# **8.1** Naming Alcohols, Phenols, and Ethers

#### Alcohols

Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbon substituents bonded to the hydroxyl-bearing carbon.

A primary (1°) alcohol A secondary (2°) alcohol A tertiary (3°) alcohol

Simple alcohols are named in the IUPAC system as derivatives of the parent alkane, using the suffix -ol. As always, the locant indicating the position of the hydroxyl group in the parent chain is placed immediately before the -ol suffix in the newer, post-1993 naming system.

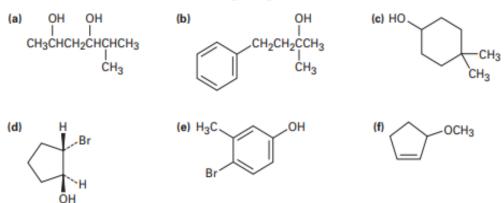
- Select the longest carbon chain containing the hydroxyl group, and replace STEP 1 the -e ending of the corresponding alkane with -ol. The -e is deleted to prevent the occurrence of two adjacent vowels: propanol rather than propaneol, for example.
- STEP 2 Number the carbons of the parent chain beginning at the end nearer the hydroxyl group.
- Number all substituents according to their position on the chain, and write STEP 3 the name listing the substituents in alphabetical order and identifying the position to which the -OH is bonded. Note that in naming cis-cyclohexane-1,4-diol, the final -e of cyclohexane is not deleted because the next letter (d) is not a vowel; that is, cyclohexanediol rather than cyclohexandiol.

#### **Ethers**

Simple ethers that contain no other functional groups are named by identifying the two organic groups and adding the word *ether*.

If other functional groups are present, the ether part is named as an *alkoxy* substituent. For example:

#### Problem 8.1 Give IUPAC names for the following compounds:



Problem 8.2 Identify the alcohols in Problem 8.1 as primary, secondary, or tertiary.

#### Problem 8.3 Draw structures corresponding to the following IUPAC names:

- (a) 2-Methylhexan-2-ol
- (b) Hexane-1,5-diol
- (c) 2-Ethylbut-2-en-1-ol
- (d) Cyclohex-3-en-1-ol
- (e) o-Bromophenol
- (f) 2,4,6-Trinitrophenol

#### Problem 8.4 Name the following ethers by IUPAC rules:

# Properties of Alcohols and Phenols: Hydrogen Bonding and Acidity

Alcohols, phenols, and ethers can be thought of as organic derivatives of water in which one or both of the hydrogens have been replaced by organic parts: H—O—H becomes R—O—H, Ar —O—H, or R—O—R'. Thus, all three classes of compounds have nearly the same geometry as water. The C—O—H or C—O—C bond angles are approximately tetrahedral—109° in methanol and 112° in dimethyl ether, for instance—and the oxygen atoms are  $sp^3$ -hybridized.

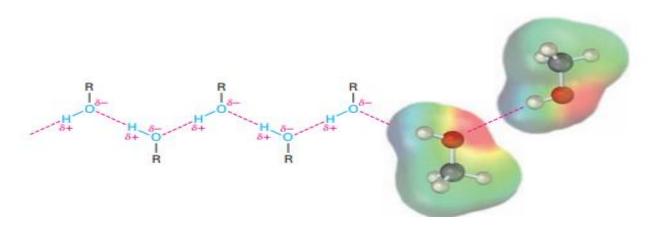
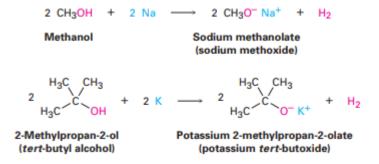


Figure 8.1 Hydrogen bonding in alcohols and phenols. The weak attraction between a positively polarized - OH hydrogen and a negatively polarized oxygen holds molecules together. The electrostatic

potential map of methanol shows the positively polarized - OH hydrogen (blue) and the negatively polarized oxygen (red).

Table 8.1	Acidity of Some Alcoho	ols and Phenols
Compound	pK <sub>a</sub>	
$(CH_3)_3COH$	18.00	Weaker acid
CH <sub>3</sub> CH <sub>2</sub> OH	16.00	
H <sub>2</sub> O	15.74	
CH <sub>3</sub> OH	15.54	
p-Methylphenol	10.17	
Phenol	9.89	
p-Nitrophenol	7.15	Stronger acid

The data in Table 8.1 show that alcohols are about as acidic as water. Thus, they don't react with weak bases such as amines or bicarbonate ion and they react to only a limited extent with metal hydroxides, such as NaOH. They do, however, react with alkali metals to yield alkoxides that are themselves strong bases. Alkoxides are named commonly by replacing the -ane suffix of the corresponding alkane with -oxide: methane gives methoxide, for instance. They are named systematically by adding the -ate suffix to the name of the alcohol. Methanol becomes methanolate, for instance.



**Phenol**, any of a family of <u>organic compounds</u> characterized by a hydroxyl (—OH) group attached to a <u>carbon</u> atom that is part of an aromatic ring. Besides serving as the generic name for the entire family, the term *phenol* is also the specific name for its simplest member, mono-hydroxy benzene (C<sub>6</sub>H<sub>5</sub>OH), also known as benzenol, or <u>carbolic acid</u>.

Phenols are similar to <u>alcohols</u> but form <u>stronger hydrogen bonds</u>. Thus, they are more soluble in <u>water</u> than are alcohols and have higher <u>boiling points</u>. Phenols occur either as colourless <u>liquids</u> or white <u>solids</u> at room temperature and may be <u>highly toxic and caustic</u>.

Phenols are widely used in household products and as intermediates for industrial synthesis. For example, phenol itself is used (in low concentrations) as a disinfectant in household cleaners and in mouthwash. Phenol may have been the first surgical antiseptic. In 1865 the British surgeon Joseph Lister used phenol as an antiseptic to sterilize his operating field. With phenol used in this manner, the mortality rate from surgical amputations fell from 45 to 15 percent in Lister's ward. Phenol is quite toxic, however, and concentrated solutions cause severe but painless burns of the skin and mucous membranes. Less-toxic phenols, such as *n*-hexylresorcinol, have supplanted phenol itself in cough drops and other antiseptic applications. Butylated hydroxytoluene (BHT) has a much lower toxicity and is a common antioxidant in foods.

In industry, phenol is used as a starting material to make <u>plastics</u>, <u>explosives</u> such as <u>picric acid</u>, and <u>drugs</u> such as <u>aspirin</u>. The common phenol <u>hydroquinone</u> is the component of photographic developer that reduces exposed silver bromide crystals to black metallic silver. Other substituted phenols are used in the <u>dye</u> industry to make intensely coloured <u>azo dyes</u>. Mixtures of phenols (especially the <u>cresols</u>) are used as components in wood preservatives such as <u>creosote</u>.

#### Natural sources of phenols

Phenols are common in nature; examples include <u>tyrosine</u>, one of the standard <u>amino acids</u> found in most proteins; epinephrine (adrenaline), a stimulant <u>hormone</u> produced by the adrenal medulla; <u>serotonin</u>, a <u>neurotransmitter</u> in the brain; and urushiol, an irritant secreted by <u>poison</u>

ivy to prevent animals from eating its leaves. Many of the more complex phenols used as flavorings and aromas are obtained from essential oils of plants. For example, vanillin, the principal flavoring in vanilla, is isolated from vanilla beans, and methyl salicylate, which has a characteristic minty taste and odour, is isolated from wintergreen. Other phenols obtained from plants include thymol, isolated from thyme, and eugenol, isolated from cloves.

Phenol, the cresols (methyl phenols), and other simple alkylated phenols can be obtained from the distillation of coal tar or crude petroleum.

Nomenclature of phenols Many phenolic compounds were discovered and used long before chemists were able to determine their structures. Therefore, trivial names (i.e., vanillin, salicylic acid, pyrocatechol, resorcinol, cresol, hydroquinone, and eugenol) are often used for the most common phenolic compounds.

### Classification of phenols

Phenols are about a million times more acidic than alcohols and are therefore soluble in dilute aqueous NaOH.

Phenols are more acidic than alcohols because the phenoxide anion is resonance-stabilized by the aromatic ring. Sharing the negative charge over the ring increases the stability of the phenoxide anion and thus increases the tendency of the corresponding phenol to dissociate (Figure 8.2).

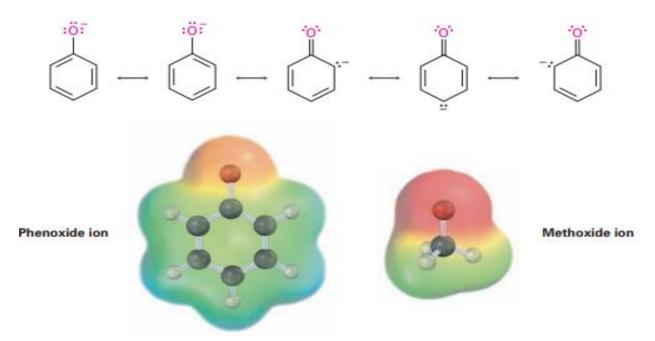


Figure 8.2 A resonance-stabilized phenoxide ion is more stable than an alkoxide ion. Electrostatic potential maps show how the negative charge is more concentrated on oxygen in the methoxide ion but is less concentrated on the phenoxide oxygen.

#### Synthesis of phenols

Most of the phenol used today is produced from <u>benzene</u>, through either <u>hydrolysis</u> of <u>chlorobenzene</u> or oxidation of isopropylbenzene (cumene).

#### Hydrolysis of chlorobenzene (the Dow process)

Benzene is easily converted to chlorobenzene by a variety of methods, one of which is the Dow process. Chlorobenzene is hydrolyzed by a strong <u>base</u> at high temperatures to give a phenoxide salt, which is acidified to phenol.

#### **General synthesis of phenols**

To make more-complicated phenolic compounds, a more general synthesis is needed. The cumene hydroperoxide reaction is fairly specific to phenol itself. The Dow process is somewhat more general, but the stringent conditions required often lead to low yields, and they may destroy any other functional groups on the molecule. A milder, more general reaction is the diazotization of an arylamine (a derivative of aniline, C6H5NH2) to give a diazonium salt, which hydrolyzes to a phenol. Most functional groups can survive this technique, as long as they are stable in the presence of dilute acid

$$NH_2$$
 $NH_2$ 
 $N = N + CI^ N = NH_2$ 
 $N = NH_2$ 
 $N$ 

R = alkyl group or functional group at any position

## **8.5** Reactions of Phenols

#### **Alcohol-Like Reactions of Phenols**

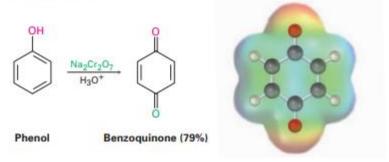
Phenols and alcohols behave very differently despite the fact that both have  $\neg OH$  groups. Phenols can't be dehydrated by treatment with acid and can't be converted into halides by treatment with HX. Phenols can, however, be converted into ethers by  $S_N 2$  reaction with alkyl halides in the presence of base. Williamson ether synthesis with phenols occurs easily because phenols are more acidic than alcohols and are more readily converted into their anions.

#### **Electrophilic Aromatic Substitution Reactions of Phenols**

The -OH group is an activating, ortho- and para-directing substituent in electrophilic aromatic substitution reactions (Sections 5.6 and 5.7). As a result, phenols are reactive substrates for electrophilic halogenation, nitration, and sulfonation.

#### **Oxidation of Phenols: Quinones**

Phenols don't undergo oxidation in the same way that alcohols do because they don't have a hydrogen atom on the hydroxyl-bearing carbon. Instead, oxidation of a phenol with sodium dichromate yields a cyclohexa-2,5-diene-1,4-dione, or quinone.



## Inter and intra hydrogen bond

## Aldehyde and ketone

Aldehyde: 
$$R^1$$
 and/or  $R^2 = H$ 
 $C = 0$ 
 $Ketone$ :  $R^1$  and  $R^2 = alkyl$  or aryl

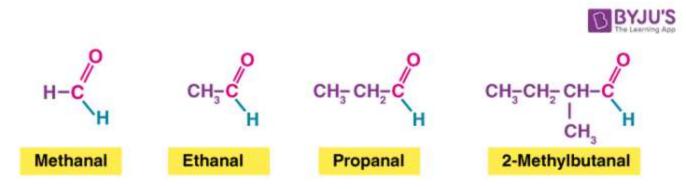
#### Table of contents

- What Are Aldehydes?
- What Are Ketones?
- Occurrence Of Ketones And Aldehydes
- Preparation Of Ketones And Aldehydes
- Uses Of Aldehydes And Ketones
- FAQs

## What are Aldehydes?

In aldehydes, the carbonyl group has one hydrogen atom attached to it together with either a 2nd hydrogen atom or a hydrogen group which may be an alkyl group or one containing a benzene ring.

#### **Example:**

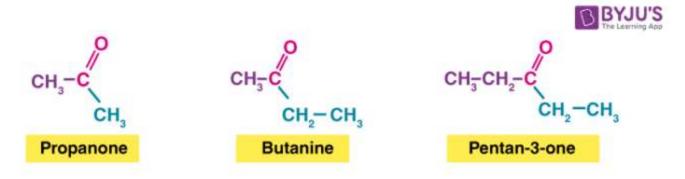


One can notice that all these have the exact same end to the molecule. The only difference is the complexity of the other attached group.

#### What are Ketones?

In ketones, the carbonyl group has 2 hydrocarbon groups attached to it. These can be either the ones containing benzene rings or alkyl groups. Ketone does not have a hydrogen atom attached to the carbonyl group.

#### **Example:**



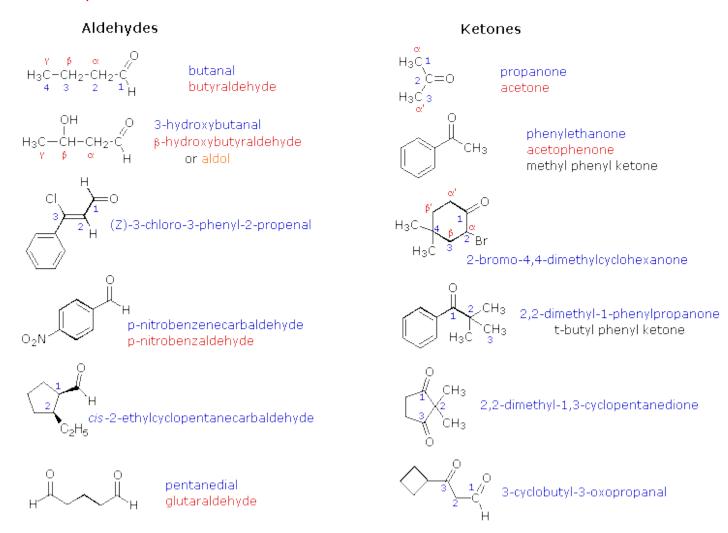
Propane is generally written as CH3COCH3. In pentanone, the carbonyl group could be in the middle of the chain or next to the end – giving either pentan-3-one or pentan-2-one.

## 1. Nomenclature of Aldehydes and Ketones

Aldehydes and ketones are organic compounds which incorporate a **carbonyl functional group**, C=O. The carbon atom of this group has two remaining bonds that may be occupied by hydrogen or alkyl or aryl substituents. If at least one of these substituents is hydrogen, the compound is an **aldehyde**. If neither is hydrogen, the compound is a **ketone**.

The IUPAC system of nomenclature assigns a characteristic suffix to these classes, **al** to aldehydes and **one** to ketones. For example, H<sub>2</sub>C=O is methanal, more commonly called formaldehyde. Since an aldehyde carbonyl group must always lie at the end of a carbon chain, it is by default position #1, and therefore defines the numbering direction. A ketone carbonyl function may be located anywhere within a chain or ring, and its position is given by a locator number. Chain numbering normally starts from the end nearest the carbonyl group. In cyclic ketones the carbonyl group is assigned position #1, and this number is not cited in

the name, unless more than one carbonyl group is present. If you are uncertain about the IUPAC rules for nomenclature you should <u>review</u> them now. Examples of IUPAC names are provided (in blue) in the following diagram. Common names are in red, and derived names in black. In common names carbon atoms near the carbonyl group are often designated by Greek letters. The atom adjacent to the function is alpha, the next removed is beta and so on. Since ketones have two sets of neighboring atoms, one set is labeled  $\alpha$ ,  $\beta$  etc., and the other  $\alpha'$ ,  $\beta'$  etc.



Very simple ketones, such as propanone and phenylethanone (first two examples in the right column), do not require a locator number, since there is only one possible site for a ketone carbonyl function. Likewise, locator numbers are omitted for the simple dialdehyde at the bottom left, since aldehyde functions must occupy the ends of carbon chains. The hydroxy butanal and propenal examples (2nd & 3rd from the top, left column) and the oxopropanal example (bottom right) illustrate the nomenclature priority of IUPAC suffixes. In all cases the aldehyde

function has a higher status than an alcohol, alkene or ketone and provides the nomenclature suffix. The other functional groups are treated as substituents. Because ketones are just below aldehydes in nomenclature suffix priority, the "oxo" substituent terminology is seldom needed.

Simple substituents incorporating a carbonyl group are often encountered. The generic name for such groups is **acyl**. Three examples of acyl groups having specific names are shown below.

## 2. Occurrence of Aldehydes and Ketones

#### **Natural Products**

## Occurrence of Ketones and Aldehydes

Combined with other functional group aldehydes and ketone are widespread in nature. Compounds such as cinnamaldehyde (cinnamon bark), vanillin (vanilla bean), Citra (lemongrass), helminthosporal (a fungal toxin), carvone (spearmint and caraway), and camphor (camphor trees) are found chiefly in microorganisms or plants. Whereas, compounds such as muscone (musk deer), testosterone (male sex hormone), and progesterone (female sex hormone), cortisone (adrenal hormone) have animal and human origin.

## 3. Synthetic Preparation of Aldehydes and Ketones

Aldehydes and ketones are obtained as products from many reactions discussed in previous sections of this text. The following diagram summarizes the most important of these. To review the previous discussion of any of these reaction classes simply click on the number (1 to 5) or descriptive heading for the group.

## Synthetic Preparation of Aldehydes and Ketones

Aldehydes and ketones are obtained as products from many reactions discussed in previous sections of this text. The following diagram summarizes the most important of these. To review the previous discussion of any of these reaction classes simply click on the number (1 to 5) or descriptive heading for the group.

#### 1. Oxidation of 1° & 2° Alcohols

$$C_{5}H_{11}-C \equiv C-CH_{2}-OH \xrightarrow{PCC \text{ in } CH_{2}Cl_{2}} C_{5}H_{11}-C \equiv C-C \xrightarrow{O} H$$

$$OH \xrightarrow{OH} \xrightarrow{Jones' \text{ reag. + acetone}} CrO_{3} \text{ in aq, } H_{2}SO_{4})$$

#### 2. Friedel-Crafts Acylation

#### 3. Hydration of Alkynes

#### 4. Glycol Cleavage

#### 5. Ozonolysis of Alkenes

$$H_3C$$
  $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

With the exception of Friedel-Crafts acylation, these methods do not increase the size or complexity of molecules. In the following sections of this chapter we shall find that one of the most useful characteristics of aldehydes and ketones is their reactivity toward carbon nucleophiles, and the resulting elaboration of molecular structure that results. In short, aldehydes and ketones are important intermediates for the assembly or synthesis of complex organic molecules.

## 4. Properties of Aldehydes and Ketones

A comparison of the properties and reactivity of aldehydes and ketones with those of the alkenes is warranted, since both have a double bond functional group. Because of the greater electronegativity of oxygen, the carbonyl group is polar, and aldehydes and ketones have larger molecular dipole moments (D) than do alkenes. The resonance structures on the right illustrate this polarity, and the relative dipole moments of formaldehyde, other aldehydes and ketones confirm the stabilizing influence that alkyl substituents have on carbocations (the larger the dipole moment the greater the polar character of the carbonyl group). We expect, therefore, that aldehydes and ketones will have higher boiling points than similar sized alkenes. Furthermore, the presence of oxygen with its non-bonding electron pairs makes aldehydes and ketones hydrogen-bond acceptors, and should increase their water solubility relative to hydrocarbons. Specific examples of these relationships are provided in the following table.

For a review of the intermolecular forces that influence boiling points and water solubility Click Here.

Compound	Mol. Wt.	<b>Boiling Point</b>	Water Solubility
$(CH_3)_2C=CH_2$	56	-7.0 ℃	0.04 g/100
$(CH_3)_2C=O$	58	56.5 °C	infinite
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	70	30.0 °C	0.03 g/100
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH=O	72	76.0 °C	7 g/100
CH <sub>2</sub>	96	103.0 °C	insoluble
O <sup>°</sup>	98	155.6 °C	5 g/100

The polarity of the carbonyl group also has a profound effect on its chemical reactivity, compared with the non-polar double bonds of alkenes. Thus, reversible addition of water to the carbonyl function is fast, whereas water addition to alkenes is immeasurably slow in the absence of a strong acid catalyst. Curiously, relative bond energies influence the thermodynamics of such

addition reactions in the opposite sense.

The C=C of alkenes has an average bond energy of 146 kcal/mole. Since a C–C  $\sigma$ -bond has a bond energy of 83 kcal/mole, the  $\pi$ -bond energy may be estimated at 63 kcal/mole (i.e. less than the energy of the sigma bond). The C=O bond energy of a carbonyl group, on the other hand, varies with its location, as follows:

H<sub>2</sub>C=O 170 kcal/mole RCH=O 175 kcal/mole R<sub>2</sub>C=O 180 kcal/mole

The C–O  $\sigma$ -bond is found to have an average bond energy of 86 kcal/mole. Consequently, with the exception of formaldehyde, the carbonyl function of aldehydes and ketones has a  $\pi$ -bond energy greater than that of the sigma-bond, in contrast to the pi-sigma relationship in C=C. This suggests that addition reactions to carbonyl groups should be thermodynamically disfavored, as is the case for the addition of water. All of this is summarized in the following diagram ( $\Delta$ H $^{\circ}$  values are for the addition reaction).

Although the addition of water to an alkene is exothermic and gives a stable product (an alcohol), the uncatalyzed reaction is extremely slow due to a high activation energy . The reverse reaction (dehydration of an alcohol) is even slower, and because of the kinetic barrier, both reactions are practical only in the presence of a strong acid. The microscopically reversible mechanism for both reactions was described earlier.

In contrast, both the endothermic addition of water to a carbonyl function, and the exothermic elimination of water from the resulting <u>geminal</u>-diol are fast. The inherent polarity of the carbonyl group, together with its increased basicity (compared with alkenes), lowers the transition state energy for both reactions, with a resulting increase in rate. Acids and bases catalyze both the addition and elimination of water. Proof that rapid and reversible addition of water to carbonyl

compounds occurs is provided by experiments using isotopically labeled water. If a carbonyl reactant composed of <sup>16</sup>O (colored blue above) is treated with water incorporating the <sup>18</sup>O isotope (colored red above), a rapid exchange of the oxygen isotope occurs. This can only be explained by the addition-elimination mechanism shown here.

#### Uses of Aldehydes and Ketones

<u>Formaldehyde</u> is the simplest aldehyde whereas acetone is the smallest ketone. There are a number of aldehydes and ketones which find application due to their chemical properties. A few uses of Aldehydes and Ketones are listed below.

#### 1. Uses of Aldehydes

- Formaldehyde is a gas. With 40% solution in water, it forms Formalin which is used in preserving biological specimens.
- Formaldehyde is used in embalming, tanning, preparing glues and polymeric products, as germicides, insecticides, and fungicides for plants. It is also used in drug testing and photography.
- When reacted with phenol, formaldehyde forms Bakelite, which is used in plastics, coatings, and adhesives.
- Acetaldehyde is largely used for the production of acetic acid and pyridine derivatives.
- Benzaldehyde is used in perfumes, cosmetic products, and dyes. It is added to provide almond flavour to food products and also used as a bee repellent.

#### 2. Uses of Ketones

- The most common ketone is acetone which is an excellent solvent for a number of plastics and synthetic fibers.
- In the household, acetone is used as a nail paint remover and paint thinner.
- In medicine, it is used in chemical peeling and for acne treatments.
- Methyl ethyl ketone (<u>MEK</u>), chemically butanone, is a common solvent. It is used in the production of textiles, varnishes, plastics, paint remover, paraffin wax, etc.
- MEK is also used as a welding agent for plastics due to its dissolving properties.

• Cyclohexanone is another important ketone which is primarily used in the production of nylon.

#### Frequently Asked Questions

How are Aldehydes and Ketones Different?

The carbonyl carbon of an aldehyde has a hydrogen atom attached to it whereas that of a ketone is attached to two alkyl or aryl groups. The C-H bond in aldehydes makes them easily oxidizable (they are strong reducing agents).

Why are Aldehydes more Reactive towards Nucleophilic Substitutions than Ketones?

The two alkyl/aryl groups in ketones offer steric hindrance during substitution reactions. Since the hydrogen atom is relatively small, it barely offers any steric hindrance. This is the primary reason why aldehydes are more susceptible to Nucleophilic substitutions. Also, the partially positive charge on the carbonyl carbon is stabilized by the two R groups in ketones.

Why are the Boiling Points of Ketones Higher than those of Aldehydes?

The presence of two electron-donating R-groups in ketones makes them more polar than aldehydes. The dipole moments that arise from this polarity account for the higher boiling points of ketones.

## Reaction of carbonyl compounds (aldehyde and ketone)

The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions because they form H-bonds with water.

$$\begin{array}{c}
R \\
C = O \\
R'
\end{array}$$

$$\begin{array}{c}
\delta_{+} \\
O \\
H
\end{array}$$

$$\begin{array}{c}
\delta_{-} \\
O \\
H
\end{array}$$

$$\begin{array}{c}
\delta_{+} \\
O \\
R'
\end{array}$$

Solubility of aldehydes and ketones decreases rapidly on increasing the length of the alkyl group.

The lower aldehydes have a sharp pungent odour. As molecular mass increases, the odour becomes less pungent and more fragrant.

#### **Chemical Reactions of Aldehydes and Ketones:**

**1. Nucleophilic addition Reactions:** On the attack of a nucleophile on the carbonyl carbon, the hybridization of C changes from sp<sup>2</sup> to sp<sup>3</sup>.

Trigonal planar (C:sp<sup>2</sup> hybridized)

Tetrahedral intermediate

Addition product (C: sp<sup>3</sup> hybridized)

<u>Aldehydes are more susceptible to Nucleophilic addition reactions than ketones</u> due to steric and electronic factors.

The reactivity of aldehydes and ketones towards Nucleophilic addition reactions is

$$H = 0$$
  $CH_3 = 0$   $CH_3 = 0$   $CH_5 = 0$   $CH_5 = 0$   $C_2H_5 = 0$   $C_2H_5 = 0$   $C_2H_5 = 0$ 

The polarity of the carbonyl group is reduced in benzaldehyde due to resonance and hence it is less reactive than propanal

Addition of Grignard's reagent: They give 1°, 2°, 3° alcohols.

(a) H 
$$C = O + R Mg X \rightarrow \begin{bmatrix} H \\ R - C - O Mg X \end{bmatrix} \xrightarrow{H_3O^+} R - C H_2OH$$
(Formaldehyde)  $H$ 

(b) 
$$CH_3$$
 $C=O+R-MgX \rightarrow \begin{bmatrix} H \\ CH_3 \\ H \end{bmatrix}$ 
 $C-OMgX$ 

$$\xrightarrow{H_3O^+} CH_3 - CH - OH$$
(2° alcohol)

(c) 
$$CH_3$$
  $C=O+CH_3MgBr \rightarrow [(CH_3)_3COMgX] \xrightarrow{H_3O^+} (CH_3)_3C (OH)$ 
(Acetone) (3° alcohol)

4. Addition of ammonia and its derivatives [Addition-Elimination].

 $Z = alkyl, aryl, OH, NH_2, C_6H_5NH, NHCONH_2 etc.$ 

Z	Reagent name	Carbonyl derivative	Product name
—н	Ammonia	C = NH	Imine
−R	Amine	C = NR	Substituted imine (Schiff's base)
—ОН	Hydroxyl- amine	> C = N—OH	Oxime
→NH <sub>2</sub>	Hydrazine	$> C = N-NH_2$	'Hydrazone

Z	Reagent name	Carbonyl derivative	Product name
-HN-	Phenyl- hydrazine	> C = N—	Phyenyl-
		NH—	hydrazone
		C = N—NH	2,4-Dinitro- phenyl-
-HN	NO <sub>2</sub> 2, 4-Dinitro- phenyl- hydrazine (2, 4-DNP)*	O <sub>2</sub> N NO <sub>2</sub>	hydrazone
O     -NH-C-NH <sub>2</sub>	Semicarbazide	O II >C = N-NH-C-NH <sub>2</sub>	Semi- carbozone

[Table: Some N-Substituted Derivatives of aldehydes and ketones

$$C = N-Z$$

2, 4-DNP-derivatives are yellow, orange or red solids, useful for characterization of aldehydes and ketones.

#### 2. Reduction:

**a.** Reduction to alcohols: Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride (NaBH<sub>4</sub>) or lithium aluminium hydride (LiAlH<sub>4</sub>) as well as by catalytic hydrogenation.

R—CHO 
$$\xrightarrow{\text{NaBH}_4}$$
 R—CH<sub>2</sub>OH

aldehyde (primary alcohol)

R COR'  $\xrightarrow{\text{NaBH}_4}$  R CH—R' (Secondary alcohol)

OH

**b.** Reduction to hydrocarbons: The carbonyl group of aldehydes and ketones is reduced to CH2 group on treatment with zinc-amalgam and concentrated hydrochloric acid [Clemmensen reduction) or with hydrazine followed by heating with sodium or potassium hydroxide in a high boiling solvent such as ethylene glycol (Wolff-Kishner reduction).

$$C = O \xrightarrow{Zn - Hg} CH_2 + H_2O \text{ (Clemmensen reduction)}$$

$$C = O \xrightarrow{NH_2NH_2} C = NNH_2 \xrightarrow{KOH/\text{ethylene glycol} \atop \text{heat}} CH_2 + N_2$$
(Wolf-Kishner reduction)

3. Oxidation: Aldehydes differ from ketones in their oxidation reactions,

$$R-CHO \xrightarrow{[O]} RCOOH$$
 aldehyde 
$$Carboxylic acid$$
 
$$R-CH_2 \xrightarrow{C} CH_2 - R' \xrightarrow{[O]} RCOOH + R'CH_2COOH \text{ (by clevage of $C_1$-$C_2 bond)}$$
 
$$RCH_2COOH + R'COOH \text{ (by cleavage of $C_2$-$C_3 bond)}$$

Due to the easy oxidation of aldehydes as compared to ketones, they can be distinguished from the following two steps:

a. Tollen's test:

R—CHO + 2  $[Ag(NH_3)_2]^+$  + 3 OH<sup>-</sup>  $\rightarrow$  RCOO<sup>-</sup> + Ag (s) + 2  $H_2O$  + 4 NH<sub>3</sub> On warming an aldehyde with freshly prepared ammonical AgNO<sub>3</sub> solution (Tollen's reagent), a bright silver mirror is produced.

b. Fehling's Test: On heating an aldehyde with Fehling reagent, a reddish-brown precipitate is obtained.

 $RCHO + 2 Cu^{2+} + 5 OH^{-} \rightarrow RCOO^{-} + Cu_{2}O + 3 H_{2}O.$  (red-brown ppt.)

→ Oxidation of methyl ketones by haloform reaction: All those carboxyl compounds containing the – COCH<sub>3</sub> group respond to this test.

$$R \longrightarrow C \longrightarrow CH_3 \longrightarrow R COONa + CHX_3[X = Cl, Br, I]$$

$$CH_3CH = C \longrightarrow COCH_3 \longrightarrow CH_3CH = C \longrightarrow COONa + CHCl_3$$

$$CH_3 \longrightarrow CH_3$$

$$CH_3 \longrightarrow CH_3$$

$$CH_3 \longrightarrow CH_3$$

If NaOI is used, yellow ppt. of  $CHI_3$  is formed which is used to detect the  $CH_3C = O$  group.

4. Reactions due to  $\alpha$ -hydrogen atom:  $\alpha$ -hydrogens in aldehydes and ketones are acidic in nature due to the strong electron-withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.

4.1. Aldol Condensation: Aldehydes and ketones having at least one  $\alpha$ -hydrogen undergo Aldol Condensation in the presence of dil. alkali to form  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$ -hydroxy ketones [ketol] respectively.

$$2 \, \text{CH}_{3}\text{--CHO} \stackrel{\text{dil. NaOH}}{\longleftrightarrow} \text{CH}_{3}\text{--CH---CH}_{2}\text{CHO}$$

$$0 \, \text{OH}$$

$$(\text{Aldol})$$

$$\frac{\Delta}{-\text{H}_{2}\text{O}} \, \text{CH}_{3}\text{--CH----CHCHO}$$

$$(\text{But-2-enal})$$

$$C \, \text{H}_{3}$$

$$2 \, \text{CH}_{3}\text{COCH}_{3} \stackrel{\text{Ba}(\text{OH})_{2}}{\longleftrightarrow} \text{CH}_{3} \stackrel{\text{I}}{-\text{C}}\text{--CH}_{2}\text{COCH}_{3}$$

$$0 \, \text{H}$$

$$(4\text{--Hydroxy-4-methyl pantan-2-one}) \, \text{(Ketol)}$$

$$C \, \text{H}_{3}$$

$$\frac{\Delta}{-\text{H}_{2}\text{O}} \stackrel{\text{C}}{\text{CH}_{3}} - \stackrel{\text{C}}{\text{C}} = \text{CHCOCH}_{3}$$

$$4\text{--Methyl pent-3-en-2-one}$$

4.2. Cross Aldol Condensation: When aldol condensation is carried out between two different aldehydes and/or ketones, it is called Cross aldol condensation.

$$\begin{array}{c} \text{CH}_3\text{CHO} \\ + \\ \text{CH}_3\text{CH}_2\text{CHO} \end{array} \xrightarrow{1.\text{NaOH}} \begin{array}{c} \text{CH}_3\text{—CH} = \text{CH}\text{—CHO} \ + \\ \text{But-2-enal} \end{array}$$

$$\begin{array}{c} \text{CH}_3\text{—CH}_2\text{—CH} = \text{C}\text{—CHO} \ + \\ \text{CH}_3 \end{array}$$

$$\begin{array}{c} \text{(2-Methylpent-2-enal)} \end{array}$$

$$\begin{array}{c} \text{CH}_3\text{—CH} = \text{C}\text{—CHO} + \\ \text{CH}_3 \end{array}$$

$$\begin{array}{c} \text{CH}_3\text{—CH}_2\text{—CHO} + \\ \text{CH}_3 \end{array}$$

$$\begin{array}{c} \text{2-Methyl but-2-enal} \end{array}$$

$$\begin{array}{c} \text{CH}_3\text{—CH}_2\text{—CH} = \text{CH}\text{—CHO} \end{array}$$

Ketones can also be used as one component in the cross aldol condensation.

O  

$$CHO *$$
 $CHO *$ 
 $OHO *$ 
 $O$ 

## 5. Other Reactions:

5.1. Cannizzaro Reactions: Aldehydes that do not have an a- hydrogen atom, undergo self oxidation-reduction called Disproportionation reactions on treatment with concentrated alkali.

2 HCHO + NaOH (conc.) → CH<sub>3</sub>OH + HCOONa Methanol Sod. formate

2 
$$\bigcirc$$
 CHO + Conc. NaOH  $\rightarrow$   $\bigcirc$  CH<sub>2</sub>OH (Benzyl alcohol)

(Sodium benzoate)

## **Amines**

## Introduction to Amines – Compounds Containing Nitrogen

Amines are one of the most important classes of organic compounds which can be derived when we replace one or more hydrogen atoms of ammonia molecules with an alkyl group.

#### Table of contents

- What are Amines?
- Recommended video for ammine
- Structure of Amine
- Types of Amines
- Preparation of Amines
- Basicity of Amines
- Uses of Amines
- FAQs

#### What are Amines?

An amine is generally a functional group with a nitrogen atom having a lone pair. Amines resemble ammonia structurally where nitrogen can bond up to 3 hydrogen atoms. It is also characterized by various properties that are based on carbon connectivity.

Compounds of nitrogen connected to a carbonyl group are called as amides, they have a structure R–CO–NR'R" and vary in properties with amines.

Amines are organic compounds that contain nitrogen atoms with a lone pair. Basically, they are derived from ammonia (NH<sub>3</sub>) in which one or more hydrogen atom is replaced by an alkyl or aryl group, and so they are known as alkyl amines and aryl amines respectively.

## **Amine Structure**

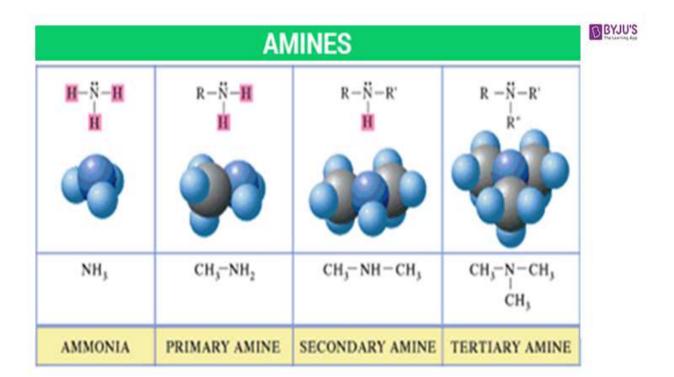
Nitrogen has 5 valence electrons and so is trivalent with a lone pair. As per <u>VSEPR theory</u>, nitrogen present in amines is sp3 hybridized and due to the presence of lone pair, it is pyramidal instead of tetrahedral shape which is a general structure for most sp3 hybridized molecules. Each of the three sp3 hybridized orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the configuration of amines. Due to the presence of lone pair, the C-N-H angle in amines is less than 109 degrees which is a characteristic angle of tetrahedral geometry. The angle of amines is near about 107 degrees.

## Occurrence of Amines

Naturally, amines occur in proteins, vitamins, hormones, etc. and they are also prepared synthetically to make polymers, drugs, and dyes.

## Types of Amines

On the basis of how the hydrogen atoms are replaced by an ammonia molecule, amines can be divided into 4 types.



## 1. Primary Amines

when one of the hydrogen atoms of the ammonia molecule is replaced by an alkyl or aryl group.

Eg: Methylamine CH<sub>3</sub>NH<sub>2</sub>, Aniline C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>

## 2. Secondary Amines

Two organic substituents replace the hydrogen atoms of the ammonia molecule forming an amine.

Eg: Dimethylamine (CH<sub>3</sub>)2NH, Diphenylamine (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH

## 3. Tertiary Amines

When all 3 of the hydrogen atoms are replaced by an organic substituent, it could be an aryl or aromatic group.

Eg: Trimethylamine N(CH<sub>3</sub>)<sub>3</sub>, Ethylenediaminetetraacetic acid (EDTA)

## 4. Cyclic Amines

These are secondary or tertiary amines in an aromatic ring structure. Eg: Piperidine (CH<sub>2</sub>)<sub>5</sub>NH, Aziridines C<sub>2</sub>H<sub>5</sub>N

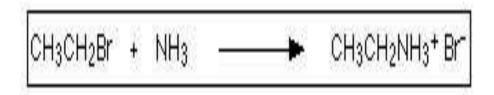
## **Preparation of Amines**

Some processes for preparing primary amines are mentioned below.

**Preparation of Primary Amines** 

## 1. Making of amines from halogenoalkanes

This process will be carried out in a sealed tube. Here haloalkanes will be heated with the concentrated solution of ammonia in ethanol. The mixture cannot be heated under the reflux as ammonia would move out in the form of gas from a container.



Now coming to the preparation of primary amine from halogenoalkane the reaction takes place in two stages. Salt will be formed at the first stage. Here ethyl ammonium bromide is the salt. It is similar to ammonium bromide except for the fact that one of the hydrogens in the ammonium atom is replaced by an ethyl group.

A reverse reaction can occur between ammonia and the salt. It is illustrated in the above reaction.

## 2. Reduction of nitriles

We can get primary amines when nitriles are reduced with lithium aluminium hydride. This method is mainly used for the preparation of amines which contain one carbon atom more than the starting amine.

## 3. Gabriel phthalimide synthesis

We can get primary amines easily by Gabriel synthesis. In this process, on the treatment of phthalimide with ethanolic potassium hydroxide, we get potassium salts of phthalimide. When this is further heated with alkyl halide followed by alkaline hydrolysis then primary amine is produced. We cannot prepare aromatic primary amines because aryl halides do not undergo nucleophilic substitution with the anion which is formed by phthalimide.

$$\begin{array}{c|c}
O \\
C \\
N-R
\end{array}$$

$$\begin{array}{c|c}
N = R
\end{array}$$

$$\begin{array}{c|c}
N = R
\end{array}$$

$$\begin{array}{c|c}
O = O \cdot Na^{+} \\
C = O \cdot Na^{+}
\end{array}$$

$$\begin{array}{c|c}
C = O \cdot Na^{+}
\end{array}$$

$$\begin{array}{c|c}
C = O \cdot Na^{+}
\end{array}$$

$$\begin{array}{c|c}
(1^{\circ} \text{ amine})
\end{array}$$

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## **Basicity of Amines**

Similar to ammonia, primary & secondary amines have protic hydrogens and thus they showcase a degree of acidity. Whereas tertiary amines have no protic hydrogen and thus do not possess a degree of acidity.

 $pK_a$  value for primary & secondary amines is about 38, which makes them a real weak acid. Whereas if we take the  $pK_b$ , it is about 4. This makes the amines much more basic than acidic. Thus, an aqueous solution of an amine is strongly alkaline.

## Uses of Amines

Amines have a widespread application in our daily lives. Some uses of amines are listed below:

- It is used in water purification, medicine manufacturing and development of insecticides and pesticides.
- It is involved in the production of amino acids which is the building block of proteins in living beings. Many varieties of vitamins are also made by amines.

- Serotonin is an important amine that functions as one of the primary neurotransmitters. It controls the feelings of hunger and is critical for the speed with which the brain operates in general.
- Pain-relieving medicines such as Morphine and Demerol which are also known as analgesics are made from amines.

From the above discussion, students would have gained some understanding of the basic concepts of amines but to know more about amines, chemical and <u>physical properties of amines</u>, register with BYJU'S.

# Frequently Asked Questions – FAQS

What is the order of basicity of Amines?

Ans: Due to the presence of lone pair electrons on the nitrogen atom of amine, it has the ability to donate a pair of electrons to form a base. The basicity of amines depends upon following factors, stectric factors, Electronic factor and solvent factor,

In the gaseous state the order of basicity of amine, when R=Me,  $3^0 > 2^0 > 1^0$ .

In the aqueous solution the order of basicity of amine, when R=Me,  $2^0 > 1^0 > 3^0$ 

In the aqueous solution the order of basicity of amine, when R= Et,  $2^0 > 3^0 > 1^0$ 

What is the difference between amine and amide?

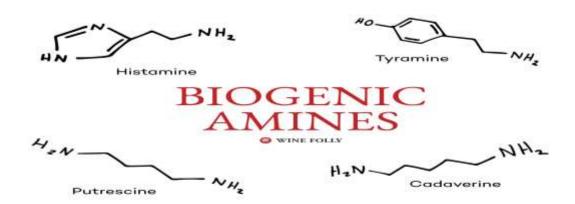
Ans. Amines and amides are two different types of organic compounds. The difference between amine and amide is the presence of a carbonyl group in their structure; amines have no carbonyl groups attached to the nitrogen atom; the formula of amine is RNH<sub>2</sub> whereas amides have a carbonyl group attached to a nitrogen atom; the formula of amide is R-CO-NH<sub>2</sub>.

## What are the uses of amines?

Amines are used as water purification, medicine manufacturing and development of insecticides and pesticides. It is also involved in the production of amino acids which is the building block of proteins .

# Are amines harmful?

Generally most of the aliphatic amine found in the food, are involved in the production of amino acids, which is the building block of proteins. So these are not highly toxic in nature, however some aromatic amines cause irritants on the skin and may be toxic in nature.



## **Reactions of Amines**

Due to the unshared electron pair, amines can act as both bases and nucleophiles.

# Reaction with acids

When reacted with acids, amines donate electrons to form ammonium salts.

## Reaction with acid halides

Acid halides react with amines to form substituted amides.

$$CH_3 - CH_2 - C = O \xrightarrow{1. CH_3NH_2} CH_3 - CH_2 - C - NH - CH_3$$
propanoyl chloride
$$CH_3 - CH_2 - C = O \xrightarrow{1. CH_3NH_2} CH_3 - CH_2 - C - NH - CH_3$$
N-methylpropanamide

Aldehydes and ketones react with primary amines to give a reaction product (a carbinolamine) that dehydrates to yield aldimines and ketimines (Schiff bases).

$$\begin{array}{c} O \\ || \\ CH_3CH_2NH_2 + CH_3CCH_3 \end{array} \longrightarrow \begin{array}{c} CH_3CH_2N - C - CH_3 \\ || \\ || \\ CH_3CH_2N - C - CH_3 \\ || \\ CH_3 \end{array}$$

If you react secondary amines with aldehydes or ketones, enamines form.

# Reaction with sulfonyl chlorides

Amines react with sulfonyl chlorides to produce sulfonamides. A typical example is the reaction of benzene sulfonyl chloride with aniline.

N-phenylbenzenesulfonamide

# Oxidation

Although you can oxidize all amines, only tertiary amines give easily isolated products. The oxidation of a tertiary amine leads to the formation of an amine oxide.

Arylamines tend to be easily oxidized, with oxidation occurring on the amine group as well as in the ring.

## Reaction with nitrous acid

Nitrous acid is unstable and must be prepared in the reaction solution by mixing sodium nitrite with acid.

Primary amines react with nitrous acid to yield a diazonium salt, which is highly unstable and degradates into a carbocation that is capable of reaction with any nucleophile in solution. Therefore, reacting primary amines with nitrous acid leads to a mixture of alcohol, alkenes, and alkyl halides.

$$CH_3CH_2NH_2$$
  $\xrightarrow{NaNO_2}$   $CH_3CH_2 - \stackrel{+}{N} \equiv NCI^-$  ethanamine  $0^\circ$  ethyl diazonium chloride (ethylamine) (unstable)

$$CH_{3}CH_{2}\overset{+}{N} \equiv NCl^{-} \longrightarrow \begin{bmatrix} CH_{3}CH_{2}^{+} \end{bmatrix} + N_{2} \overset{HOH}{\longrightarrow} CH_{3}CH_{2}Cl \\ \longrightarrow CH_{2} = CH_{2} + H^{+}$$

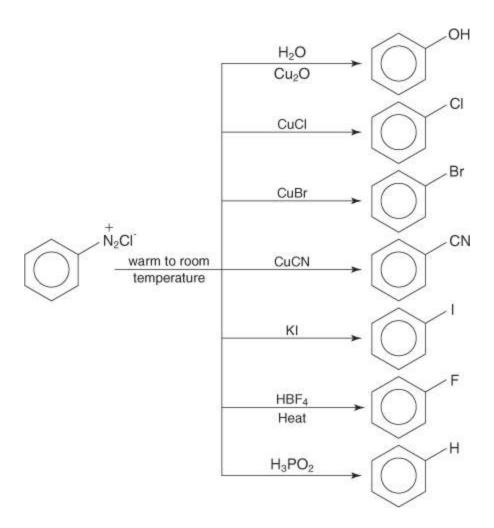
Primary aromatic amines form stable diazonium salts at zero degrees.

Secondary aliphatic and aromatic amines form nitrosoamine with nitrous acid.

Tertiary amines react with nitrous acid to form N-nitroso ammonium compounds.

# Reactions of aromatic diazonium salts

Diazonium salts of aromatic amines are very useful as intermediates to other compounds. Because aromatic diazonium salts are only stable at very low temperatures (zero degrees and below), warming these salts initiates decomposition into highly reactive cations. These cations can react with any anion present in solution to form a variety of compounds. Figure 1 illustrates the diversity of the reactions.



# What is Carboxylic Acid?

A Carboxylic Acid is an organic compound containing a carboxyl functional group. They occur widely in nature and are also synthetically manufactured by humans. Upon deprotonation, carboxylic acids yield a *carboxylate anion with the general formula R-COO*<sup>-</sup>, which can form a variety of useful salts such as soaps.

The carboxylic acids are the *most important functional group that present C=O*. This type of organic compounds can be obtained by different routes, some carboxylic acids, such as <u>citric acid</u>, lactic acid or fumaric acid are produced from by fermentation most of these type of carboxylic acids are applied in the food industry.

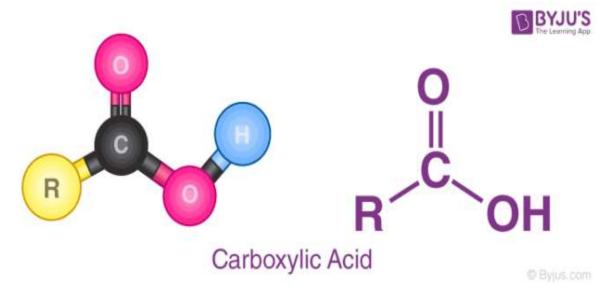
# Carboxylic Acid Structure

The *general formula of a carboxylic acid is R-COOH*, were COOH refers to the carboxyl group, and R refers to the rest of the molecule to which this group is attached. In this carboxyl group, there exists a carbon which shares a double bond with an oxygen atom and a single bond with a hydroxyl group.

A carboxylic acid's general formula is R-COOH, where COOH denotes the carboxyl group and R denotes the remainder of the molecule to which this group is linked. There is a carbon in this carboxyl group that has a double connection with an oxygen atom and a single bond with a hydroxyl group.

The first four carboxylic acids derived from alkanes are methanoic acid (HCOOH), ethanoic acid (CH<sub>3</sub>COOH), propanoic acid (C<sub>2</sub>H<sub>5</sub>COOH) and butanoic acid (C<sub>3</sub>H<sub>7</sub>COOH).

The general structure of a carboxylic acid is illustrated below.



From the illustration provided above, it can be observed that a carboxylic acid contains a hydroxyl group attached to a carbonyl carbon. Due to the electronegativity of the oxygen atom, this functional group can undergo ionization and discharge a proton.

The carboxylate ion, produced from the removal of a <u>proton</u> from the carboxyl group, is stabilized by the presence of two oxygen atoms (through which the negative charge can move). Some common examples of carboxylic acids include acetic acid (a component of vinegar) and Formic acid.

# Nomenclature of Carboxylic Acids

Generally, these organic compounds are referred to by their trivial names, which contain the suffix "-ic acid". An example of a *trivial name* for a carboxylic acid is acetic acid  $(CH_3COOH)$ . In the IUPAC nomenclature of these compounds, the suffix "-oic acid" is assigned.

The guidelines that must be followed in the IUPAC nomenclature of carboxylic acids are listed below.

• The suffix "e" in the name of the corresponding alkane is replaced with "oic acid".

- When the aliphatic chain contains only one carboxyl group, the carboxylic carbon is always numbered one. For example, CH<sub>3</sub>COOH is named as ethanoic acid.
- When the aliphatic chain contains more than one carboxyl group, the total number of carbon atoms is counted and the number of carboxyl groups is represented by Greek numeral prefixes such as "di-", "tri-", etc.
- A carboxylic acid is named by adding these prefixes and suffixes to the parent alkyl chain. Arabic numerals are used for indicating the positions of the carboxyl group.
- The name "carboxylic acid" or "carboxy" can also be assigned for a carboxyl substituent on a carbon chain. An example of such nomenclature is the name 2-carboxyfuran for the compound 2-Furoic acid.

## Carboxylic Acid Examples

Some examples describing the nomenclature of carboxylic acids as per IUPAC guidelines are provided below.

Trivial Name and Formula	IUPAC Name of the Carboxylic Acid
Formic acid, H-COOH	Methanoic acid
Crotonic acid, CH <sub>3</sub> CH=CH-COOH	But-2-enoic acid
Carbonic acid, OH-COOH	Carbonic acid
Butyric acid, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	Butanoic acid

# Properties of Carboxylic Acids

Most of the properties of carboxylic acids are a result of the presence of the <u>carboxyl group</u>. Some physical and chemical properties of these compounds are discussed in this subsection.

## 1. Physical Properties of Carboxylic Acids

- Carboxylic acid molecules are polar due to the presence of two electronegative oxygen atoms.
- They also participate in hydrogen bonding due to the presence of the carbonyl group (C=O) and the hydroxyl group.
- When placed in nonpolar solvents, these compounds form *dimers* via hydrogen bonding between the hydroxyl group of one carboxylic acid and the carbonyl group of the other.

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- The solubility of compounds containing the carboxyl functional group in water depends on the size of the compound. The smaller the compound (the shorter the R group), the higher the solubility.
- The boiling point of a carboxylic acid is generally higher than that of water.
- These compounds have the ability to donate protons and are therefore *Bronsted-Lowry acids*.
- They generally have a strong sour smell. However, their esters have pleasant odours and are therefore used in perfumes.

# 2. Chemical Properties of Carboxylic Acids

• The a-carbon belonging to a carboxylic acid can easily be halogenated via the <u>Hell-Volhard-Zelinsky reaction</u>.

- These compounds can be converted into amines using the Schmidt reaction.
- A carboxylic acid can be reduced to an alcohol by treating it with hydrogen to cause a hydrogenation reaction.
- Upon reaction with alcohols, these compounds yield esters.

# Uses of Carboxylic Acids

- Fatty acids that are essential to human beings are made up of carboxylic acids. Examples include omega-6 and omega-3 fatty acids.
- Higher fatty acids are also used in the *manufacture of soaps*.
- The production of soft drinks and many other food products involve the use of many carboxylic acids.
- The manufacture of rubber involves the use of acetic acid as a *coagulant*.
- Hexanedioic acid is used in the *manufacture of nylon-6,6*.
- Carboxylic acids have numerous applications in the rubber, textile, and leather industries.
- Ethylenediaminetetraacetic acid is a widely used *chelating agent*.
- The synthesis of many drugs involves the use of these compounds. Therefore, carboxylic acids are very important in *pharmaceuticals*.
- The production of many polymers involves the use of compounds containing the carboxyl functional group.

# Frequently Asked Questions – FAQs

# What foods contain carboxylic acids?

In plants and animals, certain carboxylic acids exist naturally. There is citric acid in citrus fruits, such as oranges and lemons. A large carboxylic acid with three ionizable hydrogen atoms is citric acid. It is present in citrus fruits and provides them with a sour or tart taste.

# Preparation of Carboxylic acids

## By using primary Alcohols and Aldehyde

We will notice that the primary alcohol gets oxidized to carboxylic acid when oxidizing agents are added such as potassium permanganate (KMnO<sub>4</sub>) in an acidic, alkaline or neutral medium. On using a mild oxidizing agent we can get carboxylic acids from aldehydes.

R—
$$CH_2$$
-OH

or

 $CH_2$ -OH

or

 $CH_2$ -OH

 $CH_2$ -OH

## From Alkylbenzenes

We can get aromatic carboxylic acids after vigorous oxidation of alkylbenzenes with chromic acid. Irrespective of the length of the chain the whole side chain is oxidized to a carbonyl group. The oxidation of primary and secondary alkyl groups can be done in this manner while the tertiary group is unaffected.

From Nitriles and Amides

Amides are prepared by the hydrolysis of nitriles and then is converted to acids in the presence of catalysts (H<sup>+</sup> or OH<sup>-1</sup>). In order to stop the reaction at the amide stage, mild reaction conditions are used.

$$R-CN \xrightarrow{\overset{+}{H} \text{ or } \overline{O}H} R-C-NH_2 \xrightarrow{\overset{+}{H} \text{ or } \overline{O}H} RCOOH$$

$$CH_3CONH_2 \xrightarrow{\overset{+}{A}} CH_3COOH + NH_3$$

$$Ethanamide \xrightarrow{CONH_2} \xrightarrow{\overset{+}{H_3O}} CH_3COOH + NH_3$$

$$Ethanoic acid + NH_3$$

$$Benzamide \xrightarrow{Benzoic acid}$$

By using Grignard Reagents

When <u>Grignard reagent</u> reacts with carbon dioxide its forms salts of carboxylic acids which after some time gives corresponding carboxylic acid after the acidification with any mineral acid. We can prepare Grignard reagents as well as nitriles from alkyl halides. These methods are very useful for the conversion of alkyl halides into corresponding carboxylic acids which has one carbon atom more than what is present in alkyl halides.

$$R-Mg-X + O=C=O$$
 dry ether  $R-C$   $\xrightarrow{O}$   $\xrightarrow{H_1O^*}$   $RCOOH + Mg(OH)Br$   $OMgX$ 

By using Esters

A carboxylic acid is produced after the acidic hydrolysis of esters and carboxylates are produced after the basic hydrolysis of an ester.

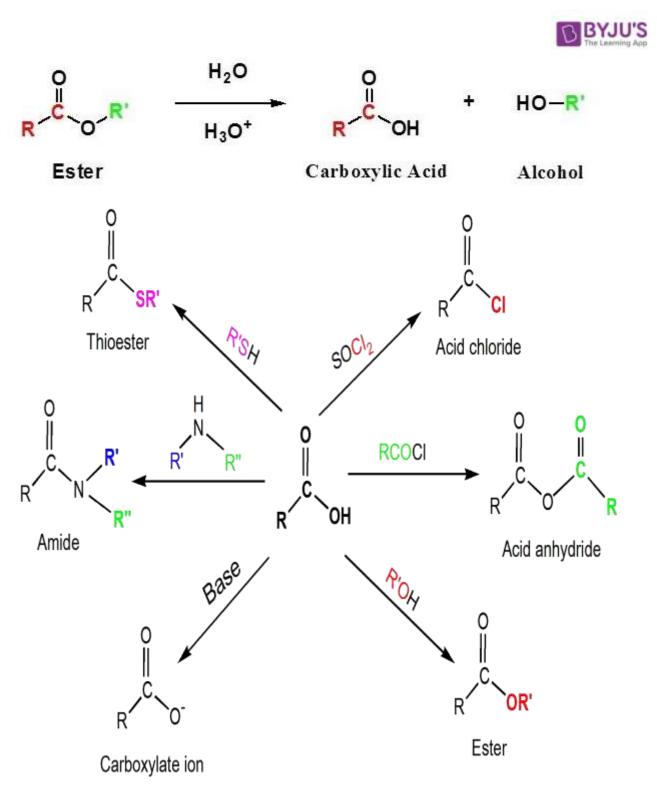


Diagram overview of carboxylic molecule reactions

Let's list down some common properties for the above shown carboxylic acid derivatives

- Each derivative contains a common group, termed as an *acyl* group (R-C=O), which is attached to a heteroatom
- They can all be synthesized from the "parent" carboxylic acid
- They are all formed through a nucleophilic substitution reaction
- On hydrolysis (i.e. reaction with H\_{2}2start subscript, 2, end subscriptO), they all convert back to their parent carboxylic acid Now let's discuss each carboxylic acid derivative individually, and outline the reaction mechanism by which they are formed starting from the parent carboxylic acid

## Acid chloride (ROCl)

Acid chlorides are formed when carboxylic acids react with thionyl chloride (SOCl\_{2}2start subscript, 2, end subscript), PCl\_{3}3start subscript, 3, end subscript or PCl\_{5}5start subscript, 5, end subscript. They are the most reactive derivatives of carboxylic acid.

Ester (RCOOR')

Esters are derived when a carboxylic acid reacts with an alcohol. Esters containing long alkyl chains (R) are main constituents of animal and vegetable fats and oils. Many esters containing small alkyl chains are fruity in smell, and are commonly used in fragrances.

Diagram of the formation of ester (RCOOR')

The acid-catalyzed esterification of carboxylic acids with alcohols to give esters is termed *Fischer esterification* 

# Acid anhydride

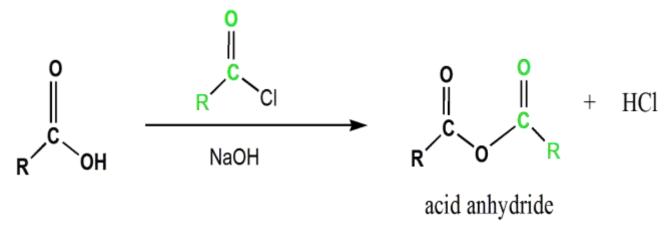


Diagram of the formation of acid anhydride

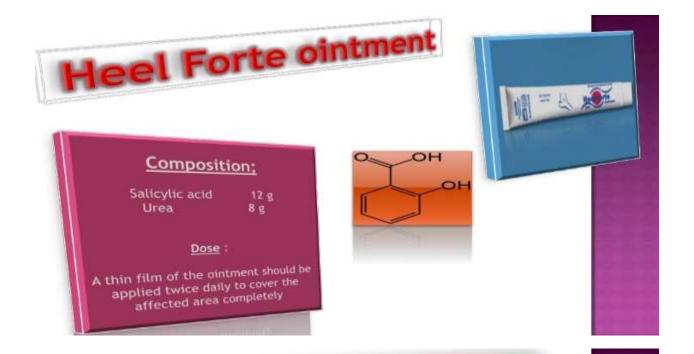
As you can see, an acid anhydride is a compound that has *two acyl* groups(R-C=O) bonded to the same oxygen atom. Anhydrides are commonly formed when a carboxylic acid reacts with an acid chloride in the presence of a base.

## **Amide**

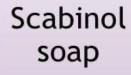
The direct conversion of a carboxylic acid to an amide is difficult because amines are very basic and tend to convert carboxylic acids to their highly unreactive carboxylate ions. Therefore, DCC (Dicyclohexylcarbodiimide) is used to drive this reaction.

Diagram of the formation of amide





Examples for soaps containing carboxylic acids



**INGREDIANTS** 

benzyl benzoate 15% sulpher 15%

USES:

For scabies and pediculosis.

# Dermacid soap

- Acidic Soap.
   Restores and
  maintains the natural
  acidity of the skin.
   Used for mycotic
  skin infections, prickly
  heat, sweat and diaper
  rashes, acne, etc.

# Salicylic acid soap

INGREDIANTS 2% salysilic acid.

> USES: for infectious skin disease.

CHAPTER



A fennel plant is an aromatic herb used in cooking. A phenyl group (pronounced exactly the same way) is the characteristic structural unit of "aromatic" organic compounds.



# **Aromatic Compounds**

- **5.1** Structure of Benzene
- **5.2** Naming Aromatic Compounds
- **5.3** Electrophilic Aromatic Substitution Reactions: Bromination
- **5.4** Other Electrophilic Aromatic
- Substitution Reactions
- 5.5 The Friedel–Crafts Alkylation and Acylation Reactions
- 5.6 Substituent Effects in Electrophilic Aromatic Substitution
- **5.7** An Explanation of Substituent Effects
- **5.8** Oxidation and Reduction of Aromatic Compounds
- **5.9** Other Aromatic Compounds
- 5.10 Organic SynthesisInterlude—Aspirin, NSAIDs, and COX-2Inhibitors

In the early days of organic chemistry, the word *aromatic* was used to describe fragrant substances such as benzene (from coal distillate), benzaldehyde (from cherries, peaches, and almonds), and toluene (from tolu balsam).

It was soon realized, however, that substances classed as aromatic differed from most other organic compounds in their chemical behavior.

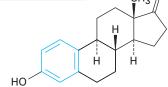
Today, the association of aromaticity with fragrance has long been lost, and we now use the word **aromatic** to refer to the class of compounds that contain six-membered benzene-like rings with three double bonds. Many valuable compounds are aromatic in part, such as the steroidal hormone estrone and the cholesterol-lowering drug atorvastatin, marketed as Lipitor. Benzene itself causes a depressed white blood cell count (leukopenia) on prolonged exposure and should not be used as a laboratory solvent.

**OWL** 

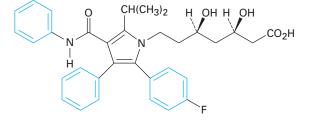
Online homework for this chapter can be assigned in OWL, an online homework assessment tool.



Benzene



Estrone



Atorvastatin (Lipitor)

## WHY THIS CHAPTER?

Aromatic rings are a common part of many organic structures and are particularly important in nucleic acid chemistry and in the chemistry of several amino acids. In this chapter, we'll find out how and why aromatic compounds are different from such apparently related compounds as alkenes.

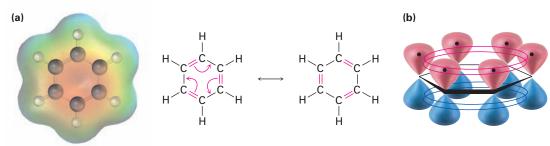
# **5.1** Structure of Benzene

Benzene  $(C_6H_6)$  has eight fewer hydrogens than the corresponding six-carbon alkane  $(C_6H_{14})$  and is clearly unsaturated, usually being represented as a six-membered ring with alternating double and single bond. Yet it has been known since the mid-1800s that benzene is much less reactive than typical alkenes and fails to undergo typical alkene addition reactions. Cyclohexene, for instance, reacts rapidly with  $Br_2$  and gives the addition product 1,2-dibromocyclohexane, but benzene reacts only slowly with  $Br_2$  and gives the substitution product  $C_6H_5Br$ .

Further evidence for the unusual nature of benzene is that all its carbon-carbon bonds have the same length—139 pm—intermediate between typical single (154 pm) and double (134 pm) bonds. In addition, the electron density in all six carbon–carbon bonds is identical, as shown by an electrostatic potential map (Figure 5.1a). Thus, benzene is a planar molecule with the shape of a regular hexagon. All C–C–C bond angles are 120°, all six carbon atoms are  $sp^2$ -hybridized, and each carbon has a p orbital perpendicular to the plane of the six-membered ring.

Because all six carbon atoms and all six p orbitals in benzene are equivalent, it's impossible to define three localized  $\pi$  bonds in which a given p orbital overlaps only one neighboring p orbital. Rather, each p orbital overlaps equally well with both neighboring p orbitals, leading to a picture of benzene in which all six  $\pi$  electrons are free to move about the entire ring (Figure 5.1b). In resonance terms (Sections 4.9 and 4.10), benzene is a hybrid of two equivalent forms. Neither form is correct by itself; the true structure of benzene is somewhere in between the two resonance forms but is impossible to draw with our usual conventions. Because of this resonance, benzene is more stable and less reactive than a typical alkene.

Figure 5.1 (a) An electrostatic potential map of benzene and (b) an orbital picture. Each of the six carbon atoms has a p orbital that can overlap equally well with neighboring p orbitals on both sides. The  $\pi$  electrons are thus shared around the ring in two doughnut-shaped clouds, and all C-C bonds are equivalent.



#### Problem 5.1

Line-bond structures appear to imply that there are two different isomers of 1,2-dibromobenzene, one with the bromine-bearing carbon atoms joined by a double bond and one with the bromine-bearing carbons joined by a single bond. In fact, though, there is only one 1,2-dibromobenzene. Explain.

# **5.2** Naming Aromatic Compounds

Aromatic substances, more than any other class of organic compounds, have acquired a large number of common names. IUPAC rules discourage the use of most such names but allow some of the more widely used ones to be retained (Table 5.1). Thus, methylbenzene is commonly known as *toluene*, hydroxybenzene as *phenol*, aminobenzene as *aniline*, and so on.

Table 5.1 Common Names of Some Aromatic Compounds			
Structure	Name	Structure	Name
CH <sub>3</sub>	Toluene (bp 111 °C)	СНО	Benzaldehyde (bp 178 °C)
ОН	Phenol (mp 43 °C)	CO <sub>2</sub> H	Benzoic acid (mp 122 °C)
NH <sub>2</sub>	Aniline (bp 184 °C)	CH <sub>3</sub>	ortho-Xylene (bp 144 °C)
O CH <sub>3</sub>	Acetophenone (mp 21 °C)	H	Styrene (bp 145 °C)

Monosubstituted benzenes are systematically named in the same manner as other hydrocarbons, with *-benzene* as the parent name. Thus,  $C_6H_5Br$  is bromobenzene,  $C_6H_5NO_2$  is nitrobenzene, and  $C_6H_5CH_2CH_3$  is ethylbenzene. The name **phenyl**, pronounced **fen**-nil and sometimes abbreviated as Ph or  $\Phi$  (Greek phi), is used for the  $-C_6H_5$  unit when the benzene ring is considered as a substituent. In addition, a generalized aromatic substituent is called an

**aryl group**, abbreviated as Ar, and the name **benzyl** is used for the  $C_6H_5CH_2$ -group.

Disubstituted benzenes are named using one of the prefixes ortho- (o), meta- (m), or para- (p). An ortho-disubstituted benzene has its two substituents in a 1,2 relationship on the ring; a meta-disubstituted benzene has its two substituents in a 1,3 relationship; and a para-disubstituted benzene has its substituents in a 1,4 relationship.

As with cycloalkanes (Section 2.7), benzenes with more than two substituents are named by choosing a point of attachment as carbon 1 and numbering the substituents on the ring so that the second substituent has as low a number as possible. The substituents are listed alphabetically when writing the name.

Br 
$$\frac{3}{4}$$
 CH<sub>3</sub>  $\frac{3}{1}$  CH<sub>3</sub>  $\frac{1}{1}$  CH<sub>3</sub>  $\frac{1}{1}$ 

Note in the second and third examples shown that *-phenol* and *-toluene* are used as the parent names rather than *-benzene*. Any of the monosubstituted aromatic compounds shown in Table 5.1 can be used as a parent name, with the principal substituent (–OH in phenol or –CH<sub>3</sub> in toluene) considered as C1.

#### Worked Example 5.1

#### Naming an Aromatic Compound

What is the IUPAC name of the following compound?

#### Solution

Because the nitro group  $(-NO_2)$  and chloro group are on carbons 1 and 3, they have a meta relationship. Citing the two substituents in alphabetical order gives the IUPAC name m-chloronitrobenzene.

#### **Problem 5.2** Tell whether the following compounds are ortho, meta, or para disubstituted:

(a) 
$$CI$$
  $CH_3$  (b)  $NO_2$  (c)  $SO_3H$   $OH$ 

#### **Problem 5.3** Give IUPAC names for the following compounds:

(a) CI 
$$\longrightarrow$$
 Br (b)  $\longrightarrow$  CH<sub>3</sub> (c)  $\longrightarrow$  NH<sub>2</sub>  $\longrightarrow$  CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>3</sub> (f)  $\longrightarrow$  CH<sub>3</sub>  $\longrightarrow$  CH

#### **Problem 5.4** Draw structures corresponding to the following IUPAC names:

- (a) p-Bromochlorobenzene
- **(b)** *p*-Bromotoluene
- (c) *m*-Chloroaniline
- (d) 1-Chloro-3,5-dimethylbenzene

# **Electrophilic Aromatic Substitution**Reactions: Bromination

The most common reaction of aromatic compounds is **electrophilic aromatic substitution**, a process in which an electrophile (E<sup>+</sup>) reacts with an aromatic ring and substitutes for one of the hydrogens.

Many different substituents can be introduced onto the aromatic ring by electrophilic substitution. To list some possibilities, an aromatic ring can be substituted by a halogen (-Cl, -Br, -I), a nitro group (-NO<sub>2</sub>), a sulfonic acid group (-SO<sub>3</sub>H), an alkyl group (-R), or an acyl group (-COR). Starting from

only a few simple materials, it's possible to prepare many thousands of substituted aromatic compounds (Figure 5.2).

**Figure 5.2** Some electrophilic aromatic substitution reactions.

Before seeing how these electrophilic substitution reactions occur, let's briefly recall what was said in Sections 3.7 and 3.8 about electrophilic addition reactions of alkenes. When a reagent such as HCl adds to an alkene, the electrophilic H<sup>+</sup> approaches the  $\pi$  electrons of the double bond and forms a bond to one carbon, leaving a positive charge at the other carbon. This carbocation intermediate then reacts with the nucleophilic Cl<sup>-</sup> ion to yield the addition product.

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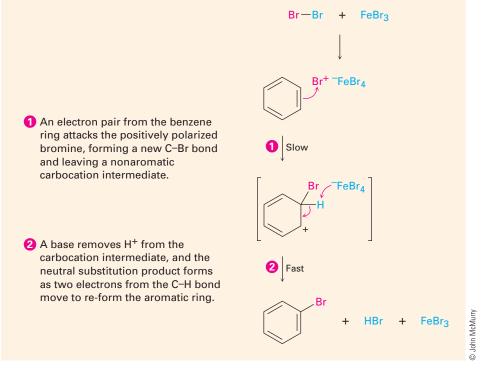
An electrophilic aromatic substitution reaction begins in a similar way, but there are a number of differences. One difference is that aromatic rings are less reactive toward electrophiles than alkenes are. For example,  $Br_2$  in  $CH_2Cl_2$  solution reacts instantly with most alkenes but does not react with benzene at room temperature. For bromination of benzene to take place, a catalyst such as  $FeBr_3$  is needed. The catalyst makes the  $Br_2$  molecule more electrophilic by reacting with it to give  $FeBr_4^-$  and  $Br^+$ . The electrophilic  $Br^+$  then reacts with the electron-rich (nucleophilic) benzene ring to yield a nonaromatic carbocation intermediate. This carbocation is doubly allylic (Section 4.9) and is a hybrid of three resonance forms.

Although more stable than a typical nonallylic carbocation because of resonance, the intermediate in electrophilic aromatic substitution is much less stable than the starting benzene ring itself. Thus, reaction of an electrophile with a benzene ring has a relatively high activation energy and is rather slow.

Another difference between alkene addition reactions and aromatic substitution reactions occurs after the electrophile has added to the benzene ring and the carbocation intermediate has formed. Instead of adding  $Br^-$  to give an addition product, the carbocation intermediate loses  $H^+$  from the bromine-bearing carbon to give a substitution product. The net effect is the substitution of  $H^+$  by  $Br^+$  by the overall mechanism shown in Figure 5.3.

#### **MECHANISM**

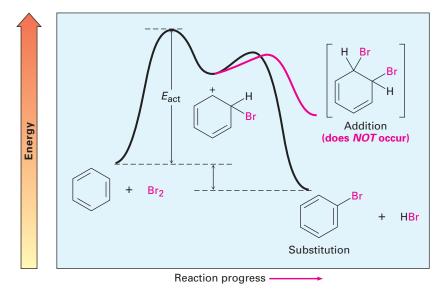
Figure 5.3 The mechanism of the electrophilic bromination of benzene. The reaction occurs in two steps and involves a resonance-stabilized carbocation intermediate.



Why does the reaction of Br<sub>2</sub> with benzene take a different course than its reaction with an alkene? The answer is straightforward: if *addition* occurred, the resonance stabilization of the aromatic ring would be lost and the overall reaction would be energetically unfavorable. When *substitution* occurs, though, the resonance stability of the aromatic ring is retained and

the reaction is favorable. An energy diagram for the overall process is shown in Figure 5.4.

Figure 5.4 An energy diagram for the electrophilic bromination of benzene. The reaction occurs in two steps and releases energy.



Problem 5.5 There are three products that might form on reaction of toluene (methylbenzene) with Br<sub>2</sub>. Draw and name them.

# **5.4** Other Electrophilic Aromatic Substitution Reactions

Many other electrophilic aromatic substitutions occur by the same general mechanism as bromination. Let's look at some briefly.

#### **Chlorination and Iodination**

Aromatic rings react with  $Cl_2$  in the presence of  $FeCl_3$  catalyst to yield chlorobenzenes, just as they react with  $Br_2$  and  $FeBr_3$  to give bromobenzenes. This kind of reaction is used in the synthesis of numerous pharmaceutical agents, including the antiallergy medication loratedine, marketed as Claritin.

Electrophilic aromatic halogenations also occur in the biological synthesis of many naturally occurring molecules, particularly those produced by marine organisms. In humans, the best-known example occurs in the thyroid gland

Loratadine

during the biosynthesis of thyroxine, a thyroid hormone involved in regulating growth and metabolism. The amino acid tyrosine is first iodinated by thyroid peroxidase, and two of the iodinated tyrosine molecules then couple. The electrophilic iodinating agent is an  $I^+$  species, perhaps hypoiodous acid (HIO), that is formed from iodide ion by oxidation with  $H_2O_2$ .

#### **Nitration**

Aromatic rings are nitrated by reaction with a mixture of concentrated nitric and sulfuric acids. The electrophile is the nitronium ion,  $NO_2^+$ , which is formed from  $HNO_3$  by protonation and loss of water and which reacts with benzene in much the same way  $Br^+$  does.

Aromatic nitration does not occur in nature but is particularly important in the laboratory because the nitro-substituted product can be reduced by reagents such as iron, tin, or SnCl<sub>2</sub> to yield an amino-substituted product, or *arylamine*, ArNH<sub>2</sub>. Attachment of an amino group to an aromatic ring by the two-step nitration/reduction sequence is a key part of the industrial synthesis of many dyes and pharmaceutical agents.

Nitric acid

$$H_2SO_4$$
 $H_2SO_4$ 
 $H_2SO_4$ 

#### **Sulfonation**

Aromatic rings are sulfonated by reaction with so-called fuming sulfuric acid, a mixture of SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. The reactive electrophile is HSO<sub>3</sub><sup>+</sup>, and substitution occurs by the usual two-step mechanism seen for bromination. Aromatic sulfonation is a key step in the synthesis of such compounds as the sulfa drug family of antibiotics.

$$\begin{bmatrix} O & + & H_2SO_4 & \longrightarrow & O \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$$

#### Worked Example 5.2

#### Writing the Mechanism of an Electrophilic Aromatic Substitution Reaction

Show the mechanism of the reaction of benzene with fuming sulfuric acid to yield benzenesulfonic acid.

Strategy The reaction of benzene with fuming sulfuric acid to yield benzenesulfonic acid is a typical electrophilic aromatic substitution reaction, which occurs by the usual two-step mechanism. An electrophile first adds to the aromatic ring, and H<sup>+</sup> is then lost. In sulfonation reactions, the electrophile is HSO<sub>3</sub><sup>+</sup>.

Solution

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Carbocation intermediate

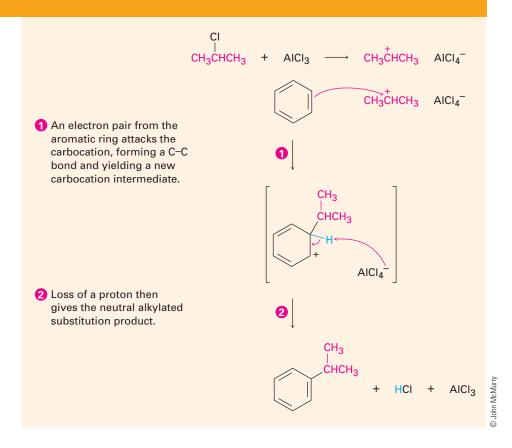
- Problem 5.6 Show the mechanism of the reaction of benzene with nitric acid and sulfuric acid to yield nitrobenzene.
- Problem 5.7 Chlorination of *o*-xylene (*o*-dimethylbenzene) yields a mixture of two products, but chlorination of *p*-xylene yields a single product. Explain.
- **Problem 5.8** How many products might be formed on chlorination of *m*-xylene?

# 5.5 The Friedel-Crafts Alkylation and Acylation Reactions

One of the most useful electrophilic aromatic substitution reactions is *alkylation*—the introduction of an alkyl group onto the benzene ring. Called the **Friedel-Crafts alkylation reaction** after its discoverers, the reaction is carried out by treating the aromatic compound with an alkyl chloride, RCl, in the presence of AlCl<sub>3</sub> to generate a carbocation electrophile, R<sup>+</sup>. Aluminum chloride catalyzes the reaction by helping the alkyl halide to dissociate in much the same way that FeBr<sub>3</sub> catalyzes aromatic brominations by helping Br<sub>2</sub> dissociate (Section 5.3). Loss of H<sup>+</sup> then completes the reaction (Figure 5.5).

#### **MECHANISM**

Figure 5.5 Mechanism of the Friedel–Crafts alkylation reaction. The electrophile is a carbocation, generated by AlCl<sub>3</sub>-assisted ionization of an alkyl chloride.



Despite its utility, the Friedel–Crafts alkylation reaction has several limitations. For one, only *alkyl* halides can be used. Aromatic (aryl) halides such as chlorobenzene don't react. In addition, Friedel–Crafts reactions don't succeed on aromatic rings that are already substituted by the groups  $-NO_2$ ,  $-C\equiv N$ ,  $-SO_3H$ , or -COR. Such aromatic rings are much less reactive than benzene for reasons we'll discuss in the next two sections.

Closely related to the Friedel-Crafts alkylation reaction is the **Friedel-Crafts acylation reaction**. When an aromatic compound is treated with a

166

#### Problem 5.9

What products would you expect to obtain from the reaction of the following compounds with chloroethane and AlCl<sub>3</sub>?

- (a) Benzene
- **(b)** *p*-Xylene

#### Problem 5.10

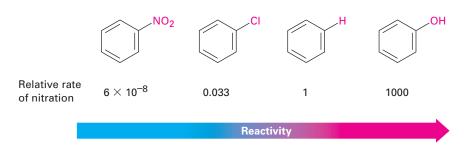
What products would you expect to obtain from the reaction of benzene with the following reagents?

- (a)  $(CH_3)_3CCl$ ,  $AlCl_3$
- (**b**) CH<sub>3</sub>CH<sub>2</sub>COCl, AlCl<sub>3</sub>

# **5.6** Substituent Effects in Electrophilic Aromatic Substitution

Only one product can form when an electrophilic substitution occurs on benzene, but what would happen if we were to carry out an electrophilic substitution on a ring that already has a substituent? A substituent already present on the ring has two effects:

• Substituents affect the *reactivity* of an aromatic ring. Some substituents activate a ring, making it more reactive than benzene, and some deactivate a ring, making it less reactive than benzene. In aromatic nitration, for instance, the presence of an -OH substituent makes the ring 1000 times more reactive than benzene, while an -NO<sub>2</sub> substituent makes the ring more than 10 million times less reactive.

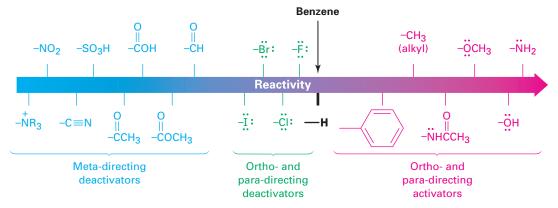


• Substituents affect the *orientation* of a reaction. The three possible disubstituted products—ortho, meta, and para—are usually not formed in equal amounts. Instead, the nature of the substituent already present on the ring determines the position of the second substitution. An -OH group directs further substitution toward the ortho

and para positions, for instance, while a -CN directs further substitution primarily toward the meta position.

Substituents can be classified into three groups, as shown in Figure 5.6: meta-directing deactivators, ortho- and para-directing deactivators, and ortho- and para-directing activators. There are no meta-directing activators. Note how the directing effect of a group correlates with its reactivity. All meta-directing groups are deactivating, and all ortho- and para-directing groups other than halogen are activating. The halogens are unique in being ortho- and para-directing but deactivating.

Figure 5.6 Substituent effects in electrophilic aromatic substitutions. All activating groups are ortho- and para-directing, and all deactivating groups other than halogen are meta-directing. The halogens are unique in being deactivating but ortho- and para-directing.



#### Worked Example 5.3

#### Predicting Relative Reactivity in Electrophilic Aromatic Substitution Reactions

Which would you expect to react faster in an electrophilic aromatic substitution reaction, chlorobenzene or ethylbenzene? Explain.

Strategy

Look at Figure 5.6, and compare the relative reactivities of chloro and alkyl groups.

Solution

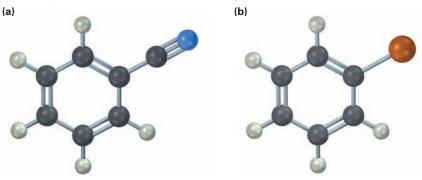
A chloro substituent is deactivating, whereas an alkyl group is activating. Thus, ethylbenzene is more reactive than chlorobenzene.

Problem 5.11

Use Figure 5.6 to rank the compounds in each of the following groups in order of their reactivity toward electrophilic aromatic substitution:

- (a) Nitrobenzene, phenol (hydroxybenzene), toluene
- (b) Phenol, benzene, chlorobenzene, benzoic acid
- (c) Benzene, bromobenzene, benzaldehyde, aniline (aminobenzene)

Problem 5.12 Draw and name the products you would expect to obtain by reaction of the following substances with  $Cl_2$  and  $FeCl_3$  (blue = N, reddish brown = Br):



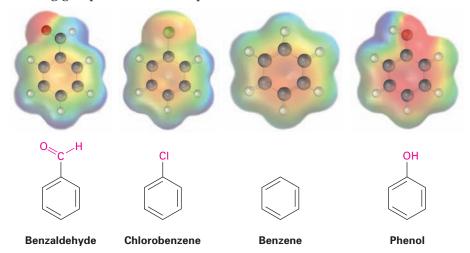
# 5.7 An Explanation of Substituent Effects

We saw in the previous section that substituents affect both the reactivity of an aromatic ring and the orientation of further aromatic substitutions. Let's look at the effects separately.

## **Activating and Deactivating Effects in Aromatic Rings**

What makes a group either activating or deactivating? The common characteristic of all activating groups is that they *donate* electrons to the ring, thereby making the ring more electron-rich, stabilizing the carbocation intermediate, and lowering the activation energy for its formation. Conversely, the common characteristic of all deactivating groups is that they *withdraw* electrons from the ring, thereby making the ring more electron-poor, destabilizing the carbocation intermediate, and raising the activation energy for its formation.

Compare the electrostatic potential maps of benzaldehyde (deactivated), chlorobenzene (weakly deactivated), and phenol (activated) with that of benzene. The ring is more positive (yellow) when an electron-withdrawing group such as -CHO or -Cl is present and more negative (red) when an electron-donating group such as -OH is present.



Electron donation or withdrawal may occur by either an inductive effect (Section 1.9) or a resonance effect (Section 4.10). An inductive effect is the withdrawal

or donation of electrons through a  $\sigma$  bond due to an electronegativity difference between the ring and the attached substituent atom, while a resonance effect is the withdrawal or donation of electrons through a  $\pi$  bond due to the overlap of a p orbital on the substituent with a p orbital on the aromatic ring.

#### **Orienting Effects in Aromatic Rings: Ortho and Para Directors**

Let's look at the nitration of phenol as an example of how ortho- and paradirecting substituents work. In the first step, reaction with the electrophilic nitronium ion  $(NO_2^+)$  can occur either ortho, meta, or para to the -OH group, giving the carbocation intermediates shown in Figure 5.7. The ortho and para intermediates are more stable than the meta intermediate because they have more resonance forms—four rather than three—including a particularly favorable one that allows the positive charge to be stabilized by electron donation from the substituent oxygen atom. Because the ortho and para intermediates are more stable than the meta intermediate, they are formed faster.

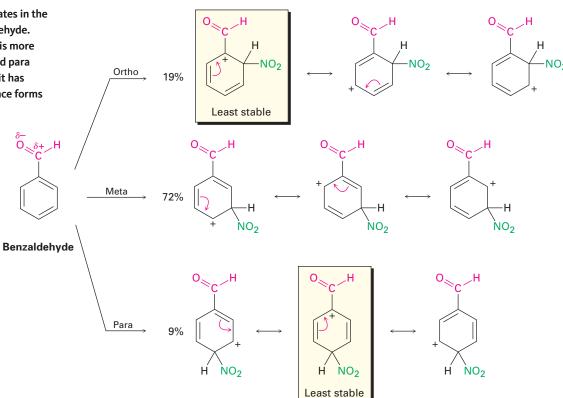
**Figure 5.7** Carbocation intermediates in the nitration of phenol. The ortho and para intermediates are more stable than the meta intermediate because they have more resonance forms, including a particularly favorable one that involves electron donation from the oxygen atom.

In general, any substituent that has a lone pair of electrons on the atom directly bonded to the aromatic ring allows an electron-donating resonance interaction to occur and thus acts as an ortho and para director.

#### **Orienting Effects in Aromatic Rings: Meta Directors**

The influence of meta-directing substituents can be explained using the same kinds of arguments used for ortho and para directors. Look at the chlorination of benzaldehyde, for instance (Figure 5.8). Of the three possible carbocation intermediates, the meta intermediate has three favorable resonance forms, while the ortho and para intermediates have only two. In both ortho and para intermediates, the third resonance form is particularly unfavorable because it places the positive charge directly on the carbon that bears the aldehyde group, where it is disfavored by a repulsive interaction with the positively polarized carbon atom of the C=O group. Hence, the meta intermediate is more favored and is formed faster than the ortho and para intermediates.

Figure 5.8 Intermediates in the chlorination of benzaldehyde.
The meta intermediate is more favorable than ortho and para intermediates because it has three favorable resonance forms rather than two.



In general, any substituent that has a positively polarized atom  $(\delta+)$  directly attached to the ring makes one of the resonance forms of the ortho and para intermediates unfavorable, and thus acts as a meta director.

### Worked Example 5.4

### Predicting the Product of an Electrophilic Aromatic Substitution Reaction

What product(s) would you expect from bromination of aniline, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>?

**Strategy** 

Look at Figure 5.6 to see whether the  $-\mathrm{NH}_2$  substituent is ortho- and paradirecting or meta-directing. Because an amino group has a lone pair of electrons on the nitrogen atom, it is ortho- and para-directing and we expect to obtain a mixture of o-bromoaniline and p-bromoaniline.

**Solution** 

**Problem 5.13** What product(s

What product(s) would you expect from sulfonation of the following compounds?

- (a) Nitrobenzene
- (b) Bromobenzene
- (c) Toluene

- (d) Benzoic acid
- (e) Benzonitrile

Problem 5.14

Draw resonance structures of the three possible carbocation intermediates to show how a methoxyl group (-OCH<sub>3</sub>) directs bromination toward ortho and para positions.

Problem 5.15

Draw resonance structures of the three possible carbocation intermediates to show how an acetyl group, CH<sub>3</sub>C=O, directs bromination toward the meta position.

# **5.8** Oxidation and Reduction of Aromatic Compounds

Despite its unsaturation, a benzene ring does not usually react with strong oxidizing agents such as  $KMnO_4$ . (Recall from Section 4.6 that  $KMnO_4$  cleaves alkene C=C bonds.) Alkyl groups attached to the aromatic ring are readily attacked by oxidizing agents, however, and are converted into carboxyl groups  $(-CO_2H)$ . For example, butylbenzene is oxidized by  $KMnO_4$  to give benzoic acid. The mechanism of this reaction is complex and involves attack on the side-chain C-H bonds at the position next to the aromatic ring (the **benzylic position**) to give radical intermediates.

$$\begin{array}{c} CH_2CH_2CH_2CH_3 \\ \hline \\ H_2O \end{array}$$

Butylbenzene

Benzoic acid (85%)

Analogous oxidations occur in various biological pathways. The neurotransmitter norepinephrine, for instance, is biosynthesized from dopamine by a benzylic hydroxylation reaction. The process is catalyzed by the coppercontaining enzyme dopamine  $\beta$ -monooxygenase and occurs by a radical mechanism.

Just as aromatic rings are usually inert to oxidation, they are also inert to reduction under typical alkene hydrogenation conditions. Only if high temperatures and pressures are used does reduction of an aromatic ring occur. For example, *o*-dimethylbenzene (*o*-xylene) gives *cis*-1,2-dimethylcyclohexane if reduced at high pressure.

# Problem 5.16 What aromatic products would you expect to obtain from oxidation of the following substances with KMnO<sub>4</sub>?

## **5.9** Other Aromatic Compounds

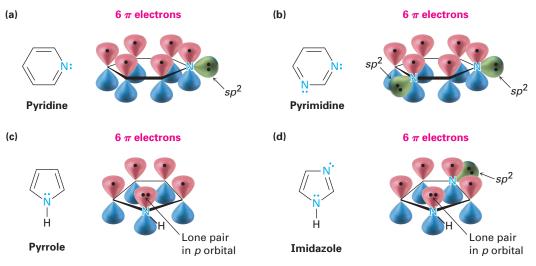
The concept of aromaticity—the unusual chemical stability present in cyclic conjugated molecules like benzene—can be extended beyond simple monocyclic hydrocarbons. Naphthalene, for instance, a substance familiar for its use in mothballs, has two benzene-like rings fused together and is thus a **polycyclic aromatic compound**.

Perhaps the most notorious polycyclic aromatic hydrocarbon is benzo[a]pyrene, which has five benzene-like rings and is a major carcinogenic (cancer-causing) substance found in chimney soot, cigarette smoke, and well-done barbecued meat. Once in the body, benzo[a]pyrene is

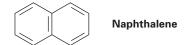
metabolically converted into a diol epoxide that binds to DNA, where it induces mutations.

In addition to monocyclic and polycyclic aromatic hydrocarbons, some aromatic compounds are **heterocycles**—cyclic compounds that contain atoms of two or more elements in their rings. Nitrogen, sulfur, and oxygen atoms are all found along with carbon in various aromatic compounds. We'll see in Chapter 12, for instance, that the nitrogen-containing heterocycles pyridine, pyrimidine, pyrrole, and imidazole are aromatic, even though they aren't hydrocarbons and even though two of them have five-membered rather than six-membered rings (Figure 5.9). They are aromatic because they all, like benzene, contain a cyclic conjugated array of six  $\pi$  electrons. Pyridine and pyrimidine have one  $\pi$  electron on each of their six ring atoms. Pyrrole and imidazole have one  $\pi$  electron on each of four ring atoms and an additional two  $\pi$  electrons (the lone pair) on their N-H nitrogen.

Figure 5.9 Orbital views of the nitrogen-containing compounds (a) pyridine, (b) pyrimidine, (c) pyrrole, and (d) imidazole. All are aromatic because, like benzene, they contain a cyclic conjugated system of six  $\pi$  electrons. Pyridine and pyrimidine have one  $\pi$  electron on each of their six ring atoms. Pyrrole and imidazole have one  $\pi$  electron on each of four ring atoms and an additional two  $\pi$  electrons (the lone pair) on their N-H nitrogen.



Problem 5.17 There are three resonance structures of naphthalene, of which only one is shown. Draw the other two.



# **5.10** Organic Synthesis

The laboratory synthesis of organic molecules from simple precursors might be carried out for many reasons. In the pharmaceutical industry, new organic molecules are often designed and synthesized for evaluation as medicines. In the chemical industry, syntheses are often undertaken to devise more economical routes to known compounds. In this book, too, we'll sometimes devise syntheses of complex molecules from simpler precursors, but the purpose here is simply to help you learn organic chemistry. Devising a route for the synthesis of an organic molecule requires that you approach chemical problems in a logical way, draw on your knowledge of organic reactivity, and organize that knowledge into a workable plan.

The only trick to devising an organic synthesis is to *work backward*. Look at the product and ask yourself, "What is the immediate precursor of that product?" Having found an immediate precursor, work backward again, one step at a time, until a suitable starting material is found. Let's try some examples.

### Worked Example 5.5

#### Synthesizing a Substituted Aromatic Compound

Synthesize m-chloronitrobenzene starting from benzene.

Strategy

Work backward by first asking, "What is an immediate precursor of *m*-chloronitrobenzene?"

m-Chloronitrobenzene

There are two substituents on the ring, a -Cl group, which is ortho- and paradirecting, and an  $-\text{NO}_2$  group, which is meta-directing. We can't nitrate chlorobenzene because the wrong isomers (o- and p-chloronitrobenzenes) would result, but chlorination of nitrobenzene should give the desired product.

Nitrobenzene

"What is an immediate precursor of nitrobenzene?" Benzene, which can be nitrated.

**Solution** We've solved the problem in two steps:

### Worked Example 5.6

### Synthesizing a Substituted Aromatic Compound

Synthesize *p*-bromobenzoic acid starting from benzene.

**Strategy** Work backward by first asking, "What is an immediate precursor of *p*-bromobenzoic acid?"

#### p-Bromobenzoic acid

There are two substituents on the ring, a  $-\text{CO}_2\text{H}$  group, which is meta-directing, and a -Br atom, which is ortho- and para-directing. We can't brominate benzoic acid because the wrong isomer (m-bromobenzoic acid) would be formed. We've seen, however, that oxidation of alkylbenzene side chains yields benzoic acids. An immediate precursor of our target molecule might therefore be p-bromotoluene.

"What is an immediate precursor of *p*-bromotoluene?" Perhaps toluene, because the methyl group would direct bromination to the ortho and para positions, and we could then separate isomers. Alternatively, bromobenzene might be an immediate precursor because we could carry out a Friedel–Crafts alkylation and obtain the para product. Both methods are satisfactory.

#### Bromobenzene

"What is an immediate precursor of toluene?" Benzene, which can be methylated in a Friedel-Crafts reaction.

"Alternatively, what is an immediate precursor of bromobenzene?" Benzene, which can be brominated.

$$\begin{array}{c|c} & & & \\ \hline & \\ \hline & & \\ \hline & & \\ \hline & & \\ \hline & \\ \hline & \\ \hline$$

**Solution** Our backward synthetic (*retrosynthetic*) analysis has provided two workable routes from benzene to *p*-bromobenzoic acid.

### **Problem 5.18** Propose syntheses of the following substances starting from benzene:

(a) 
$$O$$
 (b)  $NO_2$   $CI$ 

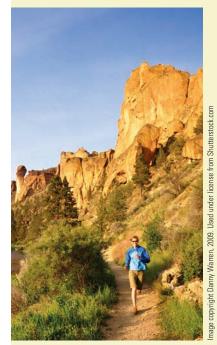
#### **Problem 5.19** Synthesize the following substances from benzene:

(a) o-Bromotoluene (b) 2-Bromo-1,4-dimethylbenzene

### Problem 5.20 How would you prepare the following substance from benzene? (Yellow-green = Cl.)



## Aspirin, NSAIDs, and COX-2 Inhibitors



Long-distance runners sometimes call ibuprofen "the fifth basic food group" because of its ability to control aches and pains.

hatever the cause—tennis elbow, a sprained ankle, or a wrenched knee—pain and inflammation seem to go together. They are, however, different in their origin, and powerful drugs are available for treating each separately. Codeine, for example, is a powerful *analgesic*, or pain reliever, used in the management of debilitating pain, while cortisone and related steroids are potent *anti-inflammatory* agents, used for treating arthritis and other crippling inflammations. For minor pains and inflammation, both problems are often treated at the same time by using a common, over-the-counter medication called an *NSAID*, or non-steroidal anti-inflammatory drug.

The most common NSAID is aspirin, or acetylsalicylic acid, whose use goes back to the late 1800s. It had been known from before the time of Hippocrates in 400 BC that fevers could be lowered by chewing the bark of willow trees. The active agent in willow bark was found in 1827 to be an aromatic compound called *salicin*, which could be converted by reaction with water into salicyl alcohol and then oxidized to give salicylic acid. Salicylic acid turned out to be even more effective than salicin for reducing fever and to have analgesic and anti-inflammatory action as well. Unfortunately, it also turned out to be too corrosive to the walls of the stomach for everyday use. Conversion of the phenol –OH group into an acetate ester, however, yielded acetylsalicylic acid, which proved just as potent as salicylic acid but less corrosive to the stomach.

Acetylsalicylic acid (aspirin)

Although extraordinary in its powers, aspirin is also more dangerous than commonly believed. A dose of only about 15 g can be fatal to a small child, and aspirin can cause stomach bleeding and allergic reactions in long-term users. Even more serious is a condition called *Reye's syndrome*, a potentially fatal reaction to aspirin sometimes seen in children recovering from the flu. As a result of these problems, numerous other NSAIDs have been developed in the last several decades, most notably ibuprofen and naproxen.

Like aspirin, both ibuprofen and naproxen are relatively simple aromatic compounds containing a side-chain carboxylic acid group. Ibuprofen, sold under the names Advil, Nuprin, Motrin, and others, has



roughly the same potency as aspirin but is less prone to cause stomach upset. Naproxen, sold under the names Aleve and Naprosyn, also has about the same potency as aspirin but remains active in the body six times longer.

Aspirin and other NSAIDs function by blocking the cyclooxygenase (COX) enzymes that carry out the body's synthesis of compounds called prostaglandins (Section 6.3). There are two forms of the enzyme: COX-1, which carries out the normal physiological production of prostaglandins, and COX-2, which mediates the body's response to arthritis and other inflammatory conditions. Unfortunately, both COX-1 and COX-2 enzymes are blocked by aspirin, ibuprofen, and other NSAIDs, thereby shutting down not only the response to inflammation but also various protective functions, including the control mechanism for production of acid in the stomach.

Medicinal chemists have devised a number of drugs that act as selective inhibitors of the COX-2 enzyme. Inflammation is thereby controlled without blocking protective functions. Originally heralded as a breakthrough in arthritis treatment, the first generation of COX-2 inhibitors, including Vioxx, Celebrex, and Bextra, turned out to cause potentially serious heart problems, particularly in elderly or compromised patients. The second generation of COX-2 inhibitors now under development promises to be safer but will be closely scrutinized for side effects before gaining approval.

## **Summary and Key Words**

acyl group 166
aromatic 155
aryl group 158
benzyl group 158
benzylic position 171
electrophilic aromatic substitution
reaction 159
Friedel-Crafts acylation
reaction 165
Friedel-Crafts alkylation
reaction 165
heterocycle 173
phenyl group 157
polycyclic aromatic compound 172

Aromatic rings are a common part of many biological molecules and pharmaceutical agents and are particularly important in nucleic acid chemistry. In this chapter, we've seen how and why aromatic compounds are different from such apparently related compounds as alkenes, and we've seen some of their most common reactions.

The word **aromatic** refers to the class of compounds structurally related to benzene. Aromatic compounds are named according to IUPAC rules, with disubstituted benzenes referred to as either ortho (1,2 disubstituted), meta (1,3 disubstituted), or para (1,4 disubstituted). Benzene is a resonance hybrid of two equivalent forms, neither of which is correct by itself. The true structure of benzene is intermediate between the two.

The most common reaction of aromatic compounds is **electrophilic aromatic substitution**. In this two-step polar reaction, the  $\pi$  electrons of the aromatic ring first attack the electrophile to yield a resonance-stabilized carbocation intermediate, which then loses H<sup>+</sup> to give a substituted aromatic product. Bromination, chlorination, iodination, nitration, sulfonation, **Friedel–Crafts alkylation**, and **Friedel–Crafts acylation** can all be carried out. Friedel–Crafts alkylation is particularly useful for preparing a variety of alkylbenzenes but is limited because only alkyl halides can be used and strongly deactivated rings do not react.

Substituents on the aromatic ring affect both the reactivity of the ring toward further substitution and the orientation of that further substitution. Substituents can be classified as either activators or deactivators, and as either ortho and para directors or meta directors.

The side chains of alkylbenzenes have unique reactivity because of the neighboring aromatic ring. Thus, an alkyl group attached to the aromatic ring can be degraded to a carboxyl group ( $-CO_2H$ ) by oxidation with aqueous  $KMnO_4$ . In addition, the aromatic ring can be reduced to yield a cyclohexane on catalytic hydrogenation at high pressure.

In addition to substituted benzenes, polycyclic hydrocarbons such as naphthalene are also aromatic, and nitrogen-containing **heterocycles** such as pyridine, pyrimidine, pyrrole, and imidazole are aromatic because their rings have the same  $\sin \pi$ -electron electronic structure as benzene.

## **Summary of Reactions**

Electrophilic aromatic substitution
 (a) Bromination (Section 5.3)

continued

180

## **(b)** Chlorination (Section 5.4)

### (c) Nitration (Section 5.4)

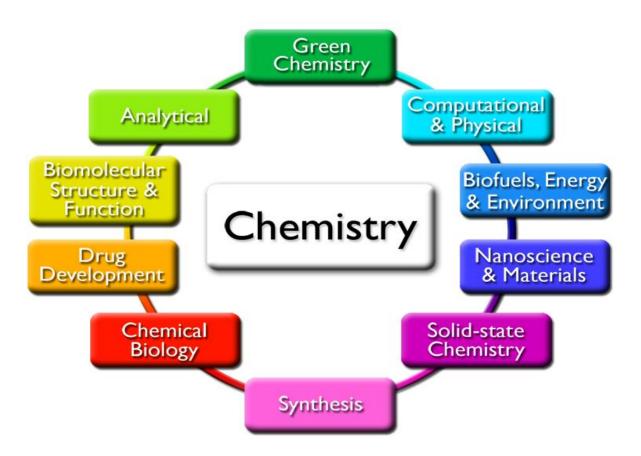
### (d) Sulfonation (Section 5.4)

### (e) Friedel–Crafts alkylation (Section 5.5)

#### (f) Friedel–Crafts acylation (Section 5.5)

### 2. Oxidation of aromatic side chains (Section 5.8)

## 3. Hydrogenation of aromatic rings (Section 5.8)



# **NOMENCLATURE** OF **ALKENES** AND **ALKYNES**

## All About Chemistry 🛂



## Branches of Chemistry-

- 1. Organic chemistry
- 2. Inorganic chemistry
- 3. Physical chemistry
- 4. Analytical chemistry
- 5. Biochemistry
- 6. Theoretical chem

## INTRODUCTION TO ORGANIC CHEMISTRY

Organic chemistry is a chemistry of carbon compounds.

Example: methane, DNA, urea, DDT (insecticide),
penicillin, nicotine, aspirin etc...

But not all carbon compounds are organics. Example:

carbonate (CO<sub>3</sub><sup>2</sup>; cyanide (CN), bicarbonate (HCO<sub>3</sub>), carbon dioxide and carbon monoxide.



## **Organic Chemistry**

- Introduction
- Functional Groups
- Alkanes
- Alkenes
- Alkynes
- Alcohols
- Acids, Esters and Amides

H <sub>3</sub> C-COOH	но ОН	AgO-CN	
Aceto destillato	ОН	Silver cyanate	O II
H <sub>3</sub> CCH <sub>2</sub> -OH Spiritus vini	Glycerol (Glycerine)	AgCNO	H <sub>2</sub> N NH <sub>2</sub> Urea
Et-O-Et	✓ COOH	Silver fulminate	Orod
Sweet oil of vitriol	Valeric acid	Some early organic chemicals	

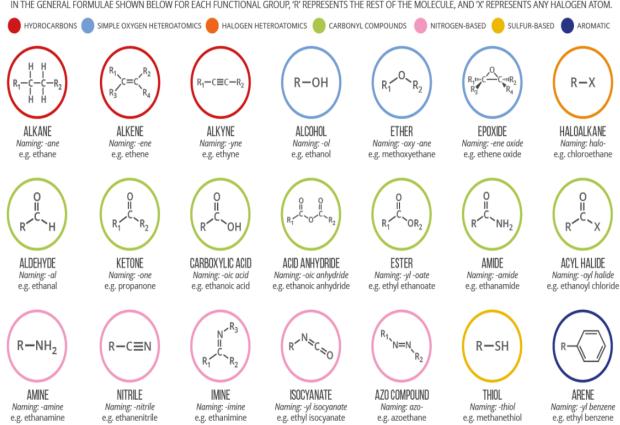
$$H_3C$$
— $CH_3$  Alkanes ( $C_nH_{2n+2}$ )

 $H_2C$ = $CH_2$  Alkenes ( $C_nH_{2n}$ )

 $HC$ = $CH$  Alkynes ( $C_nH_{2n-2}$ )

# FUNCTIONAL GROUPS IN ORGANIC CHEMISTRY

FUNCTIONAL GROUPS ARE GROUPS OF ATOMS IN ORGANIC MOLECULES THAT ARE RESPONSIBLE FOR THE CHARACTERISTIC CHEMICAL REACTIONS OF THOSE MOLECULES. IN THE GENERAL FORMULAE SHOWN BELOW FOR EACH FUNCTIONAL GROUP, 'R' REPRESENTS THE REST OF THE MOLECULE, AND 'X' REPRESENTS ANY HALOGEN ATOM.



e.g. azoethane

e.g. methanethiol



e.g. ethanamine

e.g. ethanenitrile

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e.g. ethanimine



# **Alkanes**

General chemical formula:  $C_{\scriptscriptstyle n} H_{\scriptscriptstyle 2n+2}$ 

Saturated - All bonds are single bonds

Some examples of alkanes are:

No. of C atoms	Name of Alkane	Molecular Formula
1	Methane	$CH_4$
2	Ethane	$C_2H_6$
3	Propane	$C_3H_8$
4	Butane	$C_4H_{10}$
5	Pentane	$C_{\scriptscriptstyle 5}H_{\scriptscriptstyle 12}$
6	Hexane	$C_6H_{14}$
7	Heptane	$C_{7}H_{16}$
8	Octane	$C_{8}H_{18}$
9	Nonane	$C_9 H_{20}$
10	Decane	$C_{10}H_{22}$

$$CH_3$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_4$ 
 $CH_5$ 
 $CH_5$ 
 $CH_5$ 
 $CH_5$ 
 $CH_5$ 

3-methylpentane

$$\begin{array}{c|c} & CH_3 & CH_3 \\ 1 & 2 & 3 & 4 \\ CH_3 - CH - CH - CH_2 - CH_3 \end{array} \quad \text{2,3-dimethylpentane}$$

$$\begin{array}{c|c} & C_2H_5 \\ \stackrel{1}{C}H_3 - \stackrel{2}{C}H - \stackrel{2}{C} - \stackrel{2}{C}H_2 - \stackrel{5}{C}H_3 \\ \stackrel{1}{C}H_3 - \stackrel{1}{C}H_3 \end{array} \qquad \text{3-ethyl-2, 3-dimethylpentane.}$$

# Isomers and common names of simple alkenes





Ethene (ethylene)

vinyl chloride

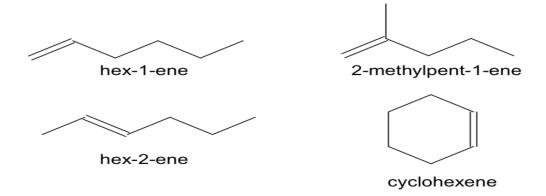
Propene (propylene)

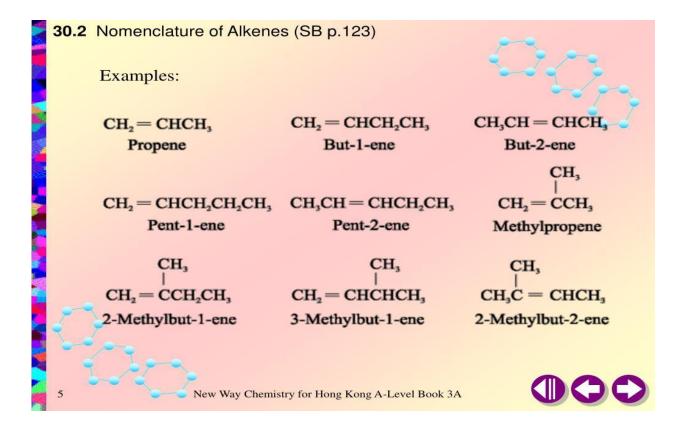
Allyl chloride

cis-2-butene

trans-2-butene

2-methyl-1-propene (isobutene)





## **Alkenes**

## Nomenclature of Alkenes

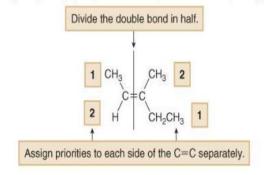
## ilenciature of Aikeries

How To Assign the Prefixes E and Z to an Alkene

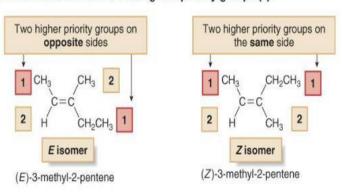
### Step [1]

Assign priorities to the two substituents on each end of the C=C by using the priority rules for R,S nomenclature.

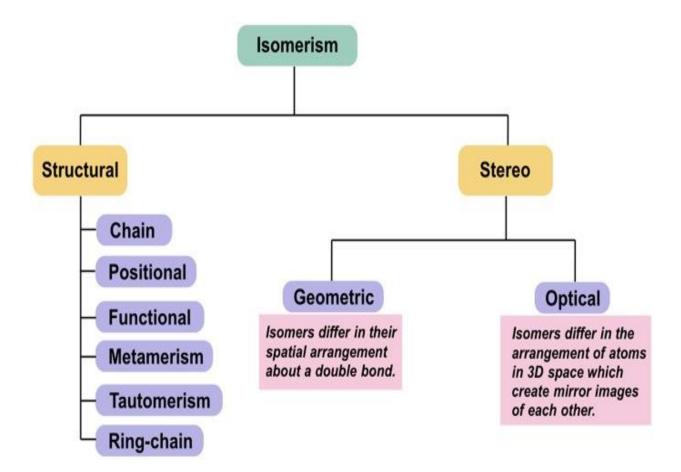
Divide the double bond in half, and assign the numbers 1 and 2 to indicate the relative priority of the two
groups on each end—the higher priority group is labeled 1, and the lower priority group is labeled 2.



Step [2] Assign E or Z based on the location of the two highest priority groups (1).



- The E isomer has the two higher priority groups on the opposite sides.
- The Z isomer has the two higher priority groups on the same side.



## **ISOMERISIM TYPES**

## **Tautomerism**

This isomerism is due to spontaneous intreconversion of two isomeric forms with different functional groups. The prerequisites for this is the presence of the C=O, C==N or N=O in the usual cases and an alpha H atom. The most usual is the â€~keto-enol' tautomerism, but there can be others like nitro-aci and amine-imine forms.

In general the Keto form is more stable. Enols can be forms by acid or base catalysis from the ketone and are extensively used in making C-C single bonds in organic synthesis.

# Ring-Chain isomerism

Here one isomer is an open chain molecule and the other a cyclic molecule.

Propene is an alkene and cyclopropane an alkane, two different classes of compounds.

# Types of organic chemistry reactions



Br

Br

# Substitution

## **Elimination**

## Rearrangement

# **Hybridization of Carbon**



1s **C**: ↑ ↓ 2s ↑ ↓

 $\begin{array}{c|c} 2p_x & 2p_y & 2p_z \\ \hline \uparrow & \downarrow & \end{array}$ 

**Ground state** 

1s 2s 2p<sub>x</sub> 2p<sub>y</sub> 2p<sub>z</sub> Excited state

**C**: ↑ ↓

 $2p_x 2p_y 2p_z$ 

sp<sup>3</sup>

1s **C**: ↑ ↓ 2p<sub>z</sub>

sp<sup>2</sup>

1s **C**: ↑ ↓ 2s 2p<sub>x</sub>

2p<sub>y</sub> 2p<sub>z</sub>

 $\rightarrow$ 

sp

