ESTERS, ORGANIC

Esters can be defined as compounds that, on hydrolysis, yield alcohols or phenols and acids according to the equation

$$ RA + H_2O = ROH + HA $$

in which R is a hydrocarbon radical and A is the anion of an organic or inorganic acid. For carboxylic acid esters, the reaction may be represented as follows:

$$ RCOOR' + H_2O = ROH + R'COOH $$

in which R and R' are the same or different radicals. The reverse reaction constitutes the usual method for preparing esters.

Although esters have been likened to salts because of the similarity in formulas and preparation, the reaction leading to esters is not a simple ionic one as is salt formation; thus in the formation of esters of carboxylic acids, it is usually the hydroxy group (rather than the hydrogen atom) of the carboxy group that is replaced by the alkoxy group (rather than the alkyl group) of the alcohol. Hydroxy carboxylic acids in which the carboxy and hydroxy groups are separated by at least two carbon atoms may form internal esters, or lactones, as shown by

$$ HO\text{C}(\text{CR}_{1}\text{C})_{n}\text{OOH} \rightarrow \text{OC}(\text{CR}_{1}\text{C})_{n}\text{O} \rightarrow H_{2}O $$

in which n ≥ 1. When n = 1 or n > 4, hydroxy carboxylic acids have a strong tendency to form polyesters (by intermolecular esterification) rather than lactones:

$$ HO\text{C}(\text{R})\text{COOH} \rightarrow H_{2}\text{O}, \text{C}(\text{R})\text{COOH} $$

Methylenes and carboxylic acids form an analogous series of compounds, the thiol esters:

$$ RNH + RC\text{OHH} \rightarrow RN\text{C}(\text{R})\text{COOH} $$
Esters of polyhydric alcohols in which the hydroxyl groups are on different carbon atoms (as in ethylene glycol and its homologs) may be prepared by the usual methods; they undergo reactions similar to those of esters of monohydric alcohols. Acylal, RCH(OCOR')₂, are esters of 1,1-diols or aldehydic hydrates. Neither their methods of preparation nor their reactions are typical of those of ordinary esters. They have little technical or commercial value. The ortho esters, RC(OR')₃, resemble acetals more than they do the simple esters with which this article is mainly concerned, although like ordinary esters they give alcohols and carboxylic acids on hydrolysis (1). The methods of preparation and reactions of vinyl esters, in which the carbon atom carrying the alcoholic oxygen atom is unsaturated (RCH═CHCOR'), are also not typical of those of simple esters.

Since the number and types of acids and alcohols that may react to form them are very great, an extremely large number of esters is theoretically possible. This article deals only with simple esters of carboxylic acids and principally with esters of the fatty acid series. Further information on esters of other organic acids and esters of inorganic acids is given in articles such as Benzoic acid, Citric acid, Phthalic acid, Phosphoric acid, for triethyl(tetralyl)phosphates and other phosphates, Sulfuric and sulfurous esters, Acetoacetic acid and ester, Carboxylic esters and chloroformic esters, Urethanes (for esters of carboxylic acid), Glycols, Fats and fatty oils (for fatty acid esters of glycerol (called glycerides)), Rosin (for rosin acid esters or glycerol (called ester gums)), Waxes (for esters of certain higher polyhydric alcohols and higher acids), Oils, essential, and Perfumes (for esters of terpenes like borneol and geraniol), Cellulose derivatives and Cellulose derivatives—plastics (for cellulose esters, such as cellulose acetate and nitrocellulose (cellulose nitrate)), and Starch derivatives (for starch esters). Polyester esters, whether derived from glycols and dibasic acids or from hydroxy acids, are described under Polyesters.

**Various types of esters find widespread uses as solvents (qv), plasticizers (qv), perfumes (qv), flavors (qv), and medicinals; certain polymerized esters are used as resins, plastics, and textile fibers.** Esters, because of their wide variation in composition and properties, are among the most important classes of organic compounds.

**Nomenclature (2).** The names of esters are derived from those of the hydroxy compounds and acids they yield on hydrolysis, as ethyl acetate, geranyl acetate (trans-, 8,7-dimethyl-2,6-octadienyl acetate), butyl hydrogen phthalate, dibutyl phthalate, and phenyl salicylate. Ester of complex hydroxy compounds are somtimes designated as derivatives of these compounds by prefixing the name of the appropriate acid radical; for example, acetycellulose (cellulose acetate) and acetyl triethyl citrate (triethyl citrate acetate). The prefix nitro has been incorrectly used to designate esters of nitric acid, as in nitrocellulose, nitroglycerin, and nitrocellulose, which are better called cellulose nitrate, glycercyl trinitrate, and starch nitrate, respectively. In naming esters containing one or more substituents, it is necessary to indicate specifically in which portion of the molecule the substituents occur and to distinguish between isomers, such as ethyl chloroacetate, CH₃CICOOC₂H₅, and 2-chloroethyl acetate, CH₂COC₂H₅Cl.

Esters, RC(O)R', formed by esterification of a carboxylic acid with a mercaptan, are known as thiol esters; the isomers, RC(OR')₂, are thio esters.

Ortho esters, RC(OR')₃, are named on the basis of the ortho acids, as HC(O)C₂H₅, triethyl orthoformate. Imido esters (often named imido ethers or imino ethers), RCl(═NH)OR', are preferably named as derivatives of imidoic acids; thus, C₂H₅C(═NH)OC₂H₅ is ethyl benzimidate.
Physical and Chemical Properties

The lower esters are colorless, volatile liquids, and many of them are pleasantly aromatic. Most of the monoesters of the higher saturated fatty acids are colorless, odorless, crystalline solids. Esters of the very long chain acids and alcohols are hard, brittle, lustrous, crystalline solids, which are generally referred to as waxes. Most of the higher esters of this class are not known in pure form, but only as complex mixtures comprising the naturally occurring waxes.

In general, the melting points of the esters of fatty acids are lower than those of the corresponding acids, and the boiling points of the methyl, ethyl, and propyl esters are lower than those of the corresponding acids. With increasing chain length of the alcohol, the boiling points increase and ultimately become much higher than those of the corresponding acids. Since many of the monoesters are relatively stable toward heat in the absence of moisture, they are generally distillable without decomposition. They are, therefore, often employed in processes of separation and identification of mixed fatty acids.

The data for the methyl and ethyl esters of the saturated fatty acid series are fairly complete and relatively well known, but data for the esters of the higher alcohols are often lacking. Data on boiling point, density, molar volume, viscosity, solubility, heat of combustion, and other physical constants of esters of aliphatic acids have been tabulated by Markley (3).

The esters are generally insoluble in water but are soluble in various organic liquids. The lower esters are themselves good solvents for many organic compounds, including most liquids. They are especially good solvents for cellulose-type lacquers.

Reactions

Hydrolysis (4, 5). Monoesters are neutral substances but those of low molecular weight slowly hydrolyze in water to form free acids and alcohols. This reaction is accelerated by high temperature and the presence of alkalies, acids, or various other catalysts. As the molecular weight increases, the tendency to hydrolyze decreases, so that elevated temperatures and the presence of an alkali or catalyst are necessary for rapid reaction.

Although esters have been observed to hydrolyze by six different mechanisms, depending upon the ester and the hydrolysis conditions, only two of these are important for most esters (4). Equations 1 and 2 illustrate the most common paths for basic hydrolysis and for acid-catalyzed hydrolysis, respectively:

\[
\begin{align*}
\text{HO}^- + \text{O}^\cdot \text{OR}' \overset{\text{slow}}{\rightarrow} \left[\begin{array}{c} \text{HO} \\
\text{R}
\end{array}\right] \underset{\text{fast}}{\rightarrow} \text{HO} \cdot \text{OR}' \rightarrow \text{RCOO}^- + \text{R'OH} (1)
\end{align*}
\]

\[
\begin{align*}
\text{RCOR'} + \text{H}^+ \rightarrow \text{R} \cdot \text{C} \cdot \text{O} \cdot \text{H} \overset{\text{+H}_2\text{O}, \text{slow}}{\rightarrow} \left[\begin{array}{c} \text{R} \\
\text{H}
\end{array}\right] \rightarrow \text{RCOOH} + \text{H}_2\text{O} \overset{\text{fast}}{\rightarrow} \text{R} \cdot \text{C} \cdot \text{O} \cdot \text{H} \rightarrow \text{RCOOH} + \text{H}^+ + \text{R'OH, slow} (2)
\end{align*}
\]
The mechanism represented by equation 1 correctly predicts observed steric and electronic effects in ester hydrolysis. In forming intermediate (1), both the density of negative charge at the reaction center and the extent of crowding are increased. It would, therefore, be predicted that electron-attracting substituents would facilitate and bulky substituents retard hydrolysis.

The following saponification rates, relative to methyl acetate, illustrate the polar effect:

<table>
<thead>
<tr>
<th>Ester</th>
<th>Rate Constant Relative to Methyl Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COOCH₃</td>
<td>1.0</td>
</tr>
<tr>
<td>(COOCH₃)₂</td>
<td>761</td>
</tr>
<tr>
<td>170,000</td>
<td>0.80</td>
</tr>
</tbody>
</table>

The following two series of saponification rates, relative to ethyl acetate, illustrate the effect of increasing steric hindrance in the acyl and alkyl substituents, respectively:

<table>
<thead>
<tr>
<th>Ester</th>
<th>Rate Constant Relative to Ethyl Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COOCH₂H₅</td>
<td>1.0</td>
</tr>
<tr>
<td>(CH₃)₂COOCH₂H₅</td>
<td>0.47</td>
</tr>
<tr>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>(CH₃)₄COOCH₂H₅</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Steric effects in acid-catalyzed hydrolysis are similar to those in basic hydrolysis, but polar effects are much less important in the acid-catalyzed reactions.

**Basic Hydrolysis.** The hydrolysis of esters with alkali is one of the oldest known chemical reactions. The early Romans and Gauls treated fats with wood ashes to obtain a solution with detergent properties, but it was not until the time of Scheele (1779) and Chevreul (1813-1823) that the reaction was understood. Today, this reaction is the basis of the soap industry. For complete saponification of esters slightly more than the theoretical amount of alkali is required, but the free acid may be obtained with catalytic amounts (0.3-1.0%) of basic materials, such as the oxides of calcium, magnesium, barium, and lead, by autoclaving at 8-10 atm.

**Acid Hydrolysis.** Hydrolysis of esters with dilute acid is slow, owing to the poor emulsifying power of acids. However, the Twitchell reagent (the reaction product of benzene, oleic acid, and concentrated sulfuric acid), which was introduced in the early 1900s, markedly increased the efficiency of the acid hydrolysis of esters, particularly fats. A large number of these fat-splitting compounds has been reported.

**Hydrolysis by Steam (0).** High-pressure steam alone at 183-300°C hydrolyzes fats directly to high-grade fatty acids. This method offers advantages to the soap industry over basic hydrolysis, and continuous commercial processes have been developed.

**Hydrolysis by Enzymes.** The metabolism of fats in both animal and plant systems is closely associated with enzymes (lipases) which have the ability to hydrolyze fatty esters. There are also certain enzymes that are capable of splitting the lower esters, but which show little activity with the higher esters.

**Alcoholysis, Acidolysis, and Ester–Ester Interchange.** See Ester interchange.
Ammonolysis. Ammonia reacts with esters to give alcohols and amides. This reaction is analogous to hydrolysis of esters, which gives alcohols and acids (7). The reaction is usually carried out in aqueous or alcoholic ammonia. Simple esters react with ammonia at a satisfactory rate at room temperature; higher esters may require elevated temperatures and pressures. Sometimes ester ammonolysis is carried out at low temperatures to avoid attack of another reactive group:

\[
\text{CICH}_2\text{COOC}_2\text{H}_5 + \text{NH}_2 \xrightarrow{\text{aq}} \text{CICH}_2\text{CONH}_2 + \text{C}_2\text{H}_5\text{OH}
\]

Other ammonia derivatives, such as primary and secondary amines, react analogously to give N-substituted amides:

\[
\text{RCOOR'} + \text{R''NH} \rightarrow \text{RCOOR''R''} + \text{R''OH}
\]

Hydrazine reacts the same way to give hydrazides:

\[
\text{RCOOR'} + \text{HNNH}_2 \rightarrow \text{RCOHNH}_2 + \text{R''OH}
\]

The mechanism of these reactions has been studied extensively (8).

When esters are passed with ammonia in the vapor phase over contact catalysts at temperatures around 400–500°C, they are rapidly converted to nitriles. Thus, Maillié in 1920 prepared acetonitrile by passing a mixture of ammonia and methyl ethyl over alumina at 500°C or over thoria at 480–490°C. These reactions may also be carried out in the liquid phase in the presence of suitable catalysts. This conversion of esters to nitriles is actually an ammonolysis, followed by catalyzed dehydration of the amide:

\[
\text{RCOOR'} + \text{NH}_2 \rightarrow \text{RCO NH}_2 + \text{ROH}
\]

\[
\text{RCO NH}_2 \xrightarrow{\text{catalyst}} \text{RCN} + \text{H}_2\text{O}
\]

Reduction (9). Hydrogenation of esters over copper chromite at 200–300°C and 100–300 atm reduces them to alcohols:

\[
\text{RCOOH} + 2 \text{H}_2 \rightarrow \text{RCOH} + \text{H}_2\text{O}
\]

When R is saturated and when no halogen or sulfur is present, the reaction is smooth and almost quantitative; but when R is an aromatic nucleus, such as benzene or pyrrole, the reaction proceeds beyond the alcohol step, as in the reduction of ethyl benzoate to toluene. This cleavage may be minimized by carrying out the reaction at low temperatures with a high ratio of catalyst to ester. An important commercial use of this reaction is the reduction of coconut oil and other fats to alcohols, chiefly lauryl and cetyl alcohols, which are used to prepare the sulfated alcohol-type detergent. The reaction may also be used to prepare diols for use as polymer intermediates, as in the reduction of dimethyl 1,4-cyclohexanedicarboxylate to 1,4-cyclohexanediol.

The use of sodium in alcoholic solutions to reduce esters to alcohols was first reported by Bouveault and Blain in 1904 (10). Since then it has been used for the commercial production of lauril alcohol, but this process is probably gradually being superseded for the production of saturated alcohols by the catalytic process. Detailed procedures for the reduction of oleic acid esters with sodium in ethyl or butyl alcohol have been given by Adkins, Reid, and co-workers (11,12). Yields of 80–84% were reported. 4-Methyl-2-pentanol is a preferred solvent for the commercial reduction of esters by this method.

Complex metal hydrides, particularly lithium aluminum hydride (lithium tetrahydroaluminate), are exceedingly useful and widely used reagents for reducing esters to alcohols in the laboratory (see Hydrides). Practically any ester can be reduced by
this method, and alcohols of high purity are obtained in excellent yield. Carbon–carbon double bonds are normally not affected (13).

Grignard Reaction (14). The reaction of esters with Grignard reagents is similar to that of ketones. The esters of formic acid yield secondary alcohols, whereas other esters yield tertiary alcohols.

\[
\begin{align*}
R_{2}\text{CHCOOR'} & \xrightarrow{\text{MgBr}} R_{2}\text{CCCH}_{2}\text{COOR'} & \xrightarrow{\text{H}_{2}\text{O}} R'_{2}\text{CCR}''\text{R}''
\end{align*}
\]

The overall yield in the preparation of triphenyl methanol from ethyl benzoate and phenylmagnesium bromide is 91%.

Acetoacetic Ester Condensation (15). In the presence of certain bases, an ester having hydrogen on the \(\alpha\)-carbon atom will react with a second molecule of the same ester or with another ester (which may or may not have hydrogen on the \(\alpha\)-carbon atom) to form a \(\beta\)-keto ester:

\[
R_{2}\text{CHCOOR'} + R_{2}\text{CCCOOR'} \rightarrow R_{2}\text{CCCH}_{2}\text{COOR'} + R'_{2}\text{OH}
\]

This reaction is a special case of the Claisen reaction which includes ketone–ester condensation to form 1,3-diketones.

Preparation of Acyloins (16). When aliphatic esters are allowed to react with metallic sodium in inert solvents, acyloins (\(\alpha\)-hydroxyketones) are formed:

\[
2\text{RCOOR'} + 4\text{Na} \rightarrow \frac{\text{RC} = \text{ONa}}{\text{RC} = \text{ONa}} + 2\text{NaOR'} + \frac{\text{H}_{2}\text{O}}{\text{RC} = \text{ONa}} \rightarrow \left[ \frac{\text{R} = \text{C} = \text{OH}}{\text{R} = \text{C} = \text{OH}} \right] + 2\text{NaOH}
\]

Pyrolysis (17). The pyrolysis of simple esters of the formula \(\text{RCOOCR'}R''\text{CHR}'''\) to form the free acid and an olefin is a general reaction which is frequently used for producing olefins. The pyrolysis is generally carried out at temperatures of 300–500°C over an inert heat-transfer agent, such as 96% silica glass chips. Esters of tertiary alcohols pyrolyze more readily than esters of secondary alcohols, and esters of primary alcohols are the most difficult to pyrolyze. Some of the higher-boiling esters of tertiary alcohols cannot be distilled without decomposition. tert-Pentyl acetate decomposes to pentenes and acetic acid below 200°C. This reaction does not require a catalyst; it has been shown to be intramolecular and to involve a cyclic transition state:

\[
\begin{align*}
\text{R} = \text{C} = \text{CHR}'' & \xrightarrow{\Delta} \text{R} = \text{C} = \text{CHR}'' + \text{R}'\text{R}''\text{C} = \text{CR}''
\end{align*}
\]

The double bond does not move along the carbon chain, but mixtures of isomeric olefins are produced by pyrolysis of unsymmetrical secondary or tertiary esters which contain more than one carbon atom capable of losing hydrogen by the above mecha-
nism. The production of methyl acrylate by pyrolysis of methyl 2-acetoxypropionate (methyl 2-hydroxypropionate acetate) has been extensively investigated:

\[ \text{CH}_3\text{CH(OOCCH}_2\text{OOCCH}_2\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCOOH} + \text{CH}_3\text{COOH} \]

Methyl esters and esters of the formula RCOOCH_2CR_3, which do not contain hydrogen atoms capable of elimination by the mechanism given above, must be heated to much higher temperatures before they decompose, and their pyrolysis products are complex. The pyrolysis of these esters is not a synthetically useful reaction. The enhanced thermal stability of these esters makes them very valuable for certain purposes; however, some acids from which esters are derived are not stable and decompose under the pyrolysis conditions. Diethyl malonate, for example, pyrolyzes to ethylene, methanol, and carbon dioxide; tert-butyl esters of \( \beta \)-keto acids decompose smoothly to isobutylene (2-methylpropane), carbon dioxide, and a ketone. Two molecules of esters of \( \alpha \)-amino acids, such as alanine, lysine, histidine, leucine, and phenylalanine, condense at 150-180°C to give a piperazine derivative and two molecules of alcohol.

Miscellaneous Reactions. Ketones can be obtained in substantial yields from fatty acid esters as well as from the fatty acids by heating them in the presence of certain metals or their oxides. For example, ethyl laurate in the vapor phase over a thoria-gel catalyst at 300°C gives a 92.5% yield of laurone (12-tricosanone), and ethyl undecenoate gives an 80% yield of didecyl ketone. Other vapor-phase catalysts are manganese chromite and zinc chromite. When the reaction is run in the liquid phase, the yields are lower, and metallic iron is probably the best catalyst. Aluminum and magnesium and the oxides of iron, silicon, copper, zinc, titanium, aluminum, and magnesium have all been reported as catalysts for this reaction to give ketones (18).

A few other reactions that esters may undergo can be illustrated with ethyl acetate. Chlorine in boiling ethyl acetate yields acetyl chloride, whereas bromine at 150–160°C yields ethyl bromide and monoor dibromoacetic acids. Phosphorus pentachloride at 150°C yields ethyl chloride and acetyl chloride. Alcoholic sodium hydrogen sulfide at about 180°C yields ethyl mercaptan (ethanethiol).

Certain esters, particularly those of di-substituted acetic acids, may be dehydrogenated to the corresponding \( \alpha, \beta \)-unsaturated esters. Methyl isobutyrinate, for example, gives methyl methacrylate (19):

\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{CH}_3\text{CHCOOCH}_2 \frac{\text{catalyst}}{} \text{CH}_2=\text{CHCOOH} + \text{H}_2 \]

Analysis of Esters

The analysis of esters usually includes the determination of such physical properties as the boiling range, melting point or freezing point, specific gravity, refractive index, the amount of nonvolatile residue or ash, and color; and such chemical properties as free acidity and the actual ester content. The physical properties are determined by well-known methods. The free acidity is determined by titrating a sample in either water or an alcohol–water mixture, with standard alkali. The ester content is generally denoted by the saponification number, which is the number of milligrams of potassium hydroxide required to saponify one gram of the ester, or by the saponification equivalent, which is the number of milliequivalents of potassium hydroxide
required to saponify one gram of the ester. The saponification number (SN) and the
saponification equivalent (SE) are related by the following formula:

\[
SE = \frac{56.1 \times 1000}{SN}
\]

The RCOOR' group of simple esters is comparatively easy to identify from characteristic bands in the infrared spectrum. The carbonyl group absorbs strongly at 1750-1735 cm⁻¹, and a second strong band, characteristic of the other linkage, is present in the region between 1300-1100 cm⁻¹. The location of this second band gives an indication of the type of acid from which the ester is derived (20).

The phenacyl esters and the p-halo- or p-nitrophenacyl esters have been used as a means of identifying fatty acids and the fatty acid portion of esters. The acid portion of the ester is also readily identified by cleaving the ester with hydrazine to form the hydrazide as described previously.

**Health and Safety Factors**

Esters, as a class, are not considered health hazards, and any harmful effects of esters, other than those based on their solvent properties, are generally due to the toxicity of the acid or alcohol which is formed by hydrolysis of that particular ester. The lower esters are quite volatile and must be kept away from sources of ignition.

Prolonged exposure to the vapors of esters and particularly esters of unsaturated compounds often causes irritation of the skin or mucous membranes. The regulations for rail shipment require that containers for all compounds having a flash point (Cleveland open-cup) below 80°F (26.67°C) have a red warning label and be marked "flammable."

**Occurrence and Preparation**

Today, most of the simple esters used commercially are of synthetic origin, although a number of them do occur in nature. Some of the naturally occurring esters, other than fats and waxes, and some of their sources are as follows (21, 22): ethyl acetate, in many wines, brandy, wine vinegar, and some fruits, as pineapples; amyl acetate, in apples, bananas, and other fruits; geranyl formate and citronellyl formate and acetate, in geranium oil; terpinyl acetate, in cypress oil; bornyl acetate, in pine-needle oil; geranyl acetate, in lemon grass oil; menthol acetate, in peppermint oil; benzyl acetate, in jasmine, hyacinth, and gardenia; methyl benzoate, in clove oil; methyl salicylate, in the oils of wintergreen and sweet birch; ethyl, benzyl, and cin-
mamyl cinnamates in oil of styrax; methyl anthranilate, in jonquil, tuberoses, ylang-ylang, jasmine, and mandarin-leaf oil (see Oils, essential). Most of these naturally occurring esters have very pleasant odors and either they or their synthetic counterparts are used in the confectionery, beverage, perfume, cosmetic, and soap industries.

Recovery of naturally occurring esters is accomplished by steam distillation, extraction or pressing, or a combination of these. Synthetic esters are generally prepared by reaction of an alcohol with an organic acid in the presence of a catalyst such as sulfuric acid or p-toluenesulfonic acid. A number of other reactions may be used industrially for preparing certain esters, however. In the presence of certain metal acetolate catalysts, two molecules of an aldehyde condense to give an ester (23):

\[
2 \text{RCHO} \xrightarrow{\text{ROM}} \text{RCH}_2\text{OCOR}
\]
This is the Tishchenko reaction; its potential importance has increased with the ready availability of aldehydes from the oxo reaction.

Esters may also be made by the reaction of an olefin, an alcohol, and carbon monoxide under pressure in the presence of either strong acids, or, preferably, nickel or cobalt carbonyl:

\[ RCH=CH_2 + R'OH + CO \rightarrow RCH=CHCOOR' + RCH=CHCOOR' \]

Mixtures of isomeric esters are produced by this reaction since the reaction occurs to some extent on both sides of the double bond of the olefin, and since the double bond itself migrates along the carbon chain. This method for preparing esters has been the subject of a number of patents.

One important variation of this reaction is the preparation of acrylates from acetylene, carbon monoxide, and alcohol in the presence of a nickel catalyst (24):

\[ CH≡CH + CO + ROH \rightarrow CH≡CHOOR \]

Vinyl esters, which are derivatives of the enol form of aldehydes, cannot be prepared by simple esterification. They may be made from acetylene and an acid in the presence of zinc or cadmium soaps:

\[ RCOOH + HC≡CH \rightarrow RCOCH≡CH \]

### Table 1. Typical Specifications of Representative Commercial Esters

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ester content (min), %</th>
<th>Color (max), APHA</th>
<th>Density, ( \rho_20^0 )</th>
<th>Distillation range, 760 mm</th>
<th>Flash pt, °F</th>
<th>Acidity (max), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl acetate</td>
<td>85.0</td>
<td>10</td>
<td>0.883-0.886</td>
<td>72.0-78.0</td>
<td>30</td>
<td>0.01</td>
</tr>
<tr>
<td>propyl acetate</td>
<td>99.6</td>
<td>10</td>
<td>0.865-0.869</td>
<td>73.5-78.0</td>
<td>30</td>
<td>0.01</td>
</tr>
<tr>
<td>isopropyl acetate</td>
<td>98.5</td>
<td>10 (Pt-Co scale)</td>
<td>0.858-0.863</td>
<td>95-113</td>
<td>70</td>
<td>0.01</td>
</tr>
<tr>
<td>butyl acetate</td>
<td>99.0</td>
<td>10 (Pt-Co scale)</td>
<td>0.854-0.856</td>
<td>122.5-128.0</td>
<td>100</td>
<td>0.01</td>
</tr>
<tr>
<td>isobutyl acetate</td>
<td>98.0</td>
<td>10</td>
<td>0.854-0.856</td>
<td>118.0-128.0</td>
<td>90</td>
<td>0.01</td>
</tr>
<tr>
<td>sec-butyl acetate</td>
<td>99.5</td>
<td>10 (Pt-Co scale)</td>
<td>0.852-0.853</td>
<td>122.5-128.0</td>
<td>100</td>
<td>0.01</td>
</tr>
<tr>
<td>amyl acetate</td>
<td>98.0</td>
<td>&lt;5 (Pt-Co scale)</td>
<td>0.897-0.873</td>
<td>118.0-120.0</td>
<td>87</td>
<td>0.01</td>
</tr>
<tr>
<td>(mixed isomers)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-ethylhexyl acetate</td>
<td>95.0</td>
<td>15</td>
<td>0.871-0.873</td>
<td>125-150</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>isobutyl acetate</td>
<td>95.0</td>
<td>15</td>
<td>0.870-0.875</td>
<td>119.0-206.0</td>
<td>190</td>
<td>0.02</td>
</tr>
<tr>
<td>isobutyrinate</td>
<td>95.0</td>
<td>15</td>
<td>0.859-0.867</td>
<td>144.0-151.0</td>
<td>120</td>
<td>0.02</td>
</tr>
<tr>
<td>benzyl hexanoate</td>
<td>99.0</td>
<td>colorless</td>
<td>1.117-1.120, crys pt (25-26)</td>
<td>18.3°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>butyl oleate</td>
<td>80-90</td>
<td>1 (Gardner scale)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dibutyl sebacate</td>
<td>99.0</td>
<td>50</td>
<td>0.955-0.959</td>
<td>349</td>
<td>370</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* Tag open-cup (ASTM Method D 1310) unless otherwise noted.
* Acidity reported as free acid of each ester.
* Cleveland open-cup (ASTM Method D 92).
* Saponification number.