Chemistry 3B Fall, 1992	First Midterm 1 October 1992			ul <b>A</b> . Bartlett
Your Name:				
PLEASE CIRCLE YOUR SECTI	ION NUMBER/NAME OF TA			
101/Matthew Marx	301/Whitney Smith			
102/Bruce Ellsworth	311/Adam Matzger			
111/Jim Krom	312/Drew Thompson			
112/Jason Martin	411/Stephen Mills			
211/Corey Liu	412/Sun Yeoul Lee			
212/Chad Peterson	511/Traci Hopkins			
AT THE BEGINNING:				
This exam has SEVEN pages;  make sure that you have them all.  Please write your answers in the boxes provided.  II We will only grade the answers that are in		I	(20 pts)	
		п	(15 pts)	<u></u>
the boxes; please do your scrato backs of the pages.		Ш	(25 pts)	
bucho of the pages.		IV	(30 pts)	
		V	(20 pts)	
		VI	(40 pts)	
		VII	(50 pts)	

Total (200 pts) \_\_\_\_\_

# I. (20 points)

A. Provide systematic names for the following compounds:

CH<sub>3</sub>-CH-C Cl OCH<sub>3</sub>


ОН

B. Draw the structures that correspond to the following names:

N,N-Dimethylacetamide

Propanoic anhydride	2

## II. (15 points)

Rank the following compounds in order of DECREASING acidity.

A:

B:



MOST ACIDIC

C:

$$\downarrow$$
<sub>OH</sub>

D:

\_\_\_\_\_\_

E;

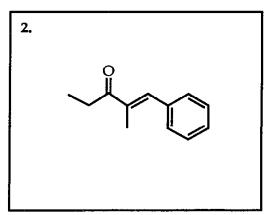
F:

LEAST ACIDIC

III. (25 points)

A. On the following molecules, show how many hydrogens can be exchanged for deuterium in NaOD, D<sub>2</sub>O by drawing in the deuteriums that would be incorporated.

Thujone: a toxic component of absinthe



B. For <u>each</u> type of exchangeable hydrogen in the two compounds, draw the structure of the enolate that accounts for the exchange. (*NOTE:* there may be more than one for each starting material)

### IV. (30 points)

For each of the equilibrium reactions depicted below, predict which side is favored ("left" or "right"), and provide a <u>brief</u> explanation for your choice.

$$+ CH_3OH$$
  $CO_2H$   $+ CH_3OH$   $CO_2CH_3$   $+ H_2O$ 

Favored side:	Why?	
Í		

$$\downarrow_{O}$$
 +  $\downarrow_{O}$  +  $\downarrow_{O}$  +  $\downarrow_{O}$ 

Favored side:	Why?	

Favored side:	Why?		 

#### V. (20 points)

The major component of "Super-Glue" is methyl  $\alpha$ -cyanoacrylate. When it is exposed to air (moisture), this material polymerizes rapidly to give the long chain structure shown.

methyl α-cyanoacrylate

To illustrate how this polymerization can start and propagate, show the mechanism for the reaction of three molecules of methyl  $\alpha$ -cyanoacrylate to give the trimer illustrated below. For the purpose of the problem, assume there is a catalytic amount of  $\neg OH$ .

3 
$$CH_2 = C$$
 $+ H_2O$ 
 $\xrightarrow{\text{catalytic OH}^-}$ 
 $+ H_2O$ 
 $\xrightarrow{\text{CO}_2CH_3}$ 
 $+ H_2O$ 
 $\xrightarrow{\text{CO}_2CH_3}$ 
 $+ H_2O$ 
 $+ H$ 

### VI. (40 points)

Dicumarol (illustrated below) is an anticoagulant used in the treatment of heart disease and (in relatively higher doses....) in rat poison. The synthesis of dicumarol starts with methyl acetyl salicylate and a strong base. Write a step-by-step mechanism for this Claisen-like condensation.

$$\begin{array}{c} \text{Strong} \\ \text{CH}_3 \text{O} \end{array} \qquad \begin{array}{c} \text{strong} \\ \text{base} \end{array} \qquad \begin{array}{c} \text{+ CH}_3 \text{OH} \\ \text{O}_- \end{array}$$

The product of the above reaction adds to formaldehyde in 2:1 stoichiometry to give dicumarol. Write a step-by-step mechanism for this aldol condensation and Michael addition.

2 
$$\longleftrightarrow$$
 +  $CH_2=0$   $\longleftrightarrow$  HO OH Dicumarol

HINT:  $\longleftrightarrow$  is an intermediate

VII. (50 points)

Show how to synthesize the following compounds from the indicated starting materials.

,  $\mathrm{CH_3I}$ , and any acidic or basic reagents

HINT: begin by analyzing which carbons in the product come from each of the starting materials

and any reagents with one carbon or less