CHEM 330

Final Exam

December 20, 2011

Your name:		

This a closed-notes, closed-book exam

The use of molecular models is allowed

This exam contains 11 pages

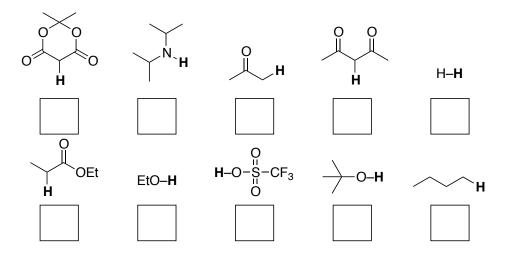
Time: 2h 30 min

- 1. _____/20
- 2. _____/20
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- 4. _____/30
- 5. _____/40
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- 7. _____/40
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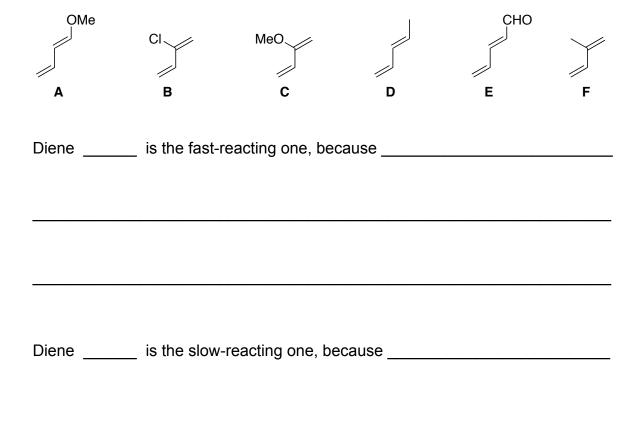
TOTAL
$$/250 = /100$$

This exam counts for 50% of your CHEM 330 final grade

1. (20 pts.) Indicate the approximate pKa for the dissociation of the H in boldface in the substances shown below



2. (20 pts) Indicate which of the following dienes is likely to undergo Diels-Alder reaction with methyl acrylate CH₂=CH–COOCH₃) at the fastest rate and which one is likely to react at the slowest rate, and briefly account for your choice (use the space provided below).



3. (20 pts.) Write a chemical equation to show an example of a reaction involving the use of the reagents listed below (**do not** write mechanisms – just the reactions).

a.
$$-Si-O-S-CF_3$$

c.
$$CH_3$$
- COO NH_4

4. (40 pts) It is found experimentally that organoboranes **A** and **B** below react stereoselectively with, e.g., benzaldehyde, to form products **C** and **D**, respectively:

(i) Write an accurate mechanism for the reaction of **A** and **B** with benzaldehyde and briefly account for the observed diastereoselectivity:

(ii) Provide a rationale for the observation that the reaction of **A** with aldehyde **E** proceeds with good diastereoselectivity to furnish **F** as the major product, but the same reaction with **B** is poorly selective and it yields comparable amounts of products **F** and **G**:

5. (30 pts.) Complete the following diagrams by writing all the missing reagents / products in the appropriate boxes. **Important**: (i) aqueous workups are understood; (ii) compounds must be drawn with the correct configuration.

6. (40 pts.) Predict the structure of the major product expected from the following reactions. Notes: (i) it is not necessary to draw mechanisms; (ii) aqueous workups at appropriate stages are understood.

a.
$$\begin{array}{c} \text{O} & \text{O} \\ \text{O} & \text{O} \\ \text{N} & \text{O} \\ \text{Bn} & \\ \end{array}$$

$$\begin{array}{c} \text{1. LDA} \\ \text{2. CH}_2 = \text{CH-CH}_2 \text{Br} \\ \text{3. DIBAL} \\ \\ \text{4. DMSO} \\ \text{Py•SO}_3, \text{Et}_3 \text{N} \\ \end{array}$$

c.
$$\begin{array}{c} O \\ Ph \end{array} \begin{array}{c} 1. \ \text{Cy}_2\text{BCI} \\ \text{Et}_3\text{N} \\ \hline 2. \quad \text{CHO} \\ \hline \hline \text{OMe} \end{array}$$

f.
$$\begin{array}{c} O & O \\ O & O \\ O & Et_3N \\ 2. \ CH_3-CHO \\ \hline \\ Ph & Et_3N \\ 4. \ LiAlH_4 \\ \end{array}$$

7. (40 pts.) Complete the following equations by indicating all the reagents that are necessary to effect the transformations shown. Provide your answers as a numbered list of reagents, in the correct order, written over/under the reaction arrows.

Note: aqueous workups are understood and need not to be included in your answers.

8. (40 pts.) Propose a method to achieve the enantioselective synthesis of the molecules shown below starting with the suggested building blocks. Be careful about protecting groups and configurations of stereocenters. Assume the availability of all needed reagents, auxiliaries, etc. Present your answer as a **clear** flowchart.

It is not necessary to draw mechanisms or to indicate aqueous workups.