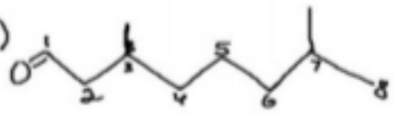
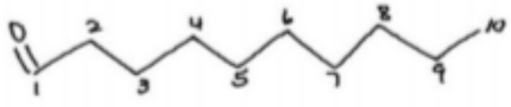
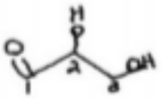
Ch 9 Problems:

9.9 in an aldehyde the carbonyl is the #1 carbon of the parent chain.
in a ketone the carbonyl must be on an interior carbon.

9.15 a) $H_2C{=}O$ b) $O{=}CHCH_2CH_3$ c) 

d)  e)  f) 

9.18 a) 3-hydroxy cyclohexanone
b) 3-hexen-2-one
c) 2,3,4-trihydroxy butanal
d) 4-amino benzaldehyde

9.21 a) ethanol
b) 3-pentanone
c) butanal
d) 2-butanol

9.36
a) 
b) 
c) 
d) 

12/12/18

Oxidizing Reagents

Dichromate orange (Cr^{6+}) $\rightarrow$ green (Cr^{3+})

$$R\text{-}C(=O)\text{-}H + Cr_2O_7^{2-} + H^+ \longrightarrow R\text{-}C(=O)\text{-}OH + Cr^{3+} + H_2O$$

Tollen's ⊕ test = silver plating

$$Ag(NH_3)_2^+ + R\text{-}C(=O)\text{-}H + OH^- \longrightarrow Ag(s) + R\text{-}C(=O)\text{-}O^- + NH_3 + H_2O$$

Benedict's Rgt (Fehling Sln) ⊕ dk red ppt

$$R\text{-}C(=O)\text{-}H + \underset{\text{(in complex)}}{Cu^{2+}} + OH^- \longrightarrow R\text{-}C(=O)\text{-}O^- + Cu_2O + H_2O$$

Iodoform

$$R\text{-}C(=O)H + I_2 + NaOH \longrightarrow NaI + H_2O + R\text{-}C(=O)O^- Na^+ + HCI_3\,(s)$$

Reducing Reagents

reduce aldehydes $\rightarrow$ 1° alcohol
reduce ketone $\rightarrow$ 2° alcohol

Lithium Aluminum Hydride

Aldehyde $$R\text{-}C(=O)H + \underset{\uparrow \text{from rgt}}{2H^+} \longrightarrow R\text{-}CH_2(OH)$$

Ketone $$4\ R\text{-}C(=O)R' + Li^+AlH_4^- \rightarrow (R\text{-}C(R')(H)\text{-}O)_4Al^-\,Li^+ \ \circlearrowright$$

$$(R\text{-}C(R')(H)\text{-}O)_4Al^- + 4H^+(aq) \rightarrow 4\ R\text{-}C(R')(H)\text{-}OH + 3Al^{3+}(aq)$$

Sodium Borohydride

Aldehyde $$R\text{-}C(=O)H + 2H^+_{\text{from Rgt}} \rightarrow R\text{-}CH_2(OH)$$

Ketone $$4\ R\text{-}C(=O)\text{-}R' + Na^+BH_4^- \rightarrow (R\text{-}C(R')\text{-}O)B^-Na^+ \ \circlearrowright$$

12/7/15

Carboxylic Acids:

Compounds containing a carboxyl group R-C(=O)-OH -C(=O)OH -COOH $-CO_2H$

The acid carbon must be carbon #1. The carboxyl group takes precidence over other functional groups (except amide).

Nomenclature:

Name the longest P.C. that contains the carboxyl group. The "C" of the carboxyl is #1 and referred to as the acid carbon. Name PC - remove "e" add "-oic acid" list other branches w/ # locators.

if double ended carboxylic groups HO-C(=O)~C(=O)-OH name parent chain - dioic acid

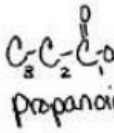
* common name is derived based on the location of acid. (where its found in life)

Attachments in order halogens - then others alphabetically

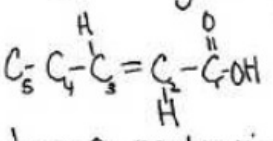
-X halogens $-NH_2$ amine (-amino)

=O carbonyl (-oxy) R'-O- ether (- R' alkyl branch + oxy)

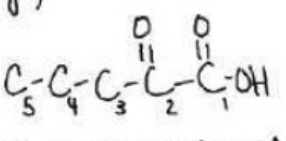
-OH hydroxyl (-hydroxy) -Cxhy alkyl (-alkyl) alkoxy



propanoic acid

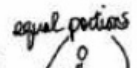
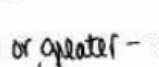


trans-2-pentenoic acid



2-oxy pentanoic acid

Properties of Carboxylic Acids

1. weak acids (pK_a 4.0-5.0)
2. distinct odors (pungent)
3. many are solid at room temp.
4. Polar, hydrogen bonds very
5. highest B.P. of comparable molecular weights
6. Solubility depends on the size of the molecule & pH of solution
   a) pH below 7.0 – Soluble in equal parts acid/water (equal portions )
   b) pH 7.0 or greater – not equal portions ( becomes )

Reactions of Carboxylic Acids:

① Fischer Esterification

$$R\text{-}COOH + HOR' \xrightarrow{H_2SO_4} R\text{-}COOR' + H_2O$$

② Saponification of an Ester

$$R\text{-}COOR' + NaOH \text{ (or KOH)} \xrightarrow[H_2O]{\text{Heat}} R\text{-}COO^-Na^+ + R'OH$$

ester — Soap (Sodium – oate) replace -oic acid w/ -oate — alcohol

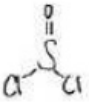
③ Formation of an acid anhydride

$$R\text{-}COOH + HOOC\text{-}R' \xrightarrow{\text{heat}} R\text{-}CO\text{-}O\text{-}CO\text{-}R' + H_2O$$

acid anhydride (names parent acid followed by anhydride)

④ Formation of an acyl halide

$R\text{-}COOH + \underbrace{SOCl_2 + PCl_5}_{\text{Reagents}} \longrightarrow$ 2 diff possibilities



$$R\text{-}COOH + SOCl_2 \longrightarrow R\text{-}COCl + HCl(aq) + SO_2(g)$$

($SOCl_2$ controls halogen)

$$R\text{-}COOH + PCl_5 \longrightarrow R\text{-}COCl + HCl(aq) + POCl_3$$

⑤ Formation of an acyl amide (2 step rxn)

[A] Step 1 – form acyl halide (as above)

Step 2 – $R\text{-}COX + R'NH_2 \xrightarrow{\text{heat}} R\text{-}CONHR' + NH_4X$

acyl halide — amine — acyl amide — ammonium halide

[B] Step 1 – form an ester

Step 2 – $R\text{-}COOR' + NH_3 \xrightarrow{\text{heat}} R\text{-}CONH_2 + R'OH$

ester — ammonia — amide — alcohol