Final Exam Chemistry 345 Professor Gellman 12 May 2009 Last Name // Wes

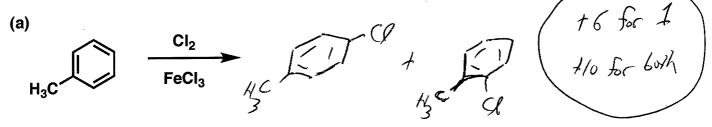
First Name

Ken

**General Instructions:** 

- (i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit.
- (ii) Print your name on each page.

1. (44 points) Show the major product or products expected from each reaction:



(b) 
$$CH_3 \xrightarrow{\text{excess Br}_2 \\ \text{excess NaOH}} H_2O$$

$$CH_3 \xrightarrow{\text{excess NaOH}} H_2O$$

$$O (16)$$

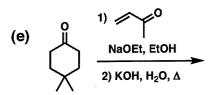
Hint: The product has a strong, broad IR signal at 3100 cm<sup>-1</sup>, which is not seen in the starting material.

(c) 
$$\frac{1) \text{ Mg}^{\circ}, \text{ Et}_{2}\text{O}}{3) \text{ H}_{3}\text{O}^{+}}$$

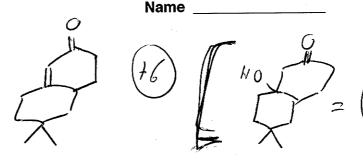
(d)  $\frac{\Delta}{A}$ 

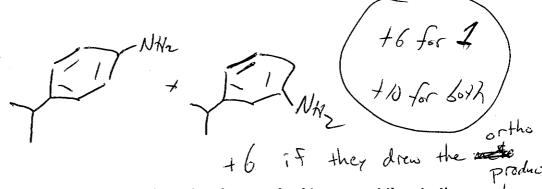
(e)  $\frac{1) \text{ Mg}^{\circ}, \text{ Et}_{2}\text{O}}{46}$ 





Hint: The product has a strong IR signal at 1675 cm<sup>-1</sup>, and no signal ≥ 3200 cm<sup>-1</sup>.



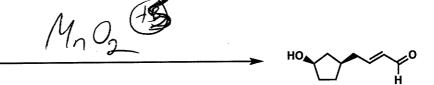


2. (47 points) Show the reagents and other organic molecules required to convert the starting material to the indicated product. Be sure to differentiate clearly between distinct steps, by using "1)", "2)", etc.

(b) 
$$\frac{\text{OH}}{\text{OH}} \frac{\text{OH}}{\text{OH}} \frac{\text{OH}}{\text{OH}} \frac{\text{OH}}{\text{OH}} + \text{HO} \frac{\text{OH}}{\text{OH}} + \text{HO}$$

## 2. (cont.)

(c) HO OH



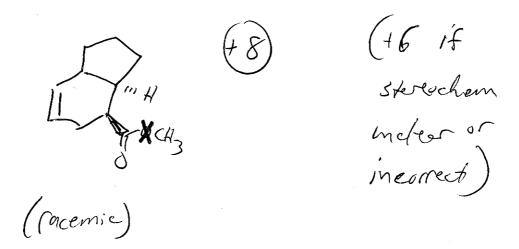
(g) 
$$\sim \frac{C \int_{\mathcal{T}} (43)}{C H_3 C H_3 G / (73)}$$
  $\sim \frac{OCH_2CH_3}{\tilde{c}_1}$  (racemic)

Name
3. (14 points) For each equilibrium shown below, circle the form (left side or right side)
that you expect to be favored in each case. BRIEFLY explain your choice, using structures as necessary to bolster your explanation.
structures as necessary to bolster your explanation.  (a)  HSO <sub>4</sub> -  NH <sub>2</sub> NH <sub>3</sub> +  NH <sub>2</sub> +  NH <sub>3</sub> +  NH <sub>2</sub> +  NH <sub></sub>
[Weaker acid/weaker Lase preferred.] Indicated side has
weaker base because of resonance - N lone poir delocalizes
more fills: Nhs.
$\Leftrightarrow \bigoplus_{\Theta \circ} \leftrightarrow \forall c.$
(b) O- Li+ O- Li+ CN +
Indicated Side has weaker base - more to delocalised
regative charge than for simple envlate:
CEN: CEN: CEN: CEN: CEN: CEN: CEN: CEN:
18. El es l'és propriée one res structu

Name	
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- 4. (8 points) When the molecule shown below is heated, compound X is formed. Propose a structure for compound X based on the observations below.
- -- Compound X is an isomer of the starting material.
- -- The <sup>1</sup>H NMR spectrum of the starting material has seven resonances (all multiplets) above 4.5 ppm, while NMR spectrum of compound X has only two resonances in this region of the NMR spectrum.
- -- Compound X takes up only one equivalent of  $H_2$  upon treatment with  $H_2$  and Pd/C.

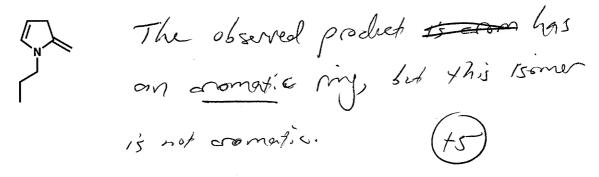
Compound X =



## 5. (25 points)

(a) Draw a mechanism (curved arrows) for the reaction shown below.

(b) Give a brief rationale (one sentence) for the fact that the product indicated above is obtained in preference to the isomer shown below.



Name		
Maille	 	

6. (14 points) Provide structures for molecules A and B, which are intermediates in the conversion of D-galactose (the starting material) to 2,6-dibenzyl-D-galactose (the final product).

HO OH Cat. HCI A Excess NaH

(remove 
$$H_2O$$
 as it forms)

A had two IR signals > 3200 cm<sup>-1</sup>, but B has

Note: A had two IR signals > 3200 cm $^{-1}$ , but B has no signal >3200 cm $^{-1}$ . In the  $^{1}$ H NMR spectrum of A dissolved in CDCl $_{3}$ , two resonances disappear when the sample is shaken with a drop of D $_{2}$ O.

$$A = \begin{cases} 0 & \text{oth} \\ 0 & \text{oth} \\ 0 & \text{oth} \end{cases}$$

7. (15 points) Draw a mechanism (curved arrows) for the reaction shown below. Show resonance forms where appropriate.

+1-for

each

145,

8. (15 points) Peptide X is analyzed as indicated below. What are the structures of peptide X and the two unknown intermediates?

Peptide X 
$$\xrightarrow{\text{CNBr}}$$
  $\xrightarrow{\text{Ph}}$   $\xrightarrow{\text{H}_2\text{N}}$   $\xrightarrow{\text{Ph}}$   $\xrightarrow{\text{Ph}}$   $\xrightarrow{\text{Ph}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{Ph}}$   $\xrightarrow{\text{C}}$ 

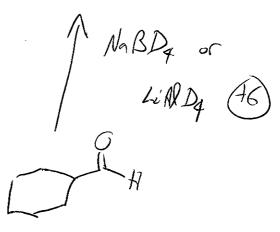
Peptide X =

+2 for no met.

Name	

9. (18 points) Propose a synthesis of each target molecule shown below from the indicated starting material shown. You may use any other reagents.





1/2, poisoned carolyst as for unpoisoned

[Pd + quinoline; not required]

Note: Order of D+H addition can be reversed.

1) Li Alty 2) PCC 3) LiAI Dy 9) H30+ +18