Chapter 21 Carboxylic Acid Practice Problems
Solutions

1

A. 3-*tert*-butyl-hexanoic acid

B. 3-bromobenzoic acid *or* meta-bromobenzoic acid

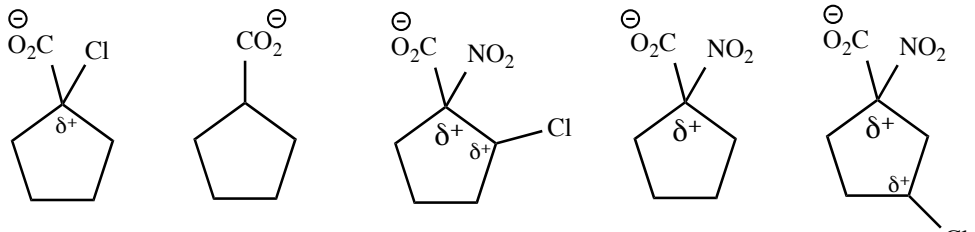
C. (R)-2-bromo-2-methylbutanoic acid

D. trans–3-methylcyclohexanecarboxylic acid

E. 2-isopropylpentanoic acid

2

• We can evaluate the acidities best by looking at stabilization of the corresponding conjugate bases of each of the carboxylic acids



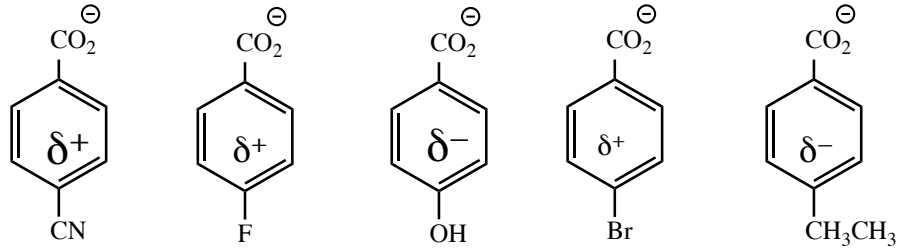
I II III IV V

• Being carboxylic acids, they are all stabilized by resonance within the CO_2^- group
• acid II has no further stabilization, but I and III-–V all have additional stabilization from the inductive effect of the nearby groups. Stabilization is provided by the δ^+ established by the polarized bonds to the groups (Cl or NO_2). I will therefore be least acidic.
• The greatest stabilization is provided by the very strong electron withdrawing NO_2 group since it creates the largest δ^+ closest to the CO_2^-. Thus, III, IV and V will be more acidic than I.
• Additional stabilization is found on III and V because of the Cl group attached. The Cl is closer to the CO_2^- group on III and therefore provides the greatest stabilization. Thus, III will be most acidic

most acidic III > V > IV > I > II least acidic

3

• We can evaluate the acidities best by looking at stabilization of the corresponding conjugate bases of each of the carboxylic acids

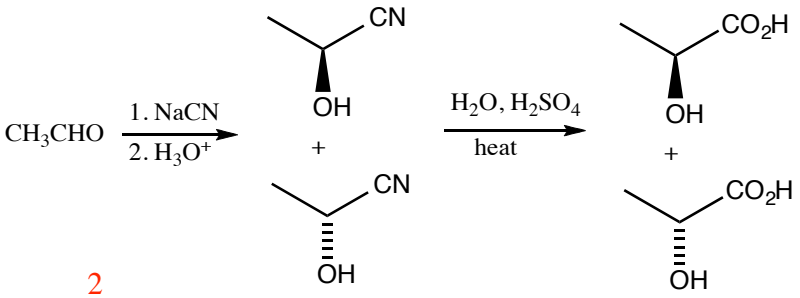


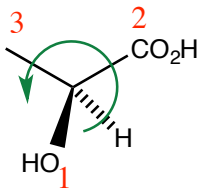
I II III IV V

• Being carboxylic acids, they are all stabilized by resonance within the CO_2^- group
• The impact of each of the attached groups at the para position is indicated by the size and sign of the charge that they induce as shown in the figures above
• Electron withdrawing groups induce a δ^+ charge, and with that from CN > F > Br. These groups stabilize the negative charge on the CO_2^- group and therefore increase acidity.
• Electron donating groups induce a δ^- charge, and with that from OH > CH_2CH_3. These groups destabilize the negative charge on the CO_2^- group and therefore decrease acidity.

most acidic I > II > IV > V > III least acidic

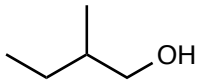
4





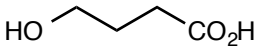
naturally occurring lactic acid has the S configuration

---

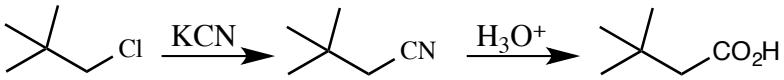
1. 

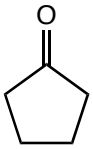
2. $KMnO_4$ *or* $Na_2Cr_2O_7$, H_2O, H_2SO_4

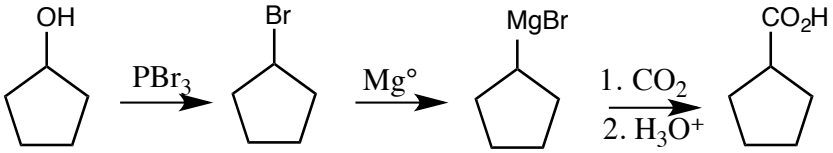
3. 1. CO_2 2. H_3O^+

4. 

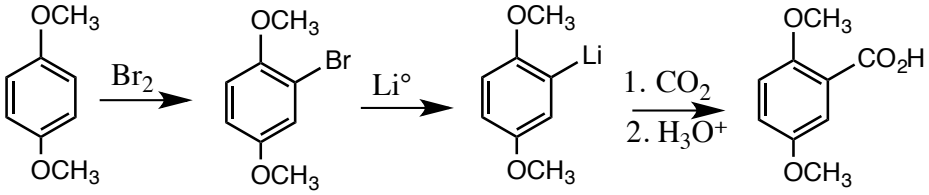
5. 1. $LiAlH_4$ 2. H_3O^+

6. 

7. 

8. 

5

9. 

10. $KMnO_4$ *or* $Na_2Cr_2O_7$, H_2O, H_2SO_4

11.