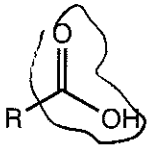
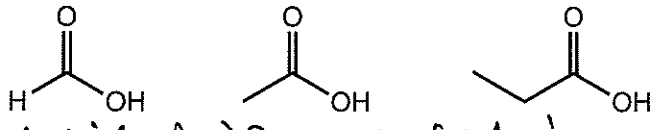
Chapter 21: Carboxylic Acids

[Sections: 21.1-21.5]

Nomenclature of Carboxylic Acids

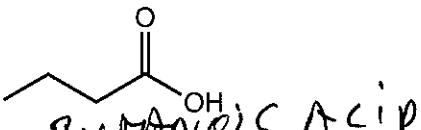


R—CO_2H R—COOH



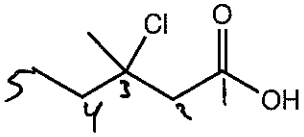
METHANOIC ACID ETHANOIC ACID

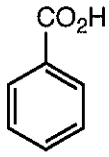
FORMIC ACID ACETIC ACID PROPANOIC ACID



BUTANOIC ACID

BUTYRIC ACID





BENZOIC ACID

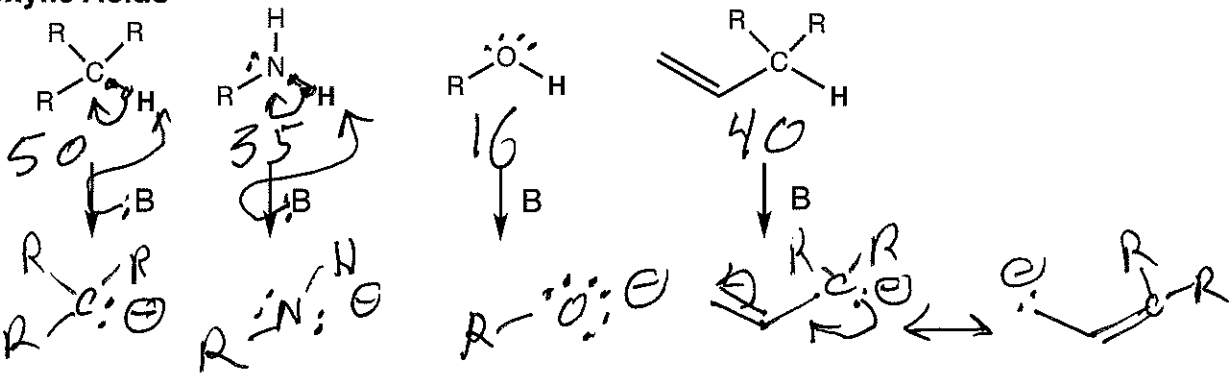
3-CHLORO-3-METHYLPENTANOIC ACID

- *the parent chain is the longest continous 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"*

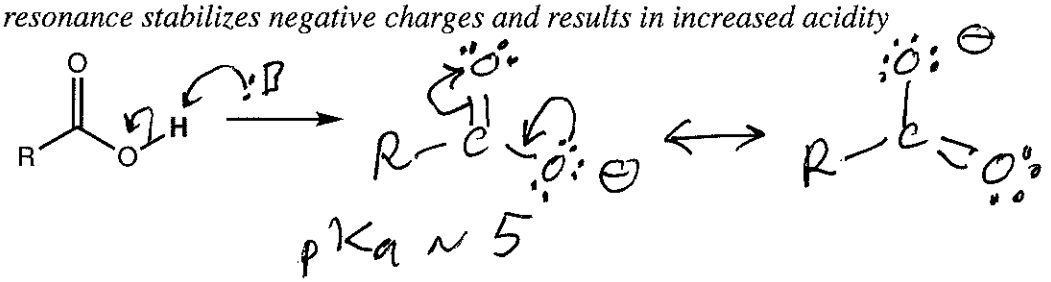
Problems: 1

Acidity of Carboxylic Acids

pKa of acid



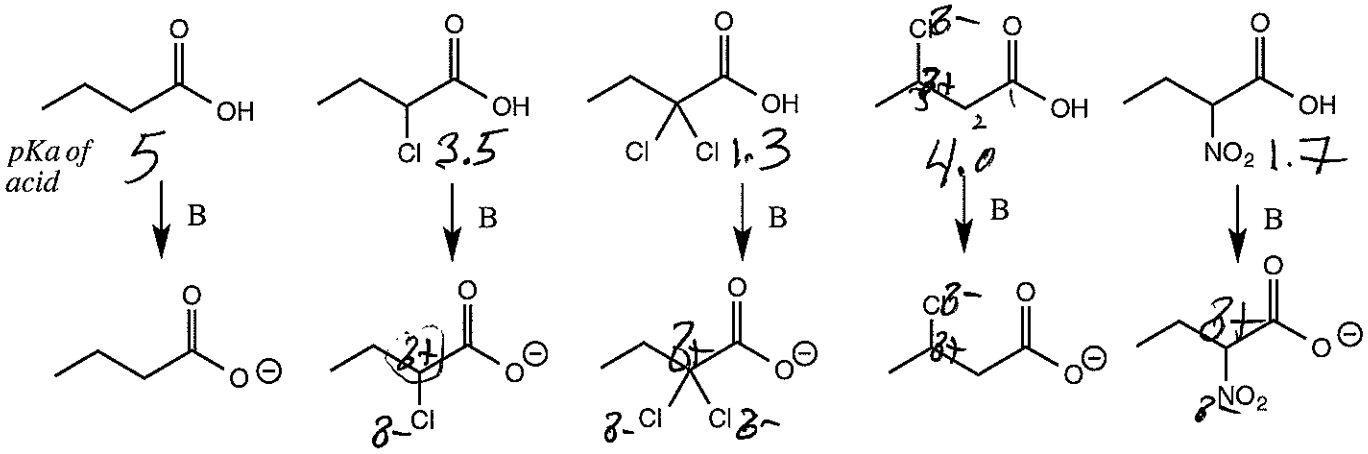
- *acidity is a measurement of how readily a proton is removed from a molecule*
- *the more stable the resulting negative charge upon removal of a proton, the more acidic is the molecule*
- *acidity in increases (i.e., pKa decreases) with increasing electronegativity of the atom to which the H is attached*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

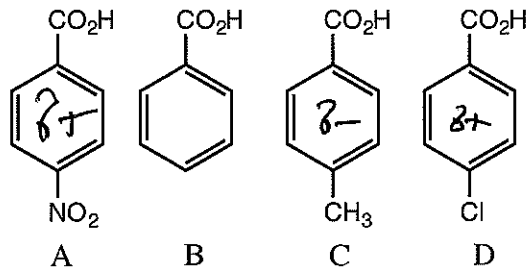
ΔpKa = 1.5

10 more R



- *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



3.41 3.98 4.20 4.26

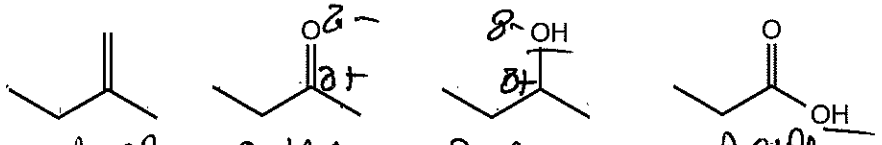
A > D > ~~B~~ > C

MOST ACIDIC

LEAST ACIDIC

Problems: 2,3

Boiling Points of Carboxylic Acids



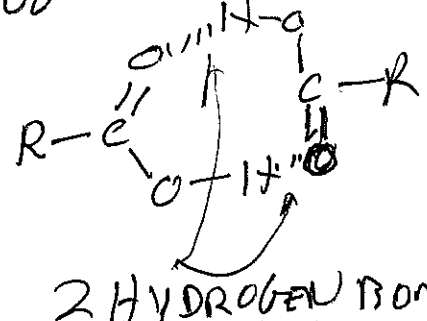
- NONPOLAR
- POLAR
- POLAR, H-BONDING
- POLAR, H-BONDING

31°C 79°C 100°C 141°C

~50° ~20° ~40°

Remember! boiling points depend upon:

- *molecular weight*
- *intermolecular forces*
- *branching*

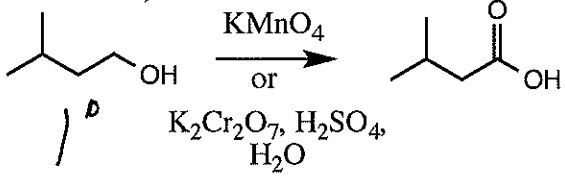


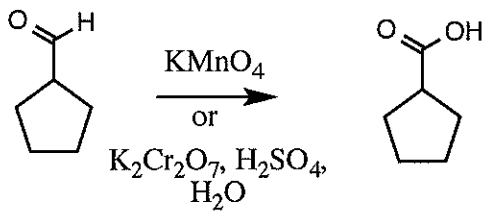
2 HYDROGEN BONDS

- *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*

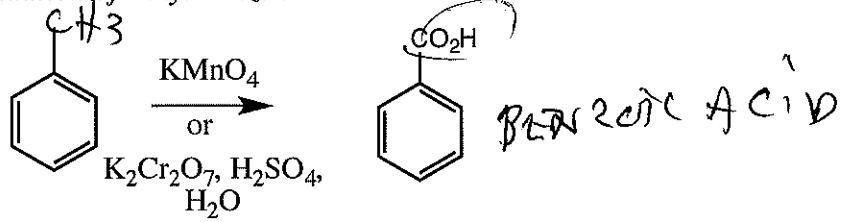
Synthesis of Carboxylic Acids

A. Oxidation of 1° alcohols or aldehydes

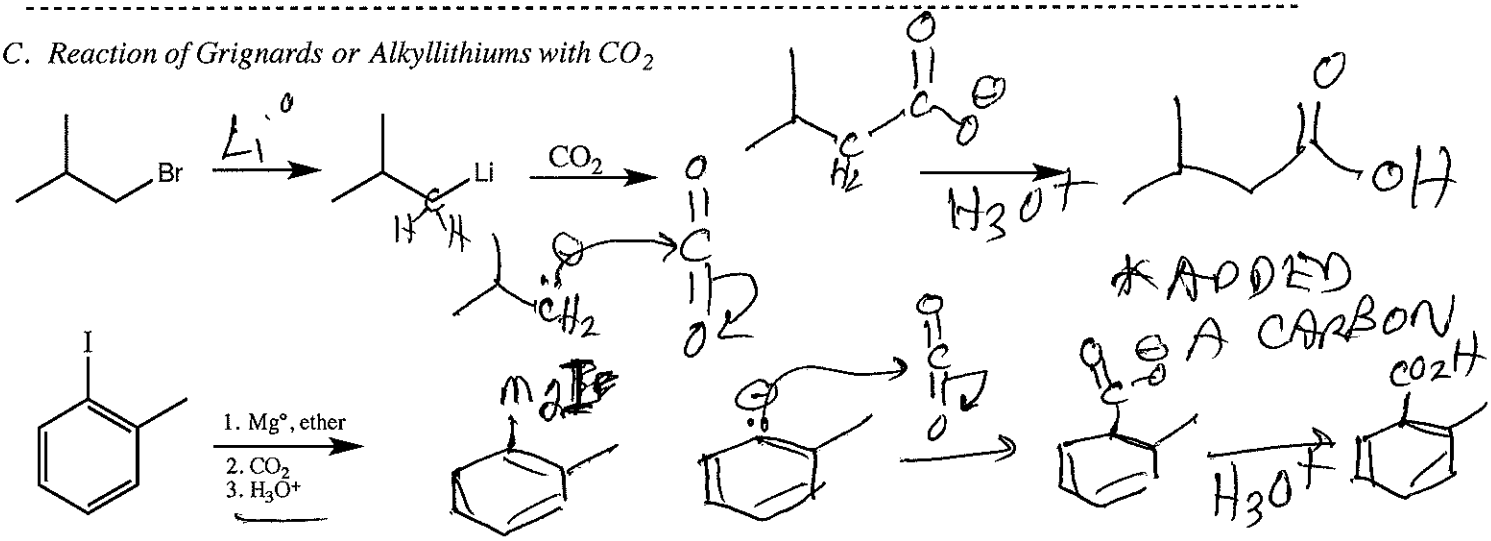




B. Oxidation of Alkyl Benzenes

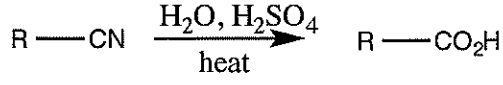


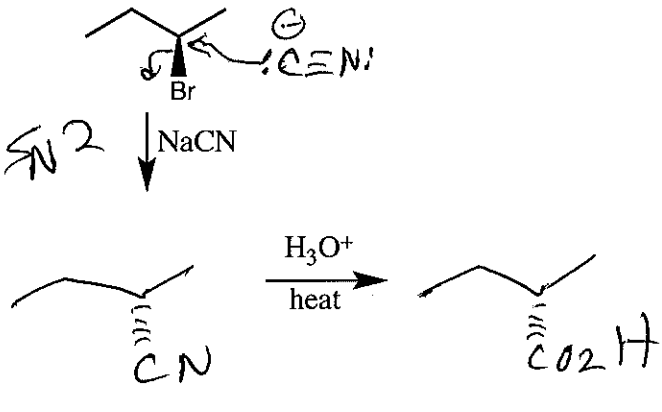
C. Reaction of Grignards or Alkyllithiums with CO_2

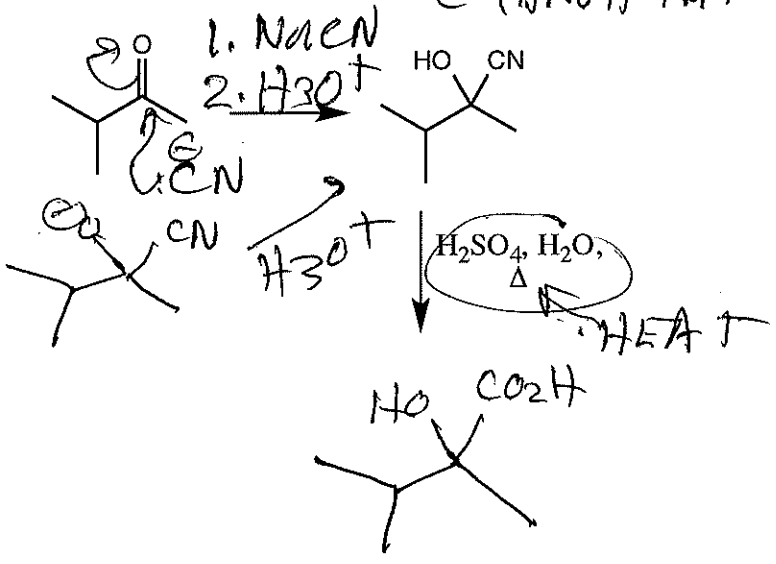


• *unlike the oxidative methods above, this method ADDS a carbon atom to the overall length in the carbon chain of the starting alkyl halide*

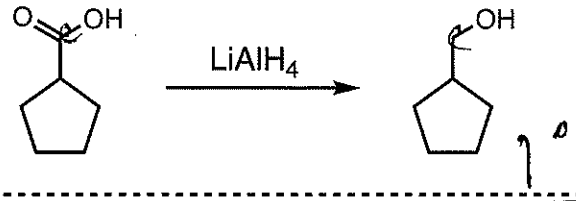
D. Hydrolysis of Nitriles R—CN R—C≡N



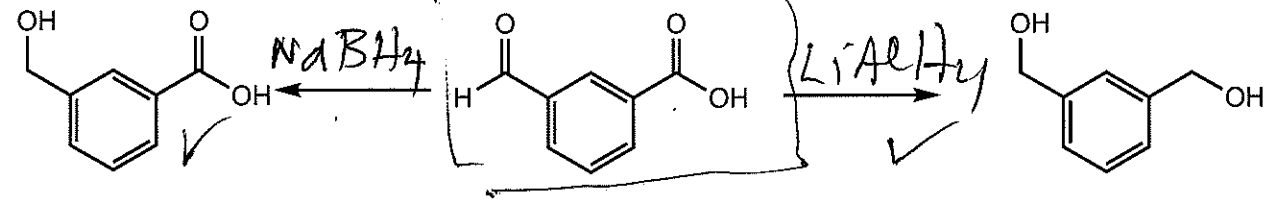


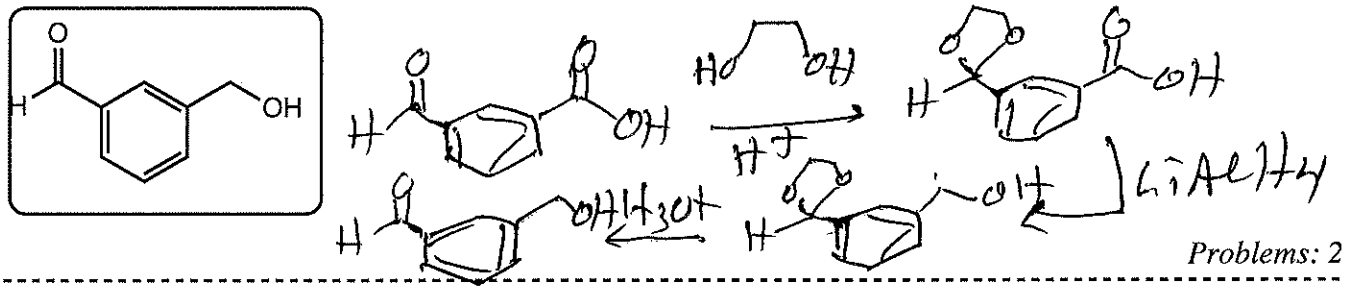


Reduction of Carboxylic Acids



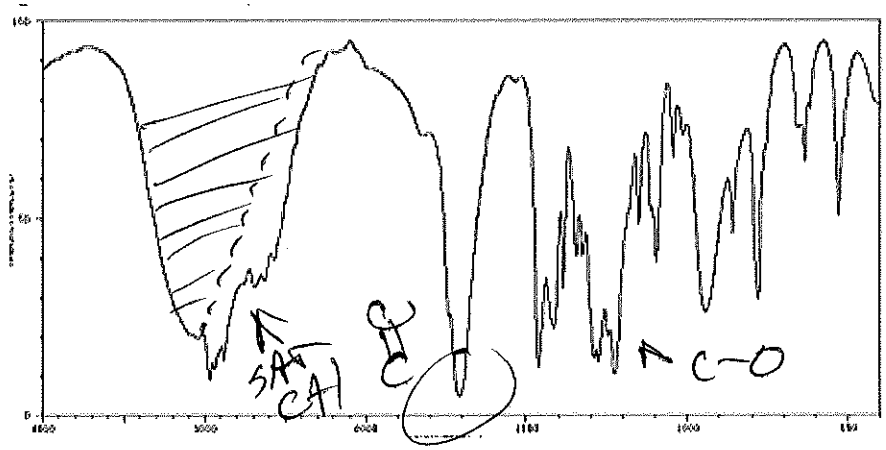
- *reduction of carboxylic acids* ***requires*** *the strong reducing agent* $LiAlH_4$
- $NaBH_4$ *is NOT effective*

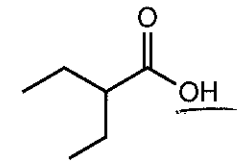




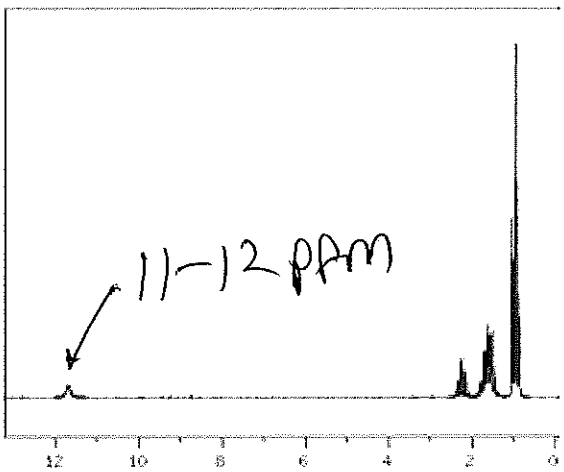
Problems: 2,4

Spectra of Carboxylic Acids





SAT CH ~~≥~~3000 cm⁻¹
C=O ~1700 cm⁻¹
OH ~3500 cm⁻¹
C-O 1,000-1,250 cm⁻¹



Problems:4,5