Microscale Organic Laboratory

with Multistep and Multiscale Syntheses

Fourth Edition

WEBSITE REFERENCE DISCUSSIONS

Dana W. Mayo          Charles Weston Pickard
Research Professor of Chemistry
Bowdoin College

Ronald M. Pike         Professor of Chemistry, Emeritus
Merrimack, College

Peter K. Trumper        University of Maine School of Law
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Sand Bath Techniques

The high sides of the crystallizing dish act to protect the apparatus from air drafts, and so the dish also operates somewhat as a hot-air bath. More uniform heating can be made by covering the crystallizing dish with aluminum foil (see Website Fig. 3.1W).

Website Figure 3.1W

Hot plate-magnetic stirrer with sand bath and reaction flask.
Metal Heat-Transfer Devices

A detailed report of the use of aluminum block systems including a number of designs has been made by Lodwig (see Lodwig, Siegfried N. J. Chem. Educ, 1989, 66, 77). Other metal systems, such as copper, have also been examined with rather promising results. To gain the advantages of both systems (sand and metal) the use of aluminum and zinc powders has been explored. Thirty-mesh zinc baths possess thermal characteristics very similar to solid aluminum blocks (see Website Fig. 3.2W).

Website Figure 3.2W

Temperature rise characteristics for several thermal devices.

Copper has nearly double the thermal conductivity of aluminum and the configuration found most attractive in this series is the copper tube-plate device. It requires relatively little copper, as it utilizes a 3-mm plate and 15-mm lengths of standard tubing (see Website Fig. 3.3W). The fabrication cost should be close to that of the aluminum block systems currently on the
market. As shown in Website Fig. 3.2W, compared to all other systems, the copper plate is far superior in temperature rise from room temperature. Thus, it is found at nearly 200 °C at the 5-min mark, whereas the aluminum block is barely above 100 °C at this time. It is also easier to achieve equilibrium conditions (see Website Fig. 3.4W).

An equilibrium temperature of 150 °C was reached in 9 min with copper, whereas it took 19 min with aluminum under the same conditions. The copper device also cools at nearly double the rate of the aluminum block. For example, to drop from 200 to 150 °C takes the aluminum block 8.1 min, whereas the copper system reaches the lower temperature in only 4.2 min. This characteristic is important in controlling temperature overruns.
Time to equilibrium (control set at high unitil the temperaturereaches 85° C, then heat control adjusted to a lower setting to give 150° C at equilibrium).

A handy plot of bath temperatures versus hot plate settings for your particular hot plate system can be obtained by using a printout of Website figure 3.5W (also see MOL4 Fig. 3.11).
Plot your bath and/or vial temperature (°C) versus hot plate control setting (reference graph provided for student printout).

Of particular significance is the observation that when distilling or refluxing organic materials, the block temperatures for the copper device are measurably lower. For example, 1 mL of p-xylene (bp 138 °C) contained in a 5-mL reaction vial refluxes at 175 °C in the copper bath. The aluminum block requires 188 °C under the same conditions and the sand bath ranks a distant third at 208 °C.

Reflux Apparatus

In microscale reactions, two basic types of reflux condensers are utilized: the air-cooled condenser, or air condenser (see Website Fig. 3.6W), and the water-jacketed condenser (see Website Fig. 3.7W).
Air condenser with conical vial, arranged for heating and magnetic stirring.
Water-jacketed condenser with 10-mL round-bottom flask, arranged for heating and magnetic stirring.

Distillation Apparatus

Reduced Pressure Distillation Systems

The high-performance low-cost atmospheric pressure 2.5-in. microspinning band distillation column has been modified to accommodate reduced pressure fractional distillation (see Website Fig. 3.8W) by: (a) replacing the
Reduced pressure microspinning band distillation column.

- Air condenser and suspended thermometer with a 14/10$\text{T}$, vacuum-tight, threaded thermometer adapter; (b) replacing the heavy-walled 3-mL conical collection vial with a thin-walled, 3-mL conical vial, which has, mounted near the bottom, a side arm with a threaded 5/5$\text{T}$ joint (a septum cap and silicone septum form a vacuum-tight seal on the side arm); and (c) a vacuum tubing
nipple replacing the Teflon stopper (7/ 10%) used to establish a vapor lock on the collection side of the system in the atmospheric still.

The system is evacuated via the vacuum tubing nipple. Fractions are efficiently collected with a gas-tight syringe and needle inserted through a septum mounted in the side arm of the 3-mL collection vial. The collection vial may be cooled externally during collection. This arrangement allows convenient collection of distillate fractions down to pressures of approximately 100 torr (successful collections have been made at pressures as low as 10 torr).

The system functions effectively under reduced pressure, even though the vapor lock present in the atmospheric still has been removed. Experimental data indicate that height equivalent/theoretical plate values remain near 0.25 in. per plate in these columns.

**Special Moisture Sensitivity Conditions**

In a few instances, reactions that are unusually moisture sensitive will be encountered. In this situation, reactions are best carried out in completely sealed systems that are scrupulously dry. The use of the Claisen head adapter with a balloon substituted for the drying tube provides a satisfactory solution to the problem (see Website Fig. 3.9W). Occasionally, it becomes
Sealed Claisen head with 3- or 5-mL conical vial, arranged for \( \text{N}_2 \) flushing, heating, and magnetic stirring.

Important to maintain dry conditions during a distillation. The Hickman stills are constructed with a 14/10\( ^\circ \) joint at the top of the head that readily accepts the drying tube (or Claisen head plus drying tube, (see Website Fig. 3.10W)).
Moisture-protected Hickman still head with 10-mL round-bottom flask, arranged for heating and magnetic stirring.

Collection of Gaseous Products

The collection, or trapping, of gases is conveniently carried out by using the capillary gas delivery tube. This item can be attached directly to the female 14/10$\text{S}$ joint of a condenser connected to a reaction flask or vial (see Website Fig. 3.11W).
Website Figure 3.11W

Water-jacketed condenser with 3- or 5-mL conical vial and capillary gas delivery tube, arranged for heating and magnetic stirring.

Collection of Gas Chromatographic Effluents

A number of the reaction products in the experimental section of the text depend on collection of gas chromatographic effluents for successful purification and isolation. The ease and efficiency of carrying out this operation is greatly facilitated by employing the 5/5s collection tube and the 0.1-mL 5/5s conical collection vial (see Website Fig. 3.12W).
Gas chromatographic collection tube and 0.1 mL conical vial.
WEBSITE DATA FOR CHAPTER 5

TECHNIQUE 2

Semimicroscale Distillation

Distillation Theory
Distillation techniques often can be used for separating two or more components on the basis of differences in their vapor pressures. Separation can be accomplished by taking advantage of the fact that the vapor phase is generally richer in the more volatile (lower boiling) component of the liquid mixture. Molecules in a liquid are in constant motion and possess a range of kinetic energies. Those with higher energies (a larger fraction for the lower boiling component) moving near the surface have a greater tendency to escape into the vapor (gas) phase. If a pure liquid (e.g., hexane) is in a closed container, eventually hexane molecules in the vapor phase will reach equilibrium with hexane molecules in the liquid phase. The pressure exerted by the hexane vapor molecules at a given temperature is called the vapor pressure and is represented by the symbol $P^\circ_H$ where the superscript $^\circ$ indicates a pure component. For any pure component $A$, the vapor pressure would be $P^\circ_A$. Suppose a second component (e.g., toluene) is added to the hexane. The total vapor pressure ($P_{\text{total}}$) is then the sum of the individual component partial vapor pressures ($P_H$, $P_T$), where $P_H$ is the partial pressure of hexane, and $P_T$ is the partial pressure of toluene as given by Dalton's law.
\[ P_{\text{total}} = P_H + P_T \]

or in general

\[ P_{\text{total}} = P_A + P_B + P_C + \ldots + P_n \]

Assuming that the vapors are ideal, the mole fraction of hexane in the vapor phase is given by

\[ Y_H = \frac{P_H}{P_{\text{total}}} \] (5.1)

It is important to realize that the vapor pressure \( P_A^\circ \) and the partial vapor pressure \( P_A \) are not equivalent, since the presence of a second component in the liquid system has an effect on the vapor pressure of the first component. If the solution is ideal, the partial vapor pressure of hexane is given by Raoult's law

\[ P_H = P_H^\circ X_H \] (5.2)

where \( X_H \) is the mole fraction of hexane in the liquid system.

For ideal solutions, Eqs. 5.1 and 5.2 may be combined to obtain the phase diagram shown in Website figure 5.1W. In this figure and
Pressure as a function of liquid composition ($X$) and vapor composition ($Y$), for hexane and toluene (temperature held constant at 69 °C).

Elsewhere we will drop the subscripts from $X_H$ and $Y_H$. Here $X$ and $Y$ will represent the mole fractions of the most volatile component (MVC) (hexane in this case) in the liquid and vapor phases, respectively.

Website figure 5.1W describes hexane and toluene mixtures at a fixed temperature. For the region above the $X$ curve, there will be only liquid present. For the region below the $Y$ curve, there will be only vapor. In the area between (the sloping, lens-shaped region), liquid and vapor will be present in equilibrium. This area is the only region of interest to us in examining the distillation process.

To understand what the phase diagram tells us about the composition of the liquid and vapor phases, let us imagine that the total pressure of the system is 500 torr, shown by the horizontal line in new figure 5.2W. At this
Pressure as a function of liquid composition ($X$) and vapor composition ($Y$), for hexane and toluene (temperature held constant at 69 °C).

pressure a liquid of composition $X_1$ will be in equilibrium with a vapor of composition $Y_1$. These two points are defined by the intersection of the constant pressure line with the $X$ and $Y$ curves. It is important to note here that $Y$ will be greater than $X$ for the equilibrium system. That is, the vapor in equilibrium with a given liquid will be richer in the more volatile component than in the liquid.

Diagrams such as Website figure 5.2W are not very useful in describing the distillation process. We need a phase diagram for the mixture at constant pressure instead of constant temperature. Website figure 5.1W may be transformed to the desired diagram if we know how $P_{H}^{\circ}$ and $P_{T}^{\circ}$ depend on $T$. This information may be supplied by the Clausius–Clapeyron equation or by appropriate experimental data.
We will obtain a qualitative diagram for temperature as a function of composition by the following reasoning: (1) The substance having the higher vapor pressure at a given temperature will have the lower boiling point at a given pressure. (2) At low temperatures, only the liquid phase will be present, and at high temperatures only the vapor phase will be present. Thus, the temperature-composition diagram is shown by Website figure 5.3W.

Website Fig. 5.3W

Temperature as a function of liquid composition (X) and vapor composition (Y).

Note that this figure may also be obtained (qualitatively) by turning Website figure 5.1W upside down.

Many pairs of liquids do not obey Raoult's law. Often, pairs of liquids encountered in organic chemistry exhibit a positive deviation from Raoult's law. The positive deviation means that the pressure above the solution is greater than would be predicted by Raoult's law. If this deviation is large, the pressure composition curve may exhibit a maximum, as shown in Website figure 5.4W. Here the curves for normal Raoult's law behavior are
Positive deviation from Raoult's law; \( L = \text{liquid}, V = \text{vapor} \).

shown as dashed lines for reference. Mixtures in which one of the components is polar and the other component is at least partly nonpolar often exhibit positive deviations from Raoult's law.

The temperature-composition diagram for systems showing a positive deviation from Raoult's law is again obtained by the simple inversion process. Such a diagram is shown in Website figure 5.5W. In this
Ethanol-water minimum boiling point phase diagram.

At a temperature of $T_1$, a liquid of composition $X_1$ will be in equilibrium with a vapor of $Y_1$. At a temperature of $T_{az}$, however, the composition of the liquid and vapor will be the same. This mixture is an azeotropic or constant-boiling mixture. Water (H$_2$O) and ethanol (CH$_3$CH$_2$OH) form one of the more familiar azeotropic systems. This mixture exhibits a positive deviation from Raoult's law and has a minimum boiling azeotrope at 78.1 °C, which consists of 95.6% ethanol by volume.

Steam Distillation

Another type of distillation and one which depends on materials which exhibit positive deviations from Raoult's law is the technique of steam distillation.
If two substances are immiscible (as the term “steam distillation” implies, one of the substances will be water), the total vapor pressure \( P_t \) above the two-phase liquid mixture is equal to the sum of the vapor pressures \( P_i \) of the pure individual components \( P_i \) according to Dalton's law.

\[
P_t = P_1 + P_2 + \ldots + P_i
\]

In other words, with an immiscible pair of liquids, neither component lowers the vapor pressure of the other. The two liquids would exert the same vapor pressure (at a given temperature) even if they were in separate containers. If a mixture of these two liquids is heated, boiling will occur when the combined vapor pressures of the liquids equals atmospheric pressure. At this point, distillation will commence. Condensation of the vapors gives a two-phase mixture (condensate or distillate) of the organic species and water. The composition of this distillate is determined by the vapor pressure and molecular weight of the compounds.

To illustrate this concept let us take an insoluble mixture of bromobenzene (bp = 156 °C) and water. At 30 °C the vapor pressure of bromobenzene is 6 torr; water is 32 torr. Therefore, the vapor pressure of the mixture is the sum of 6 + 32 or 38 torr, at this temperature. At 95 °C, the vapor pressure of bromobenzene is 120 torr; water is 640 torr. It follows that the sum is now equal to 760 torr or 1 atm. That is, \( P_A^\circ + P_B^\circ = 1 \text{ atm} \).

As a result, the mixture boils and the bromobenzene and water distill together. A further example is the isolation of cyclohexanone from nonvolatile reaction byproducts by steam distillation. The normal boiling point of pure cyclohexanone is 156 °C and that for water is 100 °C. At about 94.5 °C, the vapor pressure of cyclohexanone is 112 torr and the vapor pressure of water is 648 torr.
The vapor pressures of cyclohexanone and water add up to 760 torr. Thus the two compounds steam distill at 94.5 °C.

Several important aspects of steam distillation are summarized below:

1. The mixture **boils below** the boiling point of either pure component. In this regard the technique is similar to reduced pressure distillation in that the liquid distills and condenses at a temperature below its normal boiling point. This result occurs because compounds that are immiscible in water have very large, positive deviations from Raoult's law.

2. The **boiling point** of the mixture will **hold constant** as long as both substances are present to saturate the vapor volume.

3. The molar ratio of the two species in the **distillate** remains constant as long as aspect 2 holds.

From Dalton's law, the condensate in a steam distillation will consist of water and the compound in the same molar ratio as the ratio of their vapor pressures ($P^\circ$) at the steam distillation temperature. The relationship is

\[
\frac{\text{Moles water}}{\text{Moles of organic species}} = \frac{P^\circ \text{ water}}{P^\circ \text{ organic species}}
\]

This relationship may be altered to show the weight relationship of the organic substance to that of water.

Substituting grams per molecular weight (g/ MW) for moles we obtain

\[
\frac{\text{g/ MW water}}{\text{g/ MW organic species}} = \frac{P^\circ \text{ water}}{P^\circ \text{ organic species}}
\]

Transposition and rearrangement of this expression leads to
\[
\frac{\text{g water}}{\text{g organic species}} = \frac{P^\circ \text{ water} \times \text{MW water}}{P^\circ \text{ organic species} \times \text{MW organic species}}
\]

Based on this relationship, the weight of water required per weight of organic species can be calculated. Note that if the vapor pressure of water is known at the boiling temperature of the mixture that is being steam distilled, the vapor pressure of the organic substance is 760 torr – \(P^\circ_{\text{water}}\).

**NOTE.** These two experiments utilize Technique 3: Steam Distillation Experiments [11C] and [32].

**How Spinning Bands Function in Fractional Distillation Columns**

To understand how the spinning band improves the performance of the column, and to see some of the important characteristics of these fractionating systems, we will analyze them a bit further. Website figure 5.6W shows a very simple distillation column possessing just one plate.
Model for fractional distillation with partial reflux.

Overall, however, this system has two theoretical plates.

The compositions of the liquid in the pot and of the infinitesimal amount of liquid at the first plate are $X_0$ and $X_1$, respectively. Both $Y_0$ and $Y_1$ are compositions of the vapor in equilibrium with each of the liquids, $X_0$ and $X_1$, respectively. Since we are talking about the MVC, $Y_0 > X_0$, $Y_1 > X_1$, and we may assume that $Y_1 > Y_0$ (i.e., we have already established that the vapor will be enriched in the MVC). The parameter $V$ is the rate at which vapor is transported upward, $L$ is the rate of downward transport of liquid back to the pot, and $D$ is the rate at which material is distilled. The parameters $L$, $D$, and $V$ are related by $V = L + D$. (What goes up, must come down.)

We will first look at the process qualitatively. If $D$ and $V$ are comparable ($L$ is small), as vapor at composition $Y_1$ is removed, $X_1$ becomes smaller—the liquid in the first plate becomes less rich in the MVC as the MVC rich vapor is removed. If, on the other hand, $L$ and $V$ are both large compared with $D$, the composition at plate 1 will be maintained at $Y_0$ by the large supply of incoming vapor with composition $Y_0$. This relationship may also be seen in the following quantitative discussion.
The first relationship we have already seen:

\[ V = L + D \]  \hspace{1cm} (5.3)

In addition, if an insignificant amount of material is held up at plate 1, the moles of MVC going into plate 1 must equal the moles of MVC leaving plate 1;

\[ V \cdot Y_0 = L \cdot X_1 + D \cdot Y_1 \]  \hspace{1cm} (5.4)

We may eliminate \( V = (L + D) \) from Eq. 5.4 and rearrange to get

\[ X_1 = Y_0 - \left( \frac{D}{L} \right) \cdot (Y_1 - Y_0) \]  \hspace{1cm} (5.5)

Now, in Eq. 5.5, \( Y_1 - Y_0 \) will always be greater than 0 under ideal conditions (since they both represent the MVC). Both \( D \) and \( L \) are positive. Therefore, the upper limit for \( X_1 \) is \( Y_0 \). This situation would be the case when \( D/L = 0 \) (and nothing is being distilled). In the real world something is being distilled \( (D > 0) \) and \( X_1 \) will be less than \( Y_0 \) (and down the line the condensate will be less rich in the MVC; there will be less separation). You should be able to generalize this result for one plate for the situations in which we have \( n \) plates. When \( D/L \) is small the composition of the first plate is at a maximum; therefore, \( Y_1 \) is also a maximum and, furthermore, \( X_2 \) will be a maximum, and so on.

The purpose of the spinning band is to make \( D/L \) as small as possible so that \( X_1 \) approaches its upper limit of \( Y_0 \). The spinning band ensures that the optimum separation of a pair of liquids will be achieved. We will have a lot of vapor going up, a lot of liquid being returned by the spinning action of the spiral
band, and a relatively small amount of material actually being distilled. This result also implies that if we want to achieve a high degree of separation, the distillation rate should be low. There is, of course, a compromise between the low rate of distillation required to obtain maximum separation and a rate that will allow someone else to use the apparatus and you to get on to other things.
TECHNIQUE 3

Reduced pressure distillations with microspinning band columns

Distillation Apparatus

One of the most powerful distillation systems currently available for the instructional laboratory is the 2.5-in. vacuum-jacketed microscale spinning band distillation column shown in MOL4 text figure 3.16. This still utilizes the same type of band drive as the

MOL4 Text Fig. 3.16

Microspinning band distillation column (2.5 in.).
Hickman-Hinkle columns, but in addition the system is designed for conventional downward distillate collection, nonstopcock reflux control, and reasonably accurate temperature sensing. The column, which can develop nearly 12 theoretical plates, possesses the highest resolution in terms of HEPTs (height equivalent theoretical plates, see also discussion of distillation theory and the concept of theoretical plates in Technique 2 and a definition of HEPTs in Technique 1 discussions in text) of any standard distillation apparatus presently in use in the instructional organic laboratory.

The atmospheric pressure, 2.5-in. microspinning band distillation column can be modified to accommodate reduced pressure fractional distillation (see Website Fig. 3.8W) by: (1) replacing the air-condenser and suspended thermometer with a 14/10 standard taper (\(\Phi\)), vacuum-tight, threaded thermometer adapter; (2) replacing the heavy-walled 3-mL conical collection vial with a thin-walled 3-mL conical vial that has mounted near the bottom a side arm with a 5/5 threaded \(\Phi\) joint (a septum cap and silicone septum form a vacuum-tight seal on the side arm); (3) replacing the Teflon stopper (7/10\(\Phi\)), used to establish a vapor lock on the collection side of the system in the atmospheric still, with a 7/10\(\Phi\) inner joint connected to the vacuum system.

The still is evacuated via the 7/10\(\Phi\) joint or a vacuum tubing port (shown in drawing). Fractions are efficiently collected by employing a gas-tight syringe via the septum mounted in the side arm of the 3-mL collection vial. The collection vial should be cooled externally during the takeoff period. This arrangement allows for efficient collection of distillate fractions down to pressures of approximately 100 torr (successful collections can be made as low as 10 torr with more expensive vacuum syringes).

This micro-distillation system continues to function very effectively under reduced pressure, even though the vapor lock has been removed. Student
derived experimental data indicate that height equivalent/ theoretical plate values remain near 0.2 in/ plate as observed in these columns when operated at atmospheric pressures.

**METHYLCYCLOHEXANE/TOLUENE DISTILLATION**

at 300 Torr

**Physical Properties of Reactants**

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>MW</th>
<th>Wt/ Vol</th>
<th>bp(°C)</th>
<th>DENSITY</th>
<th>n_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylcyclohexane</td>
<td>98.19</td>
<td>1.0 mL</td>
<td>100.9</td>
<td>0.7694</td>
<td>1.4231</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.15</td>
<td>1.0 mL</td>
<td>110.6</td>
<td>0.8669</td>
<td>1.4961</td>
</tr>
</tbody>
</table>

**Assembly of the system**

Assemble the system as shown in Website figure 3.8W. In the process, make sure the Teflon band is aligned as straight as possible in the column. In particular, the pointed section extending into the pot must be straightened to minimize vibration during high speed spinning of the band. It is critically important to use a specially adapted Teflon band which has a small (1.5 cm long) Teflon filament mounted just above the magnet and running through the shaft and adjusted so the it extends equally on either side of the shaft. This filament is essential to eliminate “bumping” in the pot under reduced pressure during the distillation.

**A standard mixture of 50:50 methylcyclohexane/toluene**

Once the spinning band has been tested and rotates freely, place a mixture of 1 mL methylcyclohexane/ 1 mL toluene (to be delivered with a Pasteur pipette or an automatic delivery pipette) in the 5-mL conical distillation pot (with a greased $\mathbb{E}$ joint or $\mathbb{S}$ Teflon sleeve). Reassemble the system and lower the column and
charged conical distillation pot into the sand bath or copper tube block (the latter functions more effectively during distillations). It is important to note that the 14/10TS joint in the head also needs to be lightly greased during reduced pressure distillations and the beveled edge of the air condenser should now be oriented just off the collection cup (in atmospheric distillations the initial orientation is suggested to be 180° from the collection cup) and the ability to rotate over the collection cup under reduced pressure needs to be checked. If rotation is difficult, the joint needs to be more heavily greased. It may even be necessary to initially orient the beveled edge directly over the collection cup.

**Note**

It is important to make an aluminum foil sand bath cover or copper tube block baffle that reflects heat and hot air away from the side arm collection vial while at the same time cooling the vial in an ice bath.

The vacuum is generated by either a mechanical pump or a water pump. Employing a manostat (see below) a pressure of 300 torr is set in the still. After establishing the required pressure (see below) gently heat the copper block (see Website Fig. 3.3W) until boiling occurs. The magnetic stirrer is turned to a low spin rate when heating commences. When reflux is observed at the base of the column, the magnetic stirrer is adjusted to an intermediate spin rate. Once liquid begins to enter the column, the spin rate is increased to the maximum (1000-1500 rpm).
It is absolutely critical that the temperature of the pot be adjusted so that the vapors in the column rise very slowly.

When the vapors slowly arrive in the unjacketed section of the head of the column, the condenser joint acts as a vapor shroud to effectively remove vapors from the receiver cup area. During this total reflux period, maximum separation of the components is achieved. Once vapor reflux occurs in the head of the column, the system is left for 20-30 min. to reach thermal equilibrium. During this period of total reflux, the head thermometer will very likely read a few degrees low (below the boiling point).

Following the equilibrium period, collection of the resolved components may begin. Rotate the air condenser over the collection cup if it is not already in that position. Distillate fractions are collected in the cooled side-arm receiving vial. A gas-tight syringe is used to retrieve fractions without disturbing the vacuum during the distillation. The first fraction should be nearly 90% pure (see below). When corrected for the reduced pressure (see new Fig. 5.7W) the column resolution can be calculated by measuring the refractive
Methylcyclodohexane-toluene at 300 torr.

Index which can be related directly to the composition of the condensate (see Technique of Organic Chemistry, **Vol. IV**, Distillation, 2nd ed.; Eds. Perry, E. S.; Weissberger, A. Interscience - John Wiley & Sons, Inc., New York, p. 68) of the first fraction. If carefully distilled, the values should correspond to a HETP of approximately 0.25 in./plate. Recovery of the distillate fractions should account
for approximately 90% of the starting material. An example of a standard sample distillation is given below.

### Methylcyclohexane/Toluene Distillation at 300 Torr

<table>
<thead>
<tr>
<th>FRACTION</th>
<th>APPROXIMATE VOLUME</th>
<th>WEIGHT</th>
<th>MOLE FRACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50 mL</td>
<td>0.0425 g</td>
<td>0.895</td>
</tr>
<tr>
<td>2</td>
<td>300 mL</td>
<td>0.2300 g</td>
<td>0.855</td>
</tr>
<tr>
<td>3</td>
<td>530 mL</td>
<td>0.4080 g</td>
<td>0.815</td>
</tr>
<tr>
<td>4</td>
<td>125 mL</td>
<td>0.0965 g</td>
<td>0.825</td>
</tr>
<tr>
<td>5</td>
<td>85 mL</td>
<td>0.0780 g</td>
<td>0.778</td>
</tr>
<tr>
<td>6</td>
<td>140 mL</td>
<td>0.1100 g</td>
<td>0.470</td>
</tr>
<tr>
<td>pot</td>
<td>750 mL</td>
<td>0.5955 g</td>
<td>0.040</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>1.5605 g</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fraction purity can be further assessed by GC and IR analysis.

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### Vacuum Pumps and Pressure Regulation

The reduced pressure distillation may employ either water or mechanical types of pumps. Both have advantages and disadvantages. The water pump utilizes a very simple inexpensive aspirator. The system is based on the Venturi effect in which water is forced through a constricted throat in the pump (see Website Fig. 5.8W). If water, as an incompressible liquid,
Aspirator pump.

completely fills the water pump at all points, the same volume of liquid must pass every cross section in any given time as it is discharged out of the aspirator.

Hence,

\[ Q = A \cdot v \]

where \( Q \) = the discharge rate (cm\(^3\)/s)  
\( A \) = the cross section of the discharge  
\( v \) = the velocity of the discharge

and the Equation of Continuity follows

\[ Q = A \cdot v = A_1 v_1 = \text{constant} \]

where  
\( A_1 \) = the cross section of the throat  
\( v_1 \) = the velocity in the throat
A consequence of this relationship is that the velocity is greatest at points where the cross section is least and vice versa. Hence, the water velocity through the throat of the aspirator is much faster than the discharge velocity. Air is drawn into the low-pressure water rushing through the constricted portion (Bernoulli’s equation).

Several pressure effects are involved with the use of this type of pump. First, the pressure is limited to the vapor pressure of water at the temperature of the water supply reservoir. Second, distillations are subject to flooding (condensate overload in the column resulting from a sudden pressure drop and subsequent rapid evolution of distillate vapor into the column) if significant pressure changes occur during the distillation. Third, a drop in water pressure (caused by a laboratory neighbor turning on the water supply) will often result in a backup of water through the hose connection to the still, as the pressure momentarily is lowest on that side of the system. It is, therefore, essential that safety traps be mounted between the aspirator and the distillation apparatus.

Mechanical, motor driven pumps can obtain considerably lower pressures and are not subject to the kind of pressure variations experienced with aspirators. They are, however, considerably more expensive both to acquire and maintain. They are also very easily contaminated and the resulting corrosion may seriously effect pump performance.

Once a vacuum pump is in operation it is important to be able to monitor the pressure of the system. This measurement is carried out by using a variety of devices, depending on the pressure values being determined. Water pump pressures can vary from atmospheric (760 mm Hg or torr) to the vapor pressure of water determined by the temperature of the water supply (usually 15-25 torr).
Mechanical pump pressures can easily drop to the 0.0001 torr range, which requires more sensitive measuring devices than those obtained via the aspirator.

The manometer is the most common means of determining the system pressure. Manometers that function effectively in the 760 to 5 torr range can be easily constructed. These gauges measure the height difference between two columns of mercury—one with the system pressure above the column, and the other column (the reference column) with “zero” pressure (see Website Fig. 5.9W). When pressures below 5 torr are present an expanded scale is required to accurately observe the operating system. This can be accomplished down to 0.00005 torr by more sophisticated manometers (McLeod vacuum gauges) that employ three mercury columns, and a different type of reference system.

Website Fig. 5.9W

(a) Full-range manometer and (b) short-range manometer.
When even lower pressures are required, Venturi pumps (diffusion pumps) employing mercury or high boiling oils can be used in combination with mechanical pumps to reach pressures $<10^{-8}$ torr. When these very low pressures are required, ion pressure gauges become the measuring system of choice.

The vacuum system used in the distillation described in the example assumes the use of a water pump to furnish the reduced pressure. We will, therefore, only require a simple two-column manometer (the use of two manometers in this experiment will save on stopcock requirements—see below) for pressure measurements. In many distillations (including the example), it is essential to establish a particular pressure and to maintain that pressure throughout the distillation. Controlling the distillation pressure allows the separation to be carried out with temperatures at the column head that are low enough to prevent thermal decomposition in the pot, and high enough to establish a reasonable number of vaporization—condensation cycles in the column. The operating pressure also needs to be high enough to prevent volatilization into the pump trap by the distillate during condensation and collection in the receiver.

This pressure control is accomplished by a device termed a manostat. One of the simplest (and cheapest) monostats to be described in the literature is the "Sommer System" (see Website Fig. 5.10a&bW), which resembles a gas washing bottle in appearance.
Website Fig. 5.10a & b

(a) Sommer manostat; A, 250-mL bulb; B, 24/40; C, fluid reservoir; D, Ace-threaded adapter; E, 7-mm o.d. tubing. (b) A typical arrangement.

The Sommer manostat operates in the following fashion: The “connection from the system” (see Website Fig. 5.10aW) refers to the vacuum tubing leading to the receiver side-arm connector. The “connection to the pump” refers to vacuum tubing leading to the safety trap (see reduced pressure removal of solvent see Website Fig. 5.11W) attached to the aspirator. To set the pressure simply add fluid (usually Hg) to a predetermined height above the bottom of the inlet tube. The height of the column of fluid is equivalent (correct for fluid density) to the pressure desired in the system. The pressure on the distillation apparatus side must overcome this hydrostatic head pressure before it can escape to the pump. The operating pressure can be “fine tuned” by making small adjustments in the height of the inlet tube via the threaded adapter seal.
Consequently, the actual operating pressure in the still is most easily observed with a second manometer (see Website Fig. 5.10bW).

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**see Website Fig. 5.11W**

Vacuum trap.
TECHNIQUE 5

Crystallization

Alternate Methods for Recrystallization and/or Filtration

In recent years several alternative methods have been reported for the recrystallization and or filtration of small quantities of solid product. Several of these methods are summarized here. Consult the sited references for further details.

a. Landgrebe (see Landgrebe, J.A. J. Chem. Educ. 1988, 65, 460) has described the use of a recrystallization pipet. The method works well for 10-100 mg quantities, as long as the volume of solvent used in the recrystallization does not exceed 1.5 mL, the capacity of a Pasteur pipet. The sequence of steps follows:

1. A recrystallization tube is prepared (Website Fig. 5.12W) by pushing a plug of cotton (copper wire is used) into the Pasteur pipet so that the cotton resides 1-1.5 cm below the wider bore of the pipet.

2. The lower part of the tube is sealed below the cotton plug with a micro burner and the glass is pulled so that a very narrow tip is formed. This allows the tip to be broken easily at a later stage of the operation.
3. The solid to be recrystallized is placed in the tared tube, the tube reweighed to determine the weight of solid, and then it is clamped in a vertical position. A tared vial is placed so that the bottom tip of the recrystallization tube protrudes about 1 cm into it. (Website Fig. 5.13W).

**Website Fig. 5.13W**

Dissolution of sample in hot solvent.

4. An appropriate amount of solvent is added to the tube using a Pasteur pipet, and the suspension stirred with a copper wire. At this point a heating lamp is placed approximately 6-8 cm from the tube.

5. When the solid has dissolved, the vial is removed, the tip snapped off and the vial quickly replaced. If the filtration into the vial is too slow, pressure is applied using a pipet bulb.

6. After crystallization is complete, the mother liquor may be removed using a Pasteur filter pipet. Cold, fresh solvent may be added to wash the crystals, and
the wash solvent again removed as before using the Pasteur filter pipet. The washed crystals may be dried under reduce pressure as discussed earlier.

b. Laporterie (see A. Laporterie J. Chem. Educ. 1992, 69, A42) outlines the construction of an assembly consisting of a reaction tube fitted with a filter paper-glass wool plug supported by a one hole rubber stopper into which a hypodermic syringe needle is inserted. An adapter is inserted through the stopper hole so that the assembly can fit a filtering flask. This simple and inexpensive system allows one to filter, wash and crystallize without transferring the product crystals.

c. Durate and co-workers (see F. F. Duarte; L. L. McCoy; F. D. Popp J. Chem. Educ. 1992, 69, A314) report an apparatus for recrystallization of small amounts of material which is less imposing and/or frustrating, for the average organic laboratory student when compared to the Craig tube or filter Pasteur pipet techniques. The system is also more durable. It consists of a 10 mm x 127 mm glass tube closed on one end by a coarse frit that fits snugly in a 16 mm x 95 mm glass tube. The material to be recrystallized is placed in the outer tube, the solvent of choice is added, and the system heated as in a normal crystallization. The resulting solution is cooled and once the crystals are formed, the inner tube is placed in the outer tube and the apparatus is centrifuged. The mother liquor is forced into the inner tube. The liquor is removed with a Pasteur pipet leaving the purified material in the outer tube. The tubes are separated and the crystals dried.

d. An other alternative approach has been reported by Winkel (see C. R. Winkel J. Chem. Educ. 1993, 70, A161). A 10-mL culture tube with small holes drilled through its Bakelite screw cap is used. Filter paper (1.5 cm) is placed in the cap and secured when the cap is screwed onto the tube. The inverted tube is inserted into a neoprene rubber
connector, made from a #3 neoprene stopper, which in turn is placed in a side arm suction tube. The suction tube holds a collecting tube. The filtrate is directed into the collection tube by a plastic funnel base secured in the neoprene adapter. This assembly has several advantages. Loss of crystals and time in making sample transfers are avoided. Hot and cold filtrations can be done easily. Heat and vacuum can both be applied for fast drying. No suction trap is required to prevent back-splashing, if a spacer is used and no centrifugation is necessary in order to remove the mother liquor.

**e.** An inexpensive single-use suction microfilter has been described by McDevitt (see E. J. McDevitt J. Chem. Educ. **1994**, 71, A147).

The apparatus is prepared from two disposable polyethylene transfer pipets. The top hemispherical portions of the droppers are punctured 4 or more times with a pin. The hemispheres are then cut off each dropper. One of the punctured hemispheres is then inserted into the bulb of a cut dropper and pushed to the bottom with a rod. A small wad of glass wool is then inserted followed by the second punctured hemisphere until it rests on the glass wool. Thus, a sphere-wool-sphere sandwich is constructed at the base of the bulb. This suction filter is used in the usual manner. The collected crystals can be pushed out of the bulb or the dropper-funnel can be cut apart.

**f.** Filtration may be carried out using a Pasteur pipet, if the volume of solvent does not exceed 3.0 mL of solution (see J. W. Zubrick *The Organic Chem Lab Survival Manual* 4th ed., Wiley: New York, NY, 1997, p. 82). Push a small plug of cotton into the Pasteur pipet so that the cotton resides slightly into the narrow portion of the pipet and shorten the tip of the pipet to approximately 1.5-2 cm. Do not use too much cotton or pack it too tightly so that the solution cannot be forced through it. The warm solution to be filtered is placed in the pipet using a preheated second Pasteur pipet. The solution is then allowed to filter through the cotton plug into a clean vial (tared if
desired). If need be, pressure can be applied by a pipet bulb (careful!). It is advisable to place a heating lamp approximately 6-8 cm from the tube since a serious problem with this technique is that crystallization often occurs in the filtration tube. The shortened Pasteur filter pipet can easily be suspended over a collection vial using a cradle made by twisting two short pieces of copper wire together which are then spread apart to snugly accept the pipet.

g. Separation of crystalline solids or of impurities can often be accomplished, with care, by use of a Pasteur filter pipet (Website Fig. 5.14a-dW).

Website Fig. 5.14a-dW

Preparation of Pasteur filter pipet.

The container (conical vial or centrifuge tube) holding the crystal-mother liquor mixture is cooled in an ice-water bath. A Pasteur filter pipet is used to slightly stir the mixture. The air is then slowly pushed from the pipet as the tip of the pipet is inserted.
to the bottom of the container (the bubbles of air forced from the tip clear a path for the tip of the pipet so that it can reach the bottom of the flask without trapping crystals in the tip as it is pressed against the surface of the glass). The liquid is then drawn slowly up into the pipet leaving the crystals behind. Cold, fresh solvent may be added to wash the crystals, and the wash solvent then removed using the Pasteur filter pipet as before.

This method is not recommended for fine crystals. Large needles or granular type materials may be filtered in this manner.

**Two Examples to Practice Recrystallization on a semi-microscale are given here.**

This procedure is useful when carrying out scaled-up microscale reactions. For example, see Experiments [14], [15], or [18].

**Example [1]:** Recrystallization of Benzoin.

Place about 250 mg of benzoin in a 25 mL Erlenmeyer flask. Add a boiling stone, stirring rod or if a magnetic stirring hot plate is used, a small magnetic stir bar. Add enough preheated 95% ethanol to cover the crystals and then heat on a sand bath. When the mixture is at a low boil, add dropwise (Pasteur pipet) small amounts of the solvent just to the point where all the benzoin goes into solution.

We will assume that the solution is colored and that it also has some insoluble impurities still present.

Cool the solution somewhat and add carefully about 1–5 mg of Norit pellets to absorb the colored impurities. If powdered charcoal is used be careful during the addition, since frothing may occur. Heat the solution to boiling once again with stirring. Gravity filter the hot solution (Caution! hold the flask with tongs or use a towel) into another 25 mL Erlenmeyer flask using a short stem funnel or better a stemless one. Pre-heat the funnel with hot solvent (see Fig. 5.15W).

During the filtration crystals may appear in the funnel due to the cooling or evaporation of the solution. This can often be avoided by pre-heating the funnel or by heating the solution in the receiving flask during the process so that warm vapors envelop the funnel. Once the filtration is complete, add a small amount of hot solvent to the original flask and pass this through the filter.

Concentrate the warm filtrate by heating the flask (add a Si-C stone or stir bar) on a sand bath in the hood to the point of where the original volume of solvent used
remains. Allow the flask to cool to room temperature. If crystals do not appear, concentrate the solution further and recool. At this point it may be necessary to add a seed crystal or to scratch the walls of the flask with a glass rod (this is most successful if carried out at the interface of the solution surface with the flask) to induce crystallization. Finally, place the flask and contents in an ice-water bath for 10-15 minutes to complete the crystallization. Recover the crystals by suction filtration using a Hirsch funnel (see Filtration Techniques). Wash the crystals carefully with a small amount of cold 95% ethanol. To do this operation, vent the vacuum pump and add a small amount of ice-cold solvent over the crystals. Drain off the wash by closing the vent and repeat once or twice more, if necessary. Continue to apply reduced pressure to the filter plate to aid in drying the crystals. Determine the melting point and compare it to the literature value. Calculate the percent recovery.

**Example [2]:** Recrystallization of Naphthalene from a Solvent Pair.

Using the equipment and techniques described in the recrystallization of benzoin, dissolve about 200 mg of naphthalene in the minimum amount of warm acetone. Heat the solution to boiling and then slowly add (dropwise) warm water while stirring, until a cloudy solution is obtained. Now add more acetone dropwise until the solution is clear once again. Remove the flask and allow the solution to cool. It may be necessary to scratch the surface of the glass flask with a glass rod or add a seed crystal to initiate crystallization. Further cool the solution in a ice-water bath. Collect the crystals by suction filtration, wash and dry them in the usual manner. Weigh the dried crystals. Calculate the percent recovery. Determine the melting point and compare it to the literature value.
**TECHNIQUE 8:**

**Measurement of Specific Rotation**

**High Performance Polarimeters**

High performance polarimeters are now available with a digital readout with an accuracy of $0.001^\circ$. These instruments are based on an automatic optical-null balance principle that operates within a rotary range of $\pm 80^\circ$. The schematic diagram for two such polarimeters is shown in Website figure 5.16W. Model 241 (Website Fig. 5.16aW) has two spectral line sources (Hg and Na)

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**Website Fig. 5.16W**

Schematic diagrams of Perkin-Elmer polarimeters: (a) Model 241, (b) Model 241 MC. (Courtesy of the Perkin-Elmer Corp., Newton Centre, M A.)

and a filter wheel (F) containing five optical filters. A rotatable mirror (M) is coupled to this shaft so that when a desired wavelength is selected, the beam of the corresponding lamp is automatically reflected along the optical path.
The Model 241 MC, (Website Fig. 5.16bW) is equipped with a high-resolution grating monochrometer (M) plus deuterium (D₂) and quartz-iodine lamps (continuous sources). The desired wavelength(s) can be selected by the monochrometer.

In both instruments, the monochromatic light passes through the polarizer (P), the sample cell (K), the analyzer (A), on to the photomultiplier tube detector (PM). The polarizer and analyzer are rotatable Glan prisms of calcite. The polarizer (and thus the plane of the plane polarized light) oscillates at an amplitude of about ±0.7° at the line frequency about the optical longitudinal axis. In an unbalanced condition, the photomultiplier tube receives a frequency signal that is amplified and fed to the servo motor (SM) with the corresponding polarity (the latter gives the direction of rotation). The servo motor drives the analyzer until this signal is reduced to null (this gives the magnitude of the rotation). This condition constitutes a balanced system (optical null).

When an optically active substance is placed in the sample cell (K), the plane of the polarized light is changed based on the optical rotation of the sample. The analyzer is rotated by the servomotor to the new null balance position. The difference between the original and new balance position corresponds to the optical rotation of the sample.

**Optical rotary dispersion**

Optical rotary dispersion, the dependence of the rotation of an optically active species vs. wavelength, is a natural extension of the basic polarimetric method. The newer instruments (Website Fig. 5.16bW model 241MC) are readily adapted to this technique. Information on the degree of coiling of protein helices and the establishment of the configurations of chiral molecules indicate the wide utility of this approach.
Spectroscopic Identification of Organic Compounds

I. INTRODUCTION TO INFRARED SPECTROSCOPY

**NOTE.** It should be pointed out that a reciprocal centimeter is not a unit of frequency. Wavenumbers are only proportional to frequency. Thus, it is not correct to refer to a vibrational absorption band as having a frequency of 3000 cm\(^{-1}\) or to say that the vibration of the C—H bond possesses a frequency of 3000 cm\(^{-1}\). The C—H oscillator, however, can be said to absorb radiation with an energy of 3000 cm\(^{-1}\), or the C—H bond can be said to vibrate with a frequency of \(9 \times 10^{13}\) Hz.

**INTRODUCTION TO THEORY**

**A. MOLECULAR ENERGY**

The total molecular energy \(W\) may be expressed as the sum of the molecular translational, rotational, vibrational, and electronic energies:

\[
W_{\text{mol}} = W_{\text{trans}} + W_{\text{rot}} + W_{\text{vib}} + W_{\text{elec}}
\]

In this approximation, \(W_{\text{vib}}\) is assumed to be independent of the other types of molecular energy. Translational and rotational motion involve much smaller energies, having little influence on the spectra under observation. The parameter \(W_{\text{elec}}\) is the energy of the electrons. The energies of these latter transitions are very much larger than vibrational spacings, and their energy changes fall outside the IR. As a result, the IR region is active mainly to vibrational energy changes of ground electronic state molecules.
B. MOLECULAR VIBRATIONS

Molecules can be characterized as being in constant vibrational motion. If we are to describe this motion for nuclei of a polyatomic system, we can utilize the Cartesian coordinates $x_m, y_m, z_m$ for a nucleus of mass $m$ referred to a fixed coordinate system. Then, for $n$ nuclei, we would generate $3n$ coordinates ($3n$ degrees of freedom) to describe the motion of all the atoms. Three of these coordinates, however, may be used to locate the center of mass of the system in space. These three coordinates define the translation of the entire system through space. Because translational energies have a small impact on vibrational spectra, the three coordinates of the center of mass can be dropped from the total required to determine the vibrational degrees of freedom. Therefore, $3n - 3$ coordinates are sufficient to determine the positions of the $n$ nuclei with respect to the center of mass. However, the molecular system is still free to rotate about the center of mass. For nonlinear molecules there are three additional coordinates that are required to fully describe rotational motion about the center of mass. For linear molecules only two coordinates are necessary to define rotation, as all the nuclei lie along one of the principal axes and are considered to be point groups. Thus, for nonlinear molecules $3n - 6$ coordinates fully define the vibrational motion of the nuclei. These coordinates are often referred to as the vibrational degrees of freedom. In linear systems one rotational degree of freedom can be considered to have been transformed into a vibrational degree of freedom ($3n - 5$).

The number of vibrational degrees of freedom is directly related to the number of fundamental vibrational frequencies possessed by the molecular system. These fundamental frequencies are often referred to as the normal modes of vibration.

To get a feel for the function of the normal modes in the vibrational pattern of a molecular system, let us consider a very simple arrangement of a
single nucleus vibrating in two dimensions (see Herzberg, G. *Molecular Spectra and Molecular Structure*, Van Nostrand: New York, 1945, Vol. 2, p.62). The nucleus of mass $m$ is held by a rigid but elastic rectangular bar or rod. The mass $m$ can vibrate only in the plane perpendicular to the bar (Website Fig. 9.1W). If the nucleus is displaced along the $x$ axis and then released, the

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**Website Fig. 9.1W**

Harmonic vibration in two dimensions.

---

system will oscillate with simple harmonic motion at a frequency given by

$$\nu_x = \frac{1}{2\pi} \sqrt{\frac{k_x}{m}}$$

where $k_x$ is the force constant of the bar in the $x$ direction, where the restoring force $F = -k_x X$ for displacement $X$.

If displacement and release are carried out in the $y$ direction, a similar type of oscillation will occur with a frequency given by

$$\nu_y = \frac{1}{2\pi} \sqrt{\frac{k_y}{m}}$$
where $k_y$ is the force constant in the $y$ direction.

The frequency $\nu_x$ that results from displacement in the $x$ direction is different from the natural frequency $\nu_y$, which results from displacement in the $y$ direction, because the rectangular bar will possess different force constants $k_x$ and $k_y$. If the rectangular bar is replaced with a bar of square cross section, then the force constants that result from displacement in the $x$ and $y$ directions are equal. The frequencies of $x$ and $y$ motion also will be equal. In this situation the bar of rectangular dimensions can be referred to as having **degenerated** to a bar of square dimensions.

We now consider the displacement and release of the nucleus in a direction not along a principal axis; for example, the corner position $P$. Now on release, the motion performed by the nucleus is no longer simple harmonic. The restoring force $F$ will have components $-k_xX$ and $-k_yY$, which are unequal and not directed toward the origin.

The complex motion of the nucleus in the $x$-$y$ plane, however, will still contain components that are simple harmonic in nature. The motion of the nucleus can be represented as the sum of these “normal modes” of vibration, which are perpendicular to each other. Thus, the position of the nucleus at any point in time after release can be expressed by the two coordinates,

$$
x = x_0 \cos 2 \pi \nu_x t \quad \quad y = y_0 \cos 2 \pi \nu_y t
$$

where $x_0$ and $y_0$ are the coordinates of the initial position $P$, and $t$ is the time lapse from release.

The complicated pattern of motion performed by the nucleus on release from position $P$ is termed Lissajous motion. This type of motion is the superposition of two simple harmonic motions of differing frequency that are normal to each other. These are termed the normal modes or fundamental
frequencies of the Lissajous motion of the nucleus of mass $m$. The $x$ and $y$
coordinates, thus, become the “normal coordinates.”

In the case of a diatomic molecule the frequency (expressed as
wavenumbers) is given by

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where $k$ is the force constant, $m_1$ and $m_2$ are the atomic masses, and $\mu$ is the
reduced mass.

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \text{ or } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

### C. QUANTIZED VIBRATIONAL ENERGY

Nature has been kind in distributing vibrational energy in molecules! The
vibrational (vib) states associated with a particular normal mode are not
influenced, to a first approximation, by the energies of adjacent states. The
portion of $W_{\text{vib}}$ contributed by a particular normal mode $v_i$ is given by

$$W_{\text{vib}} = \left( v_i + \frac{1}{2} \right) \hbar \nu$$

where $v_i$ is the vibrational quantum number for the normal mode and
takes the values 0, 1, 2, . . . .

Each normal mode will possess a similar energy-quantum number
relationship, and the total vibrational energy scheme can be obtained by
summing over all $3n-6$ fundamental vibrations:

$$W_{\text{vib}} = \sum_{i=1}^{3n-6} \left( v_i + \frac{1}{2} \right) \hbar \nu$$

The characteristic energy level pattern for a normal mode as determined
by the quantum relationship dictates that the level spacings will be equal with a
value of $\hbar \nu_i$. In the upper states, however, the potential energy curve begins to
depart from the harmonic values and the vibration becomes anharmonic. In
general, anharmonicity results in lower energy transitions or a contraction in the level spacing (Website Fig. 9.2W). In rare instances the potential energy well develops steeper sides (quartic terms become important), and the spacing actually becomes greater at higher levels (negative anharmonicity). We will see a few of the more well-known departures of this type.

In addition to the equal spacing of the energy levels associated with each normal mode, the quantization of the vibrational energy requires that the lowest or zero vibrational level ($v_0$) does not occur at zero energy, but at $\frac{1}{2} \hbar \nu$. Thus, the molecule retains, even at absolute zero, some small amount of vibrational energy. This energy is termed the "zero-point" energy, and its origin lies with the Heisenberg uncertainty principle.

**Website Fig. 9.2W**

Vibrational energy-level diagram.
D. SELECTION RULES
The range of vibrational energy level transitions associated with the fundamental frequencies runs from somewhat under 5000 to approximately 100 cm⁻¹. Thus, the study of the absorption spectra of the normal modes centers on the infrared region of the spectrum. Although most molecules possess a large set of normal modes, the equal spacing of the vibrational levels and the operation of molecular selection rules greatly simplify what would otherwise be a very complex absorption pattern.

For infrared spectra the selection rules define the changes in the vibrational and rotational quantum numbers. The changes for the 3n - 6 vibrational quantum numbers follow:

1. Only one quantum number can change during a transition.
2. The change $\Delta v$ is restricted to +1, -1.
3. For certain vibrations, $\Delta v$ must always be zero.

In a very large percentage of cases, an absorbed photon excites only a single normal mode (this rule also holds true for emission spectra). Thus, each frequency observed in the spectrum corresponds to a normal mode present in the molecule. The maximum number of frequencies observed corresponds directly to the 3n - 6 (or 3n - 5 for linear molecules) vibrational degrees of freedom.

In normal modes where $\Delta v = 0$, an incomplete set of frequencies will be observed. The symmetry elements present in the molecule largely determine whether $\Delta v = 0$ for a particular normal mode. This results from the further requirement that there be a change in molecular dipole moment during the vibration for the absorption of a photon to occur.
We can see why a variation in the magnitude of the dipole moment is essential to the absorption process by considering hydrogen and hydrogen chloride molecules placed between condenser plates (Website Fig. 9.3W).

**Website Fig. 9.3W**

H₂ and HCl oscillators.

1. **The Case of HCl**

In the case of HCl, a permanent dipole moment exists along the molecular axis, with the negative pole closer to the chlorine atom and the positive pole closer to the hydrogen atom. When placed between condenser plates, as shown in Figure 9.4, the molecule will experience attractive forces at both ends, which will exert a stretching action. If the charge on the condenser plates is quickly reversed, the molecule will then experience repulsive forces at each end and be compressed. If it were possible to alternate the charge on the plates fast enough to match the natural frequency of the HCl molecule, the system would resonate. In the resonance or “tuned” condition, the oscillator will absorb energy from the condenser and expand its vibrational displacements. (If enough energy were absorbed, the molecule would dissociate.) The frequency remains constant, but the amplitude of the vibration increases (much the same way as the input of periodic energy with the correct phase into a child's swing increases the amplitude of the swing, but leaves the frequency constant). Within the band of
infrared radiation (5000–100 cm\(^{-1}\)), oscillating electric fields of the radiation will act on molecules in a fashion similar to alternating condenser fields. The frequencies in this spectral region correspond to the natural vibrational frequencies present in the molecular systems. Thus, at the particular radiation frequency that matches the vibrational frequency of the HCl molecule, resonance will occur and the photon of corresponding energy will be absorbed as the molecule moves to the next higher vibrational state. In the case of the hydrogen molecule, there is no vibrating electric dipole present because of the symmetry of the system. Thus, no interaction with the oscillating electric vector of the radiation at the natural frequency can occur (this would correspond to no interaction with the condenser plate fields). In this case the normal mode for the hydrogen molecule is not observed in the infrared spectrum, and the selection rule \( \Delta v = 0 \) applies.

Let us examine two simple examples to illustrate the preceding discussion.

2. The Case of Water

Water is a nonlinear triatomic molecule. It has, therefore, three normal modes of vibration or fundamental frequencies (3\( n \)- 6, where \( n = 3 \)). The displacements of the normal modes can be derived in much the same fashion as the two-dimensional case and are as shown in Website Figure 9.4W.

Website Fig. 9.4W

![Normal modes of water.](image-url)
All three vibrations are active in the infrared, and three absorption bands are observed. The arrows represent the relative atomic displacements involved in one phase of the vibration. The atoms all move in phase in simple harmonic motion in each fundamental mode. The high-frequency vibration $v_3$ at 3756 cm$^{-1}$ involves predominantly hydrogen motion, with one bond contracting while the other is stretching. This vibration is designated as the “antisymmetric stretching” mode. (Modes of this type are often incorrectly referred to as asymmetric vibrations. The vibration is not asymmetric, without symmetry, but a vibration of antisymmetric character, that is, opposite symmetry or opposed symmetry.) The other stretching vibration, designated $v_1$, at 3652 cm$^{-1}$ involves in-phase and identical displacements of the two O—H bonds. It is termed the symmetric stretching mode. Finally, the low-frequency mode $v_2$ at 1595 cm$^{-1}$ corresponds to a bending of the molecule about the H—O—H bond angle. It occurs at lower frequencies than do the two stretching modes, as it takes less energy to bend a bond than it does to stretch one. Thus, the force constant $k_{\text{bend}}$ is considerably smaller than $k_{\text{stretch}}$. This bending vibration is often termed the scissoring vibration because the symmetric bending motion involved is similar to the action of scissors. The complex molecular vibrational pattern of the water molecule can be resolved into three simple harmonic components or normal modes that correspond directly to three absorption bands in the infrared spectrum. The atomic displacements of these normal modes can be used to characterize the type of fundamental vibration giving rise to the infrared absorption. In the water molecule we have two O—H stretching vibrations and one O—H bending mode. These modes represent the three vibrational degrees of freedom present in the water molecule.
3. The Case of Carbon Dioxide

Carbon dioxide is a linear triatomic molecule. It possesses four vibrational degrees of freedom (one more than water). The displacements of the normal modes are given in Website Figure 9.5W.

Website Fig. 9.5W

The normal modes of carbon dioxide.

In the case of carbon dioxide only two absorption bands are observed in the infrared spectrum even though the molecule has four vibrational degrees of freedom. The high-frequency antisymmetric stretching mode \( \nu_3 \) occurs at 2350 cm\(^{-1}\). The form of this mode is close to that of the antisymmetric stretching vibration found in water. The symmetric stretching vibration \( \nu_1 \) of carbon dioxide is similar to its counterpart in water; however, this vibration does not give rise to a change of dipole moment during the vibration. The arrangement of the atoms in the carbon dioxide molecule places a center of symmetry on the carbon atom. This symmetry element remains intact during the symmetric stretching vibration, and as a consequence no change in the dipole moment occurs. Thus, \( \Delta \nu = 0 \) and no absorption occurs at this frequency in the infrared. The normal mode still exists in the molecule, but it is infrared inactive. This fundamental has been located near 1334 cm\(^{-1}\) in the Raman effect. (The Raman
effect is another spectroscopic technique used to observe vibrational energy level transitions. It does not depend on a change in dipole moment.) There are two bending frequencies present in carbon dioxide \( \nu_{2a} \) and \( \nu_{2b} \). These two modes are identical except that one is rotated by 90° with respect to the other. The bending motion does produce a change in dipole moment, and as a result it is infrared active. Since the two modes have identical frequencies, however, only one absorption band will be observed at 667 cm\(^{-1}\). Carbon dioxide can bend in two mutually perpendicular planes, and therefore two bending vibrations are required to fully characterize the vibrational motion of the molecule. The symmetry of the system dictates that the modes be identical. Vibrations possessing these characteristics are termed degenerate vibrations (remember the degeneration of the rectangular bar to a square that gave rise to two mutually perpendicular and identical modes). Thus, although carbon dioxide possesses four vibrational degrees of freedom, the observation of two absorption bands in the infrared spectrum can be satisfactorily explained. Indeed, if we examine the bending vibration present in water, we see that water can bend only in a single plane, and “bending” the molecule out of that plane results in rotation. It is this rotational degree of freedom of water that is translated into a vibrational degree of freedom in carbon dioxide as the nonlinear three-atom system is converted into a linear molecule.

If we place the carbon dioxide molecule between the plates of a condenser (Website Fig. 9.6W), we can see why some of the carbon dioxide vibrations are infrared inactive, and other vibrations are active. As carbon dioxide does not possess a permanent dipole moment, it is important to note that the antisymmetric stretching mode and the degenerate bending vibration will develop dipole moments during these vibrations as a result of the nuclear displacements involved. These dipole moments obviously undergo changes
during the different phases of the vibrations, and therefore these modes fit the requirements of the vibrational selection rules for infrared activity. In the symmetric stretching vibration, no dipole moment is developed during the vibration, and we have a case similar to that of the hydrogen molecule. Thus, no absorption band is observed in the infrared spectrum of carbon dioxide that corresponds to the symmetric stretching mode.

Website Fig. 9.6W

Carbon dioxide oscillator.

E. VIBRATIONAL COUPLING

1. Coupled Oscillators
Water and carbon dioxide are valuable examples of simple systems in which mechanical coupling between two oscillators is amply demonstrated. If we consider water to be constructed of two O—H oscillators, the individual diatomic systems would be expected to have identical frequencies. When welded together, however, the vibrations of one O—H oscillator interfere with the vibrations of the other O—H oscillator. The coupled oscillators generate two new vibrations,
one at higher frequency and one at lower frequency (much the same as the resonance that develops between two coupled identical pendulums can be considered to involve two frequencies, one higher and one lower than the natural frequency of the pendulum). The coupling interaction is frequency dependent. The closer the frequencies of the two oscillators, the stronger the interaction. When there are identical frequencies and a direct mechanical connection, the coupling effect will be maximized. Under the conditions of strong interaction, the form of the new vibrations can be quite different from that of the isolated oscillators. Coupling is also angle dependent. Oscillators normal to each other couple poorly, whereas colinear oscillators will undergo maximum coupling. [Note the wavenumber separation in water (bent system) of 104 cm\(^{-1}\), as compared with 1016 cm\(^{-1}\) for carbon dioxide (back-to-back C=O oscillators)].

2. Second-Order Coupling

The selection rules break down occasionally, particularly in condensed phases, to give overtone bands (\(\Delta v > 1\)). These departures may result from anharmonicities. The overtone frequencies are usually somewhat less than double that of the fundamental mode. The drop in expected frequency results from the compression of upper levels on the potential energy curve (Fig. 9.2W). The absorption bands that result from these transitions are usually very weak, as the mode is formally forbidden.

One of the most spectacular of the second-order events is Fermi resonance. When the first overtone (\(\Delta v = 2\)) of a fundamental possesses very nearly the same energy as the \(\Delta v = 1\) level of another normal mode, an interaction may occur in which the two close-lying levels are split into two new levels, one higher and one lower in frequency than the original modes. As a
result of this mixing, the overtone often undergoes a dramatic intensity gain at the expense of the fundamental. The resulting doublet may even possess components of approximately equal intensity. The intensity distribution is dependent to a large extent on the value of the original frequency match. The classic example of the effect is the symmetric stretching frequency (Raman active only, see above) in carbon dioxide, which should occur near 1334 cm\(^{-1}\) but which, in fact, exists as a doublet (1388 and 1286 cm\(^{-1}\)). The perturbation was explained by Fermi as the interaction of the overtone of the bending fundamental at 667 cm\(^{-1}\) with the first exited state of the symmetric stretching mode. For Fermi resonance to occur, (a) the oscillators involved must be so arranged that the anharmonic terms can interact (mechanical interaction can occur), and in addition, (b) the modes must meet certain symmetry restrictions. The large majority of all complex organic substances are of such low symmetry that the latter condition usually can be assumed to have been met.

In a few cases the overtone of a fundamental, although weak, will occur with higher than usual intensity, and in a region uncluttered by other absorptions. These bands can be utilized as confirming evidence in making assignments of fundamentals. In even rarer instances the first overtone will be observed to occur at slightly higher than double the fundamental values. These systems are considered to possess “negative anharmonicity” (see quantized vibrational energy, p. 61).

Another second-order effect is the “sum tone” or combination band. Although forbidden in the harmonic approximation, occasionally there will be absorbed a photon of the appropriate energy to simultaneously excite two normal modes. Combination bands occur as weak absorption bands that possess frequencies near the sum of the two fundamentals. If sum tones occur in regions open to observation, occasionally they can be of importance in group frequency
interpretations (see out-of-plane C—H bending modes on aromatic rings: see also Fig. 9.19W).

II. GROUP FREQUENCIES OF THE HYDROCARBONS

- Alkanes
- Alkynes
- Alkenes
- Arenes

A. Characteristic Group Frequencies of Alkanes
The saturated hydrocarbons and the alkane section of mixed structures contain only C—C and C—H bonds. The fundamental modes derived from the hydrocarbon portion of these molecules, therefore, are limited to C—C and C—H stretching and bending vibrations. These two types of oscillators are good examples of structural units that give rise to both excellent and very poor group frequencies. We have established (see p. 64) that a change in dipole moment during the vibration is essential for the absorption process to occur in the infrared. The exact relationship between the vibrational displacements and the observed band intensities is rather complex. It is related to the slope of the curve of the variation of dipole moment with the normal coordinate at the equilibrium point. The intensity of the fundamental is proportional to the square of the derivative of the dipole moment with respect to the normal coordinates. The absorptivity of infrared bands, therefore, usually can be gauged from a rough estimate of the magnitude of the oscillating dipole moment.

The C—C group is an oscillator that, at best, will possess a very small dipole moment because of the symmetry inherent in the bond. Because of the low bond polarization, the absorption bands associated with this system can be expected to be quite weak and difficult to identify. In addition, the C—C
oscillator, in most cases, will be directly connected to other C—C oscillators with similar or identical frequencies. In such an arrangement mechanical coupling effects are to be expected. This coupling will give rise to a very complex absorption pattern unique to a particular compound. Although these highly coupled vibrations have little value as group frequencies, they are the most powerful means of identifying organic materials by modern chemical instrumentation. The region of the infrared spectrum where these frequencies predominate, 1500–500 cm$^{-1}$, is often referred to as the “fingerprint region.”

The C—H oscillator is at the other extreme from the C—C case. It gives rise to excellent group frequencies. The light terminal H atom, which is connected to a relatively massive carbon atom by a strong bond (large force constant), possesses a high natural frequency. Because of the separation of this frequency from other frequencies, the only coupling that can influence the oscillator is that of other C—H groups connected to the same carbon. A rule of thumb to remember is “coupling generates as many modes as there are coupled oscillators.” The methyl group, CH$_3$—, has three stretching modes; the methylene group (—CH$_2$—), two stretching modes; and the methine group (—CH—), a single stretching mode.

Since there is very little mechanical coupling of C—H oscillators beyond the local carbon atom, the natural frequencies of the methyl, methylene, and methine groups remain relatively constant when these groups are transferred from compound to compound or from group to group within the same system. The dipole moment of the C—H bond is not large, but its derivative is sufficient to give rise to reasonably identifiable absorption bands. Because many compounds will contain several C—H bonds of similar character, they will also
possess an equal number of nearly equivalent C—H frequencies. These C—H stretching modes overlap, often to produce the most intense collection of absorption bands observed in the infrared spectrum of a material.

The three coupled C—H stretching modes of methyl groups can be described in terms of two antisymmetric vibrations that are degenerate, or nearly degenerate (p. 60), depending on the symmetry of the system, plus a symmetric mode (Website Fig. 9.7W). In most cases, the two antisymmetric

Website Fig. 9.7W

![Diagram of CH₃ and CH₂ stretching vibrations](image)

Streching vibrations of methyl and methylene groups.

methyl stretching modes, although not rigorously degenerate, will give rise to a pair of very close-lying bands that are seldom resolved. The antisymmetric methyl modes are the highest frequency vibrations of the purely sp³-hybridized
C—H bonds. These fundamentals occur near 2960 cm\(^{-1}\). The methyl symmetric stretching mode is found close to 2870 cm\(^{-1}\) (see Text Website Fig. 9.2).

The two coupled stretching modes of the methylene group are very similar in displacement pattern to the fundamental vibrations of the water molecule (see Website 9.4W). The higher frequency mode, as in water, is the antisymmetric stretch. This fundamental occurs near 2925 cm\(^{-1}\) in hydrocarbons. The symmetric stretching mode, which is particularly sensitive to adjacent heteroatoms bearing lone-pair electrons, in saturated hydrocarbons has the lowest frequency of the \(\text{sp}^3\)-hybridized coupled C—H oscillators. The symmetric stretch occurs close to 2850 cm\(^{-1}\) (see Text Fig. 9.2).

The methine group has a single uncoupled mode. As relatively few groups of this type are normally present in a structure, compared with methyl and methylene groups, this vibration gives rise to a weak fundamental, usually masked by the absorption of the other alkane groups. The absorption of the tertiary C—H bonds occurs in the 2900-cm\(^{-1}\) region.

With very few exceptions the \(\text{sp}^3\)-hybridized C—H bonds have their fundamental modes in the 3000-2800-cm\(^{-1}\) region.

Since the hydrogen atom is much lighter than other atoms, it undergoes most of the displacement. The mass term in the expression for frequency of a diatomic molecule is actually a reduced mass. In the case of hydrogen and carbon this is defined by

\[
\frac{1}{\mu} = \frac{1}{m_H} + \frac{1}{m_C}, \quad \text{since } m_C \gg m_H, \, \mu \approx m_H
\]

It is possible, therefore, to express to a very good first approximation the vibrational frequency of this system by a simple Hooke's law relationship, assuming an infinite mass for the carbon atom:
\[ \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{m_H}} \]

This expression makes it possible to predict frequency shifts on substitution by deuterium for hydrogen of \( \tilde{\nu}_H / \tilde{\nu}_D = 1.41 \). In practice these shifts are somewhat less than the theoretical values, usually falling in the range 1.32-1.38 (Website Figs. 9.8aW and 9.8bW).

**Website Fig. 9.8aW**

IR spectrum: Chloroform.

**Website Fig. 9.8bW**

IR spectrum: Chloroform-d.
If the $\tilde{\nu}_H / \tilde{\nu}_D$ ratio departs significantly from this range, the result can be taken as an indication that one or possibly both of the fundamentals are not behaving in harmonic fashion and that coupling is present. Chloroform is one of the rare exceptions to the “so called” 3000-wavenumber rule (no $sp^3$ C—H stretching modes occur above 3000 wavenumbers). The single uncoupled C—H stretching mode occurs at 3022 cm$^{-1}$. The rise in frequency in this case results from extensive substitution by the strongly electronegative chlorine atoms.

The bending frequencies of the C—H oscillator will now be discussed. As in the case of stretching modes of the alkyl groups, the bending fundamentals are coupled only with those oscillators directly bonded to the carbon. Since there are three independent H—C—H bond angles, there are three deformation or bending vibrations associated with the methyl group (Website Fig. 9.9W).

**Website Fig. 9.9W**

Bending vibrations of the methyl group.

As in the stretching fundamentals, two of these modes can be described in terms of antisymmetric degenerate or nearly degenerate, vibrations that occur near 1460 cm$^{-1}$. The third vibration is the symmetric bending mode (umbrella) close to 1375 cm$^{-1}$ (Figs. 9.2 and 9.9W), which is easily identified.
The methylene group has a single H—C—H bond angle, and a single deformation mode (scissoring, Website Fig. 9.10W) directly

Website Fig. 9.10W

Bending vibrations of the methylene group.

analogous to that of the water molecule. The symmetric bend of the —CH₂— group occurs near 1450 cm⁻¹ in hydrocarbons (Figs. 9.2 and 9.10W).

Three other bending modes are available to the methylene group (Fig. 9.10W). When the methylene group is fused into the molecule, three vibrational degrees of freedom develop, which are related to rotational motion of the isolated system, for example, the rotational motion of the water molecule. These fundamentals (wag, twist, and rock) are subject to significant coupling to adjacent methylene groups. The transitions associated with these modes are also rather weak in intensity. Thus, wag, twist, and rock are not useful group frequencies with the exception of a component of the rocking vibration (Fig. 9.10W) in certain structures. In those molecules having four or more methylene groups in a row, the coupled mode corresponding to the all-in-phase rocking vibration develops a significant dipole moment change and a stable frequency. Thus, the in-phase rock that occurs near 720 cm⁻¹ (see Fig. 9.2) in the
fingerprint region gives rise to an absorption band of sufficient intensity to allow for confident assignment. (Thus, we have all four bonds of the carbon associated with the methylene group involved in bending modes and four deformation vibrations are generated.)

The bending modes associated with the methine hydrogen are hard to identify in most hydrocarbons. (The in-plane bend of an isolated sp\textsuperscript{2} C—H group can be particularly important, however, in certain heteroatom systems; see discussion of the aldehyde functional group.)

The C—H vibrational modes of the alkanes (or mixed compounds containing alkyl groups) that are characteristic and reliable group frequencies can be summarized as in Table 9.1 (text).

**B. Characteristic Group Frequencies of Alkenes**

1. **C=C Stretching**

The stretching fundamental of the C=C group is a useful group frequency. The increase in the force constant in going from the single bond to the double bond moves the frequency to sufficiently high values ($\tilde{\nu}_{\text{C=C}} = 1616$ cm\textsuperscript{-1}, ethylene) to decouple this mode from adjacent C—C vibrations. Substitution of carbon for hydrogen on the double bond tends to raise the C=C stretching frequency, as the effective force constant has been shown to include an increased compression term (Website Fig. 9.11W).
Vinyl group double-bond stretching vibration.

It is possible to classify open-chain unsaturated systems into two groups. The high-wavenumber set (>1665-1650 cm\(^{-1}\)) has quite weak bands unless conjugation occurs. Indeed, in the tetrasubstituted case, if the four groups are identical, the C=C band is formally forbidden in the infrared. When the alkyl groups are similar but not identical, the magnitude of the dipole moment is so small that it becomes difficult to detect an absorption band. In this situation the molecule is considered to have a "pseudocenter of symmetry." In the low-wavenumber set (<1665-1660 cm\(^{-1}\)) more intense absorption bands occur, with the average intensity falling in the medium-to-strong range (see Text: Table 9.2).

2. Alkene C—H

The C—H stretching frequencies occur above 3000 cm\(^{-1}\) and are localized in two regions defining three groups as follows: (1) If two C—H groups are present on an sp\(^2\) carbon, two coupled (antisymmetric and symmetric) vibrations occur near 3080 and 3010 cm\(^{-1}\). (2) If a single C—H group is attached to an sp\(^2\)-hybridized carbon, it gives rise to a single mode near 3030 cm\(^{-1}\). (3) A vinyl group will have both sets of bands, but the lower wavenumber modes are seldom resolved from the saturated C—H stretching modes (Website Figs. 9.12W and 9.13W).
The C—H stretching vibrations of the vinyl group.

IR spectrum: 1-Pentene.

The alkene C—H bending frequencies fall into two categories: (1) There are bending modes that occur in the plane of the double bond. These fundamentals are not useful group frequencies. (2) There are bending modes that occur out of the plane of the double bond. These fundamentals are useful group frequencies.
3. Out-of-Plane Deformation Modes

a. Vinyl Groups: The vinyl group has three C—H bonds and therefore three out-of-plane bending modes. Two of these normal modes are group frequencies. The fundamental with the two trans hydrogen atoms bending in-phase occurs near 990 cm\(^{-1}\) (Website Fig. 9.14W). A second vibration involving primarily the two hydrogen atoms attached to the terminal carbon, bending in-phase together (wag), is located close to 910 cm\(^{-1}\) (Fig. 9.14W). The absorption bands resulting from both of these fundamentals are strong and easily detected in the fingerprint region.

Website Fig. 9.14W

Out-of-plane C—H bending vibrations of the vinyl group.

b. Vinylidene Groups: The 1,1-substituted system will have two bending frequencies. One of these bending modes is a good group frequency. When both hydrogen atoms wag out of the C=C plane together, a strong dipole moment change develops and gives rise to an intense absorption band near 890 cm\(^{-1}\). This mode is related to the low-frequency mode found in the vinyl group at 910 cm\(^{-1}\) (Website Figs. 9.14W and 9.15W).
c. **Trans Alkenes:** A trans alkene has two out-of-plane bending modes, but again only one gives rise to a good group frequency. The mode that involves both hydrogen atoms moving in phase together occurs close to 965 cm\(^{-1}\). This mode is directly related to the high-frequency mode of the vinyl group near 990 cm\(^{-1}\) (Fig. 9.14W).

d. **Cis Alkenes:** A cis-substituted C=C group does not possess a very good out-of-plane group frequency. The only mode with reasonable intensity involves the in-phase bend of the two hydrogen atoms. This fundamental is derived from a rotational type motion that couples to the rest of the system (Website Fig. 9.16W). Therefore, the cis mode is not localized, but occurs in a broad region near 700 cm\(^{-1}\).
e. **Trisubstituted Alkenes:** In the case of \( R_2C=CHR \) systems we have a single out-of-phase bending vibration that occurs near 820 cm\(^{-1}\). The mode is uncoupled and gives rise to a medium-intensity band.

g. **Tetrasubstituted Alkenes:** These groups have no C—H bending modes.

f. **Overtones**

The overtones of the fundamentals that involve wagging of the terminal hydrogen atoms in the vinyl and vinylidene groups occur with unusual intensity. These bands are observed at 1825 and 1785 cm\(^{-1}\), slightly more than double the fundamental frequency. Thus, these harmonics exhibit negative anharmonicity in addition to unusual intensity for forbidden vibrations (see Text: Table 9.3).

**C. Characteristic Group Frequencies of Alkynes**

1. **C≡C Stretching Vibration**

Triple-bond formation further increases the force constant involved in the C—C stretching vibration. Thus, alkynes possess the highest of all observed C—C stretching frequencies. The triple-bond group frequency is located near 2120 cm\(^{-1}\) in monosubstituted alkynes. Compression effects on the force constant similar to those observed in substituted alkenes raise the stretching mode into the 2225-wavenumber region in disubstituted alkynes. The alkyne stretching vibration involves a relatively small dipole moment change. The resulting bands, therefore, are particularly weak in the infrared. In the
disubstituted case, if the two groups are identical, the vibration is infrared inactive. Here, as in the alkenes, a pseudocenter of symmetry can operate to significantly suppress the intensity of the mode. Even though these bands occur in a region that is essentially devoid of other absorptions, their inherent weakness and variable intensity present significant problems in making confident band assignments. The high frequency of the mode effectively decouples the vibration from the rest of the system. Thus, triple bonds show little evidence of any first-order coupling. On the other hand, these vibrations are prone to second-order effects that complicate their interpretation. Triple-bond assignments must be handled with care. These vibrations constitute a set of group frequencies relatively difficult to deal with, if they can be observed at all.

2. Alkyne C—H Vibrations

The stretching of alkynyl C—H bonds gives rise to the highest carbon-hydrogen vibrations observed. These modes are relatively intense uncoupled single sharp modes that occur near 3300 cm⁻¹. Although this normal mode occurs in the same region as O—H and N—H fundamental vibrations, alkynyl C—H stretches usually can be distinguished by the sharpness of the band. These stretches are highly reliable group frequencies.

The bending modes of the C—H alkynyl group do not give rise to reliable group frequencies (see Text: Table 9.4).
D. Characteristic Group Frequencies of Arenes

Aromatic ring systems represent the final class of hydrocarbons to be considered in this section. The discussion will center on the benzene ring, but many of the more complicated systems have been examined in detail.

The infrared spectra of aromatic compounds possess many needle-sharp bands. This characteristic sets these spectra apart from the spectra of aliphatic compounds. It arises because aromatic systems are tightly bound rigid molecules having little opportunity for rotational isomerism. With aliphatic compounds the observed spectrum, is in reality, often the spectrum of a complex mixture of rotamers. These isomers all exhibit very similar but not identical spectra that overlap and result in band broadening.

1. Group Frequencies of the Phenyl Group

The group frequencies of the phenyl group can be classified as carbon-hydrogen vibrations consisting of stretching and out-of-plane bending modes, plus carbon-carbon ring stretching and out-of-plane bending modes. The in-plane bending modes in both cases are not effective group frequencies.

a. C—H Stretching Modes

The C—H stretching vibrations occur as a series of weak bands in the region 3100–3000 cm⁻¹. This observation is consistent with sp² hybridization of the carbon atom. These modes directly overlap the alkene C—H stretching fundamentals. Substitution of heteroatoms into the ring can significantly perturb
these frequencies (oxygen raises the mode into the 3200–3100-wavenumber region). As the bands are generally weak, they may be masked by strong aliphatic absorption in mixed compounds if they lie close to 3000 cm\(^{-1}\). Care must be taken in the assignment of these modes.

**b. C=C Stretching Modes**

The phenyl ring modes, which possess excellent group frequency properties, involve two pairs of closely related C=C stretching vibrations. These vibrations are related to degenerate fundamentals in unsubstituted benzene. On ring substitution the degeneracy is removed because of the lowered symmetry. The ring vibrations \(\nu_{8a}\) and \(\nu_{8b}\) (the numbering has been carried over from the benzene fundamental assignments by Wilson (see Wilson, E. B., Jr. Phys. Rev., 1934, 45, 706) involve displacements in three-carbon units at each end of the ring, which are analogous to the symmetric and antisymmetric stretching modes of water. The two modes result from the two sets of displacements, which are in phase (Website Fig. 9.17W).

**Website Fig. 9.17W**

Ring stretching vibrations of benzene, \(\nu_{8a}\), \(\nu_{8b}\).
These vibrations are degenerate and inactive in the infrared spectrum of the unsubstituted ring. In general, the higher frequency vibration, $\nu_{8a}$, is the more intense of the pair. If a substituent is conjugated to the ring system, however, the lower frequency component gains in intensity and sometimes becomes the most intense member of the pair. These two modes are also substituent independent with para disubstitution; however, if the groups are identical or nearly identical, the modes are infrared forbidden or active with greatly suppressed intensity. These modes, $\nu_{8a}$ and $\nu_{8b}$, occur near 1600 and 1580 cm$^{-1}$, respectively.

The second pair of vibrations corresponds to the identical displacements of the first pair of modes with the sets now out-of-phase (Website Fig. 9.18W).

**Website Fig. 9.18W**

Ring stretching vibrations of benzene, $\nu_{19a}$, $\nu_{19b}$.

Substitution on the ring removes the degeneracy, giving two bands corresponding to $\nu_{19a}$ and $\nu_{19b}$ in benzene.

These fundamentals, as with $\nu_{8a}$ and $\nu_{8b}$, are substituent independent on mono substitution or para substitution. The dipole moment change associated with these normal modes generally gives rise to rather intense absorption bands.
The high-frequency component, however, is sensitive to electron-withdrawing substituents that can significantly suppress the intensity of this mode. These fundamentals occur near 1500 and 1450 cm\(^{-1}\), respectively.

c. C—H Bending Vibrations

The C—H bending normal modes of group frequency value are the out-of-plane vibrations. These fundamentals are useful guides to the substitution pattern on the ring system. There will be as many out-of-plane vibrations as there are C—H groups. The modes of interest, however, are those fundamentals in which all the hydrogen atoms move in phase. These vibrations have substantial dipole moment changes and, thus, give rise to intense absorption bands. The very strong intensity of the out-of-plane deformation modes plays a key role in our ability to make confident assignments for these fundamentals, as they fall in the heart of the fingerprint region. The wavenumber values for the five all-in-phase bending vibrations are as presented in Website Figure 9.19W.
Although there is considerable overlap of the ranges, the uncertainty of the assignment can often be reduced by the identification of an additional strong band in the 690-wavenumber region. This band results from a carbon-carbon out-of-plane ring deformation, $\nu_4$, of benzene (Website Fig. 9.20W). This mode is substituent-insensitive to mono-, meta-, and 1,3,5-substitution.
Phenyl out-of-plane bending vibrations, $\nu_4$.

Thus, a band will seldom occur in this region in ortho-disubstituted systems.

**d. Sum Tone Patterns**

Some of the out-of-plane C—H bending modes can be excited simultaneously with other low-frequency fundamentals. As these sum tone transitions are formally forbidden, the resulting absorption bands are very weak. With optically thick samples, however, weak bands are observed in the 2000–1650-wavenumber region. The pattern of these bands is highly characteristic of the substitution arrangement on the ring, since they have their origin in the out-of-plane C—H bending frequencies. Unless carbonyl groups are present in the molecule, the 2000–1650-wavenumber region will be open for observation. These combination band patterns can be used to remove ambiguity about the ring substitution pattern based on assignments of the out-of-plane fundamentals (Website Fig. 9.21W also see Text: Tables 9.5 and 9.6).
III. CHARACTERISTIC FREQUENCIES OF HETEROATOM FUNCTIONAL GROUPS

A. Factors Affecting the Carbonyl Group Frequencies

The carbonyl group is perhaps the single most important functional group in organic chemistry. It is certainly the most commonly occurring functionality. Infrared spectroscopy can play a powerful role in the characterization of the
carbonyl because this group possesses all of the properties that give rise to an excellent group frequency.

- The carbonyl group has a large dipole-moment derivative, which gives rise to very intense absorption bands.

- As a result of the large force constant, it has a stretching frequency that occurs at high values outside the fingerprint region. In addition, this portion of the spectrum is devoid of most other fundamentals.

- Its stretching fundamental occurs in a range that is reasonably narrow (little coupling), 1750 ± 150 cm⁻¹, but sensitive enough to the local environment to allow for considerable interpretation of the surrounding structure.

- The range of frequencies is determined by a number of factors that are now well understood in terms of the effects outlined below.

Factors Affecting the Carbonyl Frequencies

1. Mass effects
2. Geometric effects
3. Electronic effects (inductive and conjugative effects)
4. Interaction effects

1. Mass Effects
The mode of principal interest is the stretching vibration. In this oscillator the C and O atoms undergo comparable displacements; thus, we must replace the simplified mass expression in the Hooke's law approximation that was applied to the C—H stretching fundamentals by the reduced mass \( \mu \) (where \( \mu = \frac{m_C m_O}{m_C + m_O} \), see above). On substitution of the isotopes \(^{13}\)C and \(^{18}\)O, the predicted small frequency shifts (~30–40 cm\(^{-1}\)) are observed. These results are consistent with a relatively low degree of mechanical coupling to the rest of the system. This lack of coupling is expected, because the force constant of the multiple bond is significantly different from the values of the force constants of the bonds that connect the carbonyl to the rest of the molecule.

2. Geometric Effects
Geometric effects can play a major role in determining the location of the carbonyl frequency within the 1750-wavenumber region. Although the displacement of the oxygen atom involves simply stretching or compressing the C=O bond, the displacement of the carbon atom is more complex. This latter movement also contains a compression component of the force constants in the two connecting single bonds as the carbonyl carbon is being stretched. In the opposite phase of the vibration, a stretching component of the force constants in the two connecting bonds is required, as the carbonyl carbon is being compressed. The magnitude of these additional force constant components is angle dependent. As the angle between the single bonds (C—CO—C angle) decreases, the contribution of the single-bond components to the effective C=O stretching force constant will be raised. Since the frequency of the vibration is directly proportional to the square root of the force constant, a decrease in the internal carbonyl bond angle will raise
the frequency (Table 1W and Text Table 9.7). Alternatively, an increase in the internal carbonyl bond angle will lower the carbonyl frequency.

Table 9.7W

<table>
<thead>
<tr>
<th>Ring Size:</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
<th>3</th>
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3. Electronic Effects (Resonance and Inductive)

Resonance and inductive effects can profoundly influence the vibrational frequency of the carbonyl group. In the following discussion the carbonyl stretching mode for acetone ($\tilde{\nu}_{C=O} = 1715$ cm$^{-1}$, liq) will be used as a reference frequency representative of simple alkyl substitution on the carbonyl group. Effects that perturb this reference fundamental to either higher or lower values will be examined.

a. Electronic Effects That Raise the Carbonyl Frequency

When an alkyl substituent is replaced by a more electronegative system, the balance of contributing resonance forms in the carbonyl is slightly shifted away from dipolar forms by strong inductive effects. This shift results in a larger effective C=O force constant and higher frequencies. (e.g., in hexanoyl chloride, $\tilde{\nu}_{C=O} = 1805$ cm$^{-1}$, Fig. 9.28).
b. Electronic Effects That Lower the Carbonyl Frequency

Direct conjugation of the carbonyl via $\alpha,\beta$-unsaturation will introduce new dipolar carbonyl resonance forms that lower the effective force constant values and, thus, decrease the carbonyl stretching frequency (e.g., consider cyclohexenyl methyl ketone, I, $\tilde{\nu}_{C=O} = 1685 \text{ cm}^{-1}$, and acetophenone, II, $\tilde{\nu}_{C=O} = 1687 \text{ cm}^{-1}$).

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Now let us examine ester carbonyl frequencies in somewhat greater detail.

If the ester carbonyl is directly involved with α,β unsaturation, the normal ester frequency is lowered by 20–30 cm$^{-1}$. Thus, unsaturated ester carbonyl frequencies occur very nearly in the same region as simple aliphatic ketone frequencies (e.g., in ethyl benzoate, $\tilde{\nu}_{C=O} = 1720$ cm$^{-1}$).

If the ester is conjugated, but the conjugation is located adjacent to the ether oxygen rather than alpha to the carbonyl group, then the carbonyl frequency is raised. The higher $\tilde{\nu}_{C=O}$ results from resonance competition for the lone-pair electrons of the ether oxygen by the carbonyl and the new conjugating group (e.g., phenyl acetate, $\tilde{\nu}_{C=O} = 1769$ cm$^{-1}$). These frequency shifts support the arguments concerning competition between inductive and resonance effects within the ester ether group.

If the ester group is directly conjugated on both sides, then the resonance effects should cancel, and we would expect this type of system to exhibit near normal carbonyl frequencies (e.g., phenyl benzoate, $\tilde{\nu}_{C=O} = 1743$ cm$^{-1}$) as compared with ethyl acetate, $\tilde{\nu}_{C=O} = 1742$ cm$^{-1}$.
4. Interaction Effects

Interaction effects vary from those that have a dramatic impact on the spectra to those that are barely detectable. Our understanding of these terms completes the discussion of the major factors affecting the carbonyl group frequencies. We can roughly divide this area of discussion into intramolecular and intermolecular types of interactions.

a. Intramolecular Carbonyl Interactions

First-order coupling effects are rarely observed as this oscillator is rather effectively decoupled from the rest of the molecule by differences in frequency. The most spectacular example (see p. 67) is the case of carbon dioxide. In CO$_2$ the two coupled oscillators are aligned for maximum interaction and possess identical frequencies. The splitting between the antisymmetric and symmetric levels is very large, approximately 1000 cm$^{-1}$. A second, much less dramatic, example is the case of anhydrides. In this instance the two oscillators are joined through a central oxygen. Delocalization across the connecting atom operates to maintain planarity of the system and thereby to increase the coupling. Even so, since the carbonyls are no longer held at the optimum angle and are vibrationally insulated by an intervening atom, the first-order coupling drops to about 70 cm$^{-1}$, less than 10% of the CO$_2$ value (e.g., hexanoic anhydride, $\tilde{\nu}_{C=O} = 1817$, 1750 cm$^{-1}$). The uncoupled vibration would be expected to occur near 1770 cm$^{-1}$. This latter value is consistent with an oxygen-substituted carbonyl in which conjugation of the lone-pair electrons on the ether oxygen has been nearly canceled. The full inductive effect of the ether oxygen atom on the carbonyl stretching vibration can be inferred from these data. Equalized resonance competition by both carbonyl systems of the anhydride for the ether lone-pair electrons might be expected to bring about just such an effect.
Intramolecular hydrogen bonding of carbonyls can be enhanced by resonance interactions and, thus, significantly perturb the stretching frequency. For example, let us consider the anthraquinone series shown below. In Structure I, hydrogen bonding is not present and a single stretching frequency for the quinone is observed at 1675 cm\(^{-1}\). This value reflects direct conjugation with the aromatic ring and with the methoxyl groups conjugated in equivalent fashion with both carbonyls. Little coupling between the carbonyls is observed through the ring. In Structure II a phenol group replaces one of the methoxyl groups. Resonance forms operating through a tightly hydrogen-bonded six-membered ring act to reduce the effective force constant of the carbonyl, with the result that the observed frequency, \(\tilde{\nu}_{C=O} = 1636\) cm\(^{-1}\), is lowered nearly 40 cm\(^{-1}\). In Structure III both methoxyl groups have been replaced by phenolic groups. This change results in both carbonyls undergoing strong hydrogen bonding, which involves resonance forms similar to those found in Structure II. Thus, a single band is observed at \(\tilde{\nu}_{C=O} = 1627\) cm\(^{-1}\). This downward shift approaching 50 cm\(^{-1}\) can be ascribed primarily to strong internal hydrogen bonds present in the anthraquinone system.

Several other examples of very strong intramolecular hydrogen bonding are known. In tropolone, where the hydrogen appears to be essentially equidistant from the two oxygen atoms, the absorption occurs at 1605 cm\(^{-1}\).
Second-order coupling (Fermi resonance) often occurs with carbonyl vibrations in complex organic molecules. In the large majority of cases, the frequency match of overtone and fundamental is relatively poor so that the frequency of the fundamental is not affected. The main evidence for the interaction in these cases will be weak shoulders associated with the main carbonyl peak. An example of the coupling not being trivial is the case of cyclopentanone. The Fermi interaction involves an overtone or combination of a C—H level, as the splitting collapses to a singlet in 2,2,5,5-tetra-d4-cyclopentanone.

Field effects will also perturb the carbonyl frequency. The classic case is that of the chloroacetones. In those rotamers, in which the chlorine atom is in the eclipsed position with respect to the oxygen, repulsive lone-pair interactions occur. Field effects result in suppression of the contribution of the dipolar carbonyl resonance form, and therefore cause a rise (~30 cm⁻¹) in the stretching frequency (Table 9.2W).
Table 9.2W  Field Effect in Chloroacetone

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tilde{\nu}_{C=O}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>1715</td>
</tr>
<tr>
<td>Chloroacetone</td>
<td>1752, 1726</td>
</tr>
<tr>
<td>1,1-Dichloroacetone</td>
<td>1743, 1724</td>
</tr>
<tr>
<td>1,1,1-Trichloroacetone</td>
<td>1729</td>
</tr>
</tbody>
</table>

These arguments are supported by the observation that two carbonyl frequencies are present in the mono- and dichloroacetones, and single frequencies in acetone and trichloroacetone. The small frequency rise observed in the low-frequency component is attributed to inductive effects, which, therefore, can have only a minimal influence on the high-frequency component.

Transannular interactions occur when cyclic carbonyl groups are sterically positioned so that the carbon atom of the carbonyl is oriented toward an electron-rich center lying across the ring. The interaction can greatly enhance the dipolar resonance form of the carbonyl and result in a significant drop in the stretching frequency. The effect has a major impact on the carbonyl frequency of the alkaloid protopine ($\tilde{\nu}_{C=O} = 1660$ cm$^{-1}$).

![Protopine](image)

Most interesting, however, are the results obtained from a number of model compounds (e.g., the cyclooctaaminoketone, I, $\tilde{\nu}_{C=O} = 1666$ cm$^{-1}$, and its perchlorate salt, II, which exhibits no carbonyl absorption band at all!)
b. **Intermolecular Carbonyl Interactions**

Strong intermolecular hydrogen bonding can significantly perturb carbonyl frequencies. It is known in the case of aliphatic carboxylic acids that these substances form strongly hydrogen-bonded dimers when neat or in highly concentrated solutions. Association through the carbonyl groups leads to the formation of a symmetric eight-membered ring containing two hydrogen bonds. Coupling through the tightly bonded ring results in a splitting of the carbonyl levels of approximately the same magnitude as found in anhydrides ($\tilde{\nu}_{C=O} = \text{ca. } 70 \text{ cm}^{-1}$). As the dimer possesses a center of symmetry, the in-phase mode will not be active in the infrared ($\tilde{\nu}_{C=O} = \text{ca. } 1650 \text{ cm}^{-1}$). The out-of-phase stretch of the carbonyls, however, will be active. The antisymmetric C=O stretch gives rise to a strong band in the infrared ($\tilde{\nu}_{C=O} = \text{ca. } 1720 \text{ cm}^{-1}$). In very dilute solution, it is sometimes possible to observe these systems in the monomeric state. Under these conditions the carbonyl frequencies return to expected values ($\tilde{\nu}_{C=O} = \text{ca. } 1770 \text{ cm}^{-1}$).

As the discussion of group frequencies expands, we will see several other examples of the effect of intermolecular hydrogen bonding on the carbonyl group frequency.

The interaction of weak hydrogen bonds is relatively hard to detect in the infrared, as the shifts are measured in terms of a few wavenumbers. One of the better examples is the effect on the carbonyl stretch of acetone ($\tilde{\nu}_{C=O} = 1722 \text{ cm}^{-1}$) as measured in hexane solution. When the hydrocarbon solvent is replaced by
chloroform, weak hydrogen bonds (O···H—C) develop, and the carbonyl mode drops 12 wavenumbers to 1710 cm⁻¹.

Weak dipolar interactions between carbonyls can also be observed in the infrared. The frequency shifts caused by these interactions parallel the development of polarization in the carbonyl group, as can be judged by the data in Table 9.3W.

**TABLE 9.3W Carbonyl Dipolar Interactions**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Δν (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl chloride</td>
<td>15</td>
</tr>
<tr>
<td>Phosgene</td>
<td>13</td>
</tr>
<tr>
<td>Acetone</td>
<td>21</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>23</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>50</td>
</tr>
</tbody>
</table>

* Shift measured between dilute non-polar solution and neat sample.

This completes the discussion of factors affecting carbonyl group frequencies. A number of additional examples will be discussed in detail in the following section on Characteristic Frequencies of Other Heteroatom Functional Groups, in which a survey of the infrared spectra of functional groups is considered.

**B. CHARACTERISTIC FREQUENCIES OF FUNCTIONAL GROUPS**

Now that we have examined the major group frequencies associated with the common hydrocarbon platforms (platform = hydrocarbon structural unit supporting a functional group) and the principal parameters affecting the carbonyl group, let us consider the vibrations associated with the common
functional groups that lead to good group frequency correlations. For the most part we will use, in these discussions, a series of infrared spectra derived from straight-chain aliphatic C₆ compounds.

**Group Frequencies of the following heteroatom functional groups are considered next:**

(Alkanes)

1. Alcohols  
2. Aldehydes  
3. Ketones  
4. Esters  
5. Acid halides  
6. Carboxylic acids  
7. Anhydrides  
8. Ethers

9. Amines  
10. Nitriles  
11. Amides, primary  
12. Amides, secondary  
13. Isocyanates  
14. Thiols  
15. Halogens  
16. Phenyl

*(n-Hexane)*

The spectrum of n-hexane (see Text Fig. 9.2) obtained with the pure liquid, as expected, contains simply the group frequencies of an aliphatic hydrocarbon. The antisymmetric and symmetric methyl stretching modes occur below 3000 cm⁻¹ at \(\tilde{\nu} = 2960\) and 2876 cm⁻¹. The antisymmetric and symmetric methylene stretching fundamentals occur near \(\tilde{\nu} = 2938\) and 2860 cm⁻¹. The antisymmetric methyl deformation (\(\tilde{\nu} = 1467\) cm⁻¹) overlaps the symmetric methylene scissoring vibration, which is found as a difficult-to-identify shoulder at \(\tilde{\nu} = 1455\) cm⁻¹. The symmetric methyl bend (umbrella mode) is easily assigned to the sharp band at 1379 cm⁻¹. Finally, the all-in-phase rocking mode of a sequence of four or more methylene groups can be identified by its intensity in the fingerprint region near 725 cm⁻¹. We often will be able to identify this collection of platform group
frequency bands as we progress through the infrared spectra of the following series of compounds (see Text: Table 9.1, p. 537).

1. 1-Hexanol

If an oxygen atom is inserted across one of the terminal C—H bonds, we obtain the alcohol, 1-hexanol. The change in the infrared spectrum obtained with a sample path length of less than one half that used to obtain the spectrum of hexane is remarkable (Website Fig. 9.22W; see Text: Table 9.8; 9.9, p. 540). A very intense band appears at 3350 cm⁻¹, which is assigned to the stretching mode of the single O—H group (Table 9.8). The very broad

Website Fig. 9.22W

IR spectrum: 1-Hexanol.

and intense properties of this absorption are characteristic of the stretching of hydrogen-bonded hydroxyl groups. The increase in intensity of this mode also reflects an increase in the polarity of the bond involved in the vibration over that of the C—H bond in hexane. A second strong band in the spectrum is located
near 1058 cm\(^{-1}\). This absorption has been identified as the C—O stretching mode. The vibrational displacements of this fundamental are similar to the antisymmetric stretch of water. Since the vibration involves significant displacement of the adjacent C—C oscillator, the vibration will be substitution sensitive. These latter shifts can be of value in determining the nature of the alcohol (primary, secondary, or tertiary, see Table 9.9).

The only other new modes observed in going from hexane to 1-hexanol are the O—H bending vibrations. Two types of bending vibrations would be expected, the in-plane and out-of-plane displacements. The in-plane bend of the O—H oscillator is not a very good frequency because it is coupled to adjacent methylene group bending vibrations (wagging). It can be found because of its breadth (O—H hydrogen bonding) as an underlying absorption running across the 1500-1300-wavenumber region (Table 9.8). The out-of-plane O—H bending fundamental occurs at lower frequencies as a broad band (H-bonding) near 650 cm\(^{-1}\). The group frequencies of the hydrocarbon portion of the molecule are easily identified, including the rocking fundamental (727 cm\(^{-1}\), which is superimposed on the broad O—H out-of-plane bending mode. The normal modes of the hydroxyl group possess many of the characteristics that lead to excellent group frequency correlations (Fig. 9.22W).

2. Hexanal

If two terminal hydrogen atoms of hexane are replaced by a single oxygen atom, we have hexanal. The aldehyde functional groups gives rise to several good group frequencies (Website Fig. 9.23W; see Text: Table 9.10, p. 540). The system has strong bonds and a large dipole moment, and it is
essentially decoupled from the rest of the molecule by the low-frequency C—C connecting bond. A component of the C—H stretching mode of the aldehyde group can be assigned to a band of weak-to-medium intensity at $\tilde{\nu} = 2723$ cm$^{-1}$. The low frequency of this mode is interpreted on the basis of a Fermi resonance interaction. The aldehyde in-plane C—H bending fundamental found at 1390 cm$^{-1}$ would be expected to generate an overtone very close to the aldehyde group C—H stretching mode, which must occur near 2775 cm$^{-1}$. The two levels interact and split to give two components. The more easily identified low-frequency component is very characteristic of the aldehyde group and is located near 2730 cm$^{-1}$. The higher frequency component often is masked by other aliphatic C—H stretching absorptions in the 2900–2800-wavenumber region. For hexanal, the upper band is observed as a distinct shoulder occurring at 2823 cm$^{-1}$. The carbonyl stretching frequency is the most intense band in the spectrum and is located at 1728 cm$^{-1}$. The structural change in going from ketone to aldehyde will produce mass and inductive effects that will lower the frequency and bond angle and
hyperconjugative effects that will raise the carbonyl frequency. The outcome of this competition is that aliphatic aldehyde carbonyl stretching modes generally occur at slightly higher values than do those of the saturated ketones. The only other identifiable group frequency associated with the aldehyde system is the C—H in-plane bending fundamental ($\tilde{\nu} = 1390 \text{ cm}^{-1}$) responsible for the overtone that undergoes Fermi resonance with the aldehyde C—H stretching mode. Note that the aldehyde group perturbs one of the aliphatic chain group frequencies. Thus, the frequency of the symmetric deformation (scissoring) of the methylene group alpha to the carbonyl is lowered ($\tilde{\nu} = 1408 \text{ cm}^{-1}$), and intensified by hyperconjugation with the carbonyl. It is also evident that the vibrational modes of the aliphatic portion of the molecule now contribute a much smaller fraction of the overall absorption by the sample. Hence, the spectrum is obtained with a path length even shorter than that of 1-hexanol.

3. 3-Heptanone

If we insert a carbonyl group between the first two methylene groups of hexane, we have the ketone 3-heptanone. The only group frequency mode associated with this group is the stretching frequency ($\tilde{\nu}_{C=O} = 1718 \text{ cm}^{-1}$), which occurs within the expected region for an aliphatic ketone (Website Fig. 9.24W; see Text: Table 9.11, p. 540).
As in the case of aldehydes having $\alpha$-methylene groups, the symmetric bending modes (scissoring) of the adjacent methylene groups at carbon atoms 2 and 4 (C-2 and C-4) in 3-heptanone are perturbed to lower frequencies ($\tilde{\nu} = 1425$ cm$^{-1}$) by hyperconjugation with the carbonyl. The shift of the methylene bending frequency is a useful indication of the substitution surrounding the ketone. The very weak band at 3425 cm$^{-1}$ can be confidently assigned as the overtone of the carbonyl stretching frequency ($2 \times \tilde{\nu}_{C=O} = 3444$ cm$^{-1}$). The drop in intensity from that of the fundamental and the frequency contraction are typical of these forbidden transitions. Note that in this molecule the sequence of methylene groups has dropped below 4, and the rocking vibration ($\sim 720$ cm$^{-1}$) is no longer easily detectable.

4. **n-Hexyl Acetate**

Replacing the O—H hydrogen of hexanol with CH$_3$CO— gives n-hexyl acetate. The very strong band found at 1743 cm$^{-1}$ is typical of the carbonyl frequency of
an aliphatic ester, particularly acetate esters (Website Fig. 9.25W; see Text: Table 9.12, p. 541). Two very intense bands occur in the spectra

**Website Fig. 9.25W**

IR spectrum: 1-Hexylacetate.

of acetate esters in the 1250-1000-wavenumber region. In primary acetates these bands are found near 1250 and 1050 cm\(^{-1}\) (hexyl acetate, 1242, 1042 cm\(^{-1}\)). The higher frequency mode is assigned to the antisymmetric C—CO—O stretch (similar to that in water), and the lower frequency mode to the antisymmetric O—CH\(_2—\)C stretch. Although there is some coupling of these vibrations to the adjacent structure, resonance through the carbonyl group by the ether oxygen tends to localize the higher of the two vibrations. The lower mode, which would be expected to be more highly coupled, is in fact more subject to substitution effects. The upper mode is found in most saturated esters at frequencies (1210-1160 cm\(^{-1}\) slightly lower than those that occur in acetates. The only other absorption to note in acetate esters is the methyl symmetric bending mode. Here the umbrella deformation of the methyl adjacent to the carbonyl occurs at a
slightly lower (hyperconjugation) frequency ($\tilde{\nu} = 1366$ cm$^{-1}$), and the band is significantly intensified by the interaction with the carbonyl as compared with the deformation of the methyl at the end of the hexyl chain ($\tilde{\nu} = 1384$ cm$^{-1}$).

5. Hexanoyl Chloride

Hexanoyl chloride can be formed from hexane by the exchange of three terminal methyl hydrogen atoms for an oxygen and a chlorine. The carbonyl stretching mode dominates the spectrum (Website Fig. 9.26W; see Text: Table 9.13, p. 541). It is an extremely intense band occurring near 1802 cm$^{-1}$.

**Website Fig. 9.26W**

IR spectrum: Hexanoyl chloride.

The high frequency and intensity result from inductive effects of chlorine substitution directly on the carbonyl group. The chlorine modes, on the other hand, are not easy to identify, and these vibrations do not develop good group frequencies. The symmetric deformation (scissoring) of the methylene group adjacent to the carbonyl group again shows the same frequency decrease.
resulting from hyperconjugation as observed with the ketones and aldehydes. In this case the mode ($\tilde{\nu} = 1408 \text{ cm}^{-1}$) gains considerable intensity via interaction with the highly polarized carbonyl group.

6. **Hexanoic Acid**

Hexanoic acid is obtained from hexane by substituting a carbonyl oxygen and an $-\text{OH}$ group for the terminal hydrogen atoms. The acid possesses a very intense band with a width at one-half peak height of about $1000 \text{ cm}^{-1}$, which covers the region $3500-2200 \text{ cm}^{-1}$ (Website Fig. 9.27W; see Text: Table 9.14, p. 541). This absorption is characteristic of very strongly hydrogen-bonded carboxylic acid groups. The relatively weak $\text{C—H}$ stretching absorption of the aliphatic chain is superimposed on the $\text{O—H}$ stretch between $3000$ and $2800 \text{ cm}^{-1}$.

---

**Website Fig. 9.27W**

IR spectrum: Hexanoic acid.
Also occurring along this broad absorption are a characteristic set of weak overtone and combination bands running from about 2800 to 2200 cm$^{-1}$. The spectrum of the neat material will be that of the hydrogen-bonded dimer, which as noted earlier (see p. 102), has a center of symmetry. The carbonyl mode (out-of-phase stretch) is found at 1709 cm$^{-1}$. Two rather broad and intense bands located between 1450 and 1400 and between 1300 and 1200 cm$^{-1}$ are associated with the in-plane O—H bend and the antisymmetric CH$_2$—CO—O stretch. These modes show evidence of considerable mixing, a situation quite different from the case of alcohols. A strong broad absorption band at 930 cm$^{-1}$ is assigned to an out-of-plane bending mode of the hydrogen-bonded dimer ring. Thus, this latter band is present only when detectable concentrations of the dimers exist. In dilute solution the dimer band vanishes. This low-wavenumber absorption is termed the acid dimer band. It is worth noting that even in carboxylic acids, in which the normal modes of a large, highly polarized functional group dominate the spectrum, the group frequencies of the aliphatic molecular backbone are still identifiable.

7. Hexanoic Anhydride

Hexanoic anhydride can be formed from two molecules of hexanoic acid by removing the elements of water. Coupling of the carbonyls through the ether oxygen splits the carbonyls ($\nu_{C=O} = 1831, 1761$ cm$^{-1}$) by about 70 cm$^{-1}$ (Website Fig. 9.28; see Text: Table 9.15, p. 542). In this instance the higher frequency mode is the in-phase vibration. Strong bands occur in aliphatic
IR spectrum: Hexanoic anhydride.

Anhydrides, near 1050 cm\(^{-1}\), which are directly related to C—O stretching modes. The scissoring deformation of the —CH\(_2—\) groups alpha to the carbonyls is assigned to the band near 1415 cm\(^{-1}\).

8. Dihexyl Ether

Dihexyl ether is obtained by removing the elements of water from two molecules of 1-hexanol. Long-chain aliphatic ethers have many physical properties similar to those of the hydrocarbons, and the infrared spectrum of dihexyl ether (Website Fig. 9.29W; see Text: Table 9.16, p. 542) is not very different from that of tridecane. The single major departure in the spectrum is the presence
IR spectrum: Dihexyl ether.

of a very strong band near 1100 cm\(^{-1}\). In dihexyl ether this absorption is found at 1130 cm\(^{-1}\). The vibration responsible for this absorption band must involve a considerable amount of antisymmetric C—O—C stretch. Heavy coupling, however, is also involved in this level. Because of the extensive mechanical coupling with the chain carbon atoms, substitution adjacent to the ether linkage can rather significantly shift this frequency. Fortunately, the large intensity associated with this fundamental relative to the other bands occurring in this region makes it possible, in most cases, to assign with confidence the antisymmetric C—O—C stretching mode (see Text: Table 9.16).

9. n-Hexylamine

If an NH group is inserted across one of the terminal C—H bonds of n-hexane, we obtain 1-hexylamine. Compare the infrared spectrum of 1-hexylamine (Website Fig. 9.30W; see Text: Table 9.17, p. 542) with those of 1-hexanol (Fig. 9.22W) and n-hexane (Fig. 9.2).
The difference in the region above 3310 cm\(^{-1}\) is quite remarkable. Although n-hexane is essentially devoid of absorption in this region and 1-hexanol exhibits a very strong band, 1-hexylamine possesses two bands (\(\tilde{\nu}_{N-H} = 3380, 3290\) cm\(^{-1}\)) of medium-to-weak intensity. These latter bands are the antisymmetric and symmetric N—H stretching modes, respectively, of the primary amino group (Text: Table 9.17 p. 542). Hydrogen-bond intensification of the N—H group in simple primary amines does not equal that of the hydroxyl system. A band of medium intensity just above 1600 cm\(^{-1}\) is assigned to the symmetric (scissoring) deformation of the amino group. This vibration is directly related to the methylene mode near 1450 cm\(^{-1}\). The occurrence of this fundamental requires that the amino group be unsubstituted, as the two hydrogen atoms undergo major displacements during the vibration. A second bending mode of primary amino groups can sometimes be observed. This vibration resembles the methylene wagging motion in which the hydrogen atoms are displaced more or less parallel to the molecular axis. As is usual for hydrogen-bonded bending fundamentals, the mode occurs as a fairly broad and quite strong band near 800 cm\(^{-1}\). Frequencies
related to the normal modes of single bonded C—N systems are highly coupled to the surrounding C—C oscillators and cannot be assigned with any confidence.

10. Hexanenitrile
Replacement of three terminal hydrogen atoms of hexane by a nitrogen gives hexanenitrile. The nitrile group is a very simple two-atom oscillator. The very strong triple bond (as in the case of the alkynes) contributes to an unusually high stretching frequency (Website Fig. 9.31W; see Text: Table 9.18, p. 542), and the polar character of the group gives rise to very strong bands. These two factors allow for easy distinction of nitrile bands from alkynyl absorption. The stretching fundamental of saturated nitriles falls in the region 2260–2240 cm\(^{-1}\). As expected, conjugation lowers this fundamental (2240–2210 cm\(^{-1}\)). In hexanenitrile the normal mode occurs at 2255 cm\(^{-1}\). Primary nitrile groups can interact through hyperconjugation with the adjacent methylene groups so that the symmetric deformation (scissoring) mode is lowered into the

**Website Fig. 9.31W**

IR spectrum: Hexanenitrile.
1425-wavenumber region. In hexanenitrile this bending vibration is assigned to a band at 1430 cm\(^{-1}\). The remaining absorption bands are the aliphatic group frequencies.

11. **Hexanamide**

Hexanamide is obtained by replacing the terminal hydrogen atoms of hexane with the elements ONH\(_2\). The highly polar amide group leads to very strong hydrogen bonding, which in turn leads to greatly intensified N—H antisymmetric and symmetric stretching modes (\(\tilde{\nu}_{\text{N—H}} = 3375, 3200\) cm\(^{-1}\); Website Fig. 9.32W; see Text: Table 9.19, p. 543). The carbonyl stretch occurs at low values

**Website Fig. 9.32W**

[Graph showing IR spectrum of Hexanamide]

IR spectrum: Hexanamide.

(1675 cm\(^{-1}\)) for a saturated system substituted with an electronegative atom. Resonance between the carbonyl and the nitrogen lone pair, plus strong hydrogen bonding, appears to overcome the inductive effect. The carbonyl band is accidentally degenerate (two fundamentals occurring at the same frequency by chance rather than being required to have the same frequency by symmetry...
restrictions), but does not interact to any appreciable extent with the symmetric bending mode of the $-\text{NH}_2$ group in hexanamide (symmetry constraints restrict the interaction in this case). In some situations both bands can be resolved, but they will often occur as a single band. The wagging vibration of the amino group in which the hydrogen atoms are displaced parallel to the chain axis is found in the 700-wavenumber region as a strong broad band. The symmetric deformation of the methylene group adjacent to the amide carbonyl undergoes the conventional frequency drop to the 1425-wavenumber region. The perturbed scissoring fundamental, however, gains considerable intensity from the interaction with the highly polarized amide carbonyl. Because of the presence of very strong intermolecular hydrogen bonds, the overall spectra of solid or pure liquid amides exhibit broad, rather ill-defined bands.

12. N-Methylhexanamide

If we substitute on the amide group by replacing a hydrogen with a methyl group, we obtain the secondary amide, N-methylhexanamide. The single N—H group gives rise to a very strong band at about 3300 cm$^{-1}$, which is very indicative of strong hydrogen bonding (Website Fig. 9.33W;
IR spectrum: N-Methylhexanamide.

see Text: Table 9.20, Table 9.21, p. 543). A medium intensity band near 3100 cm⁻¹ is the overtone of the N—H bending mode identified at 1570 cm⁻¹ in Fermi resonance with the N—H stretching fundamental. The overtone does not match the fundamental particularly well, but it is close enough to acquire substantial intensity enhancement. The carbonyl stretching mode at 1650 cm⁻¹ exhibits the very intense and broad characteristics of the amide C=O system. The N—H in-plane bend of the single oscillator occurs near 1570 cm⁻¹. The drop in frequency from that of the primary scissoring mode near 1600 cm⁻¹ allows for confident assignment of the substitution on secondary amide groups (see Text: Table 9.20, p. 543). The band at 1570 cm⁻¹, although often referred to as the N—H bending mode, is in reality a heavily mixed mode. The pure in-plane N—H bend naturally falls near 1450 cm⁻¹. Resonance between the carbonyl and the nitrogen lone pair results in a stiffening of the C—N bond. The resulting C—N stretch is raised into the 1400-wavenumber region. Mechanical coupling between the N—H bend and the C—N stretch results in first-order interaction and a splitting of the levels. The upper level occurs near 1570 cm⁻¹, whereas the lower level often can be identified
near 1300 cm\(^{-1}\) as a weak-to-medium band. The out-of-plane bend of the N—H group is identified as a broad, medium-intensity band centered near 700 cm\(^{-1}\). The symmetric deformation of the methylene group alpha to the carbonyl is located at 1410 cm\(^{-1}\). The unusual intensity of this mode results from interaction with the heavily polarized C=O system.

Studies of amide carbonyl frequencies in dilute nonpolar solution indicate that hydrogen-bonding effects are largely responsible for the low frequencies observed with primary and secondary amides, but play no role in tertiary amides.

The data (see Text: Table 9.21, p. 543) indicate that when hydrogen bonding is removed in primary amides, the inductive effect of the nitrogen dominates over the influence of conjugation, but not as much as in the case of esters. This result is consistent with the relative electronegativities involved in esters and amides. In secondary amides with an electron-releasing N-alkyl group replacing a hydrogen, conjugation involving the nitrogen lone pair with the carbonyl begins to overcome the inductive effect. In tertiary amides with two N-alkyl substituents present, conjugation now dominates the inductive effect. Under these conditions polarized resonance forms make large contributions to the character of the carbonyl, and the tertiary amide C=O frequencies are observed to decrease to values in the same range as the frequency shifts generated via hydrogen bonding.

13. 1-Hexyl Isocyanate

1-Hexyl isocyanate is obtained by replacement of a terminal hydrogen atom with an \(-\text{N}=\text{C}=\text{O}\) group. The out-of-phase stretching mode of the isocyanate group attached to the hexyl chain occurs at 2275 cm\(^{-1}\), as a broad and very strong band
This functional group is representative of a number of cumulated double-bond systems that possess vibrations mechanically identical to that of carbon dioxide ($\tilde{\nu} = 2350 \text{ cm}^{-1}$). The range of stretching frequencies observed for alkyl-substituted isocyanates is very narrow, $\tilde{\nu} = 2280-2260 \text{ cm}^{-1}$, which implies little coupling to the rest of the system (see Text: Table 9.22, p. 543). Interestingly, conjugation appears not to have any significant effect on the mode. The symmetric stretching fundamental is not easily observed in the infrared as it is a weak band occurring in the fingerprint region. The remaining group frequencies in the spectrum of 1-hexyl isocyanate are those of the alkyl group.

**14. 1-Hexanethiol**

Insertion of a sulfur atom in a terminal C—H bond of $n$-hexane gives 1-hexanethiol. The spectrum of this material resembles that of hexane itself except for small changes
in the fingerprint region and a weak band near 2570 cm\(^{-1}\) (Website Fig. 9.35W). The latter absorption is assigned to the S—H stretching fundamental

Website Fig. 9.35W


(see Text: Table 9.23, p. 543). Although this mode is quite weak, it is not involved in any significant coupling, and it occurs in a region of the spectrum sparsely populated by other absorption bands. The S—H stretch, therefore, can be considered a reliable group frequency. The S—H bending and C—S stretching modes also are weak, and as they fall in the fingerprint region they are not useful as group frequencies. The remaining bands of 1-hexanethiol that can be assigned belong to the alkyl portion of the molecule.

15. 1-Chlorohexane

Replacement of a terminal hydrogen atom of n-hexane by a chlorine atom gives 1-chlorohexane. The massive chlorine atom is connected to the alkyl section by a
fairly weak but highly polarized bond, which dictates that the C—Cl stretching frequency appears as an intense band at low frequencies (Website Fig. 9.36W; see Text: Table 9.24, p. 544). The spectrum of 1-chlorohexane

Website Fig. 9.36W

IR spectrum 1-Chlorohexane.

1-Chlorohexane

CH$\text{CH}(\text{CH}_2)_5\text{CH}_2\text{Cl}$ NEAT

does possess a number of moderately intense absorption bands in the low-frequency region (800–600 cm$^{-1}$). Some coupling to the main structure adjacent to the C—Cl bond is expected, since the carbon atom will be carrying out the majority of the displacement. Reliable assignment of the halogen stretching mode, therefore, is not easy, because the surrounding C—C modes will pick up intensity from the polar C—Cl bond. In the case of 1-chlorohexane, it is possible to assign two C—Cl stretching modes ($\tilde{\nu}_{\text{C—Cl}} = 731, 658$ cm$^{-1}$), based on Raman spectral data. The presence of two modes is attributed to the presence of rotamers.
The higher frequency is assigned to the **anti** (trans) conformer, and the lower frequency to the **gauche** conformer. Note that the stretching frequency of the **anti** isomer, 731 cm\(^{-1}\), falls at the same frequency as the methylene rocking vibration of the hexyl chain. Thus, without additional data it would have been difficult to assign the C—Cl stretching modes, even in these fairly simple systems. The carbon-halogen stretching vibration must be employed with care as a group frequency.

The bending modes of the halogens usually occur at such low frequencies as to be of little use as conventional group frequencies. The remaining bands are related to the hydrocarbon portion of the molecule.

### 16. Chlorobenzene

The final spectrum to be considered in this section is the spectrum of the C\(_6\) compound chlorobenzene (Website Fig. 9.37W; see Text: Table 9.25, p. 544). Here we have introduced a new hydrocarbon platform bearing the functional group. Chlorobenzene is a material in which the oscillators
IR spectrum: Chlorobenzene.

are tightly bound together as a single conformer. The spectrum contains many needle-sharp bands as compared, for example, with the spectrum of 1-chlorohexane. Thus, it is often possible to detect the presence of either aliphatic or aromatic systems simply on the basis of overall appearance of the spectrum. Based on the above assignments the group frequencies of the complete hydrocarbon portion and the heteroatom functional group can be assigned as in see Text: Table 9.25, p. 544.

IV. Instrumentation
The infrared spectrometer is a complex and expensive instrument that you will encounter on a regular basis in the organic laboratory. TREAT THE IR SPECTROMETER WITH RESPECT. The instrument is particularly adapted to the characterization of microscale products. Data obtained from the IR spectrometer
will be used many times throughout the semester. You will become more proficient at obtaining this type of spectral information as you gain experience with the instrument. Practice in preparing the sample for instrumental analysis can significantly improve the quality of the spectra.

The late Robert B. Woodward, Nobel Laureate, one of the most outstanding synthetic organic chemists of this century, once stated: “But no single tool has had more dramatic impact upon organic chemistry than infrared measurements. The development [of easily] operated machines for the determination of infrared spectra has permitted a degree of immediate and continuous analytical and structural control in synthetic organic work which was literally unimaginable. . . The power of the method grows with each day, and further progress may be expected for a long time to come. Nonetheless, its potential is even now greater than many realize” (see Woodward, R. B. In Perspectives in Organic Chemistry; A. Todd, Ed.; Interscience: New York, 1956, p. 157).

Although the preceding statement was made some time ago (when NMR spectroscopy was in its infancy), and the more dramatic impact has shifted to high-field NMR and high-resolution mass spectrometry (MS) for structural elucidation, Woodward's final point still holds true when it comes to substance identification. Infrared data and particularly spectra obtained from gas chromatographic (GC) coupled IR interferometers, continue to play a dominant role in compound identification and characterization (where nanogram, $10^9$ g, and even picogram, $10^{12}$ g, sensitivities are routinely required in these measurements). The infrared spectrum is a reflection of the vibrational energy levels present in a molecule. As no two substances have the same exact set of vibrational frequencies, no two substances have identical infrared spectra. There
are at present a number of excellent collections of infrared spectra that may be used for reference comparisons (for example, see the text Bibliography).

The use of IR spectra to identify the presence of particular functional groups in a molecule is one of the principal applications of this technique. Many of the absorption bands present in an IR spectrum can be related to specific arrays of atoms in that material. These “group frequencies” can be extremely helpful in the interpretation of experimental results. With the recent coupling of $^{13}$C NMR data and IR group frequency arguments, the interpretation of the functional group environment has become extremely powerful.

**The Infrared Interferometer**

Infrared interferometers are now beginning to enter the instructional laboratory in significant numbers. Thus, a short description of this instrumentation becomes important for understanding how modern infrared data are acquired.

The design of the majority of current interferometers, employed in infrared measurements, is based on adaptations of a two-beam system originally developed by Michelson for photon velocity measurements (see Website Fig. 9.38W).
The optical diagram of the Perkin-Elmer model 1600 infrared interferometer.

The principal function of the optical system of the two-beam interferometer is (1) to divide (beamsplitter) the source radiation into two components traveling separate paths; (2) to introduce an oscillating path difference between these two beams (by moving one of the mirrors back and forth while keeping the other mirror fixed; this is however, not the case in the PE 1600, which introduces a slight wrinkle); and (3) to create an interference condition at the intersection of the beams during their second pass through the beamsplitter. Thus, the path difference is varied in a cyclic fashion and the resulting intensity variation of the recombined beams is measured as a function of the moving mirror or changing path length (see Fig. 9.38W). The intensity fluctuation with time generates an interferogram that ultimately yields the desired spectral information when it undergoes Fourier transformation (FT).
The path difference between the two beams where the mirror travel is \( x \) is, therefore, \( 2x \). This difference is defined as the retardation \( (d) \). When the two paths are equivalent, there is zero retardation and both beams will be in phase when they intersect at the beam splitter the second time. Under these conditions constructive interference occurs, and the intensity of the beam reaching the detector is the sum total of both beams. When the moving mirror displacement equals \( \frac{1}{4} \lambda \) (wavelength), the retardation is \( \frac{1}{2} \lambda \) and destructive interference takes place during recombination of the beams at the beamsplitter. Under these conditions, no signal reaches the detector.

If we now displace the movable mirror at a constant velocity, the signal at the detector will vary sinusoidally with a maximum occurring every time retardation is an integral multiple of \( \lambda \). The source intensity \( [I \tilde{v}] \) at the detector, is therefore a function of the retardation, \( \delta \), and \( I'(\delta) \).

At other values of \( \delta \), the intensity of the exit beam is given by:

\[
I'(\delta) = 0.5 I(\tilde{v}) \{1 + \cos 2\pi \delta \lambda\} \\
= 0.5 I(\tilde{v}) \{1 + \cos 2\pi \delta \tilde{v}\}
\]

The parameter \( I'(\delta) \) is a function that involves a constant or dc term \( [0.5 I(\tilde{v})] \) and a modulated ac term \( [0.5 I(\tilde{v}) \cos 2\pi \tilde{v} \delta] \). It is the latter part of the expression that is usually referred to as the interferogram. If we employ a monochromatic (single-frequency) source, the intensity at the detector is simply defined as

\[
I(\delta) = 0.5 I(\tilde{v}) \cos 2\pi \tilde{v} \delta
\]
Spectral information is extracted from the interferogram by calculating the cosine Fourier transform of \( I(\delta) \). Normally, as the moving mirror is displaced at constant velocity, \( v \) (cm/s), we consider how the interferogram varies with time, \( I(t) \), rather than as a function of retardation, \( I(\delta) \). In this form at \( t \) (s) from the zero point the retardation \( (\delta) \) may be expressed as \( \delta = 2vt \) in centimeters.

Substituting in the above, we obtain

\[ I(t) = 0.5I(\tilde{\nu}) \cos 2\pi\tilde{\nu}\delta \]

The units of the abscissa of the interferogram will be the inverse of the units of the spectrum, in this case reciprocal centimeters (cm\(^{-1}\)).

The amplitude of the signal at time \( t \) for the cosine wave frequency \( f \) may be expressed as

\[ A(t) = A_0 \cos 2\pi ft \quad (A_0 = \text{maximum amplitude}) \]

Thus, the frequency \( f \) of the radiation in terms of \( \tilde{\nu} \) (cm\(^{-1}\)) for the elementary case of a monochromatic interferogram, \( I(t) \), corresponds to

\[ f\tilde{\nu} = 2\tilde{\nu}v \]

Thus, in this example, in which we have obtained the interferogram of a monochromatic source, the determination of the “spectrum” via Fourier transform is simple, as the amplitude and wavelength can both be measured directly (see Website Fig. 9.39W).
Interferograms for two monochromatic sources.

The extrapolation to the case of sources that emit continuous bands of radiation, however, presents a considerably more complex interferogram, which requires the use of digital computers to compute the Fourier transform and generate the data in terms of an absorption spectrum. With the advent of high-speed computation, and mathematical tricks that have shortened the calculation routine, it is now possible to generate infrared spectral data very quickly and accurately via interferometric instrumentation.

The older generation optical null, double-beam arrangement, although not nearly as sensitive and quick as the interferometric instruments, does have some distinct advantages. For example, absorption signals from any substances present in both beams in equal quantities are automatically canceled. Although atmospheric water and carbon dioxide have particularly strong absorption
bands in the infrared, the double-beam instrument automatically subtracts the absorption of these substances from the recorded spectrum. In the case of the FT systems this problem is resolved by subtracting a background spectrum, which can only be carried out sequentially with the acquisition of the sample spectrum.
At the initial phase of your training, the unknowns to be identified will be relatively pure materials and will be known compounds. The properties of these materials are recorded in the literature, and/or in the tables on the website. Later perhaps, mixtures of compounds or samples of commercial products will be assigned for separation, analysis, and identification of the compound compounds.

Tables of Derivatives

pages 135 - 149
# Tables 10.1 - 10.17.

## Table 10.1 Derivatives of Carboxylic Acids (Liquids)

<table>
<thead>
<tr>
<th>Acid</th>
<th>bp (°C)</th>
<th>Amide</th>
<th>Anilide</th>
<th>p-Toluidide</th>
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<td>Methanoic (formic)</td>
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* Two values are given for those derivatives that may exist in polymorphic forms.
### Table 10.2  Derivatives of Carboxylic Acids (Solids)

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<td>170 (mono)</td>
<td>122 (mono)</td>
<td>201 (mono)</td>
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*a Two values are given for those derivatives that may exist in polymorphic forms.
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\(^a\) Two values are given for those derivatives that may exist in polymorphic forms or as syn and anti geometrical isomers.
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* Two values are given for those derivatives that may exists in polymorphic forms or as syn and anti geometrical isomers.
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<td>4-Chloroaniline</td>
<td>232 (mp 70)</td>
<td>179</td>
<td>192</td>
<td>178</td>
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<tr>
<td>4-Methoxyaniline</td>
<td>243 (mp 57)</td>
<td>130</td>
<td>154</td>
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<tr>
<td>2-Ethoxyaniline</td>
<td>229</td>
<td>79</td>
<td>104</td>
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<tr>
<td>4-Ethoxyaniline</td>
<td>254</td>
<td>135</td>
<td>173</td>
<td>—</td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>(mp 54)</td>
<td>101</td>
<td>180</td>
<td>182</td>
</tr>
<tr>
<td>3-Nitroaniline</td>
<td>(mp 114)</td>
<td>152</td>
<td>155</td>
<td>—</td>
</tr>
<tr>
<td>4-Nitroaniline</td>
<td>(mp 147)</td>
<td>—</td>
<td>199</td>
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* Two values are given for those derivatives that may exist in polymorphic forms.
Table 10.7 Derivatives of Tertiary Amines

<table>
<thead>
<tr>
<th>Tertiary Amine</th>
<th>bp (°C)</th>
<th>Melting Point of Derivative (°C)*</th>
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<tbody>
<tr>
<td>Trimethylamine</td>
<td>3</td>
<td>216</td>
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<tr>
<td>Triethylamine</td>
<td>89</td>
<td>173</td>
</tr>
<tr>
<td>Pyridine</td>
<td>116</td>
<td>167</td>
</tr>
<tr>
<td>2-Methylpyridine (2-picoline)</td>
<td>129</td>
<td>169</td>
</tr>
<tr>
<td>2,6-Dimethylpyridine (2,6-lutidine)</td>
<td>142</td>
<td>168 (161)</td>
</tr>
<tr>
<td>3-Methylpyridine (3-picoline)</td>
<td>143</td>
<td>150</td>
</tr>
<tr>
<td>4-Methylpyridine (4-picoline)</td>
<td>143</td>
<td>167</td>
</tr>
<tr>
<td>Tripropylamine</td>
<td>157</td>
<td>116</td>
</tr>
<tr>
<td>N,N-Dimethylaniline</td>
<td>193</td>
<td>163</td>
</tr>
<tr>
<td>Tributylamine</td>
<td>216</td>
<td>105</td>
</tr>
<tr>
<td>N,N-Diethylaniline</td>
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<td>142</td>
</tr>
<tr>
<td>Quinoline</td>
<td>237</td>
<td>203</td>
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<tr>
<td>Triisopentylamine</td>
<td>245</td>
<td>125</td>
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* Two values are given for those derivatives that may exist in polymorphic forms.
<table>
<thead>
<tr>
<th>Acid Chloride or Anhydride</th>
<th>bp (°C)</th>
<th>mp (°C)</th>
<th>Amide</th>
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<tbody>
<tr>
<td>Acetyl chloride</td>
<td>52</td>
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<td>82</td>
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<td>Propionyl chloride</td>
<td>77–79</td>
<td>—</td>
<td>81</td>
</tr>
<tr>
<td>Butyryl chloride</td>
<td>102</td>
<td>—</td>
<td>115</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>138–140</td>
<td>—</td>
<td>82</td>
</tr>
<tr>
<td>Propionic anhydride</td>
<td>167</td>
<td>—</td>
<td>81</td>
</tr>
<tr>
<td>Butyric anhydride</td>
<td>198–199</td>
<td>—</td>
<td>115</td>
</tr>
<tr>
<td>Benzoyl chloride</td>
<td>198</td>
<td>—</td>
<td>130</td>
</tr>
<tr>
<td>3-Chlorobenzoxyl chloride</td>
<td>225</td>
<td>—</td>
<td>134</td>
</tr>
<tr>
<td>2-Chlorobenzoxyl chloride</td>
<td>238</td>
<td>—</td>
<td>142</td>
</tr>
<tr>
<td>cis-1,2-Cyclohexanedicarboxylic anhydride</td>
<td>—</td>
<td>32</td>
<td>192d (acid)</td>
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<tr>
<td>Benzoic anhydride</td>
<td>—</td>
<td>39–40</td>
<td>130</td>
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<tr>
<td>Maleic anhydride</td>
<td>—</td>
<td>54–56</td>
<td>181 (mono)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>266 (di)</td>
</tr>
<tr>
<td>4-Nitrobenzoxyl chloride</td>
<td>—</td>
<td>72–74</td>
<td>201</td>
</tr>
<tr>
<td>Succinic anhydride</td>
<td>—</td>
<td>119–120</td>
<td>157 (mono)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>260 (di)</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>—</td>
<td>131–133</td>
<td>149 (mono)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>220 (di)</td>
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Table 10.9  Derivatives of Aromatic Hydrocarbons

<table>
<thead>
<tr>
<th>Aromatic Hydrocarbon</th>
<th>bp (°C)</th>
<th>mp (°C)</th>
<th>Picate Melting Point of Derivative (°C)*</th>
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<tbody>
<tr>
<td>Benzene</td>
<td>80</td>
<td>—</td>
<td>84</td>
</tr>
<tr>
<td>Toluene</td>
<td>111</td>
<td>—</td>
<td>88</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>136</td>
<td>—</td>
<td>96</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>138</td>
<td>—</td>
<td>90</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>138–139</td>
<td>—</td>
<td>91</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>143–145</td>
<td>—</td>
<td>88</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>163–166</td>
<td>—</td>
<td>97</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>168</td>
<td>—</td>
<td>97</td>
</tr>
<tr>
<td>1,2,3,4-Tetramethylbenzene</td>
<td>205</td>
<td>—</td>
<td>92</td>
</tr>
<tr>
<td>1-Methylnaphthalene</td>
<td>242</td>
<td>—</td>
<td>142</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>—</td>
<td>35</td>
<td>116</td>
</tr>
<tr>
<td>Pentamethylnaphthalene</td>
<td>—</td>
<td>51</td>
<td>131</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>—</td>
<td>81</td>
<td>149</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>—</td>
<td>94</td>
<td>161</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>—</td>
<td>100</td>
<td>144 (133)</td>
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<tr>
<td>Anthracene</td>
<td>—</td>
<td>216</td>
<td>138</td>
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* Two values are given for those derivatives that may exist in polymorphic forms.
### Derivatives of Phenols

<table>
<thead>
<tr>
<th>Phenol</th>
<th>mp (°C)</th>
<th>Bromo</th>
<th>α-Naphthylurethan</th>
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<tbody>
<tr>
<td>2-Chloro-</td>
<td>7 (bp 175)</td>
<td>48 (mono)</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>76 (di)</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>42</td>
<td>95 (tri)</td>
<td>133</td>
</tr>
<tr>
<td>4-Methyl- (p-cresol)</td>
<td>35</td>
<td>49 (di)</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td></td>
<td>108 (tetra)</td>
<td></td>
</tr>
<tr>
<td>3-Methyl- (m-cresol)</td>
<td>203 (bp)</td>
<td>84 (tri)</td>
<td>128</td>
</tr>
<tr>
<td>3,4-Dimethyl-</td>
<td>229 (bp)</td>
<td>171 (tri)</td>
<td>141</td>
</tr>
<tr>
<td>2-Methyl- (o-cresol)</td>
<td>33</td>
<td>56 (di)</td>
<td>142</td>
</tr>
<tr>
<td>4-Ethyl-</td>
<td>45</td>
<td>—</td>
<td>128</td>
</tr>
<tr>
<td>2-Nitro-</td>
<td>45</td>
<td>117 (di)</td>
<td>113</td>
</tr>
<tr>
<td>2,6-Dimethyl-</td>
<td>48</td>
<td>79</td>
<td>176</td>
</tr>
<tr>
<td>2-Isopropyl-5-methyl- (thymol)</td>
<td>50</td>
<td>55</td>
<td>160</td>
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<td>3,5-Dimethyl-</td>
<td>64</td>
<td>166 (tri)</td>
<td>—</td>
</tr>
<tr>
<td>4-Bromo-</td>
<td>66</td>
<td>95 (tri)</td>
<td>168</td>
</tr>
<tr>
<td>2,5-Dimethyl-</td>
<td>73</td>
<td>178 (tri)</td>
<td>173</td>
</tr>
<tr>
<td>1-Naphthol</td>
<td>95</td>
<td>105 (di)</td>
<td>152</td>
</tr>
<tr>
<td>3-Nitro-</td>
<td>96</td>
<td>91 (di)</td>
<td>—</td>
</tr>
<tr>
<td>4-tert-Butyl-</td>
<td>98</td>
<td>50 (mono)</td>
<td>110</td>
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<tr>
<td></td>
<td></td>
<td>67 (di)</td>
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<tr>
<td>1,2-Dihydroxy- (catechol)</td>
<td>105</td>
<td>192 (tetra)</td>
<td>175</td>
</tr>
<tr>
<td>1,3-Dihydroxy- (resorcinol)</td>
<td>110</td>
<td>112 (tri)</td>
<td>275</td>
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<tr>
<td>4-Nitro-</td>
<td>112</td>
<td>142 (di)</td>
<td>150</td>
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<tr>
<td>2-Naphthol</td>
<td>123</td>
<td>84</td>
<td>157</td>
</tr>
<tr>
<td>Pyrogallol</td>
<td>134</td>
<td>158 (di)</td>
<td>173</td>
</tr>
<tr>
<td>1,4-Dihydroxy- (hydroquinone)</td>
<td>171</td>
<td>186 (di)</td>
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<td>Compound</td>
<td>bp (°C)</td>
<td>Compound</td>
<td>bp (°C)</td>
</tr>
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<td>---------</td>
<td>---------------------</td>
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<td>Alkanes</td>
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<td>2,2,4-Trimethylpentane</td>
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<td>trans-1,4-Dimethylcyclohexane</td>
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<td>2,2-Dimethylbutane</td>
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<td>Octane</td>
<td>126</td>
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<td>2,3-Dimethylbutane</td>
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<td>Nonane</td>
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<td>2-Methylpentane</td>
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<td>Decane</td>
<td>174</td>
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<td>3-Methylpentane</td>
<td>63</td>
<td>Eicosane (mp 37)</td>
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<td>Hexane</td>
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<td>Norbornane (mp 87, subl)</td>
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<td>Cyclohexane</td>
<td>81</td>
<td>Adamantane (mp 268, sealed)</td>
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<td>Heptane</td>
<td>98</td>
<td>3-Hexyne</td>
<td>82</td>
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<td>1-Pentene</td>
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<td>Cyclohexene</td>
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<td>2-Methyl-1,3-butadiene (isoprene)</td>
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<td>2-Hexyne</td>
<td>84</td>
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<td>trans-2-Pentene</td>
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<td>1-Heptene</td>
<td>94</td>
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<td>cis-2-Pentene</td>
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<td>1-Heptyne</td>
<td>100</td>
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<td>2-Methyl-2-butene</td>
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<td>2,4,4-trimethyl-1-pentene</td>
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<td>2,4,4-Trimethyl-2-pentene</td>
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<td>1-Octene</td>
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<td>(piperylene)</td>
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<td>1-Hexene</td>
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<td>d,l-α-Pinene</td>
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<td>cis-3-Hexene</td>
<td>66</td>
<td>(−)-β-Pinene</td>
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<td>trans-3-Hexene</td>
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<td>Limonene</td>
<td>176</td>
</tr>
<tr>
<td>1-Hexyne</td>
<td>71</td>
<td>1-Decene</td>
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<td>1,3-Cyclohexadiene</td>
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### Table 10.12 Halogenated Hydrocarbons

<table>
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<th>bp (°C)</th>
<th>Compound</th>
<th>bp (°C)</th>
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<td><strong>Alkyl Halides</strong></td>
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<tr>
<td><strong>Chlorides</strong></td>
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<td><strong>Bromides</strong></td>
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<tr>
<td><em>n</em>-Propyl</td>
<td>47</td>
<td>Ethyl</td>
<td>38</td>
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<tr>
<td>tert-Butyl</td>
<td>51</td>
<td>Isopropyl</td>
<td>60</td>
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<tr>
<td>sec-Butyl</td>
<td>68</td>
<td>Propyl</td>
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<tr>
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<td>Isobutyl</td>
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<td>Neopentyl</td>
<td>85</td>
<td>sec-Butyl</td>
<td>91</td>
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<td>tert-Pentyl</td>
<td>86</td>
<td>Butyl</td>
<td>101</td>
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<td>Cyclohexyl</td>
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<td>Hexachloroethane</td>
<td>185 (mp 187, subl)</td>
<td>Neopentyl</td>
<td>109</td>
</tr>
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<td>Triphenylmethyl</td>
<td>(mp 113)</td>
<td>1-Bromoheptane</td>
<td>178–179</td>
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<td><strong>Iodides</strong></td>
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<table>
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<th>Compound</th>
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<th>mp (°C)</th>
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<tr>
<td>Bromobenzene</td>
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<td>—</td>
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<tr>
<td>2-Chlorotoluene</td>
<td>157–159</td>
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</tr>
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<td>4-Chlorotoluene</td>
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<td>—</td>
</tr>
<tr>
<td>1,3-Dichlorobenzene</td>
<td>172–173</td>
<td>—</td>
</tr>
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<td>1,2-Dichlorobenzene</td>
<td>178</td>
<td>—</td>
</tr>
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<td>2,4-Dichlorotoluene</td>
<td>196–203</td>
<td>—</td>
</tr>
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<td>3,4-Dichlorotoluene</td>
<td>201</td>
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</tr>
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<td>214</td>
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<td>1-Bromonaphthalene</td>
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<td>1,4-Dichlorobenzene</td>
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<td>54–56</td>
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<td>1,4-Bromochlorobenzene</td>
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Table 10.13  Nitriles

<table>
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<th>Compound</th>
<th>mp (°C)</th>
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<td>81</td>
<td>Malononitrile</td>
<td>34</td>
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<tr>
<td>Propionitrile</td>
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<td>Stearonitrile</td>
<td>40</td>
</tr>
<tr>
<td>Isobutyronitrile</td>
<td>108</td>
<td>2-Chlorobenzonitrile</td>
<td>41</td>
</tr>
<tr>
<td>n-Butyronitrile</td>
<td>117</td>
<td>Succinonitrile</td>
<td>48</td>
</tr>
<tr>
<td>Benzonitrile</td>
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<td>Diphenylacetonitrile</td>
<td>75</td>
</tr>
<tr>
<td>2-Methylbenzonitrile</td>
<td>205</td>
<td>4-Cyanopyridine</td>
<td>80</td>
</tr>
<tr>
<td>3-Methylbenzonitrile</td>
<td>212</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Methylbenzonitrile</td>
<td>217</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzylcyanide</td>
<td>234</td>
<td></td>
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</tr>
<tr>
<td>Adiponitrile</td>
<td>295</td>
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</table>

Table 10.14  Amides

<table>
<thead>
<tr>
<th>Compound</th>
<th>bp (°C)</th>
<th>mp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N-Dimethylformamide</td>
<td>153</td>
<td>—</td>
</tr>
<tr>
<td>N,N-Diethylformamide</td>
<td>176</td>
<td>—</td>
</tr>
<tr>
<td>N-Methylformamide</td>
<td>185</td>
<td>—</td>
</tr>
<tr>
<td>N-Formylpiperidine</td>
<td>222</td>
<td>—</td>
</tr>
<tr>
<td>N,N-Dimethylbenzamide</td>
<td>—</td>
<td>41</td>
</tr>
<tr>
<td>N-Benzoylpiperidine</td>
<td>—</td>
<td>48</td>
</tr>
<tr>
<td>N-Propylacetanilide</td>
<td>—</td>
<td>50</td>
</tr>
<tr>
<td>N-Benzylacetamide</td>
<td>—</td>
<td>54</td>
</tr>
<tr>
<td>N-Ethylacetanilide</td>
<td>—</td>
<td>54</td>
</tr>
<tr>
<td>N,N-Diphenylformamide</td>
<td>—</td>
<td>73</td>
</tr>
<tr>
<td>N-Methyl-4-acetotoluidide</td>
<td>—</td>
<td>83</td>
</tr>
<tr>
<td>N,N-Diphenylacetamide</td>
<td>—</td>
<td>101</td>
</tr>
<tr>
<td>N-Methylacetanilide</td>
<td>—</td>
<td>102</td>
</tr>
<tr>
<td>Acetanilide</td>
<td>—</td>
<td>114</td>
</tr>
<tr>
<td>N-Ethyl-4-nitroacetanilide</td>
<td>—</td>
<td>118</td>
</tr>
<tr>
<td>N-Phenylsuccinimide</td>
<td>—</td>
<td>156</td>
</tr>
<tr>
<td>N-Phenylphthalimide</td>
<td>—</td>
<td>205</td>
</tr>
</tbody>
</table>

* Also see Tables A.1 and A.2 for amides prepared as derivatives of carboxylic acids.
### Table 10.15  Nitro Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>bp (°C)</th>
<th>mp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene</td>
<td>211</td>
<td>—</td>
</tr>
<tr>
<td>2-Nitrotoluene</td>
<td>225</td>
<td>—</td>
</tr>
<tr>
<td>2-Nitro-(m)-xylene</td>
<td>225</td>
<td>—</td>
</tr>
<tr>
<td>3-Nitrotoluene</td>
<td>231</td>
<td>—</td>
</tr>
<tr>
<td>3-Nitro-(o)-xylene</td>
<td>245</td>
<td>—</td>
</tr>
<tr>
<td>4-Ethynitrobenzene</td>
<td>246</td>
<td>—</td>
</tr>
<tr>
<td>2-Chloro-6-nitrotoluene</td>
<td>—</td>
<td>36</td>
</tr>
<tr>
<td>4-Chloro-2-nitrotoluene</td>
<td>—</td>
<td>38</td>
</tr>
<tr>
<td>3,4-Dichloronitrobenzene</td>
<td>—</td>
<td>42</td>
</tr>
<tr>
<td>1-Chloro-2,4-dinitrobenzene</td>
<td>—</td>
<td>50</td>
</tr>
<tr>
<td>4-Nitrotoluene</td>
<td>—</td>
<td>54</td>
</tr>
<tr>
<td>1-Nitronaphthalene</td>
<td>—</td>
<td>56</td>
</tr>
<tr>
<td>1-Chloro-4-nitrobenzene</td>
<td>—</td>
<td>84</td>
</tr>
<tr>
<td>(m)-Dinitrobenzene</td>
<td>—</td>
<td>90</td>
</tr>
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### Table 10.16  Ethers

<table>
<thead>
<tr>
<th>Compound</th>
<th>bp (°C)</th>
<th>mp (°C)</th>
</tr>
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<tr>
<td>Furan</td>
<td>32</td>
<td>—</td>
</tr>
<tr>
<td>Ethyl vinyl ether</td>
<td>33</td>
<td>—</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>67</td>
<td>—</td>
</tr>
<tr>
<td>(n)-Butyl vinyl ether</td>
<td>94</td>
<td>—</td>
</tr>
<tr>
<td>Anisole</td>
<td>154</td>
<td>—</td>
</tr>
<tr>
<td>4-Methylanisole</td>
<td>174</td>
<td>—</td>
</tr>
<tr>
<td>3-Methylanisole</td>
<td>176</td>
<td>—</td>
</tr>
<tr>
<td>4-Chloroanisole</td>
<td>203</td>
<td>—</td>
</tr>
<tr>
<td>1,2-Dimethoxybenzene</td>
<td>207</td>
<td>—</td>
</tr>
<tr>
<td>4-Bromoanisole</td>
<td>215</td>
<td>—</td>
</tr>
<tr>
<td>Anethole</td>
<td>234–237</td>
<td>—</td>
</tr>
<tr>
<td>Diphenyl ether</td>
<td>259</td>
<td>—</td>
</tr>
<tr>
<td>2-Nitroanisole</td>
<td>273</td>
<td>—</td>
</tr>
<tr>
<td>Dibenzyl ether</td>
<td>298</td>
<td>—</td>
</tr>
<tr>
<td>4-Nitroanisole</td>
<td>—</td>
<td>50–52</td>
</tr>
<tr>
<td>1,4-Dimethoxybenzene</td>
<td>—</td>
<td>56–60</td>
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<tr>
<td>2-Methoxynaphthalene</td>
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<td>73–75</td>
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<td>Compound</td>
<td>bp (°C)</td>
<td>Compound</td>
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<tr>
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<td>---------</td>
<td>------------------------</td>
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<tr>
<td><strong>Liquids</strong></td>
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<td><strong>Liquids</strong></td>
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<tr>
<td>Methyl formate</td>
<td>32</td>
<td>Pentyl formate</td>
</tr>
<tr>
<td>Ethyl formate</td>
<td>54</td>
<td>Ethyl 3-methylbutanoate</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>57</td>
<td>Isobutyl propanoate</td>
</tr>
<tr>
<td>Isopropyl formate</td>
<td>68</td>
<td>Isopentyl acetate</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>77</td>
<td>Propyl butanoate</td>
</tr>
<tr>
<td>Methyl propanoate</td>
<td>80</td>
<td>Ethyl pentanoate</td>
</tr>
<tr>
<td>Methyl propenoate</td>
<td>80</td>
<td>Butyl propanoate</td>
</tr>
<tr>
<td>Propyl formate</td>
<td>81</td>
<td>Pentyl acetate</td>
</tr>
<tr>
<td>Isopropyl acetate</td>
<td>91</td>
<td>Isobutyl 2-methylpropanoate</td>
</tr>
<tr>
<td>Methyl 2-methylpropanoate</td>
<td>93</td>
<td>Methyl hexanoate</td>
</tr>
<tr>
<td>sec-Butyl formate</td>
<td>97</td>
<td>Isopentyl propanoate</td>
</tr>
<tr>
<td>tert-Butyl acetate</td>
<td>98</td>
<td>Butyl butanoate</td>
</tr>
<tr>
<td>Ethyl propanoate</td>
<td>99</td>
<td>Propyl pentanoate</td>
</tr>
<tr>
<td>Propyl acetate</td>
<td>101</td>
<td>Ethyl hexanoate</td>
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<tr>
<td>Methyl butanoate</td>
<td>102</td>
<td>Cyclohexyl acetate</td>
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<tr>
<td>Allyl acetate</td>
<td>104</td>
<td>Isopentyl butanoate</td>
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<tr>
<td>Ethyl 2-methylpropanoate</td>
<td>110</td>
<td>Pentyl butanoate</td>
</tr>
<tr>
<td>sec-Butyl acetate</td>
<td>112</td>
<td>Propyl hexanoate</td>
</tr>
<tr>
<td>Methyl 3-methylbutanoate</td>
<td>117</td>
<td>Butyl pentanoate</td>
</tr>
<tr>
<td>Isobutyl acetate</td>
<td>117</td>
<td>Ethyl heptanoate</td>
</tr>
<tr>
<td>Ethyl butanoate</td>
<td>122</td>
<td>Isopentyl 3-methylbutanoate</td>
</tr>
<tr>
<td>Propyl propanoate</td>
<td>122</td>
<td>Ethylene glycol diacetate</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>126</td>
<td>Tetrahydrofurfuryl acetate</td>
</tr>
<tr>
<td>Diethyl carbonate</td>
<td>127</td>
<td>Methyl octanoate</td>
</tr>
<tr>
<td>Methyl pentanoate</td>
<td>128</td>
<td>Methyl benzoate</td>
</tr>
<tr>
<td>Isopropyl butanoate</td>
<td>128</td>
<td>Ethyl benzoate</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>mp (°C)</th>
<th>Compound</th>
<th>mp (°C)</th>
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<tbody>
<tr>
<td><strong>Solids</strong></td>
<td></td>
<td><strong>Solids</strong></td>
<td></td>
</tr>
<tr>
<td>d-Bornyl acetate</td>
<td>29 (bp 221)</td>
<td>Ethyl 3,5-dinitrobenzoate</td>
<td>93</td>
</tr>
<tr>
<td>Ethyl 2-nitrobenzoate</td>
<td>30</td>
<td>Methyl 4-nitrobenzoate</td>
<td>96</td>
</tr>
<tr>
<td>Ethyl octadecanoate</td>
<td>33</td>
<td>2-Naphthyl benzoate</td>
<td>107</td>
</tr>
<tr>
<td>Methyl cinnamate</td>
<td>36 (bp 261)</td>
<td>Isopropyl 4-nitrobenzoate</td>
<td>111</td>
</tr>
<tr>
<td>Methyl 4-chlorobenzoate</td>
<td>44</td>
<td>Cyclohexyl 3,5-</td>
<td>dinitrobenzoate</td>
</tr>
<tr>
<td>1-Naphthyl acetate</td>
<td>49</td>
<td>Cholesteryl acetate</td>
<td>114</td>
</tr>
<tr>
<td>Ethyl 4-nitrobenzoate</td>
<td>56</td>
<td>Ethyl 4-hydroxybenzoate</td>
<td>116</td>
</tr>
<tr>
<td>2-Naphthyl acetate</td>
<td>71</td>
<td>tert-Butyl 4-nitrobenzoate</td>
<td>116</td>
</tr>
<tr>
<td>Ethylene glycol dibenzoate</td>
<td>73</td>
<td>Hydroquinone diacetate</td>
<td>124</td>
</tr>
<tr>
<td>Propyl 3,5-dinitrobenzoate</td>
<td>74</td>
<td>tert-Butyl 3,5-dinitrobenzoate</td>
<td>142</td>
</tr>
<tr>
<td>Methyl 4-bromobenzoate</td>
<td>81</td>
<td>Hydroquinone dibenzoate</td>
<td>204</td>
</tr>
</tbody>
</table>
Chapters 6, 7, and 8: (pages 150 - 157)
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and cis-2-Butene Experiment [9], 184

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   2-Bromobutane to Yield 1-Butene, trans-2-Butene, and
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   3-phenylpropanoic Acid: 2’-Bromostyrene
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   Piperonylnitrile
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  9,10-Dihydroanthracene-9,10-α,β-succinic Acid Anhydride
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  Hexaphenylbenzene
  Experiment [A4ab], 449

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  Bromination of (E)-Stilbene: meso-Stilbene Dibromide
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  The Benzoin Condensation of Benzaldehyde: Benzoin
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  Xanthene
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  Triphenylmethyl alcohol
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  4-Methyl-3-heptanol
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    SUBSTITUTION

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    TETRAHEDRAL CARBON

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    TRIGONAL CARBON
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    Experiment [8B], 178
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9-Bromoanthracene

G. AROMATIC
ELECTROPHILIC
SUBSTITUTION

H. AROMATIC
NUCLEOPHILIC
SUBSTITUTION

I. AROMATIC FREE RADICAL
SUSTITUTION
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- Cyclohexanol
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- cis- and trans-4-tert-Butylcyclohexanol
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Hydroboration-Oxidation of an Alkene:
- Octanol
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- Thioxanthene
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- 9-Fluorenone
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