CHEM 51C LEC A (40550)
Midterm 1 (Fall Qtr 2014) - LETTER SIZE
ver. A

Assigned Seat#: 6010 (2586)

Instructions to Instructor:
Do not alter this coversheet in ANY way. Substantial delays and additional fees may apply.

Instructions to Student:
1. Clearly print your Last Name, First Name and the Date
2. Clearly print your Student ID number in the boxes provided. Use large, dark numbers. These numbers are captured automatically during the scanning process.
3. Bubble in each number of your Student ID completely. The bubbles are used only if your written ID number is not captured.
4. Write your Name and Student ID number in the upper right corner of all following pages of your exam.

Last Name, First Name: ___________________________ Date: ______/____/____

STUDENT ID: ___________________________

For Access UCI student, leave first column blank then enter your 7-digit Student ID number.

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<thead>
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</table>

(This space for Instructor/TA use only)

<table>
<thead>
<tr>
<th>Question</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Score</td>
<td>18</td>
<td>25</td>
<td>12</td>
<td>16</td>
<td>12</td>
<td>83</td>
</tr>
</tbody>
</table>

DO NOT OPEN YOUR EXAMS UNTIL INSTRUCTED TO DO SO.
Answer the questions you understand best first.
Your answers must be neat and legible.
1. (22 points)

a. Rank highest to lowest oxidation state

\[ \text{A} \quad \text{B} \quad \text{C} \]

WS 2 #1b

b. Provide pKa's for any 6 of the following compounds (if you do them all, we will count your best 6).

\[
\begin{array}{cccccc}
\text{CH}_4 & \text{H}_3\text{C}-\text{CH}_3 & \text{H}_2\text{C}-\text{OH} & \text{H}_3\text{O}^+ & \text{H}_3\text{C}-\text{COH} & \text{Me}\text{NHMeMe} & \text{H}_2\text{SO}_4 & \text{HCl} \\
50 & 20 & 10 & -2 & 5 & 36 & -10 & -7 \\
45-55 & 18-22 & 14-18 & -4-0 & 3-6 & 32-40 & -11 to & -8 to \ -6 \\
\end{array}
\]

WS 1 #1c

acceptable range

6

6

c. Rank fastest to slowest reaction with LiAlH₄

\[
\begin{array}{ccc}
\text{MeO} & \text{Me} & \text{Me} \\
\text{A} & \text{B} & \text{C} \\
\end{array}
\]

WS 1 #1a

2

2

d. Fill in the correct nucleophile and electrophile from the table to complete the retrosyntheses.

<table>
<thead>
<tr>
<th>Nucleophiles</th>
<th>Electrophiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>A PhLi</td>
<td>E F₃C-OCH₃</td>
</tr>
<tr>
<td>B Ph₂CuLi</td>
<td>F F₃C=CH</td>
</tr>
<tr>
<td>C NaBH₄</td>
<td>G F₃C-COOH</td>
</tr>
<tr>
<td>D LiAlH₄</td>
<td>H F₃C-CNH₂</td>
</tr>
</tbody>
</table>

Products

WS 3 # dii

i. \[
\text{HO} \\
\text{F₃C} \\
\text{C} \\
\text{Me} \\
\text{F₃C-OCH₃} \\
\]

\[ \Rightarrow \text{F} + \text{A} \]

Practice 2a

ii. \[
\text{F₃C} \\
\text{C} \\
\text{NH₂} \\
\]

\[ \Rightarrow \text{D} + \text{H} \]
1. (18 points)

a. Fill in the correct nucleophile and electrophile from the table to complete the retrosyntheses.

<table>
<thead>
<tr>
<th>Nucleophiles</th>
<th>Electrophiles</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Ph₂CuLi</td>
<td>E: F₃C-CONH₂</td>
<td>G + D</td>
</tr>
<tr>
<td>B: NaBH₄</td>
<td>F: F₃C-COCH₃</td>
<td></td>
</tr>
<tr>
<td>C: LiAlH₄</td>
<td>G: F₃C-CO</td>
<td></td>
</tr>
<tr>
<td>D: PhLi</td>
<td>H: F₃C-COOH</td>
<td></td>
</tr>
</tbody>
</table>

b. Rank fastest to slowest reaction with LiAlH₄

\[ \text{MeO} \quad \text{MeO} \quad \text{Me} \]
\[ \text{OMe} \quad \text{H} \quad \text{CH₃} \]

\[ \begin{align*}
2 \quad & \text{B} > 2 \quad \text{C} > 2 \quad \text{A} \\
\end{align*} \]

c. Provide pKa's for any 6 of the following compounds (if you do them all, we will count your best 6).

\[ \begin{array}{cccccccc}
\text{H}_3\text{C-CHOH} & \text{H}_3\text{C-CHO} & \text{H}_3\text{O}^+ & \text{CH}_4 & \text{H}_3\text{C-CH}_3 & \text{H}_2\text{SO}_4 & \text{HCl} & \text{Me-NH-Me-Me} \\
5 & 16 & -2 & 50 & 20 & -10 & -7 & 36 \\
\end{array} \]

max 6

d. Rank highest to lowest oxidation state

\[ \begin{align*}
2 \quad & \text{C} > 2 \quad \text{A} > 2 \quad \text{B} \\
\end{align*} \]
1. (18 points)

a. Rank highest to lowest oxidation state

\[ \text{A} > \text{C} > \text{B} \]

b. Provide pKa's for any 6 of the following compounds (if you do them all, we will count your best 6).

\[ \begin{align*}
5 & \quad 36 & \quad 16 & \quad -2 & \quad -7 & \quad 20 & \quad -10 & \quad 50 \\
\end{align*} \]

c. Rank fastest to slowest reaction with LiAlH₄

\[ \text{B} > \text{A} > \text{C} \]

d. Fill in the correct nucleophile and electrophile from the table to complete the retrosyntheses.

<table>
<thead>
<tr>
<th>Nucleophiles</th>
<th>Electrophiles</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ( \text{Ph}_2\text{CuLi} )</td>
<td>E ( \text{F}_3\text{C} = \text{OCH}_3 )</td>
<td>( \Rightarrow \text{G} + \text{B} )</td>
</tr>
<tr>
<td>B ( \text{PhLi} )</td>
<td>F ( \text{F}_3\text{C} = \text{OH} )</td>
<td>( \Rightarrow \text{H} + \text{C} )</td>
</tr>
<tr>
<td>C ( \text{LiAlH}_4 )</td>
<td>G ( \text{F}_3\text{C} = \text{H} )</td>
<td>1 pt each</td>
</tr>
<tr>
<td>D ( \text{NaBH}_4 )</td>
<td>H ( \text{F}_3\text{C} = \text{NH}_2 )</td>
<td>1 pt each</td>
</tr>
</tbody>
</table>
1. (18 points)

a. Fill in the correct nucleophile and electrophile from the table to complete the retrosyntheses.

<table>
<thead>
<tr>
<th>Nucleophiles</th>
<th>Electrophiles</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>A NaBH₄</td>
<td>E F₃C OCH₃</td>
<td>F + C</td>
</tr>
<tr>
<td>B LiAlH₄</td>
<td>F F₃C H</td>
<td></td>
</tr>
<tr>
<td>C PhLi</td>
<td>G F₃C NH₂</td>
<td></td>
</tr>
<tr>
<td>D Ph₂CuLi</td>
<td>H F₃C COOH</td>
<td></td>
</tr>
</tbody>
</table>

i. \[ \text{OH} \quad \text{F₃C} \quad \text{CH₃} \] \[ \rightarrow \ F + C \]

ii. \[ \text{F₃C} \quad \text{NH₂} \] \[ \rightarrow \ G + B \]

1 pt each

b. Rank fastest to slowest reaction with LiAlH₄

2. A > B > C

c. Provide pKa's for any 6 of the following compounds (if you do them all, we will count your best 6).

\[ \begin{align*}
\text{H}_3\text{O}^+ & 5 \\
\text{H}_3\text{C} & 36 \\
\text{Me} & -10 \\
\text{H}_2\text{SO}_4 & -7 \\
\text{HCl} & 50 \\
\text{CH}_4 & 20 \\
\text{H}_3\text{C} & 16 \\
\end{align*} \]

max 6

d. Rank highest to lowest oxidation state

2. B > C > A
2. (25 points) Fill in the boxes with the appropriate starting material, reagent or major product. Show stereochemistry where appropriate.

What is the relationship between the products?

d. 

What is the relationship between the products?

0 points for the following structure:

0 points for the following structure:
2. (25 points) Fill in the boxes with the appropriate starting material, reagent or major product. Show stereochemistry where appropriate. Initials: ____________

a. 

What is the relationship between the products? ____________

b. 

1. SOCl₂
2. H₂NCH₃ (mild acid)

added to ketone = 0
added to both = 1

c. 

H₃C-PPH₃

(d)(1)

d. 

CH₃I

H₂C-PPH₃

(1)

e. 

H₃C-O-Si(CH₃)₂-Bu

f. 

1. H₃C-MgBr
2. H₂O

1/3

(leg.)(1)
3. Provide an arrow-pushing mechanism (10 points).

a. 

\[ \begin{align*}
\text{Mechanism:} \\
\text{H}_3\text{C} & \text{O} \text{O} \text{C} \text{H}_3 & \text{NaOCH}_3 & \rightarrow & \text{H}_3\text{C} \text{O} \text{O} \text{C} \text{H}_3 \\
\end{align*} \]

b. 

\[ \begin{align*}
\text{Mechanism:} \\
\text{H}_3\text{C} & \text{O} \text{O} \text{C} \text{H}_3 & \text{NaOCH}_3 & \rightarrow & \text{H}_3\text{C} \text{O} \text{O} \text{C} \text{H}_3 \\
\end{align*} \]

Errors: missing θ or θ charge -0.5 points
4. Propose syntheses of the targets below (10 points).
All carbons must come from the starting materials provided, you can use any reagent you wish.
YOU CAN IGNORE STEREOCHEMISTRY.

**Starting Materials:**

<table>
<thead>
<tr>
<th>Starting Materials:</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical Structures" /></td>
</tr>
</tbody>
</table>

**Target A.**

1. \( \text{PPh}_3 \)
2. \( \text{nBuLi} \)
3. \( \text{Me}_2\text{S} \)
4. \( \text{H}_2 \), \( \text{Pd/C} \)

**Target B.**

1. \( \text{LiAIH}_4 \)
2. \( \text{H}_2\text{O} \)
3. \( \text{H}_3\text{O}^+ \)
4. \( \text{Jones} \)
5. \( \text{H}_2\text{SO}_4 \)
6. \( \text{DCC} \)
5. Propose syntheses of the targets below (14 points).
All carbons must come from the starting materials provided, you can use any reagent you wish.
YOU CAN IGNORE STEREOCHEMISTRY.

**Starting Materials:**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>H₂C</td>
<td>OH/CO₃CH₃</td>
<td>H₂C</td>
<td>COOH</td>
<td>H₂C</td>
</tr>
<tr>
<td>Br</td>
<td>CH₃</td>
<td>NaCN</td>
<td>CO₂</td>
<td>CH₃</td>
</tr>
<tr>
<td>H₂C</td>
<td>OH/CO₃CH₃</td>
<td>H₂C</td>
<td>MgBr</td>
<td>Li</td>
</tr>
<tr>
<td>Br</td>
<td>CH₃</td>
<td>Li</td>
<td>Br</td>
<td>Br</td>
</tr>
</tbody>
</table>

**Target A.**

1. **Li (4eq cm)**
2. CuI

**Target B.**

racemic

1. p-Li
2. H₂O

(correct)

2. p-Polar

(note: PhLi also ok)