Review Session 3

Ch 20 The Chemistry of Carboxylic Acids
Ch 21 The Chemistry of Carboxylic Acid Derivatives
Ch 22 The Chemistry of Eneals and Enolates (22.1-22.7)

R-C=OH, R-C-OR', R-O-CR', R=O, R-CN, R-CN

R

Q: How about pKa of these carboxylic acids?

Major Reactions:

1. Reactions at the carbonyl group
   a. Reaction at the carbonyl oxygen, cyano, nitrogen
   b. Reaction at the carbonyl carbon or cyano carbon

2. Reactions involving α-carbon

3. Reactions at the carboxylate oxygen

4. Decarboxylation

5. Reactions at the nitrogen, amides

6. Reactions by enol/ enolates

1. Substitution at the carbonyl carbon/acyl substitution

\[
R-\text{C}-X + E\text{Y} \rightarrow R-\text{C}-Y + E\text{X}
\]

acyl group: \(x = \text{Cl, } -\text{OR, } -\text{OH}\)

\(y = \text{OR}\)
Hydrolysis

Esterification can be a good example, carbon addition either catalyzed by acid or base

(Fischer) Acid-catalyzed esterification cannot apply to phenol or tertiary alcohols under go cleavage

Acid

Use: react with base

Acid is catalyst

Reversible

Base-catalyzed hydrolysis

Base hydrolysis

Use: react with acid

Base is consumed

Another good example is the addition (acid/base) as regular, C-C bond formation method

Unsmoothed, but only useful when no mixture is yet

Practise A. point: Hydroxy acid - carboxylic acid
Another C-C bond formation method

2. Addition to \( \mathbf{I} \) with organometallic agent
   \( \text{CH}_3\text{Li, LiCa(C,H)}_2 \)

practice B.

3. LAH red-ox reaction

   to prepare tertiary alcohol \( \rightarrow \) ester

\[
\text{CH}_3\text{COH} \xrightarrow{\text{SN}} \text{CH}_3\text{COCl} \xrightarrow{\text{OH}} \text{H}_3\text{CAH}_2
\]

\[
\downarrow \text{LH}
\]

\[
\text{CH}_3\text{NM} \text{NHCH}_3
\]