Carboxylic Acids

#### Question

What is the major organic product of the reaction of propylmagnesium bromide with  ${
m CO}_2$  followed by addition of dilute acid?

 $CH_3CH_2CH_2MgBr + CO_2 \rightarrow$ 

- A) propanoic acid
- B) butanoic acid
- C) butanol
- D) propane

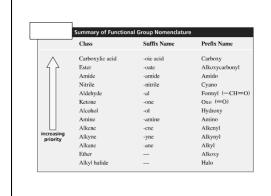
# Nomenclature of Carboxylic Acids systematic name: methanoic acid common name: formic acid acetic acid proplonic acid proplonic acid proplonic acid proplonic acid butanoic acid proplonic acid acrylic acid acrylic acid waleric acid valeric acid (aproic acid acrylic acid butyric acid benzoic acid

# Question

Which is the correct IUPAC name for the compound shown?  ${\sf CO}_2{\sf H}$ 

(CH<sub>3</sub>)<sub>2</sub>CCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>

- A) 1,1,3-trimethylpentanoic acid
- 3) 2,2,4-trimethylpentanoic acid
- C) 2,4-dimethyl-2-pentylcarboxylic acid
- D) 2,4-dimethyl-2-pentanoic acid



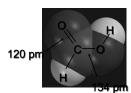
#### Question

What is the IUPAC name of the caboxylic acid at the right  $_{H_3C}$   $_{(CH_2)_4CO_2H}$ 

$$H_3C$$
  $C=C$   $(CH_2)_4CO_2H$ 

- A) cis-3-pentenoic acid
- B) trans-6-octenoic acid
- C) cis-6-octenoic acid
- D) trans-6-octenoic acid

#### Planar Geometry



#### Carboxylic Acid Acidity

Most carboxylic acids have a  $pK_a$  close to 5.

#### REVIEW Carboxylic Acids from Chem 226:

http://chemconnections.org/organic/chem226/Presentations/Chap-03-12 /Ch03-acids-12-ques.htm

http://chemconnections.org/organic/chem226/Presentations/Chap-03-12/Ch03-acids-12-ques.pdf

# Carboxylic Acids are Weak Acids

Carboxylic acids are far more acidic than alcohols.

CH<sub>3</sub>CH<sub>2</sub>OH

$$pK_a = 4.7$$

 $pK_a = 16$ 

# Question

Which compound has the lower  $pK_a$  (i.e., is more acidic)?

B)

CH<sub>3</sub>C≡CH

# 

Greater Acidity of Carboxylic Acids is Attributed Stabilization of Carboxylate Ion by

Inductive effect of carbonyl group

Plus resonance stabilization of carboxylate ion

# Substituent Effects on Acidity

standard of comparison is acetic acid (X = H)

$$pK_a = 4.7$$

# Substituent Effects on Acidity

Alkyl groups have negligible effect		Electronegative groups increase acidity	
X	p <i>K</i> <sub>a</sub>	X	p <i>K</i> <sub>a</sub>
н	4.7	н	4.7
CH <sub>3</sub>	4.9	F	2.6
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	4.9	CI	2.9

# Substituent Effects on Acidity

# Question

Which one of the following compounds is more acidic?

# Hybridization Effect

 $sp^2$ -hybridized carbon is more electron-withdrawing than  $sp^3$ , and sp is more electron-withdrawing than  $sp^2$ 

# Ionization of Substituted Benzoic Acids

#### Question

Which one of the following compounds has the highest  $pK_a$ ?

Dicarboxylic Acids

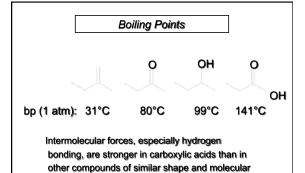
# Dicarboxylic Acids Dicarboxylic Acids Dicarboxylic Acids PK<sub>a</sub> HOC — COH Oxalic acid 1.2 HOCCH<sub>2</sub>COH Malonic acid 2.8 HOC(CH<sub>2</sub>)<sub>s</sub>COH Heptanedioic acid 4.3 One carboxyl group acts as an electron-withdrawing group toward the other; effect decreases with increasing separation

#### Question

Which of the following statements is true regarding the effect of substituents on the acidity of carboxylic acids?

- A) Alkyl substituents have a negligible effect on acidity.
- B) Electron-attracting groups increase acidity.
- C) Substituents on the  $\alpha$ -carbon increase acidity.
- D) All of the statements above are true.

Physical Properties



weight.

#### Question

Which compound has the highest boiling point?

B) /

#### Solubility in Water

Carboxylic acids are similar to alcohols in respect to their solubility in water.

Form hydrogen bonds to water.

Salts of Carboxylic Acids

Carboxylic Acids are Neutralized by Strong Bases

Equilibrium lies far to the right; *K* is ca. 10<sup>11</sup>. As long as the molecular weight of the acid is not too high, sodium and potassium carboxylate salts are soluble in water.

# Which form is favored? Acid or Conjugate Base?

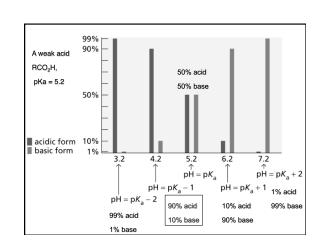
**Solution effects:** The pH of the surroundings (i.e. independent of the acid-conjugate base pH contribution) controls which form is favored, acid or conjugate base, and relates to the following equation.

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

 If the pH of the surroundings is < than a compound's pK<sub>a</sub>, the compound will exist primarily in its acidic form.

•If the pH of the surroundings is > than a compound's  $pK_a$ , the compound will exist primarily in its basic form.

 NOTE: Remember that a buffer solution (surroundings) maintains a nearly constant pH within certain parameters.



# **QUESTION**

Aspirin has a  $pK_a$  of 3.5. In the stomach,  $pH \sim 2$ , what form of aspirin is favored?

# QUESTIONS from Worksheet:

The pKa of a general anesthetic, sodium pentothal, is 7.4. If a patient is given sodium pentothal orally instead of *iv*, will it put the patient to sleep?

A drug has a pKa of 7.8 and is a known teratogen. If given *iv* to a pregnant woman whose blood pH is within normal levels, will this drug cross the placenta and affect the baby?

What information is needed to answer these anesthesiology questions?

# Question

Which is the product of the reaction of propanoic acid and Br<sub>2</sub>, PBr<sub>3</sub> in toluene at 80°C?



# Question

Select the product of the reaction of propanoic acid with thionyl chloride

# Preparation of Acyl Chlorides

from carboxylic acids and thionyl chloride

$$(CH_3)_2CHCOH \xrightarrow{SOCl_2} (CH_3)_2CHCCI + SO_2 + HO$$
(90%)

# Acid Chloride Reactions

