CHEM 20482 - Basic Organic Chemistry - Chapter 19 Review
Carboxylic Acids

Structure & Nomenclature

R-COOH carboxylic acid -oic acid Ex. $(CH_3)_2CH\text{-}CO_2H$ = 2-methylpropanoic acid

R-COO$^-$ carboxylate -(o)ate Ex. $(CH_3)_2CH\text{-}COO^{-1}$ = 2-methylpropanoate

Common Names: formic acid, acetic acid, benzoic acid

Properties

C=O bond is polar, sp^2-hybridized trigonal planar. OH group forms H-bonds

least polar *lowest b.p.*	*alkanes* *alkenes* *alkynes*	<	ethers <	*aldehydes* *ketones*	<	amines < alcohols < carboxylic acids		*most polar* *highest b.p.*
	No H-bonds		*H-bond acceptors*			*H-bond donors and acceptors*		

Acidity of Carboxylic Acids

Carboxylic acids much stronger acids than alcohols (pK_a(acids)$\sim$ 5 vs. pK_a(alcohols)$\sim$16). Explained by:

Inductive effect: Electronegative oxygen stabilizes carboxylate (product of acid/base reaction)

Resonance effect: Delocalization reduces negative charge on any one atom.

- Acidity can be varied by substituents. In general, addition of electronegative groups increases the acidity (due to an inductive effect). For example, CCl_3COOH is a much stronger acid than acetic acid.
- Dicarboxylic acids are more acidic than carboxylic acids containing a single COOH group.

Synthesis of Carboxylic Acids

- $ArCHR_2 \xrightarrow[K_2Cr_2O_7,\ H_2SO_4]{KMnO_4 \text{ or}} ArCOOH$ — Side-chain oxidation of alkylbenzenes
- $R\text{-}CH_2OH \xrightarrow{[O]} R\text{-}COOH$ — Oxidation of primary (1°) alcohols
- $R\text{-}CHO \xrightarrow{[O]} R\text{-}COOH$ — Oxidation of aldehydes

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- $R\text{-}Mg\text{-}X \xrightarrow[\text{ether}]{CO_2} \xrightarrow{H_3O^+} R\text{-}COOH$ — Carboxylation of Grignard reagents
- $R\text{-}X \xrightarrow{CN^-} R\text{-}CN \xrightarrow[\text{heat}]{H_2O,\ \text{acid}} R\text{-}COOH$ — Limited to 1° and 2° alkyl halides.

  Also works for cyanohydrins.

Reactions of Carboxylic Acids

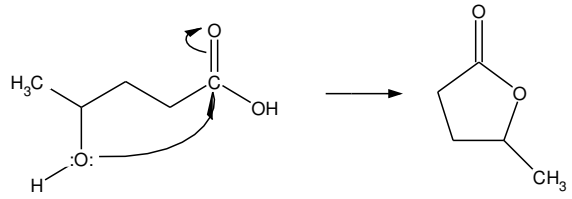
- RCOOH $\xrightarrow{SOCl_2}$ R-C(=O)-Cl — Synthesis of acyl chloride

- RCOOH $\xrightarrow[\text{ether}]{LiAlH_4}$ $\xrightarrow{H_2O}$ R-CH_2OH — Synthesis of primary (1°) alcohols

- RC(O)-O-H + R'-O-H $\overset{\text{acid}}{\rightleftharpoons}$ RC(O)-O-R' + H-O-H — Esterification - Know mechanism

- Lactone synthesis - intramolecular esterification to form 5- or 6-membered ring.

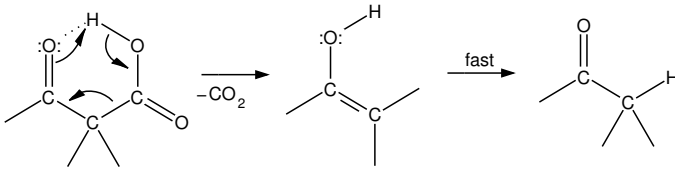
Ex.



- Hell-Volhard-Zelinsky Reaction

R-CH_2-COOH $\xrightarrow[PCl_3]{Br_2}$ R-CH(Br)-COOH — *React product with NH_3 to make amino acid*

- Decarboxylation of β-dicarbonyls



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terminal carbonyl must be carboxylic acid