Chapter 19

Carboxylic Acids

Chapter 19 suggested problems: none

Class Notes

I. Nomenclature

   A. General

      1. Longest continuous chain that contains the COOH group
      2. Substitute "oic acid" for "e" for alkane name
      3. Acids are always terminal groups
      4. Substitute "alkane 'dioic acid' " if the molecule contains two acid functionalities
      5. When an acid group is attached to a ring (-COOH) the compound is benzoic acid and the acid group is attached to C-1 on the ring
      6. If the compound contains one or more double bonds, the compound ends in "enoic acid" with the appropriate prefix indicating the number of double bonds and numbers indicating the position (eicosapentaenoic acid - 20:5)
      7. Acceptable common names of carboxylic acids (IUPAC - common name)

         a. Methanoic acid - formic acid
         b. Ethanoic acid - acetic acid
         c. Propanoic acid - propionic acid
         d. Butanoic acid - butytric acid
         e. Benzene carboxylic acid - benzoic acid
         f. Dodecanoic acid - lauric acid
         g. Tetradecanoic acid - myristic acid

h. Hexadecanoic acid - palmitic acid

i. Octadecanoic acid - stearic acid

j. Ethanedioic acid - oxalic acid

k. Propanedioic acid - malonic acid

l. Butanedioic acid - succinic acid

m. Pentanedioic acid - glutaric acid

n. Hexanedioic acid - adipic acid

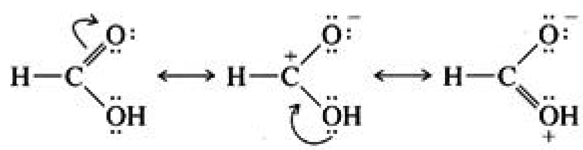
II. Properties of carboxylic acids

A. Structure and bonding

1. sp^2 hybridized carbon and oxygen in carbonyl, sp^3 hybridized oxygen in hydroxyl group

2. Trigonal planar geometry around carbonyl

3. Electron delocalization - especially lone pair donation from the hydroxyl oxygen - results in a carbonyl group that is much less electrophilic than that of aldehydes and ketones



a. The carboxylic acid carbonyl is still reasonably electrophilic

b. Remember that aldehyde/ketone carbonyls only have the first two resonance structures

B. Physical properties

1. Two polar groups per acid molecule, capable of both dipole-dipole and hydrogen bonds and a total of three intramolecular bonds per acid molecule

2. Acids exist as dimers by forming hydrogen bonds with each other

3. Highest MP/BP per molecular weight of any class yet discussed in this course (not as high as amides)

4. Solubility trends

C. Acidity

1. Carboxylic acids are weak acids

2. The most acidic class of compounds containing only C, H, and O

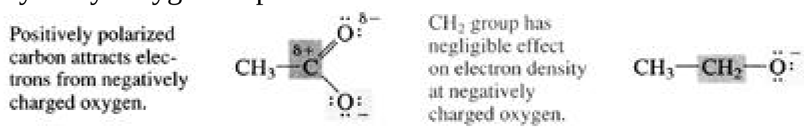
3. pK_a values of 5-10, much stronger acids than alcohols or water

4. Average percent dissociation is about 1-5% or less, as compared to the mineral acids

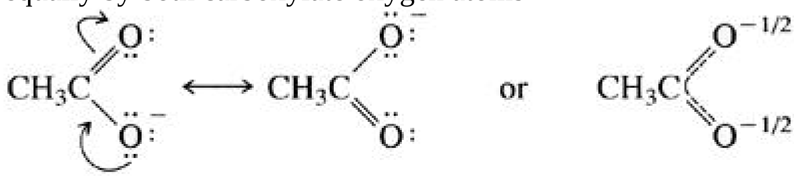
    a. Acid dissociation constants are used to calculate percent dissociation

5. The greater stability of acids relative to alcohols is a reflection of the relative stabilities of the carboxylate and alkoxy ions

    a. The inductive effect of the carbonyl carbon on the negatively-charged hydroxyl oxygen helps to stabilize the ion



    b. Electron delocalization results in the negative charge being shared equally by both carboxylate oxygen atoms



D. Substituents and acid strength

1. Electron withdrawing substituents make acids more acidic, e.g. trifluoroacetic acid

2. Electron-donating substituents make acids less acidic, e.g. benzoic acid

3. This is due to the inductive effect of the substituents acting through the sigma bonds of the molecule

    a. Trichloroacetic acid, the effect of the chlorines on the methyl carbon, its effect on the carbonyl carbon, and its effect on the oxygen ion (acetic acid: pK_a = 4.7; TCA: pK_a = 0.9)

4. The inductive effect lessens with an increasing number of sigma bonds between the substituents and the carboxylic group

E. Dicarboxylic acids: step-wise ionization, inductive effect of one carbonyl on the other when only separated by a few carbons

1. Carbonic acid is both a dicarboxylic acid and an inorganic chemical

F. Carboxylate salts

1. The product of the reaction between a carboxylic acid and a strong base

    a. Strong bases: Group I and II hydroxides, ammonium hydroxide

    b. Salts are the product of a neutralization reaction between the acid and base

    c. The salts are ionic compounds and not covalent

2. Greater solubility in aqueous solution than carboxylic acids - sodium salts of lauric, myristic, and palmitic acids are readily soluble in aqueous solution

    a. Ion-dipole interactions are stronger than dipole-dipole interactions or hydrogen bonding

3. The solubility of acids increases in basic solutions, because carboxylic acids are converted to carboxylates - think in terms of equilibrium

4. Soaps and their cleaning actions

    a. Most common soaps are sodium or potassium salts of fatty (long chain) carboxylic acids

    b. Micelle formation, hydrophobicity, hydrophilicity, and amphipathicity

    c. Detergents: substances that clean by micellar action

III. Preparation of acids

A. Natural sources: fermentation and oxidation

B. Oxidation of 1° alcohols and aldehydes using chromates, dichromates, and permanganate

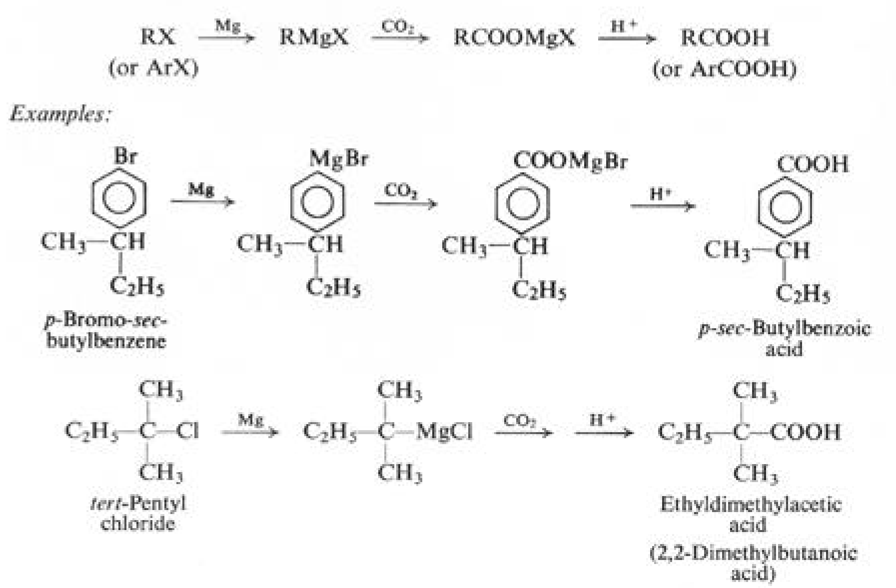
    1. The most direct method, used when possible

C. Oxidation of alkylbenzene side chains

    1. While benzene and alkyl chains are ordinarily quite unreactive toward oxidizing agents (chromates, dichromates, and permanganate), alkyl groups attached to benzene rings react strongly with oxidizing agents and are oxidized to carbon dioxide gas and a carboxylic acid group remaining on the ring at the point of attachment

D. Carboxylation of Grignard reagents

3. **Carbonation of Grignard reagents.**



1. Transforms an alkyl halide or aryl halide into a carboxylic acid and adds one carbon atom to the carbon skeleton of the molecule

2. The alkyl or aryl halide cannot have substituents that react with Grignard reagents (e.g., OH, NH, SH, carbonyls, etc.)

IV. Reactions

A. Lithium aluminum hydride reduction

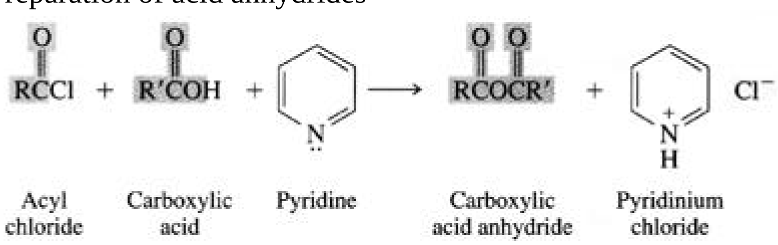
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[2.\ H_2O]{1.\ LiAlH_4,\ Et_2O} R-CH_2-OH$$

1. Esters are more easily reduced by lithium aluminum hydride than acids, the acyl group forming a primary alcohol and the alkoxy group forming a second alcohol

B. Preparation of acyl (acid) halides

1. $RCOOH + SOCl_2$ -> $RCOCl + SO_2 + HCl$

C. Preparation of acid anhydrides



1. This method can be used to prepare symmetrical and unsymmetrical

anhydrides

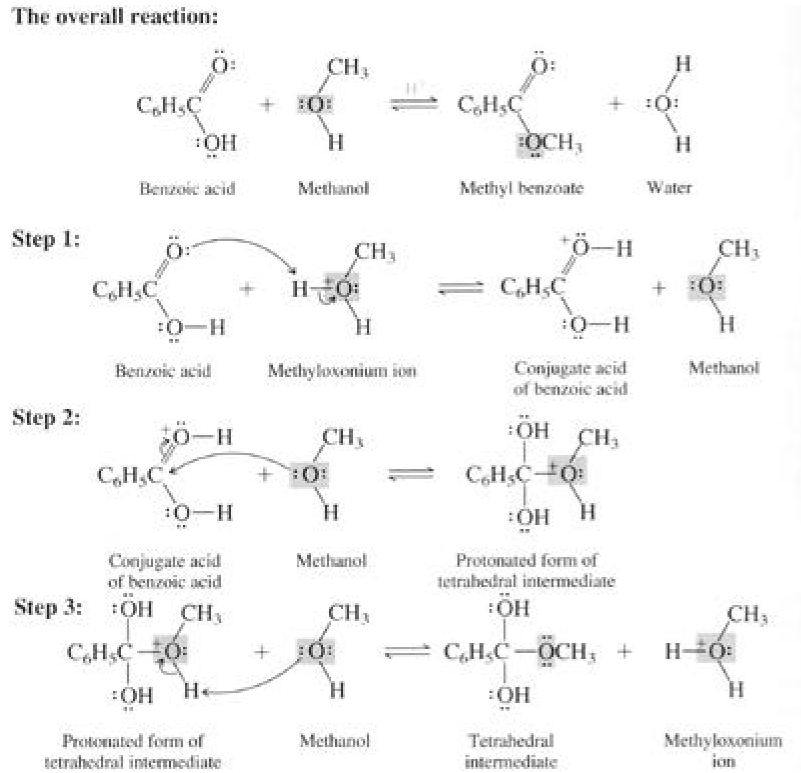
D. Preparation of amides

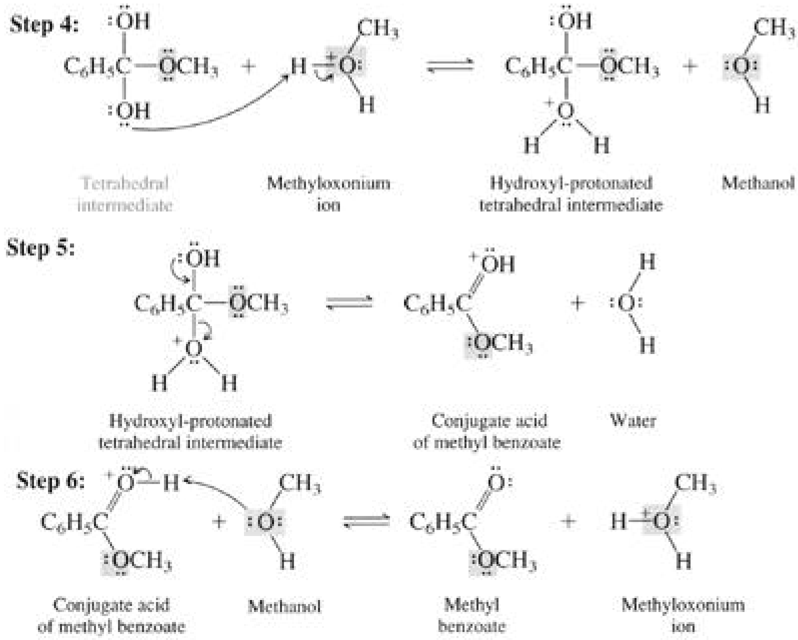
1. It is difficult to prepare amides directly from a carboxylic acid

2. Usually the acid is converted to an ester, acid halide, or acid anhydride and then reacted with ammonia or a 1° or 2° amine to form the amide

E. Acid-catalyzed esterification: a nucleophilic addition

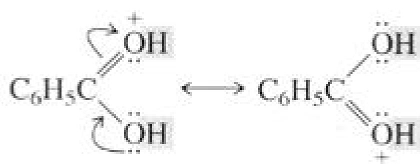
1. Mechanism





2. Nucleophilic addition of alcohol to acid is analogous to nucleophilic of alcohol to aldehyde/ketone and the subsequent hemiacetal formation

3. The carbonyl oxygen is protonated in Step 1. because it has resonance stabilization



4. Three elements of this mechanism are common to the reactions of other carboxylic acid derivatives (Ch. 20)

    a. Protonation of the carbonyl oxygen results in activation of the carbonyl group

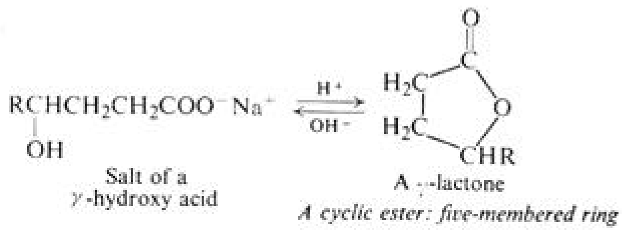
    b. An unstable tetrahedral intermediate is formed when nucleophilic addition to the carbonyl carbon occurs

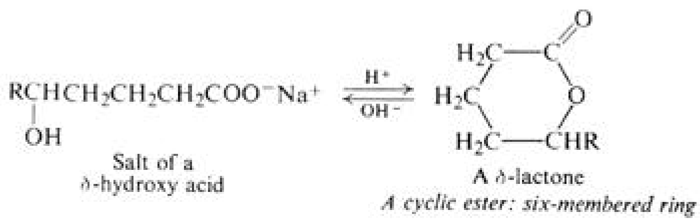
    c. The carbonyl is restored when a group is eliminated from the intermediate

F. Lactones

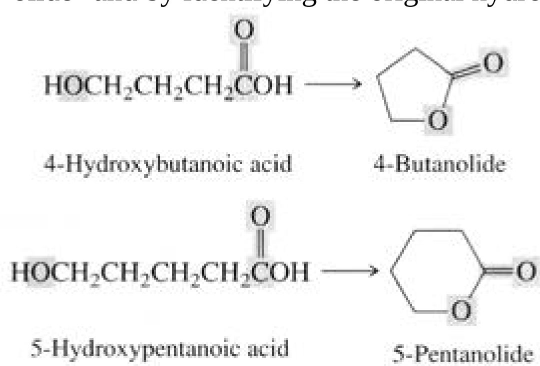
1. Cyclic esters formed by the intramolecular esterification of a hydroxy acid

2. This process is spontaneous for gamma- and delta-hydroxy acids, forming g-lactones and d-lactones (five and six member rings)





3. Lactones are named by changing the "oic acid" suffix of the parent acid to "olide" and by identifying the original hydroxyl carbon number

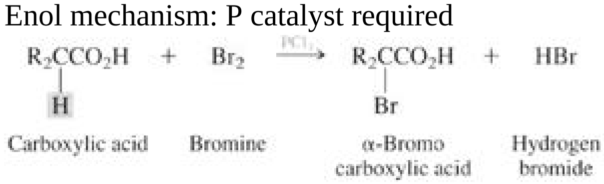


4. Many lactones occur naturally, including macrocyclic lactones

G. a-Halogenation (Hell-Volhard Zelinsky reaction)

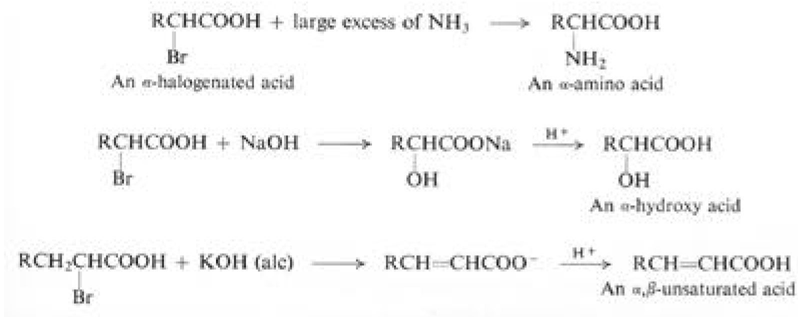
1. Halogens (Cl or Br) add to the a-carbons of carboxylic acids but not as freely as aldehydes/ketones

2. Enol mechanism: P catalyst required



3. Acids alone are generally unreative unless they have high enol concentrations

4. Significance: the a-halogen is easily displaced in nucleophilic substitutions



[Chemistry 2320 Index Page]

Last Modified Tuesday, August 06, 2002 21:37:28
