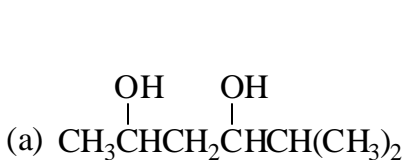
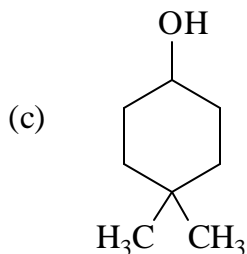


## Chapter 8

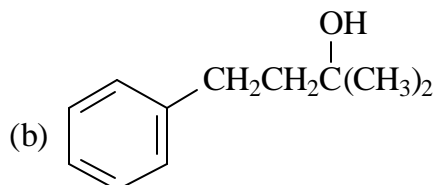
1. Give IUPAC names for the following alcohols.



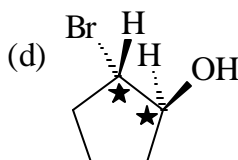
Longest chain = 6 carbons:  
 ....hexanediol.  
 OH on carbons 2&4:  
 ...-2,4-hexanediol.  
 Methyl on carbon 5:  
 5-methyl-2,4-hexanediol.



The ring has 6 carbons;  
 we set the carbon holding  
 the OH as #1:  
 ....-1-cyclohexanol.  
 There are two methyl  
 groups on atom 4:  
 4,4-dimethyl-1-cyclohexanol.



Longest chain = 4 carbons:  
 ....butanol.  
 OH on carbon 2:  
 ...-2-butanol.  
 Methyl on carbon 2, phenyl  
 on carbon 4:  
 2-methyl-4-phenyl-2-butanol.

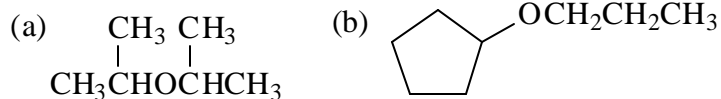


The ring has 5 carbons; we set the  
 carbon holding the OH as #1:  
 ....-1-cyclopentanol.  
 We make the carbon holding the bromine  
 #2 (which is a smaller number than 5, which  
 is what we would get going the other way):  
 -2-bromo-1-cyclopentanol.  
 Owing to the two stereocenters, we need to  
 specify their configuration, so:  
 (1S,2S)-2-bromo-1-cyclopentanol.

2. Identify the alcohols in Problem 1 as primary, secondary, or tertiary.

(a) Both hydroxy groups are attached to secondary carbons.  
 (b) Tertiary, (c) Secondary, (d) Secondary.

4. Name the following ethers by IUPAC rules.



(a) diisopropyl ether, (b) cyclopentyl propyl ether *or* propoxycyclopentane

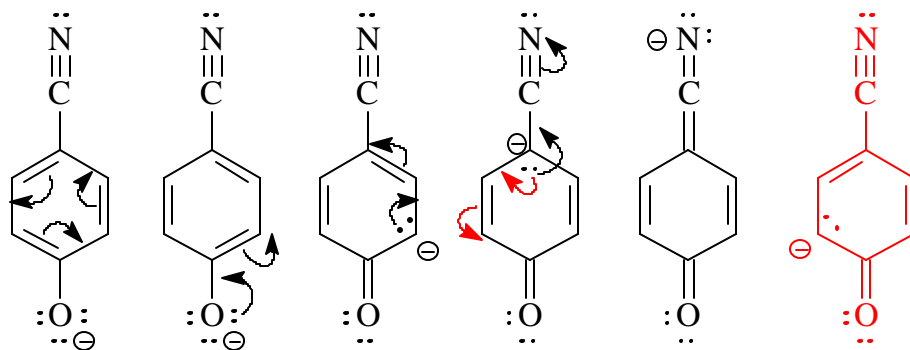
5. Rank the compounds in each group in order of increasing acidity.

(a) methanol, phenol, *p*-nitrophenol, *p*-methylphenol.

Phenols are typically a million times more acidic than alcohols owing to the resonance stabilization of the phenoxide ion that delocalizes the negative charge from the oxygen into the ring. If this is not clear, look over the lecture notes where you will find myriad resonance structures of phenol and the phenoxide anion and the comparison of phenol and alcohol acidities. Among the phenols, electron withdrawing groups increase acidity and electron donating groups decrease it. This is because electron withdrawing groups, like nitro, delocalize the negative charge of the oxygen in the phenoxide anion into the ring. Electron donating groups, like methyl, will intensify this charge.

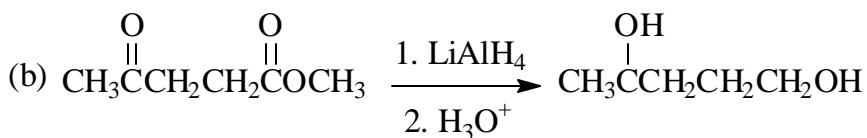
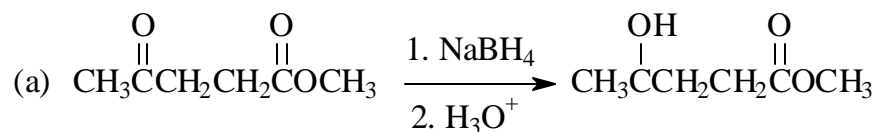
*p*-nitrophenol > phenol > *p*-methylphenol > methanol

6. Draw as many resonance structures as you can for the anion of *p*-cyanophenol.



Note that we leave the atoms alone and move only electrons. The electrons that are usually moved (and are the ones moved in this case) are unshared electrons and electrons in  $\pi$  bonds. In each case the curved arrows on one structure show how the structure to its right was generated, with the exception of red arrows on the fourth structure which show how the sixth structure was generated.

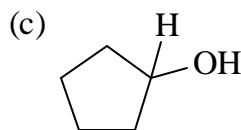
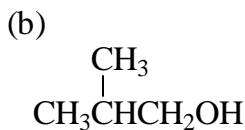
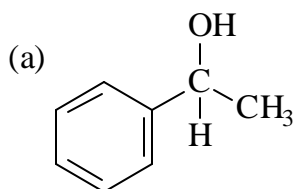
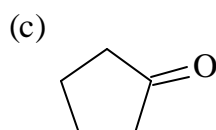
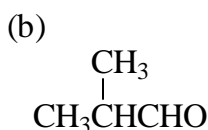
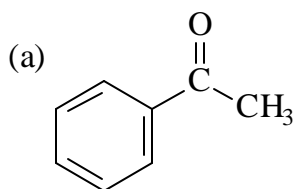
7. How would you carry out the following reactions?



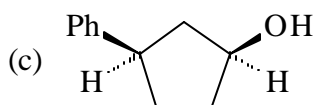
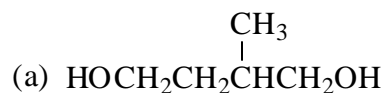
(a) The issue here is that sodium borohydride will reduce ketones but not esters.

(b) The issue here is that lithium aluminum hydride will reduce both ketones and esters.

13. What alcohols would give the following products on oxidation?



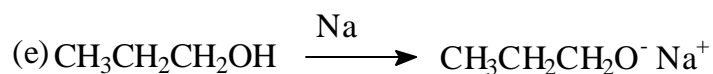
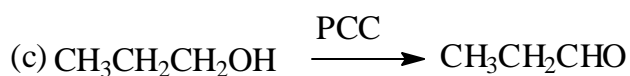
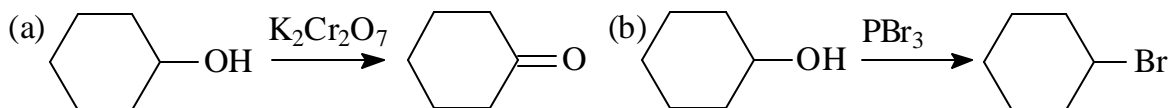
25. Name the following compounds according to IUPAC rules.



(a) 2-methyl-1,4-butanediol. In this case the OH groups do not determine the numbering because the compound would be 1,4-butanediol regardless of which end-carbon is number 1. Numbering from the right puts the methyl on the second carbon, while numbering from the left puts it on the third carbon.

(c) We make the carbon that holds the OH #1. There is one substituent on the ring, a phenyl group. Traversing the ring from carbon 1 in a clockwise direction would place the phenyl on carbon 4. Traversing the ring in a counterclockwise direction from carbon 1 would place the phenyl on carbon 3. This makes the compound 3-phenyl-1-cyclopentanol. There are two chiral centers in this molecule; we need to specify the configurations at these carbons. (1S,3R)-3-phenyl-1-cyclopentanol.

32. What reagents would you use to carry out the following transformations?



HBr would work in (b) also.

39. Reduction of 2-butanone with  $\text{NaBH}_4$  yields 2-butanol. Is the product chiral? Is it optically active? Explain.

2-Butanone and sodium borohydride are both achiral. 2-Butanol has one stereocenter (the carbon holding the OH) and is chiral. When achiral reactants produce chiral products, the products form as racemic mixtures. So, a racemic mixture of (R)- and (S)-2-butanol will form. The racemic mixture is optically inactive.

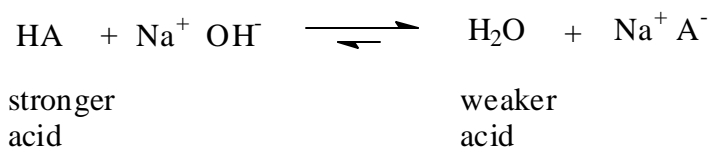
43. Rank the following substances in order of increasing acidity. [Least acidic first.]

- (a) acetone ( $\text{p}K_a = 19$ ), (b) 2,4-pentanedione ( $\text{p}K_a = 9$ ), (c) phenol ( $\text{p}K_a = 9.9$ ),  
(d) acetic acid ( $\text{p}K_a = 4.7$ )

$\text{p}K_a = -\log K_a$ , so the smaller (or more negative) the  $\text{p}K_a$  the larger the  $K_a$ . The larger the  $K_a$ , the stronger the acid.

(a) < (c) < (b) < (d)

44. Which, if any, of the substances in problem 43 are strong enough acids to react substantially with NaOH? (The  $\text{p}K_a$  of water is 15.7.)



One assumes that by “substantially” the author of the question means that the acid/base equilibrium will favor the conjugate base ( $\text{Na}^+ \text{A}^-$ ) of the acid (HA) in question, as shown above. For this to be so, HA must be a stronger acid than water. Of the compounds listed only acetone is a weaker acid than water. So, the answer would be (b), (c), and (d).