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## Alcohols and Phenols

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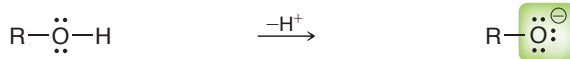
Klein, D. (2012). Alcohols and Phenols. En *Organic Chemistry* (pp. 571-574). USA: Wiley.



## 13.2 Acidity of Alcohols and Phenols

### Acidity of the Hydroxyl Functional Group

As we learned in Chapter 3, the acidity of a compound can be qualitatively evaluated by analyzing the stability of its conjugate base:



To evaluate the acidity  
of this compound...

...deprotonate...

...and assess the stability  
of the conjugate base  
(an alkoxide ion)

#### LOOKING BACK

The factors affecting the stability of a negative charge were first discussed in Section 3.4.

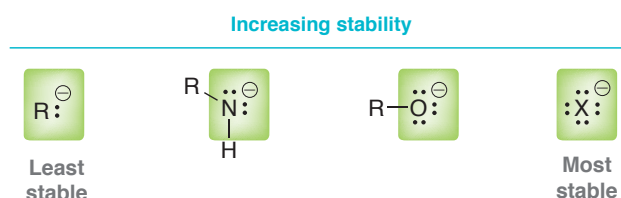
#### LOOKING BACK

Recall that a strong acid will have a low  $pK_a$  value. To review the relationship between  $pK_a$  and acidity, see SkillBuilder 3.2.

The conjugate base of an alcohol is called an **alkoxide** ion, and it exhibits a negative charge on an oxygen atom. A negative charge on an oxygen atom is more stable than a negative charge on a carbon or nitrogen atom but less stable than a negative charge on a halogen, X (Figure 13.2).

FIGURE 13.2

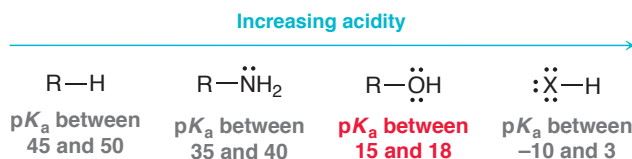
The relative stability of various anions.



Therefore, alcohols are more acidic than amines and alkanes but less acidic than hydrogen halides (Figure 13.3). The  $pK_a$  for most alcohols falls in the range of 15–18.

FIGURE 13.3

The relative acidity of alkanes, amines, alcohols, and hydrogen halides.



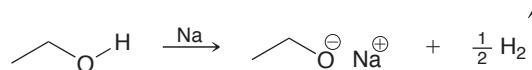
### Reagents for Deprotonating an Alcohol

There are two common ways to deprotonate an alcohol, forming an alkoxide ion.

1. A strong base can be used to deprotonate the alcohol. A commonly used base is sodium hydride (NaH), because hydride ( $\text{H}^-$ ) deprotonates the alcohol to generate hydrogen gas, which bubbles out of solution:

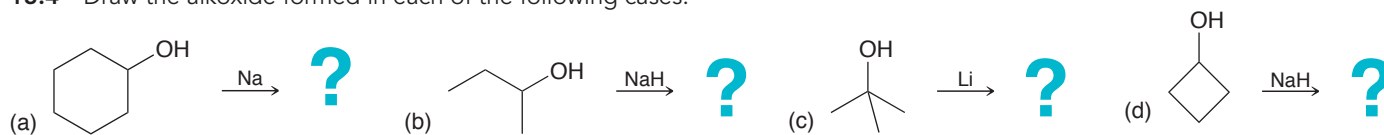


2. Alternatively, it is often more practical to use Li, Na, or K. These metals react with the alcohol to liberate hydrogen gas, producing the alkoxide ion.



### CONCEPTUAL CHECKPOINT

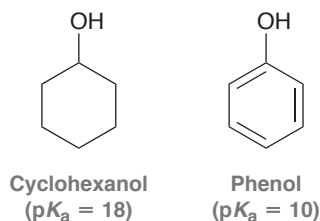
13.4 Draw the alkoxide formed in each of the following cases:



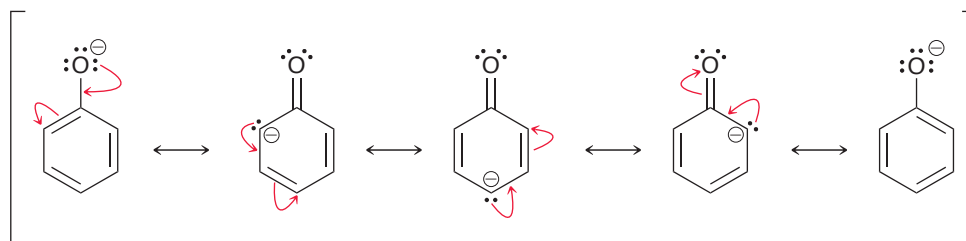
## Factors Affecting the Acidity of Alcohols and Phenols

How can we predict which, of a number of alcohols, is more acidic? In this section, we will explore three factors for comparing the acidity of alcohols.

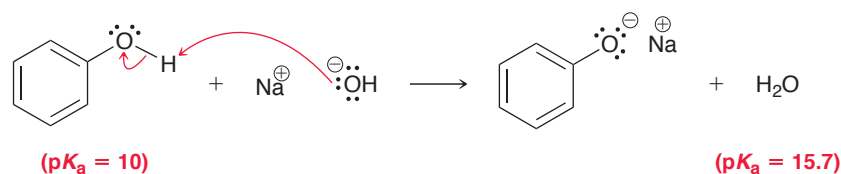
1. *Resonance.* One of the most significant factors affecting the acidity of alcohols is resonance. As a striking example, compare the  $pK_a$  values of cyclohexanol and phenol:



When phenol is deprotonated, the conjugate base is stabilized by resonance.

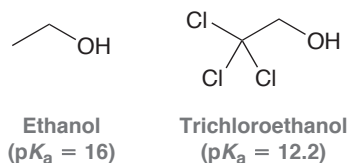


This resonance-stabilized anion is called a **phenolate**, or a **phenoxide** ion. Resonance stabilization of the phenoxide ion explains why phenol is eight orders of magnitude (100,000,000 times) more acidic than cyclohexanol. As a result, phenol does not need to be deprotonated with a very strong base like sodium hydride. Instead, it can be deprotonated by hydroxide.



The acidity of phenols is one of the reasons that phenols are a special category of alcohols. Later in this chapter and again in Chapter 19 we will see other reasons why phenols belong to a class of their own.

2. *Induction.* Another factor in comparing the acidity of alcohols is induction. As an example, compare the  $pK_a$  values of ethanol and trichloroethanol.



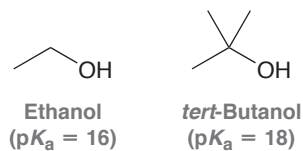
### LOOKING BACK

For a review of inductive effects, see Section 3.4.

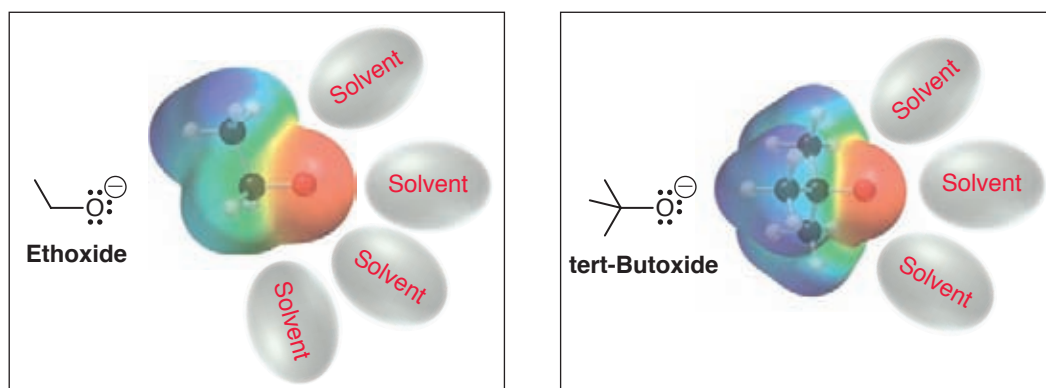
Trichloroethanol is four orders of magnitude (10,000 times) more acidic than ethanol, because the conjugate base of trichloroethanol is stabilized by the electron-withdrawing effects of the nearby chlorine atoms.



3. *Solvation effects.* To explore the effect of alkyl branching, compare the acidity of ethanol and *tert*-butanol.



The  $pK_a$  values indicate that *tert*-butanol is less acidic than ethanol, by two orders of magnitude. This difference in acidity is best explained by a steric effect. The ethoxide ion is not sterically hindered and is therefore easily solvated (stabilized) by the solvent, while *tert*-butoxide is sterically hindered and is less easily solvated (Figure 13.4). The conjugate base of *tert*-butanol is less stabilized than the conjugate base of ethanol, rendering *tert*-butanol less acidic.



**FIGURE 13.4**

An ethoxide ion is stabilized by the solvent to a greater extent than *tert*-butoxide is stabilized by the solvent.

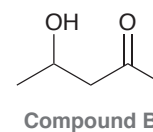
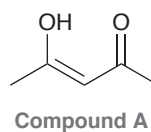
## SKILLBUILDER



### 13.2 COMPARING THE ACIDITY OF ALCOHOLS

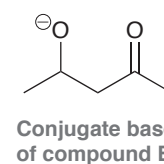
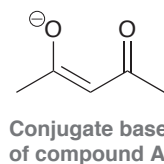
#### LEARN the skill

Identify which of the following compounds is expected to be more acidic.

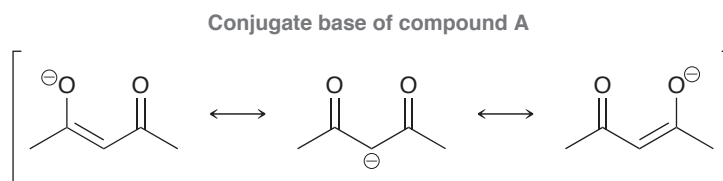


#### SOLUTION

Begin by drawing the conjugate base of each, and then compare the stability of those conjugate bases.



The conjugate base of compound **B** is not resonance stabilized, but the conjugate base of compound **A** is resonance stabilized.

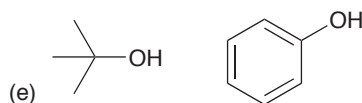
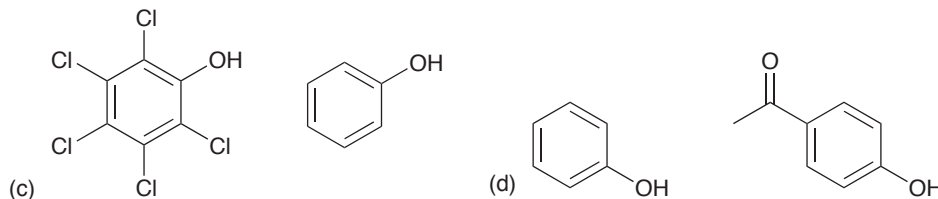
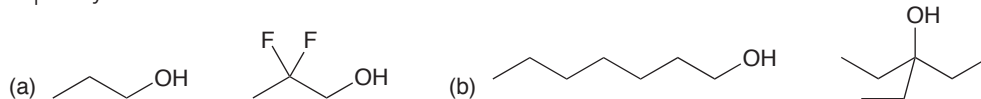


The conjugate base of compound **A** will be more stable than the conjugate base of compound **B**. Therefore, compound **A** will be more acidic.

We expect compound **B** to have a  $pK_a$  somewhere in the range of 15–18 (the range expected for alcohols). The  $pK_a$  of compound **A** will be more difficult to predict. However, we can say with certainty that it will be lower (more acidic) than a regular alcohol. In other words, the  $pK_a$  value will be lower than 15.

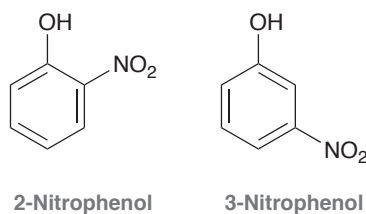
### PRACTICE the skill

**13.5** For each of the following pairs of alcohols, identify the one that is more acidic, and explain your choice:



### APPLY the skill

**13.6** Consider the structures of 2-nitrophenol and 3-nitrophenol. These compounds have very different  $pK_a$  values. Predict which one has the lower  $pK_a$ , and explain why. (**Hint:** In order to solve this problem, you must draw the structure of each nitro group.)



need more PRACTICE? Try Problems 13.33, 13.34

## 13.3 Preparation of Alcohols via Substitution or Addition

### Substitution Reactions

As we saw in Chapter 7, alcohols can be prepared by substitution reactions in which a leaving group is replaced by a hydroxyl group.



A primary substrate will require  $S_N2$  conditions (a strong nucleophile), while a tertiary substrate will require  $S_N1$  conditions (a weak nucleophile).

**Primary:**



**Tertiary:**

