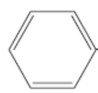
Home work

1- Write the structure for

a. 3-hydroxyhexanoic acid
b. 2-iodo-2-methyloctanoic acid
c. 2-butynoic acid
d. 5-ethyl-6-oxoheptanoic acid

2- Give an IUPAC name for

a.  $-CH_2CO_2H$
b. $Br_2CHCH_2CO_2H$
c. $CH_3CH{=}CHCO_2H$
d. $(CH_3)_3CCH_2CH_2CO_2H$

3- Write the structure for

a. *cis*-3-isopropylcyclohexanecarboxylic acid
b. *o*-nitrobenzoic acid

4- Write the formula for

a. 4-formylbenzoic acid
b. benzoyl bromide
c. octanoyl bromide
d. acetylcyclopentane

5- Phenoxide ions are also stabilized by resonance. Why are phenols weaker acids than carboxylic acids?

Solution First, the carbon atom to which the hydroxyl group is attached in a phenol is not as positive as a carbonyl carbon. Second, charge delocalization is not as great in phenoxide ions as in carboxylate ions because the contributors to the resonance hybrid are not equivalent. Some of them put the negative charge on carbon instead of on oxygen and disrupt aromaticity.

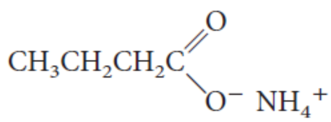
6- Write two resonance structures for the benzoate ion ($C_6H_5CO_2^-$) that show how the negative charge is delocalized over the two oxygens. Can the negative charge in the benzoate ion be delocalized into the aromatic ring?

7- Explain the acidity order for butanoic acid and its 2- and 3-chloro derivatives.

Solution The 2-chloro substituent increases the acidity of butanoic acid substantially, due to its inductive effect. In fact, the effect is about the same as for chloroacetic and acetic acids. The 3-chloro substituent exerts a similar *but much smaller* effect, because the C—Cl bond is now farther away from the carboxylate group. *Inductive effects fall off rapidly with distance.*

8-

Name the following carboxylate salt:



9-

Show how $(CH_3)_3CBr$ can be converted to $(CH_3)_3CCO_2H$.

Solution $(CH_3)_3CBr \xrightarrow[\text{ether}]{\text{Mg}} (CH_3)_3CMgBr \xrightarrow[2.\ H_3O^+]{1.\ CO_2} (CH_3)_3CCO_2H$

10- Show how 4-methylcyclohexyl chloride can be converted to 4-methylcyclohexanecarboxylic acid.

11- Devise a synthesis of butanoic acid (CH3CH2CH2CO2H) from 1-propanol (CH3CH2CH2OH).

12- Why is it not possible to convert bromobenzene to benzoic acid by the nitrile method? Instead, how could this conversion be accomplished?

13- Write equations for synthesizing phenylacetic acid from benzyl bromide by two routes.

14- Write the structure of

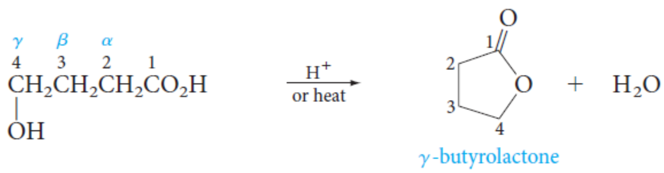
a. 3-pentyl butanoate

b. methyl 2-methylhexanoate

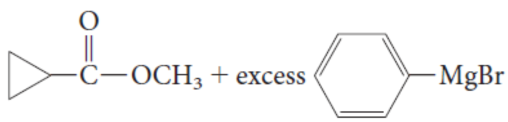
15- Write an equation for the preparation of ethyl pentanoate from the correct acid and alcohol.

16- Write out the steps in the mechanism for the acid-catalyzed preparation of ethyl acetate from ethanol and acetic acid.

17- Write the steps in the mechanism for the following reaction

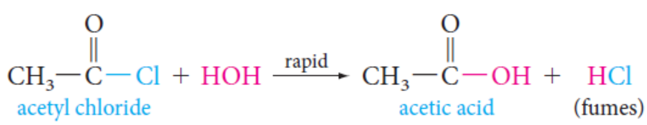


18- Write the structure of the tertiary alcohol that is obtained from

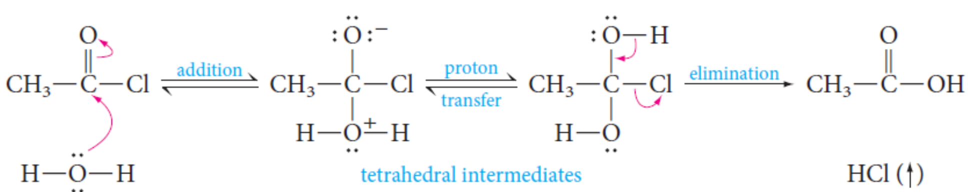


Key: Reaction of Esters with Grignard Reagents

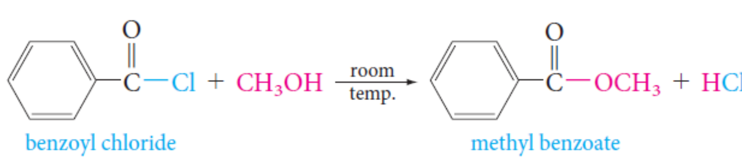
19- Write a mechanism for the following reaction



Solution Nucleophilic addition of water to the carbonyl group, followed by proton transfer and elimination of HCl from the tetrahedral intermediate, gives the observed products.



20- Write a mechanism for the following reaction

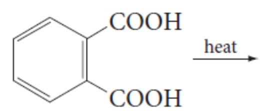


21- Devise a synthesis of 4-methylphenyl propyl ketone from toluene and butanoic acid as starting materials.

22- Write the structural formula for

a. butanoic anhydride b. benzoic anhydride

23- Predict and name the product of the following reaction:



24- Write an equation for the reaction of acetic anhydride with 1-pentanol.

25- Write equations for the reactions of maleic anhydride

a. water b. 1-propanol c. ammonia

26-

a. Name $(CH_3)_2CHCH_2CONH_2$
b. Write the structure of 1-phenylcyclopentanecarboxamide

27- Show that hydrogen bonding is possible for acetamide, but not for N,N-dimethylacetamide.