CHEM 3331, Professor M. Walczak, Spring 2016 Third hour exam, 7.00 PM, April 12th, 2016

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- (a) Which sequence represents the relative reactivities of carboxylic acid derivatives (3 points)?
- a) RCO₂R' > RCONH₂ > (RCO)₂O > RCOCI
- b) RCOCI > RCO₂R' > (RCO)₂O > RCONH₂
- c) $(RCO)_2O > RCOCI > RCO_2R' > RCONH_2$ (RCO) $_2O > RCO_2R' > RCONH_2$ (RCO) $_2O > RCO_2R' > RCONH_2$
- (b) Identify the most acidic compound (4 points). Briefly explain your reasoning why you selected this molecule.

(c) In the following reactions, circle only the reactions which may occur under the indicated conditions. D2O in all reactions is used in large excess (4 points).

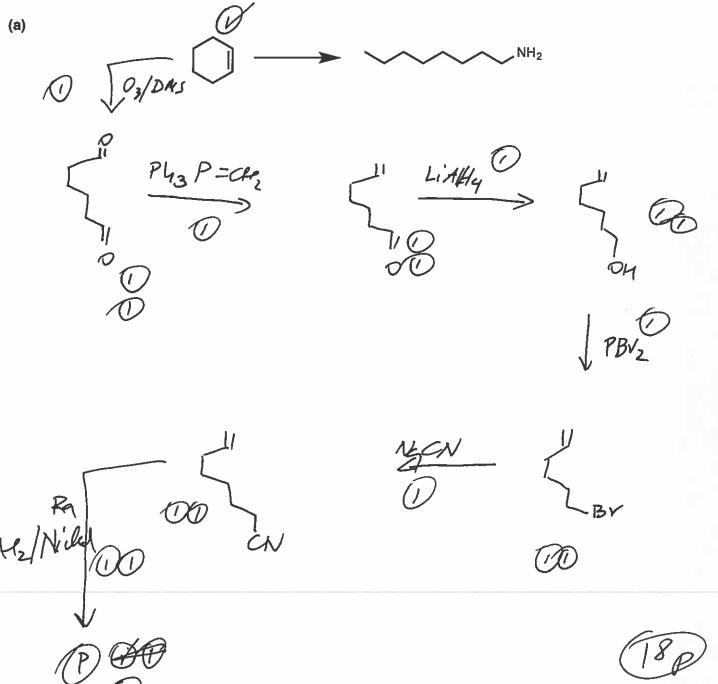
$$(a) \qquad (b)$$

$$Et_3N, D_2O \qquad (d)$$

$$D_2O \qquad (d)$$

$$DCI, D_2O \qquad heat$$

2. Provide a reasonable synthesis of the following two compounds using provided starting materials. More than one step may be required to complete the synthesis. The products are racemic but pay close attention to relative stereochemistry if applicable (32 points).



(4)

3. Complete the following syntheses using any reagents you need. You do not have to show the synthesis of the reagents you use, but you must use the starting material indicated. All chiral products are racemic mixtures (3 points each, 15 points total).

(e)

Br

$$\frac{1. \text{ Na CN}}{2. \text{ HzO}/\text{H}_300}$$
 $\frac{\text{OH}}{\text{Or}}$
 $\frac{\text{My/effrey}}{\text{CO}_{\text{L}} \text{ Lian H}_300}$

4. Provide the products of the following reactions (all reactions have an appropriate aqueous work up). If no reaction would occur, write NR. Ignore stereochemistry in the products (3 points each, 15 points total).

(a) OH
$$P$$
, Br_2 then H_2O

$$\begin{array}{c|c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

(d)
$$CI$$
 $CH_3)_2CuLi$ CH_3

then H₂O

(c)

5. Draw a plausible mechanism of the following reaction (15 points):

Phyon SOCI2

Phyon
$$+ SO_2 + HCI$$
 $OS_2 + HCI$
 $OS_3 - CI$
 $OS_4 - CI$
 $OS_5 - CI$
 $OS_5 - CI$
 $OS_6 -$

- 6. In the following questions, please circle only the correct answer (3 points each, 12 points total):
- (a) Which group or atom will undergo protonation when an amide is mixed with a strong acid?
- (a)O of CO group;
- (b) not protonation will occur;
- (c) C of CO;
- (d) nitrogen atom.
- (b) Which structure represents a tetrahedral intermediate involved in acylation of methylamine with acetic anhydride?

$$(a) \qquad (b) \qquad (c) \qquad (d) \qquad (d)$$

- (c) Which reagent(s) can convert nitriles into primary amines?
 - (a) LiAlH₄;

(b) H₂/Raney nickel;

(c) NaBH₄;

- (d) both a and b are correct;
- (e) both a and c are correct;
- (f) H₂O.
- (d) Which statement about acyl halides is incorrect?
- (a) are less reactive than anhydrides;

- (b) can react with alcohols to form esters;
- (c) can be formed using carboxylic acid and PCI₅;
- (d) can be reduced to alcohols.