## **CHEM 330**

## **Final Exam** December 19, 2005

Your name:			

This a closed-notes, closed-book exam

The use of molecular models is allowed

## This exam contains 12 pages

Time: 2h 30 min

- 1. \_\_\_\_\_/24
- 2. \_\_\_\_\_/24
- 3. \_\_\_\_\_/ 22
- 4. \_\_\_\_\_/40
- 5. \_\_\_\_\_/40
- 6. \_\_\_\_\_/40
- 7. \_\_\_\_\_/ 50
- 8. \_\_\_\_\_/60

**TOTAL** 
$$/300 = /100$$

This exam counts for 45% of your CHEM 330 final grade

1. (24 pts.) Indicate the approximate pKa's for the ionization of the protons in boldface in the following molecules (write your answer in the box):

	0			
	OEt	H- <b>H</b>	, N.H	EtO- <b>H</b>
approx. pKa =				
	<u>о</u> н	O H	O O O OEt	∕
approx. pKa =				

2. (24 pts) Check the appropriate box to indicate whether the following transformations involve overall oxidation, reduction, or neither, of the starting compound:

a.	OTMS	b. $\bigcirc$
	oxid. redn. neith.	oxid. redn. neith.
C.	$\bigcirc$ OTMS	d. OH
	oxid. redn. neith.	oxid. redn. neith.
е.	OH	f. $\downarrow$ $\rightarrow$ $\downarrow$
	oxid. redn. neith.	oxid. redn. neith.
g.	$\stackrel{O}{\not\downarrow}_{Ph} \longrightarrow \stackrel{O}{\not\downarrow}_{OPh}$	h. $2 \longrightarrow 0$ O O O O O O O O O O O O O O O O O O
	oxid. redn. neith.	oxid. redn. neith.

3. (22 pts.) Write detailed mechanisms for the following known reactions:

a. 
$$\frac{\text{MeOOC}}{\text{Et}_3\text{N}}$$
  $\frac{\text{COOMe}}{\text{CN}}$ 

4.	(40 pts.) Write a chemical equation to show an example of the following reaction encountered in class ( <b>do not</b> write mechanisms – just the reactions):	ns
	Prasad reduction:	
	Cannizzaro reaction:	
	Robinson annulation:	
	Miller silyl enol ether synthesis:	
	wither stryr enor edier synthesis.	

- 5. (40 pts) Check the appropriate box to indicate whether the following statements are true or false.
  - a. The copper atom undergoes reductive elimination in the following reaction:

uuc	iaisc		

$$Me_2CuLi + 2 HBr \longrightarrow 2 Me-H + LiBr + Cu-Br$$

b. The following transformation may be induced by the use of  $Me_2CuLi$ :

c. Treatment of **A** with metallic Na, followed by aqueous workup, will result in formation of **B**:

true	false

COOEt	metallic Na,	<b>6</b> 0
COOEt	then aq. wrkp.	OH
Δ		В

d. The reaction shown below will give compound **C** as the major product:

e. The reaction shown below is a reverse Diels-Alder:

true false

f.	Treatment of <b>D</b> with NaBH(OAc) <sub>3</sub> followed by aqueous
	workup yields E as the major product:

g. Treatment of **F** with catalytic NaOMe will cause isomerization to **G**:

h. The following sequence represents a good method for the preparation of **H**:

i. Substrate and reagent in the reaction shown below are stereochemically mismatched:

j. Compound I shown below is the product of an *endo*-Diels-Alder reaction:

6. (40 pts.) Predict the structure of the major product expected from the following reactions. Note: It is not necessary to draw mechanisms.

b. 
$$\frac{1. \text{ CH}_2 = \text{CHCu}(\text{PBu}_3)_2}{2. \text{ Bu-I, then aq. wrkp.}}$$

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

7. (50 pts.) Indicate a method to accomplish the transformations shown below. In each case, a multistep sequence (= not just one reaction, but several) may be necessary. Assume the availability of all required reagents (e.g, bases, alkyl halides, etc.). Present your answer as a flowchart. Note: It is not necessary to draw mechanisms.

8. (60 pts) Propose a method to achieve the enantioselective synthesis of the molecules shown below. Be careful about protecting groups and relative/absolute configurations of stereocenters. Assume the availability of all required reagents, chiral auxiliaries, etc.