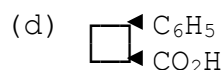
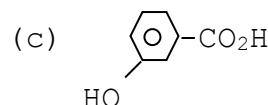
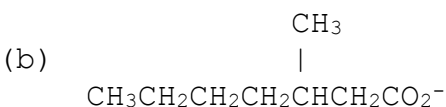
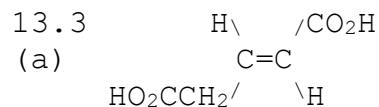


Answers to Puzzles of Chapter 13  
Carboxylic Acids

13.1 (a) no chiral atoms (b) no stereoisomers (no chiral atoms, no double bonds)

13.2 (a) 3-bromobutanoic acid (b) 2-methylpentanoic acid (c) 2-hydroxyethanoic acid  
(d) cyclohexanecarboxylic acid (e) 2-cyclohexylpropanoic acid (f) (*E*)-3-chloro-2-butenoic acid

(g) ethylpropanedioic acid (h) sodium hexanoate



13.4 (a) butanoic acid < 3-methylbutanoic acid < pentanoic acid  
because as surface area ↑, dispersion forces ↑ & bp ↑.

(b) butanoic acid > 3-methylbutanoic acid > pentanoic acid  
because as polarity ↑, solubility in water ↑.

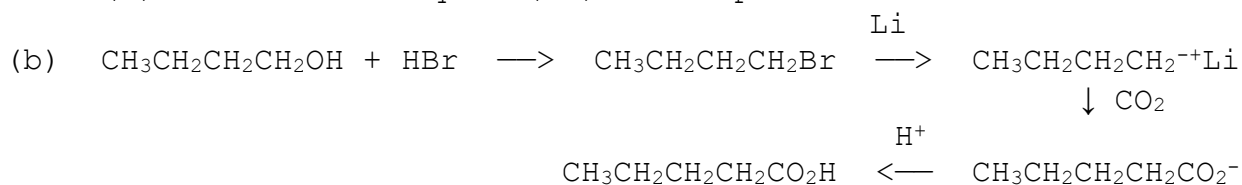
13.5 (a) diethyl ether, because both are a little polar

(b) the soap because its ionic charges make it more polar

(c) the soap because its ionic bonds are stronger than any intermolecular forces of the fatty acid

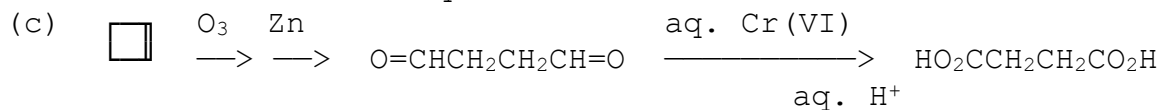
13.6 (a) Ag<sub>2</sub>O (b) anhyd. Cr(VI) (c) Ag<sub>2</sub>O; then anhyd. Cr(VI)

13.7 (a) reactant + aq. Cr(VI) → product



13.8 (a) HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH + aq. Cr(VI) → HO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H

(b) O=CHCH<sub>2</sub>CH<sub>2</sub>CH=O + aq. Cr(VI) → HO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H

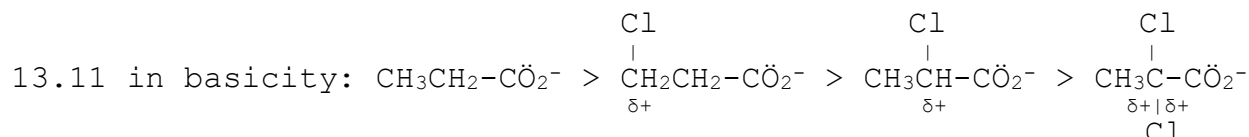
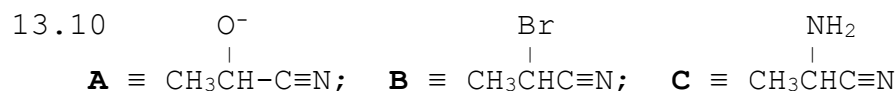
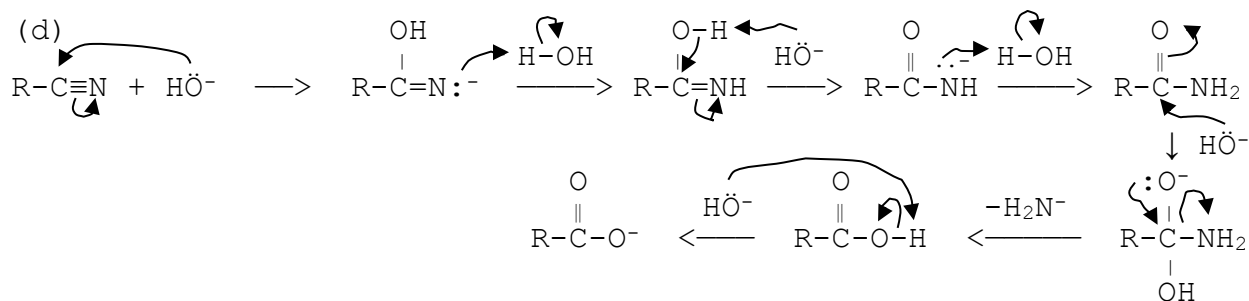


(d) BrCH<sub>2</sub>CH<sub>2</sub>Br + <sup>-</sup>C≡N → N≡CCH<sub>2</sub>CH<sub>2</sub>C≡N  $\xrightarrow{\text{aq. H}^+}$  HO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H

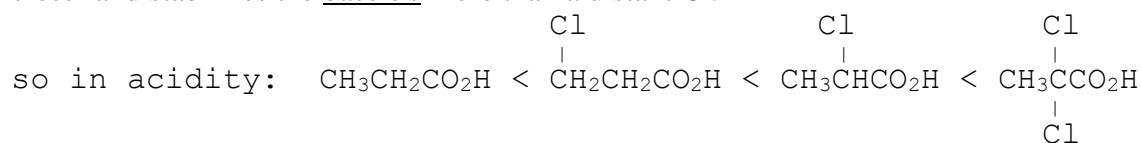
13.9 (a) For basic hydrolysis, the nucleophile is hydroxide ion.

(b) This is a stronger nucleophile than the nucleophile for acidic hydrolysis: water.

(c) Acidic hydrolysis has the stronger electrophile, the protonated, cationic nitrile: R-C≡NH<sup>+</sup>

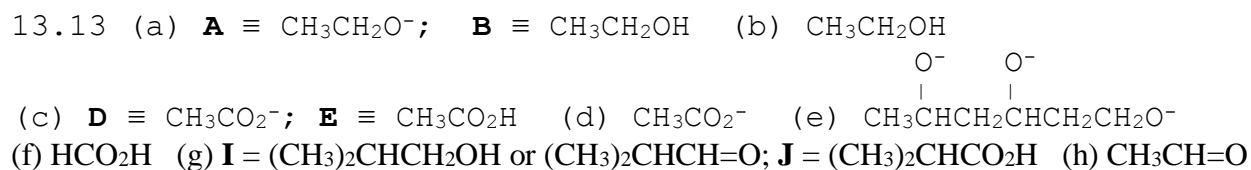


because 2 Cl's put more  $\delta+$  on a C, which stabilize the base e's more; also a nearer Cl puts its  $\delta+$  closer and stabilizes the base e's more than a distant Cl.

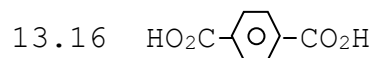
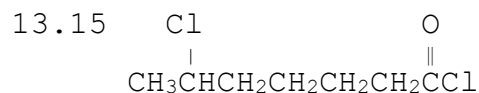


13.12

the conjugate bases' basicity:  $\text{C}_6\text{H}_5\text{CH}_2\overset{+\text{NH}_3}{\underset{|}{\text{C}}}\text{HCO}_2^- < \text{CH}_3\text{CO}_2^-$   
 because the first base's + stabilizes the base e's. So phenylalanine is more acidic.



13.14 (a)  $\text{LiAlH}_4$ ; then  $\text{H}^+$  (b)  $\text{H}_2$ , Pt (c)  $\text{LiAlH}_4$ ; then  $\text{H}^+$ ; then  $\text{H}_2$ , Pt  
 (d)  $\text{LiAlH}_4$ ; then  $\text{H}_2$ , Pt; then anhyd. Cr(VI); then Zn/Hg, HCl

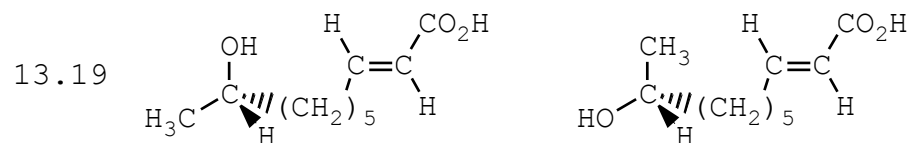


Since 2/3 of the 6 Hs resonate in the phenyl region, there are 4 phenyl Hs and 2 phenyl substituents. Since 1/3 of the 6 Hs resonate in the carboxylic acid region, there are 2 carboxylic acid groups, both on the phenyl ring. Because the phenyl H signal is a sharp singlet, all the phenyl Hs are equivalent. So, the carboxylic acid groups must be at opposite ends of the phenyl ring.

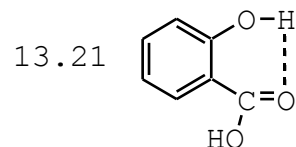
13.17  $\sim 3400 \text{ cm}^{-1}$ : alcohol O-H;  $\sim 3050 \text{ cm}^{-1}$ :  $sp^2$  C-H;  $\sim 2700, 2600 \text{ cm}^{-1}$ : carboxylic acid O-H;  $\sim 2900 \text{ cm}^{-1}$ :  $sp^3$  C-H;  $\sim 1720 \text{ cm}^{-1}$ : ketone C=O;  $\sim 1710 \text{ cm}^{-1}$ : carboxylic acid C=O;

~1660 cm<sup>-1</sup>: C=C; ~1200 cm<sup>-1</sup>: C-O; ~800 cm<sup>-1</sup>: sp<sup>2</sup> C-H

- 13.18 (a) propanoic acid: CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H (b) sodium methanoate: NaO<sub>2</sub>CH<sub>2</sub>  
 (c) e.g., 2-bromopropanoic acid: CH<sub>3</sub>CHBrCO<sub>2</sub>H (d) butanedioic acid: HO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H  
 (e) e.g., 5-hexenoic acid: H<sub>2</sub>C=CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H



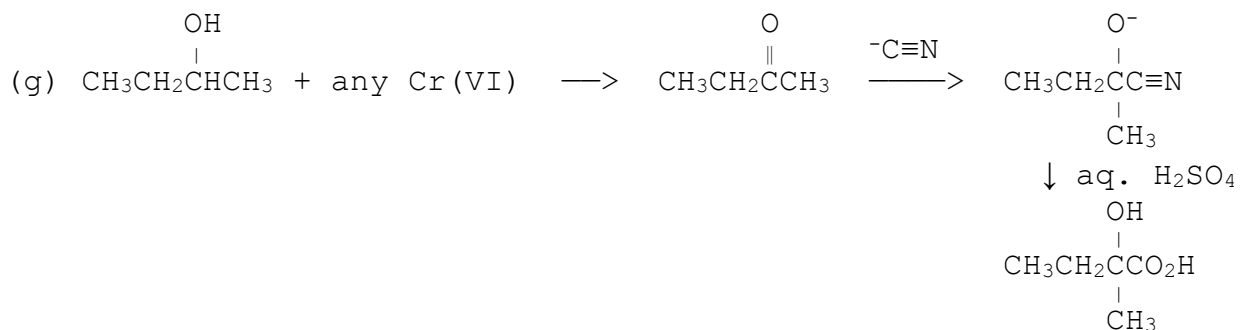
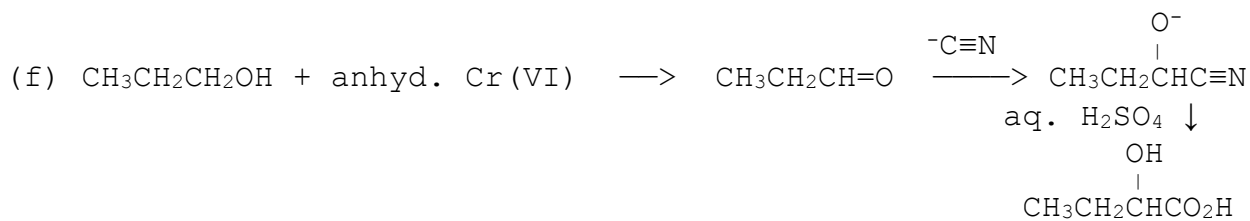
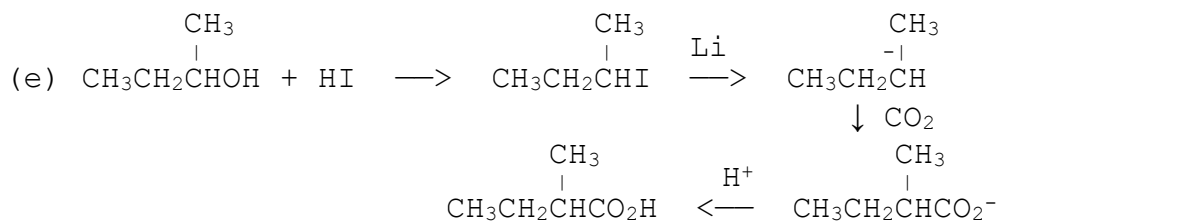
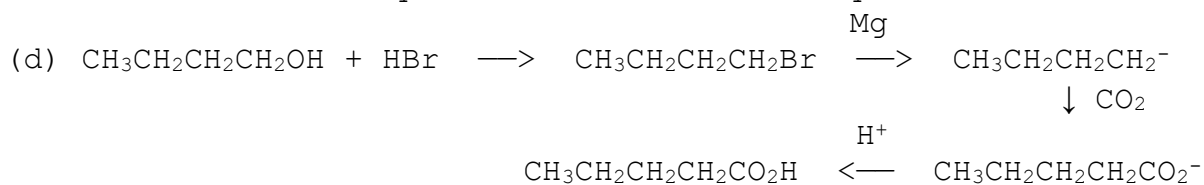
13.20 Ethanoic acid because of its tendency to form dimers with 2 H "bonds".

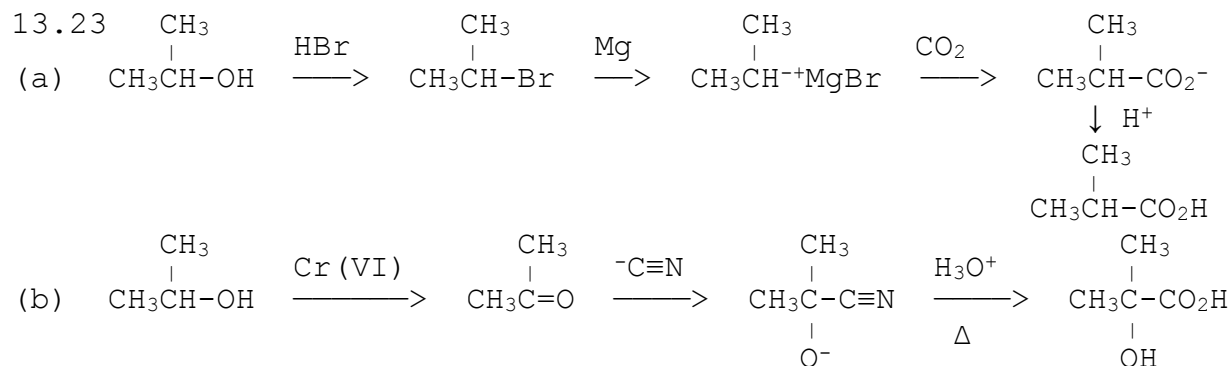


The 2-isomer has intramolecular H "bonds", which lessen the intermolecular H "bonds" & mp.

13.22 (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH + aq. Cr(VI)

(b) (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>OH + aq. Cr(VI) (c) CH<sub>3</sub>OH + aq. Cr(VI)





13.24 (a)

conjugate bases' basicity:  $\text{CH}_3\text{C}(\text{O})\text{O}^- < \text{CH}_3\text{C}(\text{O})\text{CH}_2^-$   
 because base e's are stabler on more EN O than on C. So  $\text{CH}_3\text{CO}_2\text{H}$  is more acidic.

(b) conjugate bases' basicity:  $\text{CH}_3\text{C}(\text{O})\text{O}^- \leftrightarrow \text{CH}_3\text{C}(\text{O}^-) < \text{CH}_3\text{CH}_2\text{O}^-$   
 because resonance stabilizes base e's. So  $\text{CH}_3\text{CO}_2\text{H}$  is more acidic

(c) conjugate bases' basicity:  $\overset{\delta^-}{\text{Cl}}-\overset{\delta^+}{\text{CH}_2}\text{C}(\text{O})\text{O}^- < \text{CH}_3\text{C}(\text{O})\text{O}^-$   
 because  $\delta^+$  from EN Cl stabilizes base e's. So  $\text{ClCH}_2\text{CO}_2\text{H}$  is more acidic.

(d) conjugate bases' basicity:  $\overset{\delta^-}{\text{F}}-\overset{\delta^+}{\text{CH}_2}\text{C}(\text{O})\text{O}^- < \overset{\delta^-}{\text{Cl}}-\overset{\delta^+}{\text{CH}_2}\text{C}(\text{O})\text{O}^-$   
 because larger  $\delta^+$  from more EN F stabilizes base e's more. So  $\text{FCH}_2\text{CO}_2\text{H}$  is more acidic.

(e) conjugate bases' basicity:  $\overset{\delta^-}{\text{Cl}}-\overset{\delta^+}{\text{CH}_2}\text{C}(\text{O})\text{O}^- < \overset{\delta^-}{\text{Cl}}-\overset{\delta^+}{\text{CH}_2}\text{CH}_2\text{C}(\text{O})\text{O}^-$   
 because the  $\delta^+$  from nearer Cl stabilizes base e's more. So  $\text{ClCH}_2\text{CO}_2\text{H}$  is more acidic.

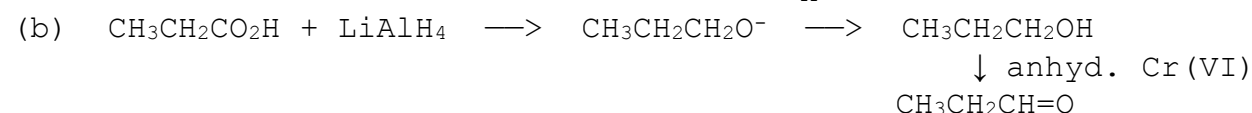
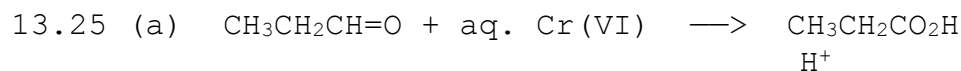
(f) conjugate bases' basicity:  $\overset{\delta^-}{\text{Cl}_2}-\overset{\delta^+}{\text{CH}}\text{C}(\text{O})\text{O}^- < \overset{\delta^-}{\text{Cl}}-\overset{\delta^+}{\text{CH}_2}\text{C}(\text{O})\text{O}^-$   
 because 2  $\delta^+$  from 2 Cl's stabilize base e's more. So  $\text{Cl}_2\text{CHCO}_2\text{H}$  is more acidic.

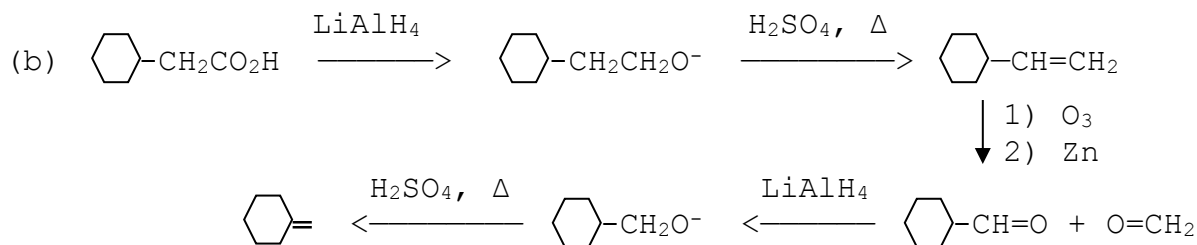
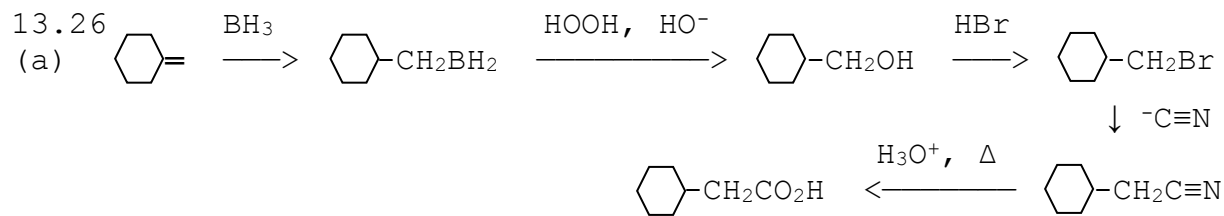
(g) conjugate bases' basicity:  $\overset{+}{\text{H}_3\text{N}}\text{CH}_2\text{C}(\text{O})\text{O}^- < \text{CH}_3\text{C}(\text{O})\text{O}^-$   
 because + stabilizes base e's. So  $\text{H}_3\text{NCH}_2\text{CO}_2\text{H}$  is more acidic.

(h) conjugate bases' basicity:  $\overset{+}{\text{O}_2\text{N}}\text{CH}_2\text{C}(\text{O})\text{O}^- < \text{CH}_3\text{C}(\text{O})\text{O}^-$   
 because + stabilizes base e's. So  $\text{O}_2\text{NCH}_2\text{CO}_2\text{H}$  is more acidic.

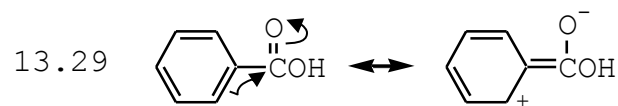
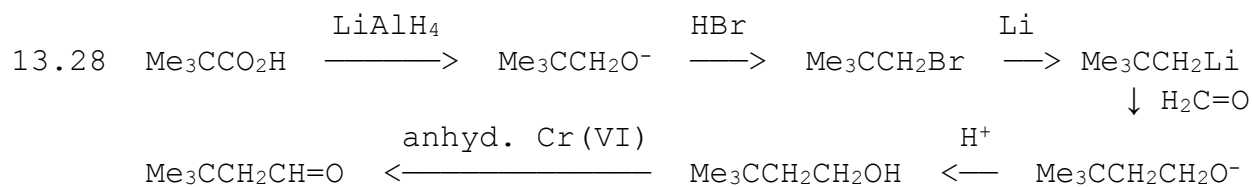
(i) conjugate bases' basicity:  $\overset{\delta^-}{\text{HO}_2}\overset{\delta^+}{\text{C}}\text{CH}_2\text{C}(\text{O})\text{O}^- < \text{CH}_3\text{C}(\text{O})\text{O}^-$   
 because  $\delta^+$  due to 2 extra EN Os stabilizes base e's. So  $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$  is more acidic.

(j) conjugate bases' basicity:  $\overset{\delta^-}{\text{HO}_2}\overset{\delta^+}{\text{CH}_2}\text{C}(\text{O})\text{O}^- < \overset{\delta^-}{\text{O}_2}\overset{\delta^+}{\text{C}}\text{CH}_2\text{C}(\text{O})\text{O}^-$   
 because extra - repels & destabilizes base e's. So  $\text{HO}_2\text{CH}_2\text{CO}_2\text{H}$  is more acidic.



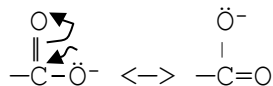


13.27 (a)  $\text{CH}_3\text{CH}_2\text{O}^-$  (b)  $\text{CH}_3\text{CO}_2^-$  (c)  $\text{CH}_3\text{COCl}$  (d)  $\text{CH}_3\text{CO}_2^-$  (e)  $\text{CH}_3\text{CO}_2^- + \text{CH}_3\text{CH}_3$   
 (f)  $\text{CH}_3\text{CO}_2^- + \text{CH}_3\text{CH}_2\text{CO}_2\text{H}$  (g) no reaction



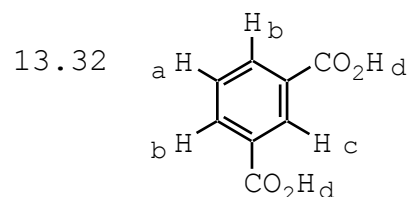
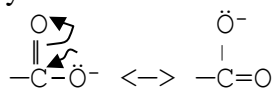
The 2nd resonance form  $\downarrow$  the C=O's bond order. A lowered bond order  $\downarrow$  IR frequency.

13.30 2 major resonance forms lower the bond order of the C=O in a carboxylate ion:



A lowered bond order  $\downarrow$  IR energy & frequency.

13.31 The 2 O's are equally basic because resonance makes them equivalent:



$\delta$  13.3 (s): 2 x  $\text{CO}_2\text{H}$  d;  $\delta$  8.6 (s):  $\text{H}$  c;  $\delta$  8.3 (d): 2 x  $\text{H}$  b;  $\delta$  7.7 (t):  $\text{H}$  a