

Chem 342 • Organic Chemistry II

Exam 03 • 01 May 2009

KEY



Please read through each question carefully and answer in the spaces provided. A good strategy is to go through the test and answer all the questions you can do easily. Then go back and tackle the more difficult problems. Please make sure your structures are drawn clearly and indicate any stereochemistry with bold or dashed bonds. Finally, think about what you know. Reason and common sense can often help you out.

The radiocarbon dating technique.

| Problem 1 | 10 pts | Problem 6 | 8 pts | |
|-----------|--------|---------------|---------|--|
| Problem 2 | 10 pts | Problem 7 | 20 pts | |
| Problem 3 | 8 pts | BONUS | 10 pts | |
| Problem 4 | 27 pts | | | |
| Problem 5 | 17 pts | TOTAL | 100 pts | |

- 1. Indicate whether the following statements are True for False. (10 pts)
 - Acid-catalyzed hydrolysis of esters is usually better than base-catalyzed hydrolysis.
 - T Acetals are relatively stable and are used as carbonyl protecting groups.
 - Grignard reagents add to give an alcohol (1,2-addition product) upon reaction with α,β -unsaturated ketones.
 - **F** Borane will reduce acids, ketones, aldehydes and esters.
 - Wittig reactions are a good way to make alkenes from carbonyls.
- 2. Place a check mark in the box for the functional group that best describes each of the following structures. (10 pts)

| Sur | detures. (10 pts) | acid | ester | amide | anhydride | acetal |
|-----|-------------------|------|-------|-------|-----------|--------|
| a) | 0 0 0 | | | | X | |
| b) | 0 0 0 | | X | | and | /or X |
| C) | OCH ₃ | | | | | X |
| d) | NH | | | X | | |
| e) | | | | | X | |

3. Identify the most acidic hydrogen in each of the following compounds (Circle the carbon or hydrogen if shown). (8 pts)



4. Provide the major product for each of the following reactions. (27 pts)

(a)
$$OH \longrightarrow OH$$
 $OH \longrightarrow OH_3OH$ OH_3OH

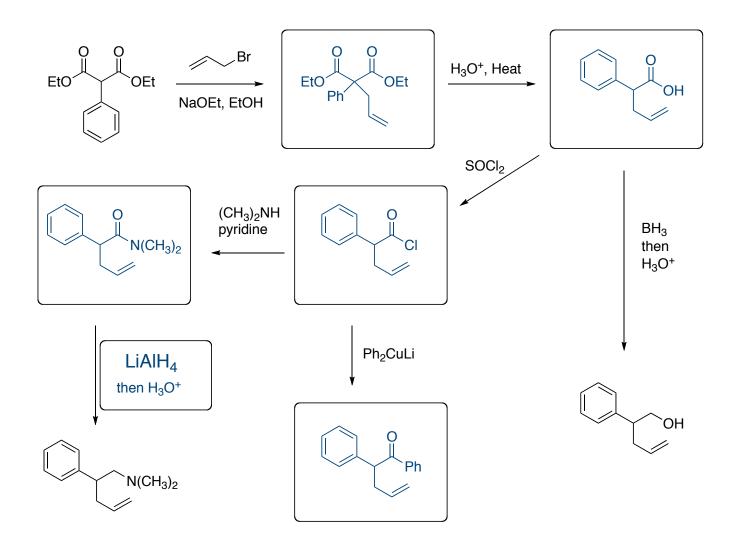
(c)
$$H_3O^+$$
 Heat OH

(d)
$$CH_3NH_2$$
 $NHCH_3$

(f)
$$(CH_3)_2CuLi$$
 CH_3

(g)
$$O$$
 1) LiAlH₄ 2) H₃O⁺ O NH₂

5. Fill in the missing structures and reactants for the following multistep synthesis. (17 pts)



6. Rank the following molecules in order of decreasing reactivity for nucleophilic acyl substitution where 1 is most reactive and 4 is least reactive. (8 pts)

7. The mechanism for the hydrolysis of an acetal is partially shown below (complete structures are circled). This is the reverse of acetal formation. The starting material, products, and an intermediate along the way have been provided. Complete this mechanism by showing all arrows for electron movements and filling out the partially drawn structures. Include any additional acid or conjugate base necessary for the mechanism. (20 pts)

Bonus: In biological systems, NADH acts as a reducing agent to reduce pyruvate to lactate. We did not discuss this in class but it is an important biological reduction reaction. Explain in detail how NADH can react as a source of hydride (H⁻) to reduce the carbonyl group. You may answer on the back of this page. (up to 10 pts)

$$\begin{array}{c} O\\ O\\ CO_2 \\ \hline\\ \text{pyruvate} \end{array}$$