Reactions of Functional Groups

2.2

In the past, mirrors were rare and valuable, made from sheets of polished copper or silver. Although they were expensive, they usually produced only warped and dim images. Modern mirrors are everywhere. They are cheaply made of glass, with a very thin layer of silver over the back of the glass. Because the surface of the glass and the layer of silver are so smooth, the image is almost perfect. One method for depositing a thin layer of silver over glass is shown in Figure 2.2.

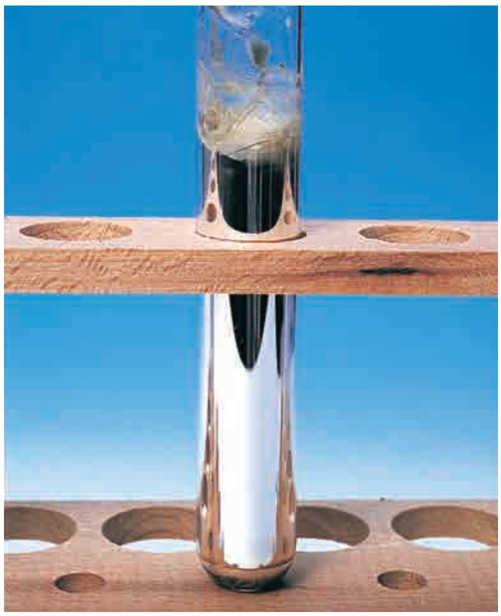


Figure 2.2 **The "silver mirror test" is used to distinguish an aldehyde from a ketone. Tollen's reagent, $Ag(NH_3)_2OH$, acts as an oxidizing agent. When it is mixed with an aldehyde, the aldehyde oxidizes to the salt of a carboxylic acid. The silver ions in Tollen's reagent are reduced to silver atoms, and coat the glass of the reaction container with solid silver metal.**

Section Preview/ Specific Expectations

In this section, you will

- **describe** various addition, substitution, elimination, oxidation, reduction, condensation, and hydrolysis reactions
- **predict**, **draw**, and **name** the products of various organic reactions
- **investigate** the oxidation of alcohols
- **communicate** your understanding of the following terms: *Markovnikov's rule, esterification reaction*

In this section, you will learn how to predict the reactions of different functional groups. You studied the most common reaction of alkanes, combustion, in your previous chemistry course. For this reason, the reactions of alkanes will not be considered here. The reactions of amines and ethers will be left for a later chemistry course.

Reactions of Alkenes and Alkynes

Because alkenes and alkynes have reactive double or triple bonds, they undergo addition reactions. Some common atoms and groups of atoms that can be added to a double or triple bond include

- H and OH (from H_2O)
- H and X (from HX), where X = Cl, Br, or I
- X and X (from X_2), where X = Cl, Br, or I
- H and H (from H_2)

Depending on which atoms are added to the multiple bond, the product may be an alcohol, alkyl halide, alkane, or alkene (if atoms are added to a triple bond).

Addition to Alkenes

The product of an addition reaction depends on the symmetry of the reactants. A *symmetrical alkene* has identical groups on either side of the double bond. Ethene, $CH_2{=}CH_2$, is an example of a symmetrical alkene. An alkene that has different groups on either side of the double bond is called an *asymmetrical alkene*. Propene, $CH_3CH{=}CH_2$, is an example of an asymmetrical alkene.

The molecules that are added to a multiple bond can also be classified as symmetrical or asymmetrical. For example, chlorine, Cl_2, breaks into two identical parts when it adds to a multiple bond. Therefore, it is a symmetrical reactant. Water, HOH, breaks into two different groups (H and OH) when it adds to a multiple bond, so it is an asymmetrical reactant.

In Figures 2.3 and 2.4, at least one of the reactants is symmetrical. When one or more reactants in an addition reaction are symmetrical, only one product is possible.

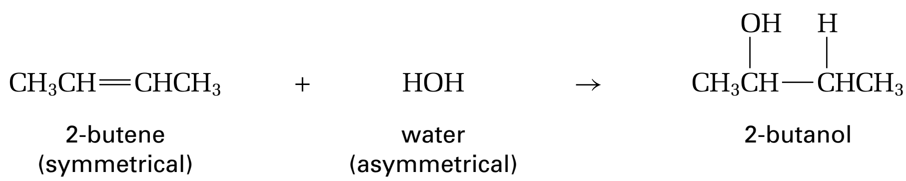


Figure 2.3 **The addition of water to 2-butene**

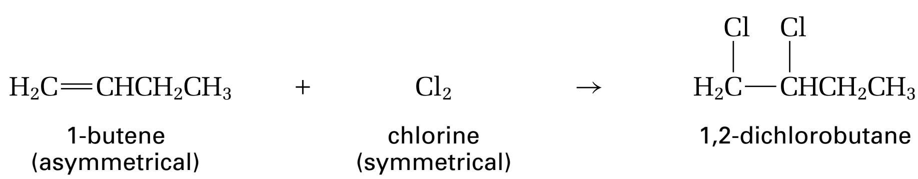


Figure 2.4 **The addition of chlorine to 1-butene**

When both reactants are asymmetrical, however, more than one product is possible. This is shown in Figure 2.5. The two possible products are isomers of each other.

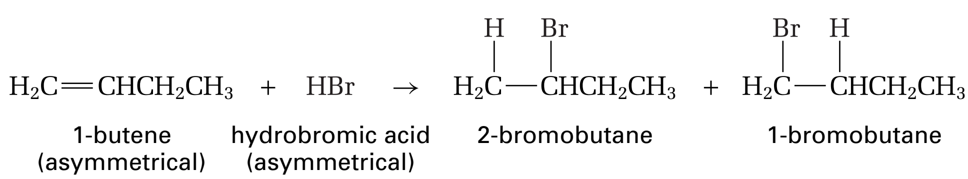


Figure 2.5 **The addition of hydrobromic acid to 1-butene**

Although both products are possible, 2-bromobutane is the observed product. This observation is explained by Markovnikov's rule. **Markovnikov's rule** states that *the halogen atom or OH group in an addition reaction is usually added to the more substituted carbon atom—the carbon atom that is bonded to the largest number of other carbon atoms*. Think of the phrase "the rich get richer." The carbon with the most hydrogen atoms receives even more hydrogen atoms in an addition reaction. According to Markovnikov's rule, the addition of two asymmetrical reactants forms primarily one product. Only a small amount of the other isomer is formed. The following Sample Problem shows how to use Markovnikov's rule to predict the products of addition reactions.

Sample Problem

Using Markovnikov's Rule

Problem

Draw the reactants and products of the following incomplete reaction.

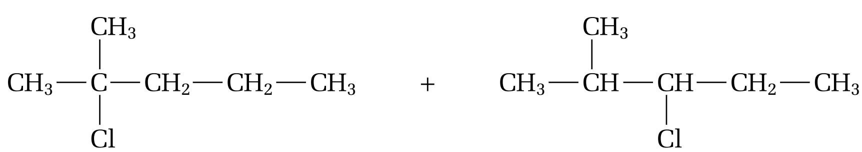
2-methyl-2-pentene + hydrochloric acid → ?

Use Markovnikov's rule to predict which of the two isomeric products will form in a greater amount.

Solution

According to Markovnikov's rule, *the hydrogen atom will go to the double-bonded carbon with the larger number of hydrogen atoms.* Thus, the chlorine atom will go to the other carbon, which has the larger number of C—C bonds. The product 2-chloro-2-methylpentane will form in the greater amount. Small amounts of 3-chloro-2-methylpentane will also form.

2-methyl-2-pentene + hydrochloric acid →



2-chloro-2-methylpentane (major product) + 3-chloro-2-methylpentane (minor product)

Practice Problems

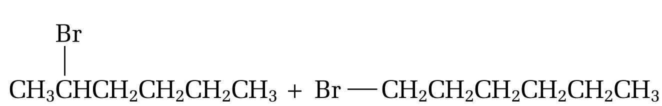
5. Draw the reactants and products of the following reaction.

3-ethyl-2-heptene + HOH → 3-ethyl-3-heptanol + 3-ethyl-2-heptanol

Use Markovnikov's rule to predict which of the two products will form in the greater amount.

6. Name the reactants and products of each reaction. Use Markovnikov's rule to predict which of the two products will form in the greater amount.

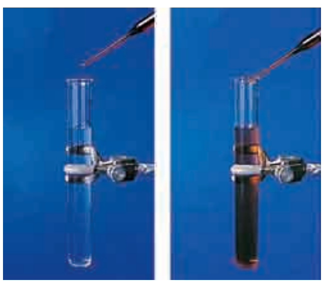
(a) $CH_2{=}CHCH_2CH_2CH_2CH_3 + HBr \rightarrow$



Continued ...

CHEM FACT

Addition reactions form the basis for tests that distinguish alkenes and alkynes from alkanes. Bromine, Br_2, has a deep reddish-brown colour. When bromine is added to an alkene or alkyne, an addition reaction takes place. As the bromine is used up, the brown colour of the bromine disappears. Since alkanes cannot undergo addition reactions, no reaction takes place when bromine is added to an alkane.



Electronic Learning Partner

Go to the Chemistry 12 Electronic Learning Partner for more information about the bonding in ethyne.

Continued ...

(b) $CH_3—C(CH_3)═CH—CH_2—CH_3 + HOH \rightarrow$

$CH_3—C(CH_3)(OH)—CH_2—CH_2—CH_3 + CH_3—CH(CH_3)—CH(OH)—CH_2—CH_3$

7. Draw the major product of each reaction.

(a) $CH_3CH═CH_2 + Br_2 \rightarrow$

(b) $CH_2═CH_2 + HOH \rightarrow$

(c) $CH_2═CHCH_2CH_3 + HBr \rightarrow$

(d) $(CH_3)_2C═CHCH_2CH_2CH_3 + HCl \rightarrow$

8. For each reaction, name and draw the reactants that are needed to produce the given product.

(a) $? + ? \rightarrow CH_3CH(Cl)CH_3$

(b) $? + ? \rightarrow Br—CH_2CH_2—Br$

(c) $? + HOH \rightarrow CH_3CH_2C(OH)(CH_3)CH_2CH_3$

(d) $CH_2═CHCH_3 + ? \rightarrow CH_3CH_2CH_3$

Addition to Alkynes

Since alkynes have triple bonds, two addition reactions can take place in a row. If one mole of a reactant, such as HCl, Br_2, or H_2O, is added to one mole of an alkyne, the result is a substituted alkene.

$H—C≡C—CH_3 + Br_2 \rightarrow H—C(Br)═C(Br)—CH_3$

propyne (1 mol) + bromine (1 mol) → 1,2-dibromopropene

If two moles of the reactant are added to one mole of an alkyne, the reaction continues one step further. A second addition reaction takes place, producing an alkane.

$H—C≡C—CH_3 + 2Br_2 \rightarrow H—CBr_2—CBr_2—CH_3$

propyne (1 mol) + bromine (2 mol) → 1,1,2,2-tetrabromopropane

Like alkenes, asymmetrical alkynes follow Markovnikov's rule when an asymmetrical molecule, such as H_2O or HBr, is added to the triple bond. An example is given below.

$H—C≡C—CH_2CH_3 + HBr \rightarrow H_2C═C(Br)—CH_2CH_3 + HC(Br)═CH—CH_2CH_3$

1-butyne (1 mol) + hydrobromic acid (1 mol) → 2-bromo-1-butene (major product) + 1-bromo-1-butene (minor product)

Reactions of Aromatic Compounds

As you learned in Chapter 1, aromatic compounds do not react in the same way that compounds with double or triple bonds do. Benzene's stable ring does not usually accept the addition of other atoms. Instead, aromatic compounds undergo substitution reactions. A hydrogen atom or a functional group that is attached to the benzene ring may be replaced by a different functional group. Figure 2.6 shows two possible reactions for benzene. Notice that iron(III) bromide, $FeBr_3$, is used as a catalyst in the substitution reaction. An addition reaction does *not* occur because the product of this reaction would be less stable than benzene.

Electronic Learning Partner

Go to the Chemistry 12 Electronic Learning Partner for more information about aspects of material covered in this section of the chapter.

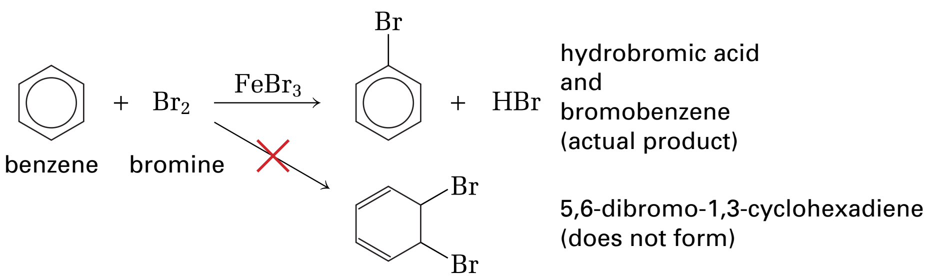


Figure 2.6 The bromine does not add to benzene in an addition reaction. Instead, one of the H atoms on the benzene ring is replaced with a Br atom in a substitution reaction.

Reactions of Alcohols

Alcohols can react in several ways, depending on the reactants and on the conditions of the reaction. For example, alcohols can undergo substitution with halogen acids, elimination to form alkenes, and oxidation to form aldehydes, ketones, or carboxylic acids.

Substitution Reactions of Alcohols

When a halogen acid, such as HCl, HBr, or HI, reacts with an alcohol, the halogen atom is substituted for the OH group of the alcohol. This is shown in Figure 2.7(A). The reverse reaction takes place when an alkyl halide reacts with OH^- in a basic solution. See Figure 2.7(B).

A $$CH_3-CH_2-OH + HCl \rightarrow CH_3-CH_2-Cl + H_2O$$

B $$CH_3-CH_2-Cl + OH^- \rightarrow CH_3-CH_2-OH + Cl^-$$

Figure 2.7 (A) Ethanol reacts with hydrochloric acid to produce chloroethane. (B) In a basic solution, the reverse reaction takes place. A hydroxide ion reacts with chloroethane to produce ethanol.

Elimination Reactions of Alcohols

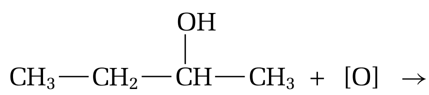
When an alcohol is heated in the presence of the strong acid and dehydrating agent, H_2SO_4, an elimination reaction takes place. This type of reaction is shown in Figure 2.8, on the next page. The OH group and one H atom leave the molecule, and water is produced. As a result, the molecule forms a double bond. Because water is produced, this type of reaction is also called a *dehydration* (meaning "loss of water") reaction.

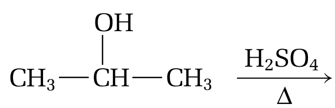
Sample Problem

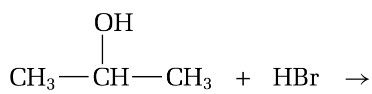
Predicting the Reaction of an Alcohol

Problem

Name each type of reaction. Then predict and name the products.

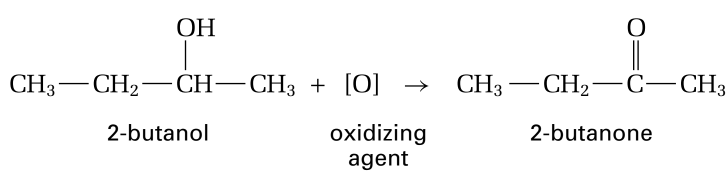
(a) 

(b) 

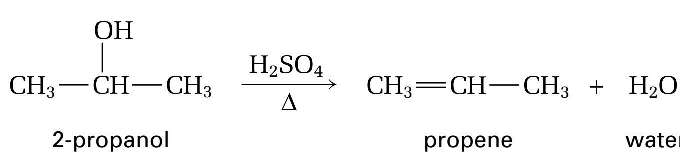
(c) 

Solution

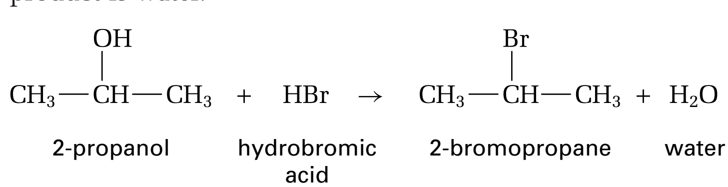
(a) The reactant is a secondary alcohol, and an oxidizing agent is present. Therefore, this must be oxidation. You know that a secondary alcohol is oxidized to a ketone. The ketone must have the same carbon-carbon bonds, and the same number of carbon atoms, as the reacting alcohol. Therefore, the ketone must be 2-butanone.



(b) This reaction takes place in the presence of heat and sulfuric acid, H_2SO_4. It is an elimination reaction. The product is an alkene, with the same number of carbon atoms as the reacting alcohol. Since this reaction is an elimination reaction, a small molecule (in this case, water) must be eliminated as the second product. The organic product is propene.



(c) In this reaction, an alcohol reacts with hydrobromic acid, HBr. This is a substitution reaction. The product is an alkyl halide, with the same carbon-carbon bonds, and the same number of carbon atoms, as the reacting alcohol. The alkyl halide is 2-bromopropane. The second product is water.



PROBLEM TIP

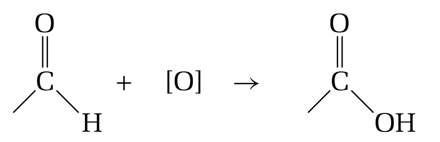
In many elimination reactions, water is produced. The formation of water is a strong driving force for many reactions.

Reactions of Aldehydes and Ketones

As you observed in the investigation, different alcohols react differently with an oxidizing agent. In the same way, aldehydes and ketones react differently with oxidizing and reducing agents, even though aldehydes and ketones have similar structures.

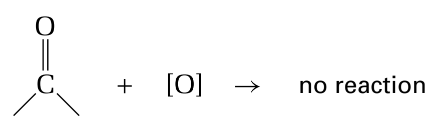
Oxidation of Aldehydes

In the presence of an oxidizing agent, an aldehyde is oxidized to produce a carboxylic acid. The hydrogen atom that is bonded to the carbon atom of the C═O bond is replaced with an OH group.



aldehyde carboxylic acid

Ketones do not usually undergo oxidation. Like tertiary alcohols, ketones do not have a hydrogen atom that is available to be removed. Carbon-carbon bonds are too strong to be broken by an oxidizing agent.



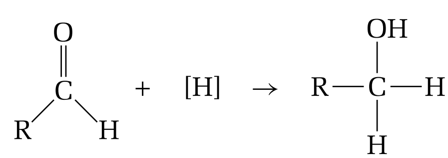
ketone

Reduction of Aldehydes and Ketones

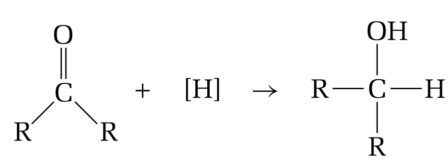
You learned earlier that primary alcohols are oxidized to aldehydes, and secondary alcohols are oxidized to ketones. You can think of the reduction of aldehydes and ketones as the reverse of these reactions. Aldehydes can be reduced to produce primary alcohols. Ketones can be reduced to produce secondary alcohols.

CONCEPT CHECK

Explain why the transformation of an aldehyde into an alcohol is a reduction not an oxidation.



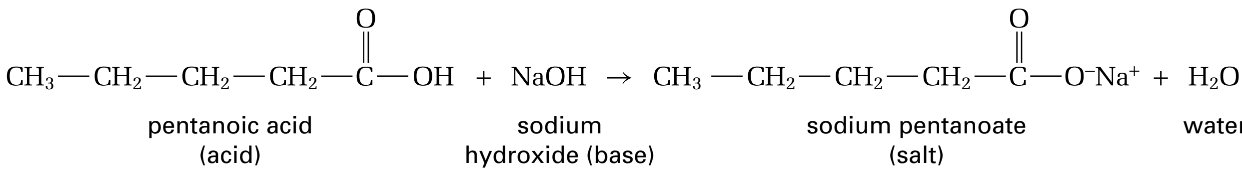
aldehyde primary alcohol



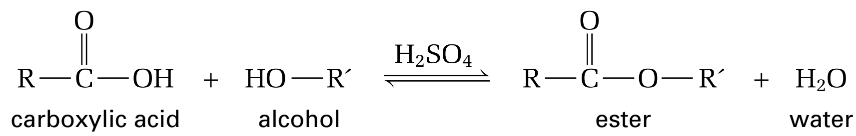
ketone secondary alcohol

Reactions of Carboxylic Acids

Like other acids, a carboxylic acid reacts with a base to produce a salt and water.



As you learned earlier, a carboxylic acid reacts with an alcohol to produce an ester. Water is the second product of this reaction. A strong acid, such as H_2SO_4, is used to catalyze (speed up) the reaction. The reverse reaction can also occur. (See "Reactions of Esters and Amides," below.)



The reaction of a carboxylic acid with an alcohol to form an ester is called an **esterification reaction**. An esterification reaction is one type of condensation reaction. In a similar type of condensation reaction, an amide can be formed from a carboxylic acid and an amine, but this process is slightly longer and will not be discussed here.

Carboxylic acids can be reduced to form aldehydes and alcohols.

Reactions of Esters and Amides

Both esters and amides undergo hydrolysis reactions. In a hydrolysis reaction, the ester or amide bond is *cleaved*, or split in two, to form two products. As mentioned earlier, the hydrolysis of an ester produces a carboxylic acid and an alcohol. The hydrolysis of an amide produces a carboxylic acid and an amine. There are two methods of hydrolysis: acidic hydrolysis and basic hydrolysis. Both methods are shown in Figure 2.9. Hydrolysis usually requires heat. In acidic hydrolysis, the ester or amide reacts with water in the presence of an acid, such as H_2SO_4. In basic hydrolysis, the ester or amide reacts with the OH^- ion, from NaOH or water, in the presence of a base. Soap is made by the basic hydrolysis of ester bonds in vegetable oils or animal fats.

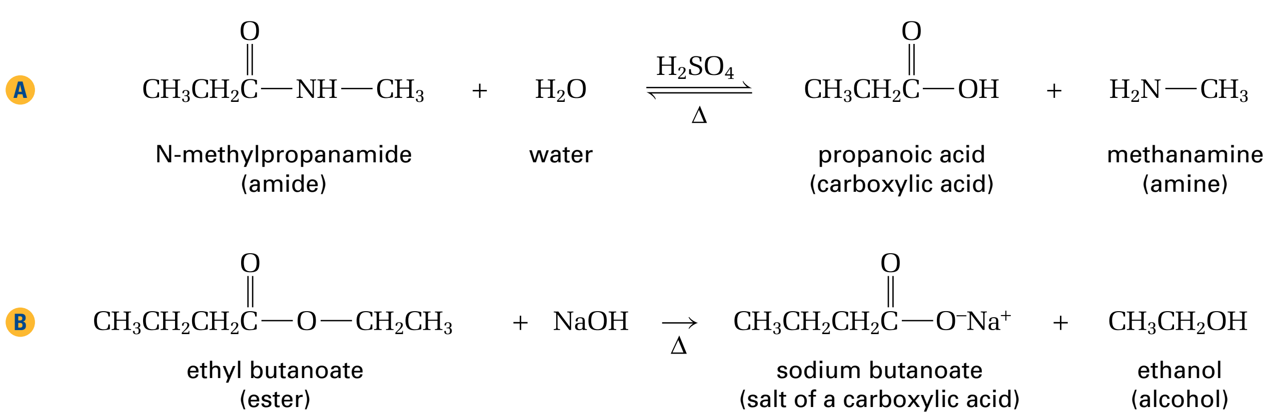


Figure 2.9 **(A) The acid hydrolysis of an amide produces a carboxylic acid and an amine. (B) The basic hydrolysis of an ester produces the salt of a carboxylic acid and an alcohol.**