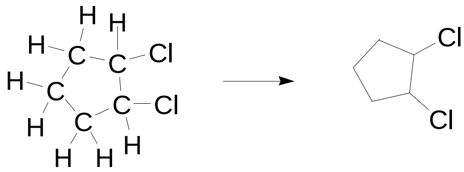
(a) Indole



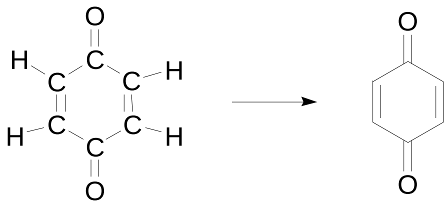

(b) 1,3-Pentadiene




(c) 1,2-Dichlorocyclopentane

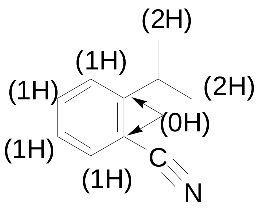



(d) Quinone



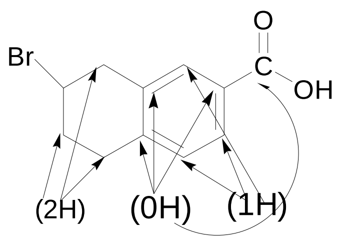
**2.28** Tell the number of hydrogens bonded to each carbon atom in the following substances, and give the molecular formula of each:

(a)



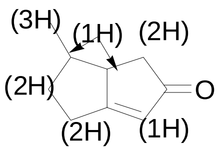

$C_{10}H_8N$

(b)




$C_{11}H_{10}O_2Br$

(c)




$C_9H_{12}O$

**2.29** Identify the most electronegative element in each of the following molecules:

(a) $CH_2FCl$ (b) $FCH_2CH_2CH_2Br$

(c) $HOCH_2CH_2NH_2$ (d) $CH_3OCH_2Li$

Solution: Ca) is F, (b) is F, (c) is O and (d) is O.

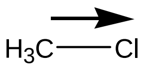
**2.30** Use the electronegativity table (see Figure 2.2) to predict which bond in each of the following sets is more polar, and indicate the direction of bond polarity for each compound.

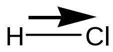
(a) $H_3C$—Cl or Cl—Cl

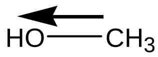
(b) $H_3C$—H or H—Cl

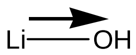
(c) HO—$CH_3$ or $(H_3C)_3Si$—$CH_3$

(d) $H_3C$—Li or Li—OH

Solution:  is more polar in the (a).

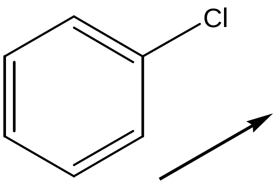
 is more polar in the (b).

 is more polar in the (c).

 is more polar in the (d).

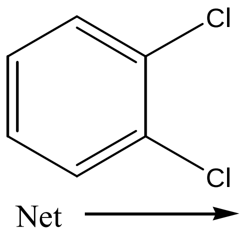
**2.31** Which of the following molecules has a dipole moment? Indicate the expected direction of each.

(a)

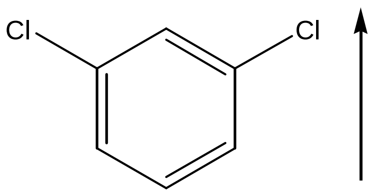



Net

(b)

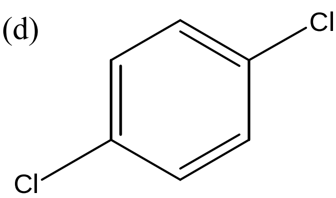



(c)



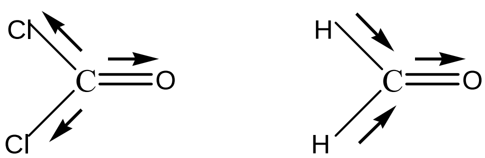

Net

(d)




No dipole moment

**2.32** Phosgene, $Cl_2C{=}O$, has a smaller dipole moment than formaldehyde, $H_2C{=}O$, even though it contains electronegative chlorine atoms in place of hydrogen, Explain.




From the above, we can see that in $Cl_2C{=}O$, the effect of individual bond polarities are partially cancel, so its dipole moment is smaller.

**2.33** The dipole moment of HCl is 1.08D, and the H-Cl bond length is 136 pm. What is the percent ionic character of the H-Cl bond?

Solution: $\mu=Q*r=1.60*10^{-19}*136*10^{-12}/(3.336*10^{-30})=6.528D$

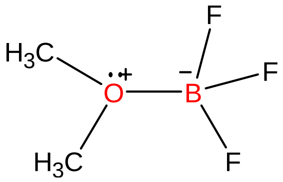
So 1.08/ 6.528*100%=16.5% ionic.

**2.34** Fluoromethane ($CH_3F$, $\mu$=1.81D) has a smaller dipole moment than chloromethane ($CH_3Cl$, $\mu$=1.87D) even through florine is more electronegative than chlorine. Explain.

Solution: Because C-F bond is much shorter than C-Cl bond.

**2.35** Calculate the formal charges on the atoms shown in red.

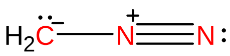
(a)



For oxygen FC=6-6/2-2=+1

For boron FC=3-8/2=-1

(b)

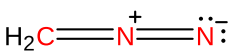


For carbon FC=4-6/2-2=-1

For the middle nitrogen FC=5-8/2=+1

For the end nitrogen FC=5-6/2-2=0

(c)

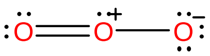


For carbon FC=4-8/2=0

For the middle nitrogen FC=5-8/2=+1

For the end nitrogen FC=5-4/2-4=-1

(d)

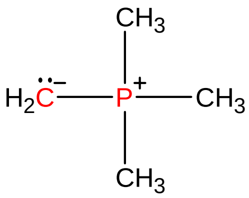


For the first oxygen FC=6-4/2-4=0

For the middle oxygen FC=6-6/2-2=+1

For the end oxygen FC=6-2/2-6=-1

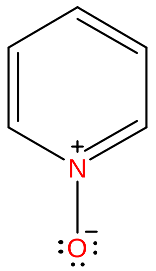
(e)



For carbon FC=4-6/2-2=-1

For phosphorus FC=5-8/2=+1

(f)

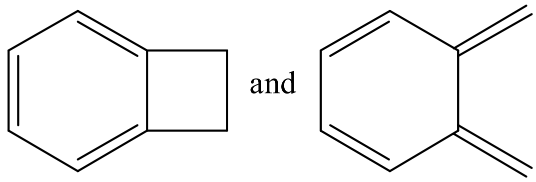


For nitrogen FC=5-8/2=+1

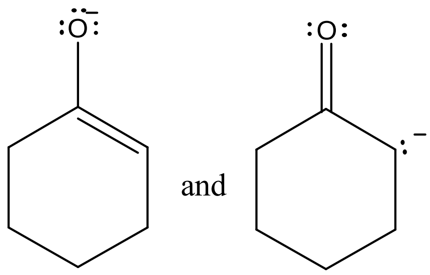
For oxygen FC=6-2/2-6=-1

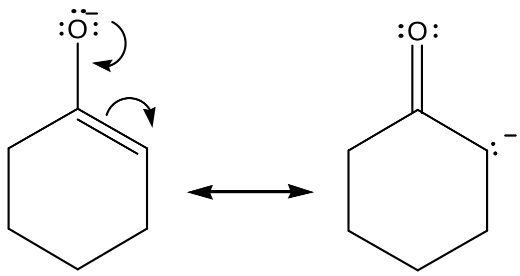
**2.36** Which of the following pairs of structures represent resonance forms?

(a)

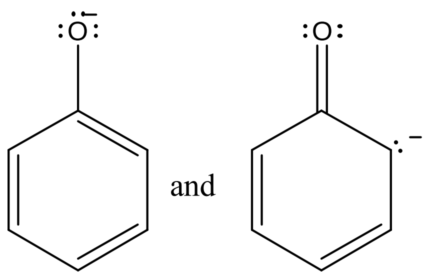


(b)

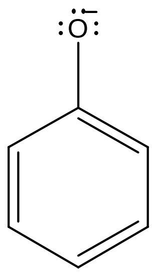




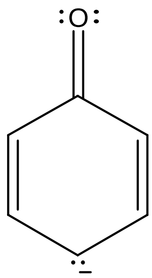
(c)

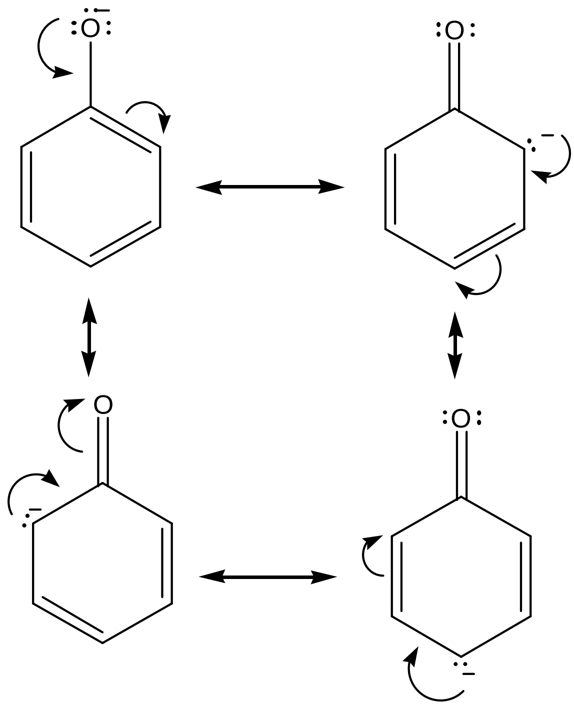


(d)



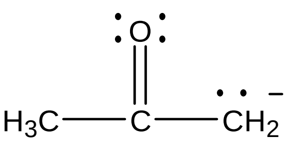
and

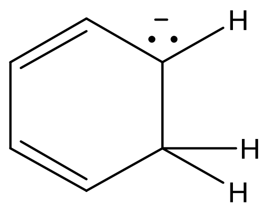


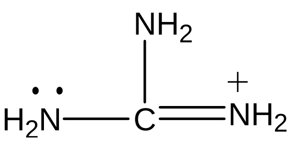


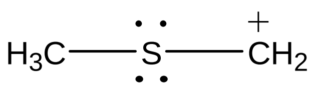
(b), (c), (d) represent resonance forms.

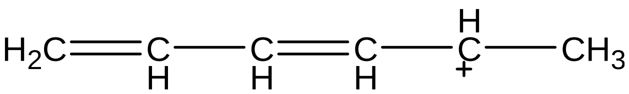
**2.37** Draw as many resonance structures as you can for the following species:

(a). 

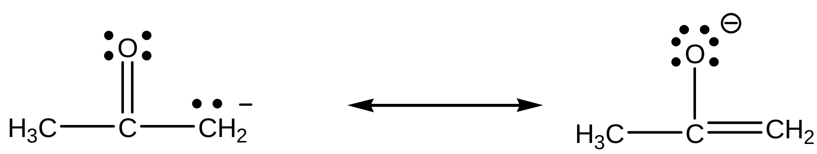

(b). 


(c). 

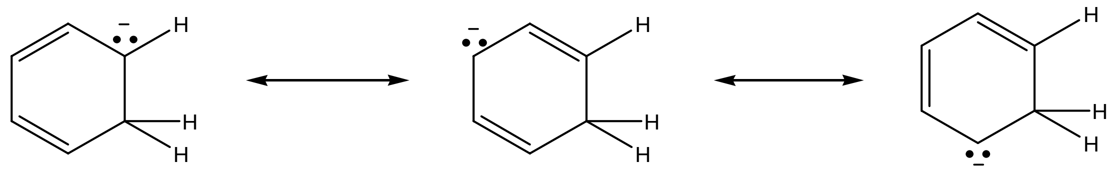

(d). 


(e). 

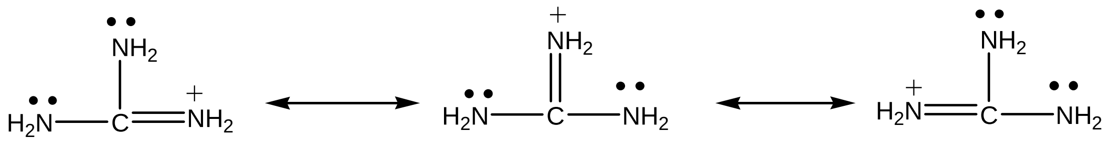

Solution:

(a). 

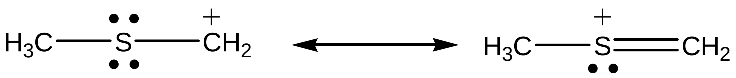
(b).



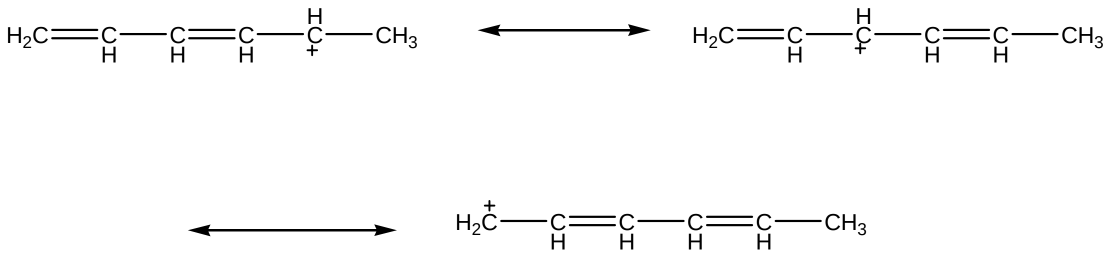
(c).



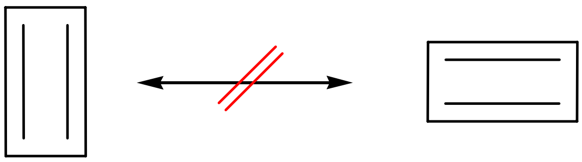
(d).



(e).



**2.38** Cyclobutadiene is a rectangular molecule with two shorter double bonds and two longer single bonds. Why do the following structures not represent resonance forms?

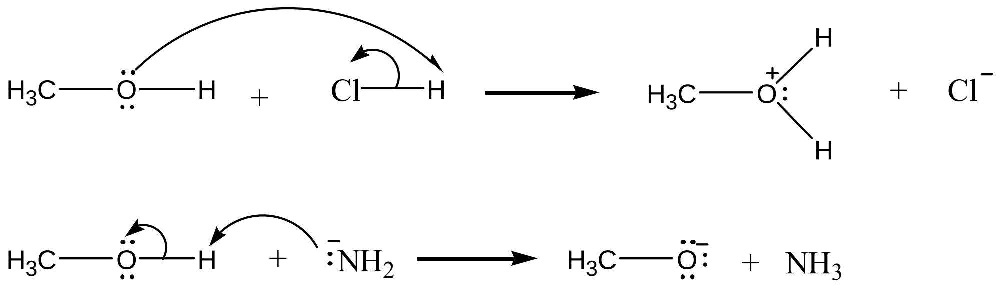


Solution:

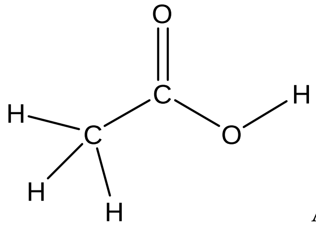
The two structures are not resonance forms because the position of carbon atoms is different in the two forms.

**2.39** Alcohols can act either as weak acids or as weal bases, just as water can. Show the reaction of methyl alcohol, $CH_3OH$, with a strong acid such as HCl and with a strong base such as $Na^{+}$ $^{-}NH_2$

Solution:



**2.40** The O-H hydrogen in acetic is much more acidic than any of the C-H hydrogens. Explain.




Acetic acid

Solution: Because electronegativity of oxygen atom (3.5) is higher than carbon atom (2.5). Acidity is due to the fact that having its negative charge on a highly electronegative oxygen atom stabilizes the conjugate base resulting from loss of $H^+$.

**2.41** Which of the following are likely to act as Lewis acids and which as Lewis bases?

(a) $AlBr_3$ (b) $CH_3CH_2NH_2$ (c) $BH_3$

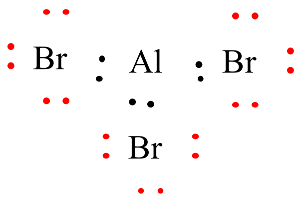
(d) HF (e) $CH_3SCH_3$ (f) $TiCl_4$

Solution: Lewis acid: (a) $AlBr_3$, (c) $BH_3$, (d) HF, (f) $TiCl_4$;

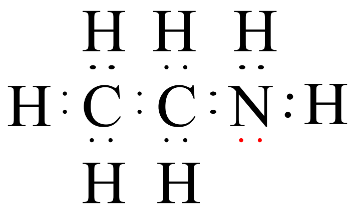
Lewis bases: (b) $CH_3CH_2NH_2$, (e) $CH_3SCH_3$.

**2.42** Draw a Lewis (electron-dot) structure for each of the molecules in Problem 2.41, indicating any unshared electron pairs.

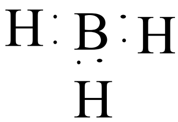
Solution: (a)



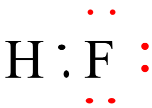

(b)



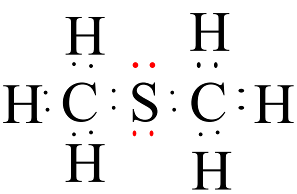

(c)



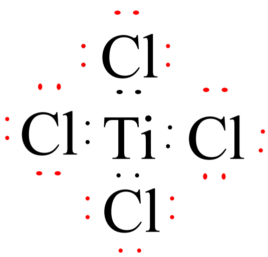

(d)




(e)




(f)




**2.43** Write the products of the following acid-base reactions:

(a) $CH_3OH + H_2SO_4 \rightleftharpoons$

(b) $CH_3OH + NaNH_2 \rightleftharpoons$

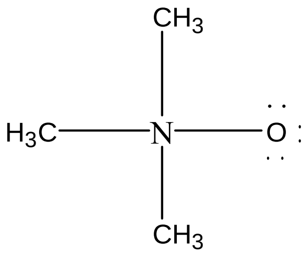
(c) $CH_3NH_3^+Cl^- + NaOH \rightleftharpoons$

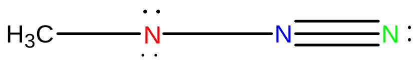
Solution: (a) $CH_3OH + H_2SO_4 \rightleftharpoons CH_3OH_2^+ + HSO_4^-$

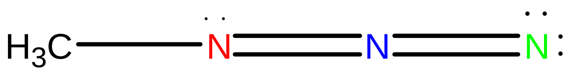
(b) $CH_3OH + NaNH_2 \rightleftharpoons CH_3ONa + NH_3$

(c) $CH_3NH_3^+Cl^- + NaOH \rightleftharpoons CH_3NH_2 + NaCl + H_2O$

**2.44** Assign formal charge to the atoms in each of the following molecules:

(a) 

(b) 

(c) 

Solution: (a) N: 5-8/2=+1

O: 6-6-2/2=-1

(b) N: 5-4-4/2=-1

N: 5-8/2=+1

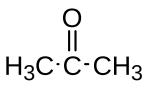
N: 5-2-6/2=0

(c) N: 5-2-6/2=0

N: 5-8/2=+1

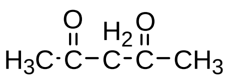
N: 5-4-4/2=-1

**2.45** Rank the following substances in order of increasing acidity:



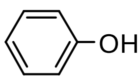
Acetone

(pKa= 19.3)



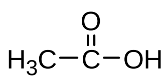
2,4-Pentanedione

(pKa= 9)



Phenol

(pKa= 9.9)



Acetic acid

(pKa= 4.76)

Solution: Acetone < Phenol < 2,4-Pentanedione < Acetic acid

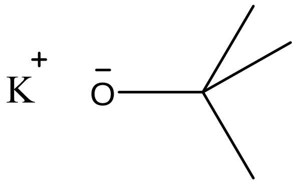
**2.46** Which, if any, of the four substances in Problem 2.45 is a strong enough acid to react almost completely with NaOH? (The pKa of $H_2O$ is 15.74.)

Solution: All substances except acetone react completely with NaOH.

**2.47** The ammonium ion ($NH_4^+$, pKa=9.25) has a lower pKa than the methylammonium ion ($CH_3NH_3^+$, pKa=10.66). Which is the stronger base, ammonia ($NH_3$) or methylamine ($CH_3NH_2$)? Explain.

Solution: Methylamine is the stronger base. Because the pKa of ammonium ion is smaller than methylammonium ion, then it is the stronger acid. As the stronger acid has the weaker conjugate base, the conjugate base of weaker acid methylamine is the stronger base.

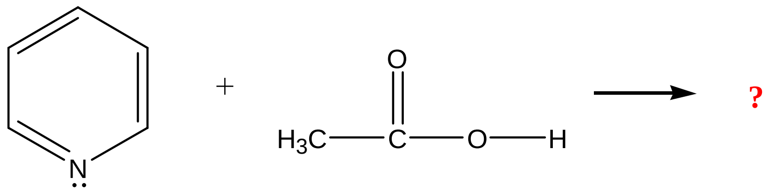
**2.48** Is tert-butoxide anion a strong enough base to react with water? In other words, can a solution of potassium tert-butoxide be prepared in water? The pKa of ter-butyl alcohol is approximately 18.



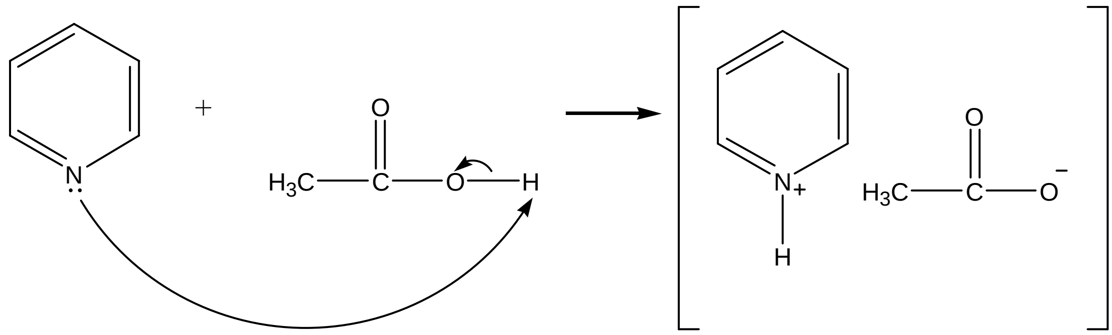

Potassium tert-butoxide

Solution: Yes, it is. Because the pKa of tert-butyl alcohol (pKa=18) is larger than the pKa of water (pKa=15.74). So it is a weaker acid, then its conjugate base is stronger than OH-. So ter-butoxide anion can react with water, in other word, a solution of potassium tert-butoxide be prepared in water can't be prepared in water.

**2.49** Predict the structure of the product formed in the reaction of the organic base pyridine with the organic acid acetic acid, and use curved arrows to indicate the direction of electron flow.




Solution:




**2.50** Calculate Ka values from the following pKa's:

(a) Acetone, $pK_a = 19.3$

Solution: $K_a = 10^{-19.3} = 5.01*10^{-20}$

(b)Formic acid, $pK_a = 3.75$

Solution: $K_a = 10^{-3.75} = 1.78*10^{-4}$

**2.51** Calculate pKa values from the following Ka's.

Solution: (a) pKa=10.301

(b) pKa=4.252

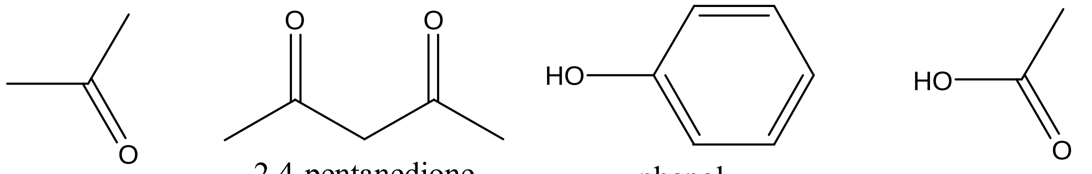
**2.52** What is the pH of a 0.050 M solution of formic acid ?

Solution:

$$[H^+] = \sqrt{Ka*c}$$

$$pH = -\lg[H^+] = \frac{1}{2}(-\lg Ka - \lg c) = \frac{1}{2}(pKa - \lg c) = \frac{1}{2}(3.75 - \lg 0.050) = 2.52$$

**2.53** Sodium bicarbonate,NaHCO3, is the sodium salt of carbonic acid (H2CO3), pKa=6.37. Which of the substances shown in Problem 2.45 will react with sodium bicarbonate?



acetone pKa=19.3 | 2,4-pentanedione pKa=9 | phenol pKa=9.9 | acetic acid pKa=4.76

Solution:

Sodium bicarbonate can react with acetic acid as base.

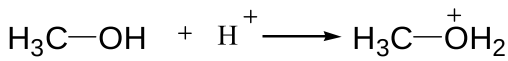
Also it can react with acetone as acid.

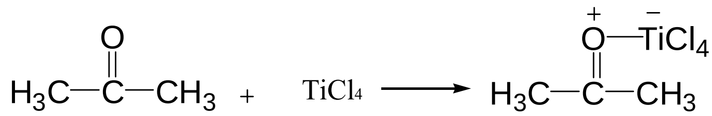
**2.54** Assume that you have two unlabeled bottles, one of which contains phenol (pKa=9.9) and one of which contains acetic acid (pKa=4.76). In light of your answer to Problem 2.53, propose a simple way to determine what is in each bottle.

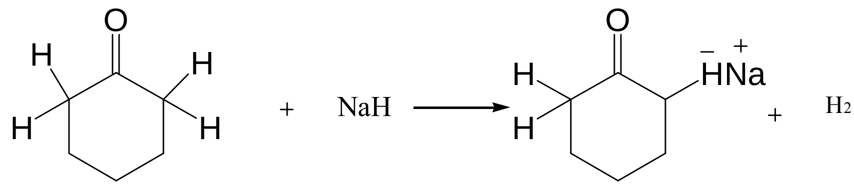
Solution:

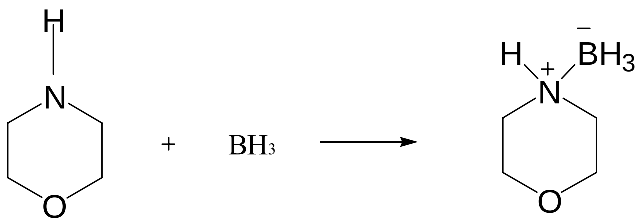
Put sodium bicarbonate into two bottles, and the bottle gives out gas ($CO_2$) contains acetic acid.

**2.55** Identify the acids and bases in the following reactions:

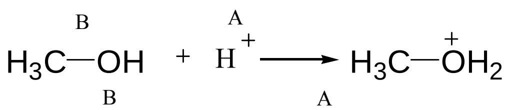
a 

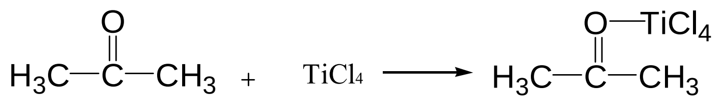
b 

c 

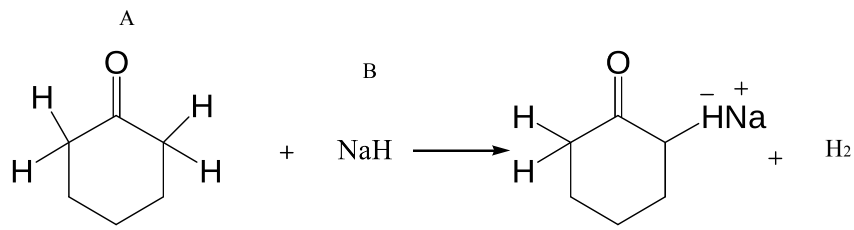
d 

Solution:

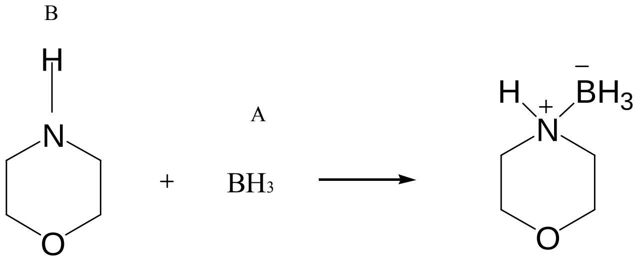
a 


b 

c



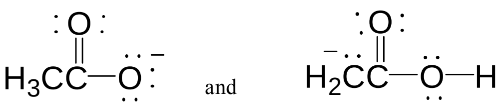
d



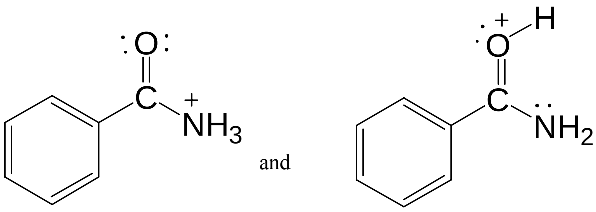
**2.56** Which of the following pairs represent resonance structures?

a

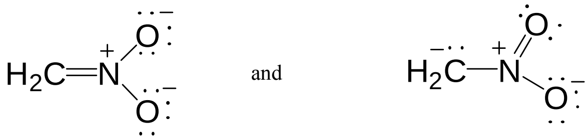
b



c



d

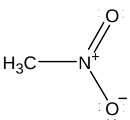


Solution:

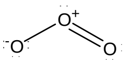
Pairs (a) and (d) represent resonance structures; pairs (b) and (c) do not.

**2.57** Draw as many resonance structures as you can for the following species, adding appropriate formal charges to each:

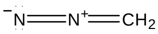
(a) Nitromethane



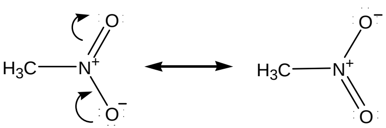
(b) Ozone

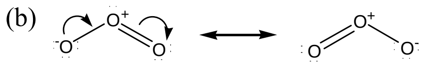


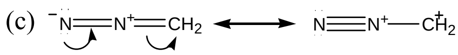
(c) Diazomethane



Solution: (a)

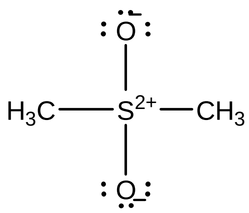


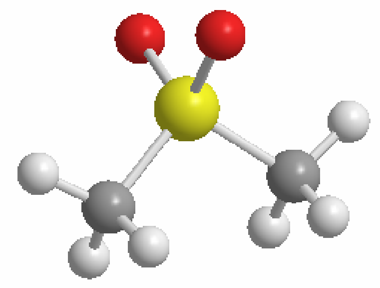




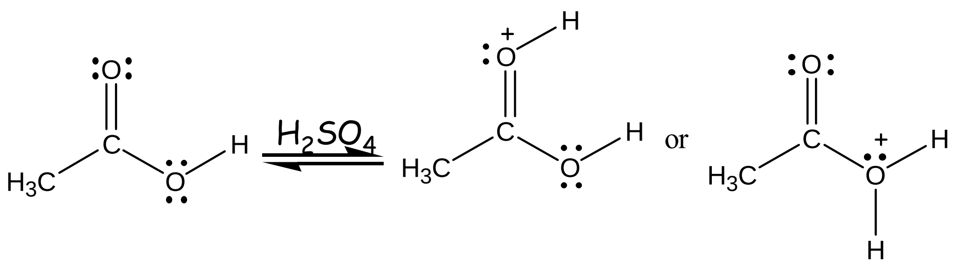
**2.58** Dimethyl sulfone has dipole moment μ=4.4 D. calculate the formal charges present on oxygen and sulfur, and suggest a geometry for the molecule that is consistent with the observed dipole moment.

Solution:

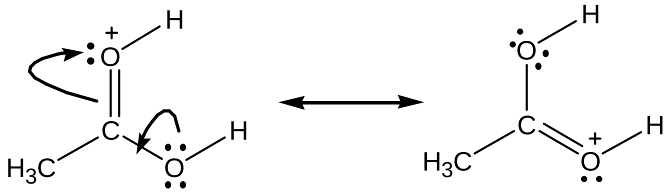


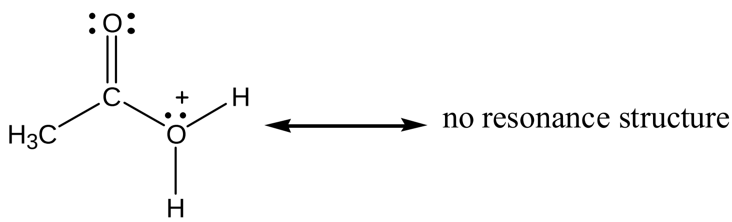


**2.59** We said in Section 2.11 that acetic acid can be protonated by $H_2SO_4$ either on its double-bond oxygen or on its single-bond oxygen. Draw resonance structures of the possible products to explain why the product of protonation on the double-bond oxygen is more stable.



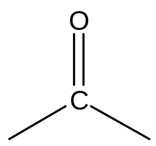
Solution:





**2.60** Organic molecules can be classified according to the functional groups they contain, where a functional group is a collection of atoms with a characteristic chemical reactivity. Use the electronegativity values given in Figure2.2 to predict the polarith of the following functional groups.

(a)

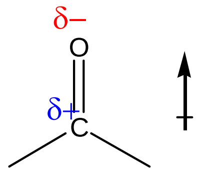



Solution:

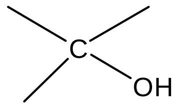
O: EN=3.5

C: EN=2.5

So the polarity:




(b)

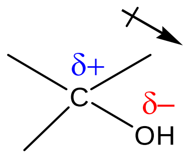



Solution:

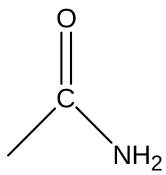
O: EN=3.5

C: EN=2.5

So the polarity:




(c)



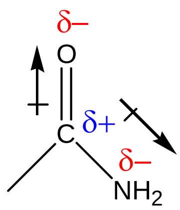

Solution:

O: EN=3.5

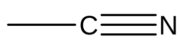
C: EN=2.5

N: EN=3.0

So the polarity:




(d)

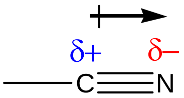



Solution:

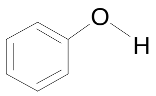
C: EN=2.5

N: EN=3.0

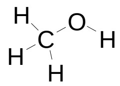
So the polarity:




**2.61** Phenol, $C_6H_5OH$, is a stronger acid than methyl alcohol, $CH_3OH$, even though both contain an O-H bond. Draw the structures of the anions resulting from loss of $H^+$ from phenol and methyl alcohol, and use resonance structures to explain the difference in acidity.

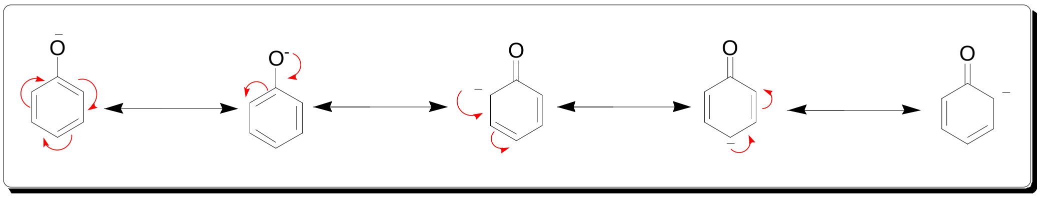



**Phenol (pKa=9.89)**




**Methyl alcohol (pKa=15.54)**

Solution:



The resonance-stabilized phenoxide ion is more stable than an alkoxoide ion, so it is a stronger acid.