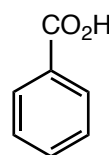
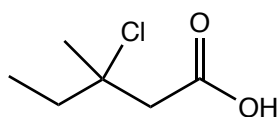
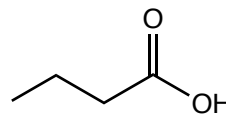
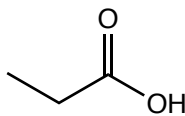
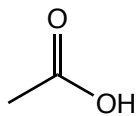
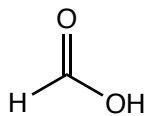
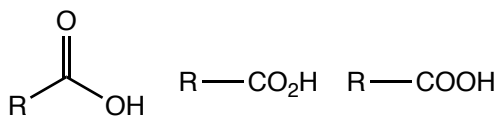


Chapter 21: Carboxylic Acids

[Sections: 21.1-21.5]



Nomenclature of Carboxylic Acids

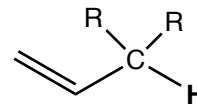
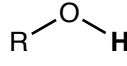
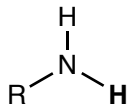
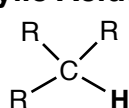


- the parent chain is the longest continuous carbon chain containing the carbon of the carbonyl group
- the carbonyl carbon is always assigned the locant value 1
- the names of carboxylic acids end in "oic acid"

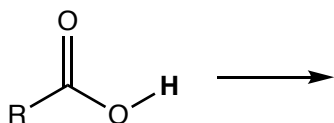
Problems: 1

Acidity of Carboxylic Acids

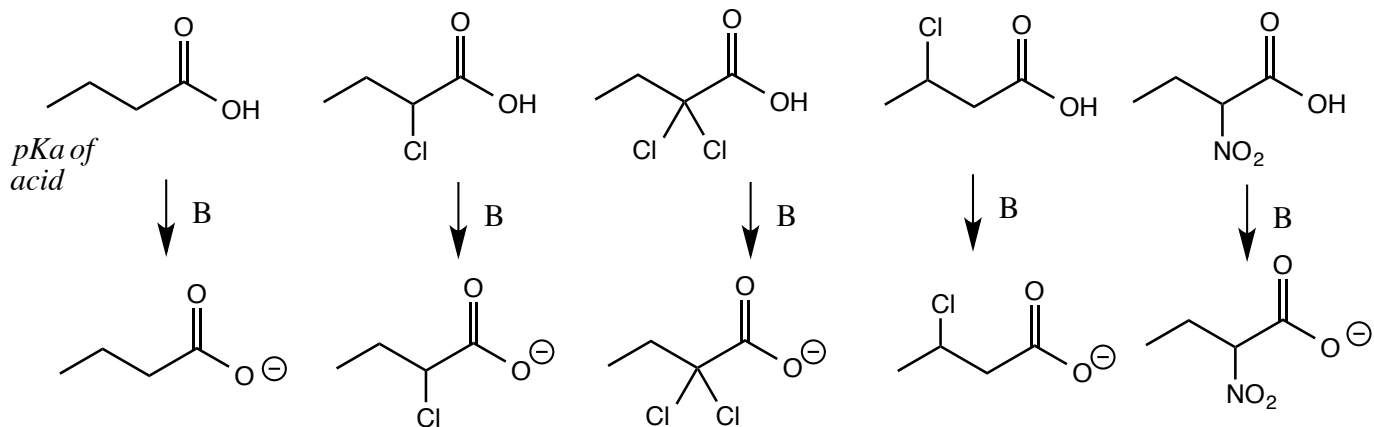
pKa of acid



- acidity is a measurement of how readily a proton is removed from a molecule
- the more stable the resulting negative charge upon removal of a proton, the more acidic is the molecule
- acidity increases (i.e., pK_a decreases) with increasing electronegativity of the atom to which the H is attached
- resonance stabilizes negative charges and results in increased acidity

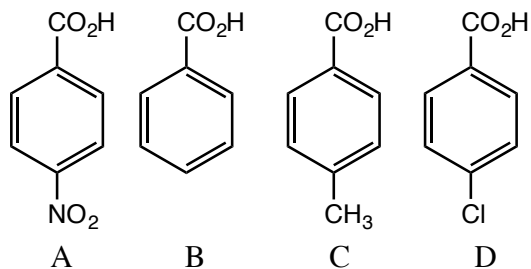


- the acidity of carboxylic acids is particularly high because: i) the negative charge is initially placed on an electronegative oxygen atom, and ii) resonance delocalizes the charge over TWO electronegative oxygen atoms



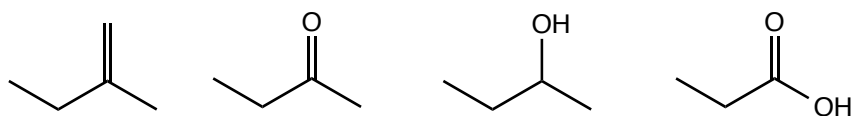
- the presence of substituents that stabilize negative charge (electron-withdrawing substituents) will also increase acidity
- the effect is strongest when the substituent is closest to the carboxylic acid group

Predict the relative acidities of the following series of benzoic acids



Problems: 2,3

Boiling Points of Carboxylic Acids



Remember! boiling points depend upon:

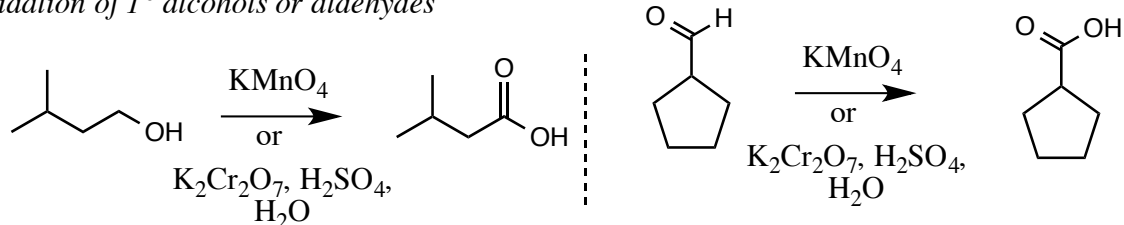
- molecular weight
- intermolecular forces
- branching



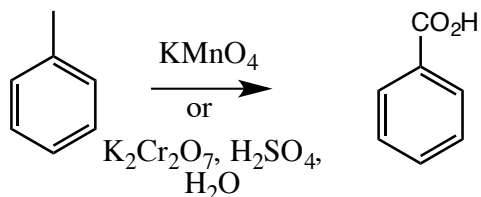
- carboxylic acids have surprisingly high boiling points due to the unusual dimer-type hydrogen bonding that is unique to their structures since it effectively doubles the intermolecular forces between molecules

Synthesis of Carboxylic Acids

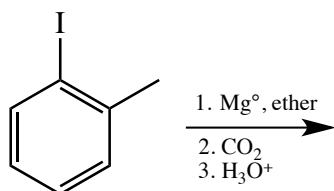
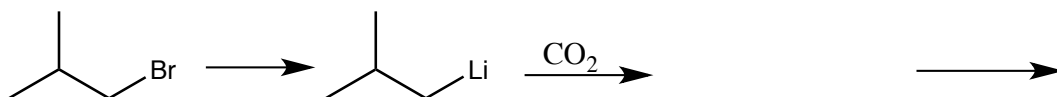
A. Oxidation of 1° alcohols or aldehydes



B. Oxidation of Alkyl Benzenes

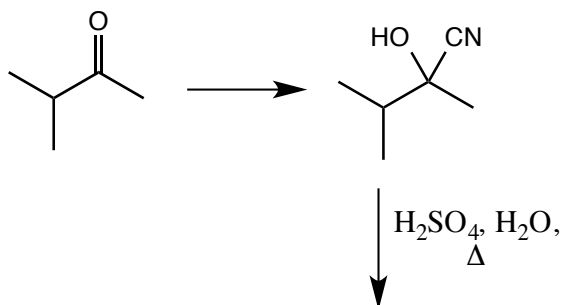
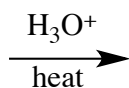
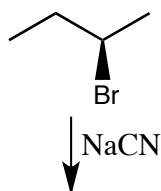
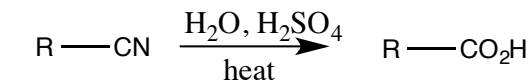


C. Reaction of Grignards or Alkylolithiums with CO_2

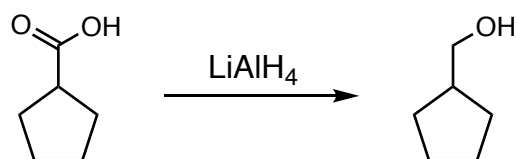


• unlike the oxidative methods above, this method ADDS a carbon atom to the overall length in the carbon chain of the starting alkyl halide

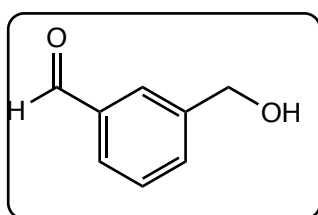
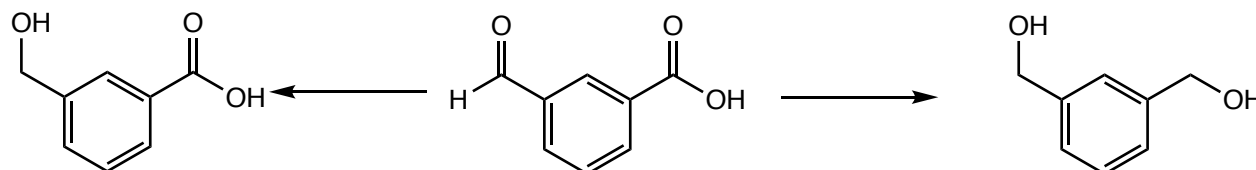
D. Hydrolysis of Nitriles $\text{R}-\text{CN}$ $\text{R}-\text{C}\equiv\text{N}$



Reduction of Carboxylic Acids

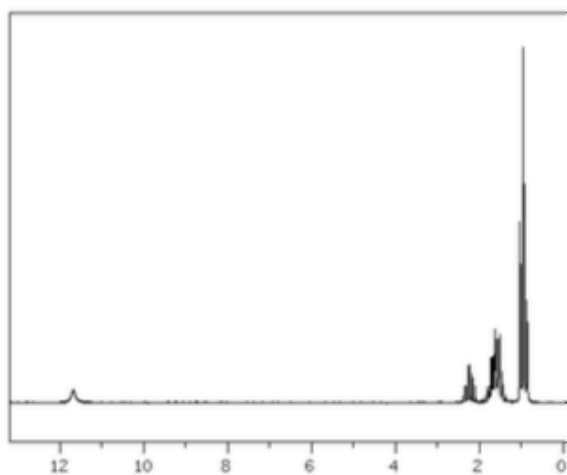
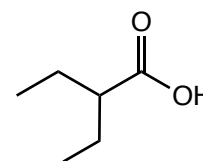
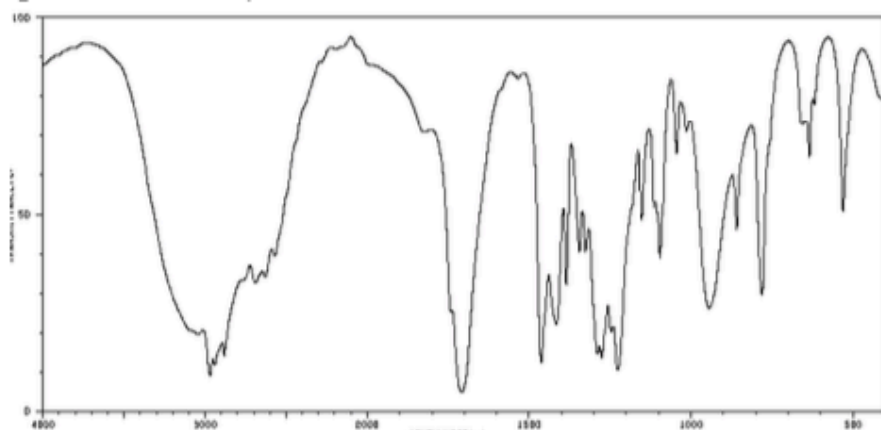


- reduction of carboxylic acids **requires** the strong reducing agent LiAlH_4
- NaBH_4 is **NOT** effective



Problems: 2,4

Spectra of Carboxylic Acids



Problems: 4,5

Chapter 24: Carboxylic Acids *Essential Concepts*

1. Know how to name simple carboxylic acids and benzoic acids. Recognize the different commonly used ways to represent the carboxylic acid group
2. Understand the unusual acidity of carboxylic acids and how substituents can affect relative pK_a's.
3. Know why carboxylic acids have unusually high boiling points
4. Know the common methods for synthesis of carboxylic acids
5. Know the reagents commonly used to reduce carboxylic acids and be able to draw products from such reactions.
6. Know how to identify carboxylic acids from IR and ¹H NMR spectra.