

## Ch 20 Carboxylic Acids and Nitriles

Carboxylic Acids ( $\text{RCO}_2\text{H}$ ) are compounds with an OH attached to a carbonyl.

Nitriles ( $\text{RC}\equiv\text{N}$ ) are compounds with a carbon-nitrogen triple bond.

### Naming Carboxylic Acids

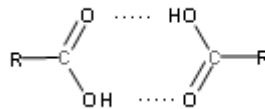
1. Replace final “e” of alkane parent with “oic”, and follow with “acid”.  
For example, pentanoic acid has a five-carbon chain.
2. Number the C’s in the parent, starting with carbonyl as #1.  
Then, precede name with the substituents, such as 2-hydroxybutanoic acid.
3. If  $\text{CO}_2\text{H}$  is the substituent on a ring, follow the parent name with “carboxylic acid”, such as cyclohexanecarboxylic acid and benzenecarboxylic acid (benzoic acid).
4. Both “oic” and “carboxylic acid” may be preceded with “di” if there are two.  
For instance, butanedioic acid and 1,4-benzenedicarboxylic acid.
5. Many common names are used. For instance, formic acid and acetic acid are used almost exclusively instead of the systematic names. (See Table 20.1)

### Naming Nitriles

1. Name alkane parent after the longest chain and include the nitrile C.  
Follow parent name with “nitrile”. For example, butanenitrile has 4 C’s total.
2. Number the C’s in the parent, starting with nitrile C as #1.  
Then, precede name with the substituents, such as 2-hydroxybutanenitrile.
3. If  $\text{C}\equiv\text{N}$  is the substituent on a ring, follow the parent name with “carbonitrile”, such as cyclohexanecarbonitrile and benzenecarbonitrile (benzonitrile).
4. Both “nitrile” and “carbonitrile” may be preceded with “di” if there are two.  
For instance, butanedinitrile and 1,4-benzenedicarbonitrile.

### Structure of Acids

- The carbonyl C is  $\text{sp}^2$  and trigonal planar with  $120^\circ$  bond angles.
- The acid H will form a hydrogen bond with the carbonyl O of another molecule.
- As a liquid or in solution, carboxylic acid molecules exist primarily in pairs.  
That is, the pairs are H-bonded dimers with two H-bonds per pair.
- Carboxylic acids have more extensive H-bonding than alcohols, and as a result, they have higher melting points and boiling points as well.
- The H-bonding properties also make the smaller acid molecules soluble in water.



### Acidity and Ionization

- Carboxylic acids have  $K_a \sim 10^{-5}$  ( $\text{p}K_a \sim 5$ ). So, they are weak acids with less acidity than mineral acids ( $\text{p}K_a < -1$ ), but much more acidic than alcohols ( $\text{p}K_a > 15$ ).
- Acidity results from dissociation of the carboxyl O-H bond.
- The carboxyl H can be removed easily because the carboxylate anion is stabilized by resonance (delocalization), so that the two O’s share the positive charge.

## Carboxylic Acid Extraction

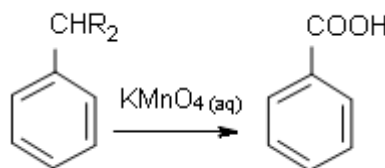
- Longer-chained carboxylic acid molecules are not water-soluble, but the ionic sodium salts of their anions are semi-soluble, and are used as soaps.
- Carboxylic acids can be extracted from an organic layer with aqueous NaOH, which ionizes the molecules so that they become water-soluble anions.
- The anions can be separated from the aqueous layer by protonating again with acid.

## Substituent Effects on Carboxylic Acids

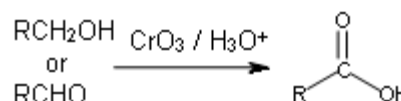
- Substituents like halogens and nitro that are  $e^{-1}$  withdrawing will stabilize the carboxylate anion, which increases acid strength.
- For example, p-nitrobenzoic acid ( $pK_a = 3.4$ ) is stronger than benzoic acid ( $pK_a = 4.2$ ) due to  $e^{-1}$  withdrawing effects from both induction ( $\sigma$  bonds) and resonance ( $\Pi$  bonds).
- Trifluoroacetic acid ( $pK_a = -0.2$ ) is much stronger than acetic acid ( $pK_a = 4.7$ ) due to  $e^{-1}$  withdrawing induction of the three C-F  $\sigma$  bonds.

## Preparation of Carboxylic Acids

- Oxidation of alkylbenzenes with potassium permanganate (see Ch 16 notes)

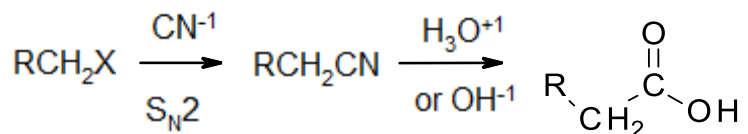


- Oxidation of  $1^\circ$  alcohols and aldehydes with chromium (VI) oxide in aqueous acid (See Ch's 17 and 19 notes)



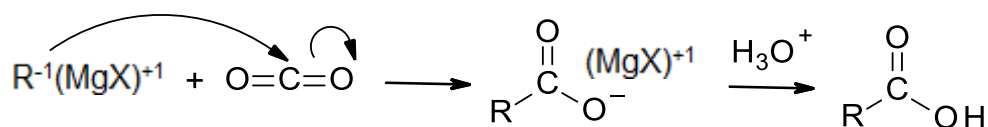
- Hydrolysis of Nitriles

A nitrile can be created by an  $S_N2$  reaction between a  $1^\circ$  alkyl halide and a cyanide anion. The nitrile can be hydrolyzed to carboxylic acid with an acid or base catalyst. Note that the carboxylic acid has one more C than the alkyl halide.



- Carboxylation of Grignard

This reaction is accomplished by introducing dry  $CO_2$  gas to a Grignard reagent. It is nucleophilic addition where the Grignard reagent's carbanion acts as a Nu to the electrophilic carbon atom of  $CO_2$ . Note that the carboxylic acid has one more C than the Grignard reagent.



## Reactions of Carboxylic Acids

### - Deprotonation

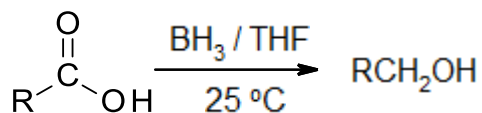
The carboxyl H can be removed by bases.

See previous section on Acidity and Ionization.

### - Reduction

Although  $\text{LiAlH}_4$  can reduce carboxylic acids,  $\text{BH}_3/\text{THF}$  is more effective.

$\text{BH}_3$  reacts with carboxylic acids faster than with any other carbonyl, and the reaction proceeds at room temperature with high selectivity.



### - Nu Acyl Subst'n

The carboxyl OH can be replaced by a stronger Nu, as seen in the introduction to carbonyls.

These reactions will be studied in chapter 21 (carboxylic acid derivatives).

### - Alpha Subst'n

An H on the alpha C can be removed to create a Nu.

See the Introduction to Carbonyls, where this Nu takes part in an  $\text{S}_{\text{N}}2$  reaction.

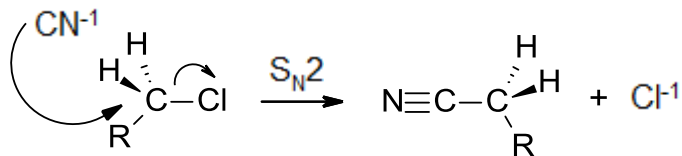
These reactions will be studied further in chapters 22 (alpha subst'n) and 23 (carbonyl condensations).

## Chemistry of Nitriles

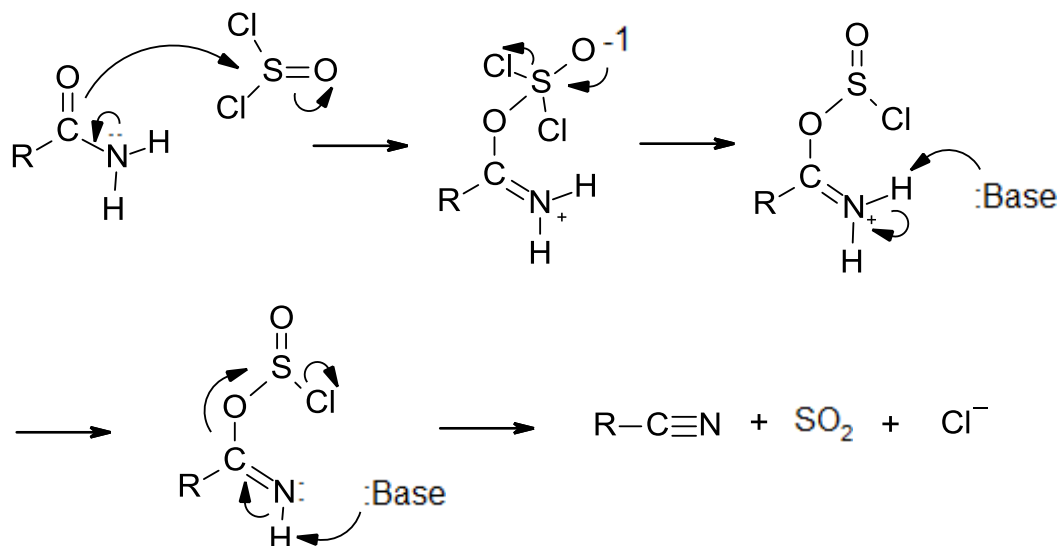
- The nitrile C is sp with two  $\Pi$  bonds, and has linear geometry.
- There is a  $180^\circ$  bond angle from the N to the other atom attached to the C.
- The negative charge on the nitrile C of  $\text{CN}^{-1}$  causes it to be nucleophilic.
- The nitrile C of an alkyl nitrile ( $\text{RCN}$ ) undergoes electrophilic additions when nucleophiles are present.

## Preparation

- A nitrile can be created most easily by an  $\text{S}_{\text{N}}2$  reaction between a  $1^\circ$  alkyl halide and a cyanide anion.



- A nitrile can also be created by dehydration of an amide ( $\text{RCONH}_2$ ). This reaction can be accomplished with dehydrating agents such as thionyl chloride ( $\text{SOCl}_2$ ) and phosphorous oxychloride ( $\text{POCl}_3$ ). Unlike the  $\text{S}_{\text{N}}2$  reaction, dehydration does not have steric requirements on the C next to the nitrile C. The first  $\pi$  bond is created from N's lone pair when  $\text{SOCl}_2$  (or  $\text{POCl}_3$ ) bonds with the carbonyl O. After the intermediate loses one  $\text{Cl}^-$ , then loses the first  $\text{H}^+$ , the second  $\pi$  bond forms when the second  $\text{H}^+$  leaves simultaneously along with  $\text{SO}_2$  and  $\text{Cl}^-$ .



### Reactions of Nitriles

- Hydrolysis of a Nitrile

A nitrile can be hydrolyzed with an acid or base catalyst to create an amide intermediate, which hydrolyzes further to a carboxylic acid.

In the base-catalyzed reaction, the first step is Nu addition of  $\text{OH}^-$ .

Then, the anionic N accepts  $\text{H}^+$  from  $\text{H}_2\text{O}$ , which creates  $\text{OH}^-$  again.

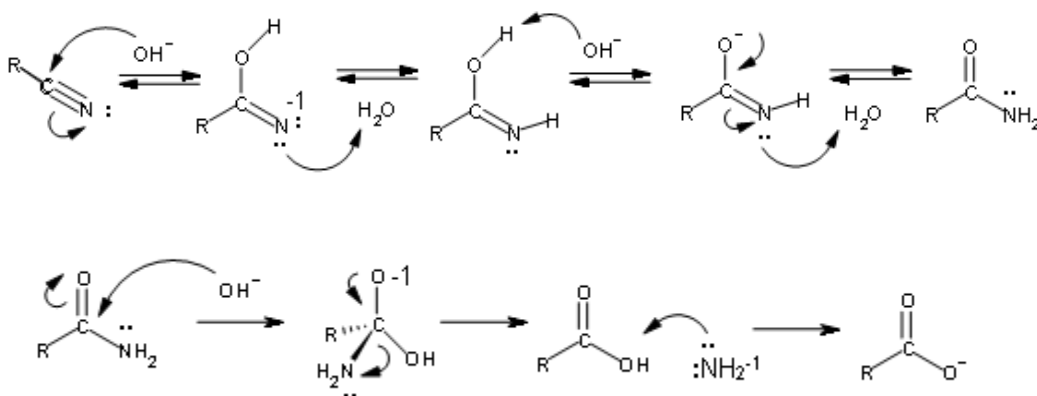
Next, an  $\text{OH}^-$  deprotonates the hydroxyl, and this creates  $\text{H}_2\text{O}$  again.

Then, the N's lone pair accepts  $\text{H}^+$  from  $\text{H}_2\text{O}$ , which creates  $\text{OH}^-$  again.

This results in an amide.

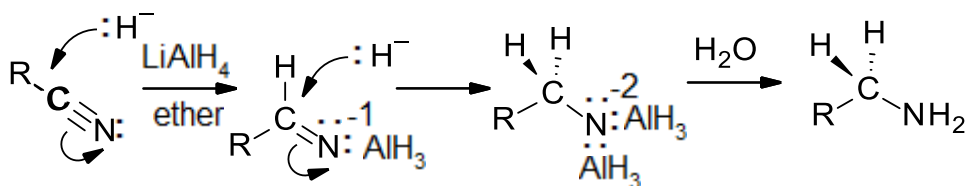
The amide undergoes substitution of  $\text{OH}^-$  for  $\text{NH}_2^-$ .

Deprotonation of the carboxylic acid by  $\text{NH}_2^-$  completes the process.



- Reduction to Amine with Hydride

Nucleophilic addition of  $\text{H}^{-1}$  happens twice, and the dianion is neutralized by water. The result is a 1° amine.



- Reduction to Ketone with Grignard Reagent

Nucleophilic addition of a carbanion is followed by replacement of the N with an O. The result is a ketone.

