

Organic Chemistry

Second Edition

Robert Thornton Morrison

and

Robert Neilson Boyd

*Professors of Chemistry
New York University*

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than some other classification. For example, the similarities between aliphatic and aromatic acids, or between aliphatic and aromatic amines, are more important than the differences.

10.2 Structure of benzene

It is obvious from our definition of aromatic compounds that any study of their chemistry must begin with a study of benzene. Benzene has been known since 1825; its chemical and physical properties are perhaps better known than those of any other single organic compound. In spite of this, no satisfactory structure for benzene had been advanced until about 1931, and it was ten to fifteen years before this structure was generally used by organic chemists.

The difficulty was not the complexity of the benzene molecule, but rather the limitations of the structural theory as it had so far developed. Since an understanding of the structure of benzene is important both in our study of aromatic compounds and in extending our knowledge of the structural theory, we shall examine in some detail the facts upon which this structure of benzene is built.

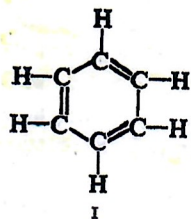
10.3 Molecular formula. Isomer number. Kekulé structure

(a) *Benzene has the molecular formula C_6H_6 .* From its elemental composition and molecular weight, benzene was known to contain six carbon atoms and six hydrogen atoms. The question was: how are these atoms arranged?

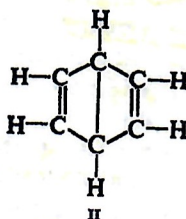
In 1858, August Kekulé (of the University of Bonn) had proposed that carbon atoms can join to one another to form *chains*. Then, in 1865, he offered an answer to the question of benzene: these carbon chains can sometimes be closed, to form *rings*.

"I was sitting writing at my textbook, but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of this kind, could now distinguish larger structures of manifold conformations; long rows, sometimes more closely fitted together; all twisting and turning in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I woke; . . . I spent the rest of the night working out the consequences of the hypothesis. Let us learn to dream, gentlemen, and then perhaps we shall learn the truth."—August Kekulé, 1865.

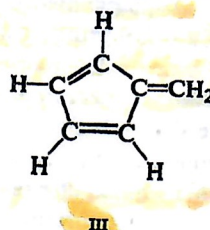
Kekulé's structure of benzene was one that we would represent today as I.



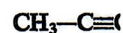
I
Kekulé formula



II
"Dewar" formula



III



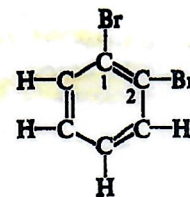
Other structures are II-V. Of all these, factory; the evidence number (Sec. 3.2).

(b) *Benzene yields* bromobenzene, C_6H_5Br ; bromine; similarly, $C_6H_5NO_2$, etc., has structure of benzene hydrogen, since the

Structure V, for isomeric monobrom hydrogens are not e are likewise unsatisf of these yield? I a

(c) *Benzene yields* Three and only three zenes, $C_6H_4ClNO_2$, of a structure; for e products would IV

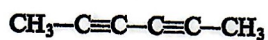
At first glance, we can expect three dibromo compound



1,2-Dibromobenzene

Closer examination (VI and VII), differ should be possible:





IV



V

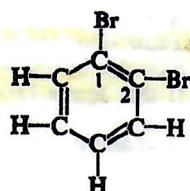
Other structures are, of course, consistent with the formula C_6H_6 : for example, II-V. Of all these, Kekulé's structure was accepted as the most nearly satisfactory; the evidence was of a kind with which we are already familiar: isomer number (Sec. 3.2).

(b) *Benzene yields only one monosubstitution product, $\text{C}_6\text{H}_5\text{Y}$.* Only one bromobenzene, $\text{C}_6\text{H}_5\text{Br}$, is obtained when one hydrogen atom is replaced by bromine; similarly, only one chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$, or one nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, etc., has ever been made. This fact places a severe limitation on the structure of benzene: each hydrogen must be exactly equivalent to every other hydrogen, since the replacement of any one of them yields the same product.

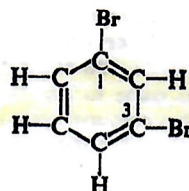
Structure V, for example, must now be rejected, since it would yield two isomeric monobromo derivatives, the 1-bromo and the 2-bromo compounds; all hydrogens are not equivalent in V. Similar reasoning shows us that II and III are likewise unsatisfactory. (How many monosubstitution products would each of these yield?) I and IV, among others, are still possibilities, however.

(c) *Benzene yields three isomeric disubstitution products, $\text{C}_6\text{H}_4\text{Y}_2$ or $\text{C}_6\text{H}_4\text{YZ}$.* Three and only three isomeric dibromobenzenes, $\text{C}_6\text{H}_4\text{Br}_2$, three chloronitrobenzenes, $\text{C}_6\text{H}_4\text{ClNO}_2$, etc., have ever been made. This fact further limits our choice of a structure; for example, IV must now be rejected. (How many disubstitution products would IV yield?)

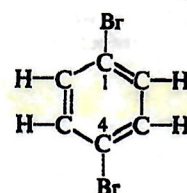
At first glance, structure I seems to be consistent with this new fact; that is, we can expect three isomeric dibromo derivatives, the 1,2-, the 1,3-, and the 1,4-dibromo compounds shown:



1,2-Dibromobenzene

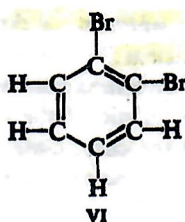


1,3-Dibromobenzene

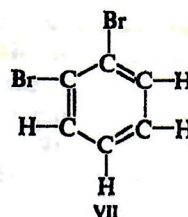


1,4-Dibromobenzene

Closer examination of structure I shows, however, that *two* 1,2-dibromo isomers (VI and VII), differing in the positions of bromine relative to the double bonds, should be possible:

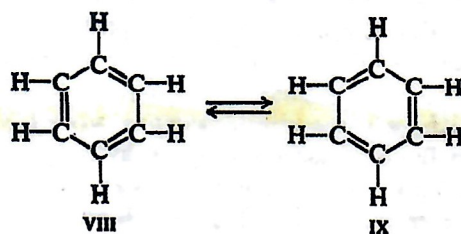


VI

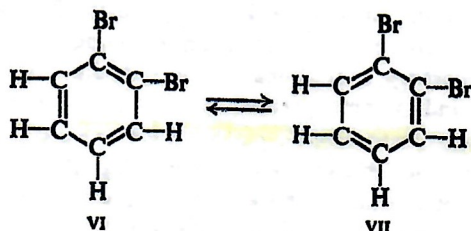


VII

But Kekulé visualized the benzene molecule as a dynamic thing: "... the form whirled mockingly before my eyes ..." He described it in terms of two structures, VIII and IX, between which the benzene molecule alternates. As a consequence,



the two 1,2-dibromobenzenes (VI and VII) would be in rapid equilibrium and hence could not be separated.



Later, when the idea of tautomerism (Sec. 8.13) became defined, it was assumed that Kekulé's "alternation" essentially amounted to tautomerism.

On the other hand, it is believed by some that Kekulé had intuitively anticipated by some 75 years our present concept of delocalized electrons, and drew two pictures (VIII and IX)—as we shall do, too—as a crude representation of something that neither picture alone satisfactorily represents. Rightly or wrongly, the term "Kekulé structure" has come to mean a (hypothetical) molecule with alternating single and double bonds—just as the term "Dewar benzene" has come to mean a structure (II) that James Dewar devised in 1867 as an example of what benzene was *not*.

10.4 Stability of the benzene ring. Reactions of benzene

Kekulé's structure, then, accounts satisfactorily for facts (a), (b), and (c) in Sec. 10.3. But there are a number of facts that are still not accounted for by this structure; most of these unexplained facts seem related to unusual stability of the benzene ring. The most striking evidence of this stability is found in the chemical reactions of benzene.

(d) *Benzene undergoes substitution rather than addition.* Kekulé's structure of benzene is one that we would call "cyclohexatriene." We would expect this cyclohexatriene, like the very similar compounds, cyclohexadiene and cyclohexene, to undergo readily the addition reactions characteristic of the alkene structure. As the examples in Table 10.1 show, this is not the case; under conditions that cause an alkene to undergo rapid addition, benzene reacts either not at all or very slowly.

Table

Reagent	C
KMnO ₄ (cold, dilute, aqueous)	F
Br ₂ /CCl ₄ (in the dark)	I
HI	I
H ₂ + Ni	I

In place of addition reactions involving substitution.

1. Nitration. Discuss
C₆H₆

2. Sulfonation. Discuss
C₆H₆ +

3. Halogenation. Discuss

4. Friedel-Crafts alkylation

5. Friedel-Crafts acylation
C₆H₆

In each of these reactions, the benzene ring is not destroyed; the hydrogen atoms of benzene are of the same kind; the fact indicates that it has retained its structure.

It would appear that the benzene ring system would be destroyed if it were not preserved.

the molecule: the carbon-carbon bonds in benzene are represented by six equivalent electron clouds, each intermediate in density between that representing a single bond and that representing a double bond.

The facts are consistent with the orbital picture of the benzene molecule. X-ray and electron diffraction show benzene (Fig. 10.4) to be a completely flat,

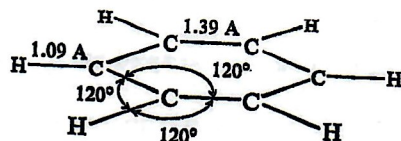


Figure 10.4. Benzene molecule: shape and size.

symmetrical molecule with all carbon-carbon bonds equal, and all bond angles 120° .

As we shall see, the chemical properties of benzene are just what we would expect of this structure. Despite delocalization, the π electrons are nevertheless more loosely held than the σ electrons. The π electrons are thus particularly available to a reagent that is seeking electrons; the typical reactions of the benzene ring are those in which it serves as a source of electrons for electrophilic (acidic) reagents. Because of the resonance stabilization of the benzene ring, these reactions lead to substitution, in which the aromatic character of the benzene ring is preserved.

Problem 10.4 The carbon-hydrogen bond dissociation energy for benzene (102 kcal) is considerably larger than for cyclohexane. On the basis of the orbital picture of benzene, what is one factor that may be responsible for this? What piece of physical evidence tends to support your answer? (Hint: Look at Fig. 10.4 and see Sec. 5.3.)

Problem 10.5 The molecules of pyridine, C_5H_5N , are flat, with all bond angles about 120° . All carbon-carbon bonds are 1.39 Å long and the two carbon-nitrogen bonds are 1.36 Å long. The measured heat of combustion is 23 kcal lower than that calculated by the method of Problem 10.2 on page 317. Pyridine undergoes such substitution reactions as nitration and sulfonation (Sec. 10.4). (a) Is pyridine adequately represented by formula I? (b) Account for the properties of pyridine by both valence-bond and orbital structures. (Check your answer in Sec. 36.6.)



Problem 10.6 The compound borazole, $B_3N_3H_6$, is shown by electron diffraction to have a flat cyclic structure with alternating boron and nitrogen atoms, and all boron-nitrogen bond lengths the same. (a) How would you represent borazole by valence-bond structures? (b) In terms of orbitals? (c) How many π electrons are there, and which atoms have they "come from"?

10.13 Representation of the benzene ring

For convenience we shall represent the benzene ring by a regular hexagon containing a circle (I); it is understood that a hydrogen atom is attached to each angle of the hexagon unless another atom or group is indicated.



I represents a resonance structure. The straight lines stand for the single bonds, and the circle stands for the cloud of six delocalized π electrons.

I is a particularly useful representation of the equivalence of the various bonds in the benzene ring. It distinguishes the benzene ring from other six-membered rings today by a plain hexagon.

There is no complete agreement on the use of the benzene ring. The student should expect to find it occasionally as a plain hexagon, and its use seems to have some advantages, and its use seems to have some disadvantages. The same representation was advanced by the University of Munich, who call it "valences".

10.14 Aromatic character

We have defined aromaticity as being aromatic. Beside which properties of benzene are being aromatic? Beside many other substances that bear little resemblance to benzene.

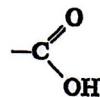
What properties do all aromatic compounds have? From the experiments whose molecular formulas and yet which are resistant to unsaturated compounds. Aromatic compounds undergo substitution reactions with benzene. Along with this, we find evidence of heats of combustion. Aromatic compounds with five-, six-, or seven-membered rings are found to have the same sort of chemical shift and its derivatives.

From a theoretical standpoint, a molecule that contains a cyclic plane of the molecule; further, it contains π electrons. That is to say, an aromatic compound, and a particular number of π electrons.

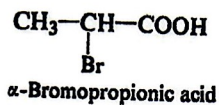
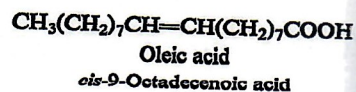
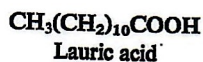
18 / Carboxylic Acids

18.1 Structure

Of the organic compounds that show appreciable acidity, by far the most important are the carboxylic acids. These compounds contain the carboxyl group



attached to either an alkyl group (RCOOH) or an aryl group (ArCOOH). For example:



Whether the group is aliphatic or aromatic, substituted or unsubstituted, the properties of the carboxyl group are essentially the same.

18.2 Nomenclature

The aliphatic carboxylic acids have been known for a long time, and as a result have common names that refer to their sources rather than to their chemical structures. The common names of the more important acids are shown in Table 18.1

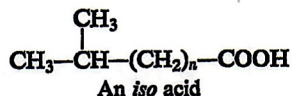
18.1 *Formic acid*, for example, adds the sting to the bite of an ant (Latin: *formica*,

Table 18.1 CARBOXYLIC ACIDS

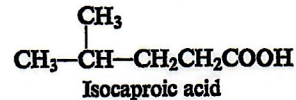
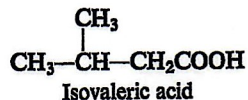
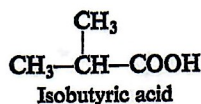
Name	Formula	M.p., °C	B.p., °C	Solub., g/100 g H ₂ O
Formic	HCOOH	8	100.5	∞
Acetic	CH ₃ COOH	16.6	118	∞
Propionic	CH ₃ CH ₂ COOH	-22	141	∞
Butyric	CH ₃ (CH ₂) ₂ COOH	-6	164	∞
Valeric	CH ₃ (CH ₂) ₃ COOH	-34	187	3.7
Caproic	CH ₃ (CH ₂) ₄ COOH	-3	205	1.0
Caprylic	CH ₃ (CH ₂) ₆ COOH	16	239	0.7
Capric	CH ₃ (CH ₂) ₈ COOH	31	269	0.2
Lauric	CH ₃ (CH ₂) ₁₀ COOH	44	225 ¹⁰⁰	i.
Myristic	CH ₃ (CH ₂) ₁₂ COOH	54	251 ¹⁰⁰	i.
Palmitic	CH ₃ (CH ₂) ₁₄ COOH	63	269 ¹⁰⁰	i.
Stearic	CH ₃ (CH ₂) ₁₆ COOH	70	287 ¹⁰⁰	i.
Oleic	<i>cis</i> -9-Octadecenoic	16	223 ¹⁰	i.
Linoleic	<i>cis,cis</i> -9,12-Octadecadienoic	-5	230 ¹⁶	i.
Linolenic	<i>cis,cis,cis</i> -9,12,15-Octadecatrienoic	-11	232 ¹⁷	i.
Cyclohexanecarboxylic	<i>cyclo</i> -C ₆ H ₁₁ COOH	31	233	0.20
Phenylacetic	C ₆ H ₅ CH ₂ COOH	77	266	1.66
Benzoic	C ₆ H ₅ COOH	122	250	0.34
<i>o</i> -Toluic	<i>o</i> -CH ₃ C ₆ H ₄ COOH	106	259	0.12
<i>m</i> -Toluic	<i>m</i> -CH ₃ C ₆ H ₄ COOH	112	263	0.10
<i>p</i> -Toluic	<i>p</i> -CH ₃ C ₆ H ₄ COOH	180	275	0.03
<i>o</i> -Chlorobenzoic	<i>o</i> -ClC ₆ H ₄ COOH	141		0.22
<i>m</i> -Chlorobenzoic	<i>m</i> -ClC ₆ H ₄ COOH	154		0.04
<i>p</i> -Chlorobenzoic	<i>p</i> -ClC ₆ H ₄ COOH	242		0.009
<i>o</i> -Bromobenzoic	<i>o</i> -BrC ₆ H ₄ COOH	148		0.18
<i>m</i> -Bromobenzoic	<i>m</i> -BrC ₆ H ₄ COOH	156		0.04
<i>p</i> -Bromobenzoic	<i>p</i> -BrC ₆ H ₄ COOH	254		0.006
<i>o</i> -Nitrobenzoic	<i>o</i> -O ₂ NC ₆ H ₄ COOH	147		0.75
<i>m</i> -Nitrobenzoic	<i>m</i> -O ₂ NC ₆ H ₄ COOH	141		0.34
<i>p</i> -Nitrobenzoic	<i>p</i> -O ₂ NC ₆ H ₄ COOH	242		0.03
Phthalic	<i>o</i> -C ₆ H ₄ (COOH) ₂	231		0.70
Isophthalic	<i>m</i> -C ₆ H ₄ (COOH) ₂	348		0.01
Terephthalic	<i>p</i> -C ₆ H ₄ (COOH) ₂	300 subl.		0.002
Salicylic	<i>o</i> -HOC ₆ H ₄ COOH	159		0.22
<i>p</i> -Hydroxybenzoic	<i>p</i> -HOC ₆ H ₄ COOH	213		0.65
Anthranilic	<i>o</i> -H ₂ NC ₆ H ₄ COOH	146		0.52
<i>m</i> -Aminobenzoic	<i>m</i> -H ₂ NC ₆ H ₄ COOH	179		0.77
<i>p</i> -Aminobenzoic	<i>p</i> -H ₂ NC ₆ H ₄ COOH	187		0.3
<i>o</i> -Methoxybenzoic	<i>o</i> -CH ₃ OC ₆ H ₄ COOH	101		0.5
<i>m</i> -Methoxybenzoic	<i>m</i> -CH ₃ OC ₆ H ₄ COOH	110		
<i>p</i> -Methoxybenzoic (Anisic)	<i>p</i> -CH ₃ OC ₆ H ₄ COOH	184		0.04

ant); *butyric acid* gives rancid butter its typical smell (Latin: *butyrum*, butter); and *caproic*, *caprylic*, and *capric acids* are all found in goat fat (Latin: *caper*, goat). The student should memorize the names of at least the first six acids and of the C_{12} , C_{16} , and C_{18} acids.

The prefix *iso-* is used to designate certain of the branched-chain acids: those with a single branch of a methyl group at the end of the molecule farthest removed from the carboxyl group.



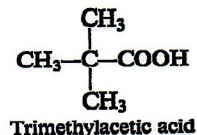
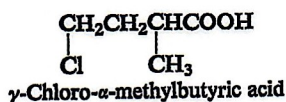
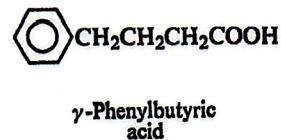
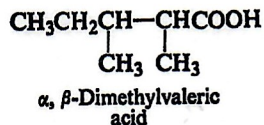
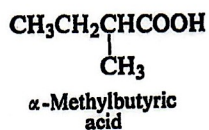
For example:



Other branched-chain acids and substituted acids are named as derivatives of the straight-chain acids. To indicate the position of attachment, the Greek letters, α -, β -, γ -, δ -, etc., are used; the α -carbon is the one bearing the carboxyl group.

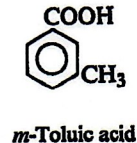
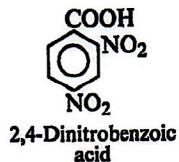
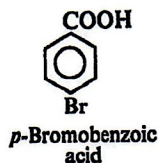


For example:



Generally the parent acid is taken as the one of longest carbon chain, although some compounds are named as derivatives of acetic acid.

Aromatic acids, ArCOOH , are usually named as derivatives of the parent acid, benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$. The methylbenzoic acids are given the special name of *toluic acids*.



The IUPAC names follow the usual pattern. The longest chain carrying the carboxyl group is considered the parent structure, and is named by replacing the *-e* of the corresponding alkane with *-oic acid*. For example:

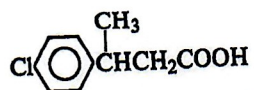


Ethanoic acid

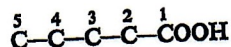


$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{2-Methylbutanoic} \\ \text{acid} \end{array}$$


3-Phenylpropanoic acid

3-(*p*-Chlorophenyl)butanoic acid

The position of a substituent is indicated as usual by a number. We should



Used in IUPAC names

notice that the carboxyl carbon is always considered as C-1, and hence C-2 corresponds to α of the common names, C-3 to β , and so on. (*Caution:* Do not mix Greek letters with IUPAC names, or Arabic numerals with common names.)

The name of a salt of a carboxylic acid consists of the name of the cation (*sodium, potassium, ammonium*, etc.) followed by the name of the acid with the ending *-ic acid* changed to *-ate*. For example:



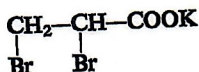
Sodium benzoate



Calcium acetate



Ammonium formate

Potassium α, β -dibromopropionate
(Potassium 2,3-dibromopropanoate)

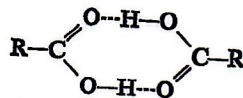
18.3 Physical properties

As we would expect from their structure, carboxylic acid molecules are polar, and like alcohol molecules can form hydrogen bonds with each other and with other kinds of molecules. The aliphatic acids therefore show very much the same solubility behavior as the alcohols: the first four are miscible with water, the five-carbon acid is partly soluble, and the higher acids are virtually insoluble. Water solubility undoubtedly arises from hydrogen bonding between the carboxylic acid and water. The simplest aromatic acid, benzoic acid, contains too many carbon atoms to show appreciable solubility in water.

Carboxylic acids are soluble in less polar solvents like ether, alcohol, benzene, etc.

We can see from Table 18.1 that as a class the carboxylic acids are even higher boiling than alcohols. For example, propionic acid (b.p. 141°) boils more than

twenty degrees higher than the alcohol of comparable molecular weight, *n*-butyl alcohol (b.p. 118°). These very high boiling points are due to the fact that a pair of carboxylic acid molecules are held together not by one but by two hydrogen bonds:

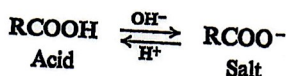


Problem 18.1 At 110° and 454 mm pressure, 0.11 g acetic acid vapor occupies 63.7 cc; at 156° and 458 mm, 0.081 g occupies 66.4 cc. Calculate the molecular weight of acetic acid in the vapor phase at each temperature. How do you interpret these results?

The odors of the lower aliphatic acids progress from the sharp, irritating odors of formic and acetic acids to the distinctly unpleasant odors of butyric, valeric, and caproic acids; the higher acids have little odor because of their low volatility.

18.4 Salts of carboxylic acids

Although much weaker than the strong mineral acids (sulfuric, hydrochloric, nitric), the carboxylic acids are tremendously more acidic than the very weak organic acids (alcohols, acetylene) we have so far studied; they are much stronger acids than water. Aqueous hydroxides therefore readily convert carboxylic acids into their salts; aqueous mineral acids readily convert the salts back into the carboxylic acids. Since we can do little with carboxylic acids without encountering



this conversion to and from their salts, it is worthwhile for us to examine the properties of these salts.

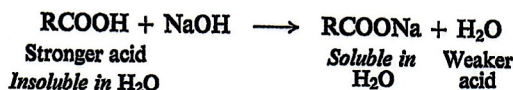
Salts of carboxylic acid—like all salts—are crystalline non-volatile solids made up of positive and negative ions; their properties are what we would expect of such structures. The strong electrostatic forces holding the ions in the crystal lattice can be overcome only by heating to a high temperature, or by a very polar solvent. The temperature required for melting is so high that before it can be reached carbon-carbon bonds break and the molecule decomposes, generally in the neighborhood of 300–400°. A decomposition point is seldom useful for the identification of a compound, since it usually reflects the rate of heating rather than the identity of the compound.

The alkali metal salts of carboxylic acids (sodium, potassium, ammonium) are soluble in water but insoluble in non-polar solvents; most of the heavy metal salts (iron, silver, copper, etc.) are insoluble in water.

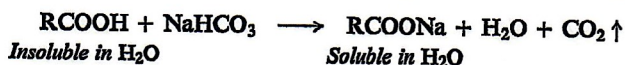
Thus we see that, except for the acids of four carbons or less, which are soluble both in water and in organic solvents, *carboxylic acids and their alkali metal salts show exactly opposite solubility behavior*. Because of the ready interconversion

of acids and their salts, this difference in solubility behavior may be used in two important ways: for *identification* and for *separation*.

A water-insoluble organic compound that dissolves in cold dilute aqueous sodium hydroxide must be either a carboxylic acid or one of the few other kinds of organic compounds more acidic than water; that it is indeed a carboxylic acid can then be shown in other ways.



Instead of sodium hydroxide, we can use aqueous sodium bicarbonate; even if the unknown is water-soluble, its acidity is shown by the evolution of bubbles of CO_2 .



We can separate a carboxylic acid from non-acidic compounds by taking advantage of its solubility and their insolubility in aqueous base; once the separation has been accomplished, we can regenerate the acid by acidification of the aqueous solution. If we are dealing with solids, we simply stir the mixture with aqueous base and then filter the solution from insoluble, non-acidic materials; addition of mineral acid to the filtrate precipitates the carboxylic acid, which can be collected on a filter. If we are dealing with liquids, we shake the mixture with aqueous base in a separatory funnel and separate the aqueous layer from the insoluble organic layer; addition of acid to the aqueous layer again liberates the carboxylic acid, which can then be separated from the water. For completeness of separation and ease of handling, we often add a water-insoluble solvent like ether to the acidified mixture. The carboxylic acid is extracted from the water by the ether, in which it is more soluble; the volatile ether is readily removed by distillation from the comparatively high-boiling acid.

For example, an aldehyde prepared by the oxidation of a primary alcohol (Sec. 16.7) may very well be contaminated with the carboxylic acid; this acid can be simply washed out with dilute aqueous base. The carboxylic acid prepared by oxidation of an alkylbenzene (Sec. 12.11) may very well be contaminated with unreacted starting material; the carboxylic acid can be taken into solution by aqueous base, separated from the insoluble hydrocarbon, and regenerated by addition of mineral acid.

Since separations of this kind are more clear-cut and less wasteful of material, they are preferred wherever possible over recrystallization or distillation.

18.5 Industrial source

As usual, the lowest members of the family are prepared by special methods. **Formic acid** is synthesized on a large scale by the reaction between carbon monoxide and aqueous sodium hydroxide at high temperature and pressure.

