Email: $\qquad$
The exam must be written in ink. No calculators of any sort allowed.
You have 2 hours to complete the exam.

## CHEM 610B

Exam 3
Spring 2002
Instructor: Dr. Brian Pagenkopf

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| Periodic table | 4 | 9 |
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|  | 10 | 4 |
|  | 11 | 9 |
|  | 12 | 4 |
|  | 13 | 4 |
|  | 14 | 6 |
|  |  | 100 |

(7 points). Miscellaneous. Show the products expected to be isolated from each of the following reactions.
a)


1. $\mathrm{Cl}_{2}, \mathrm{KOH}$ in water/dioxane
2. $\mathrm{HCl}, \mathrm{H}_{2} \mathrm{O}$
b)

c) At temperatures lower than required for a Claisen reaction, one product would be expected to form under the following reaction conditions. (It's NOT the Claisen product).


(7 points). NMR.

a) Assume complete deuterium exchange and draw the structure of $\mathbf{B}$.
b) How many signals would you expect to see in the ${ }^{1} \mathrm{H}$ NMR for $\mathbf{A}$ ?

c) After complete deuterium exchange, how many signals would you expect to see in the ${ }^{1} \mathrm{H}$ NMR of $\mathbf{B}$ ?

( 9 points). Aldol Reactions. Show the products from the following aldol condensations. For each question where more than one product is possible, show all possible aldol condensation products even if expected to be minor. In each question show the $\beta$-hydroxy aldehyde(s) or $\beta$-hydroxy ketone(s). Do not eliminate or dehydrate to the $\alpha, \beta$-unsaturated product. Do not show stereochemistry.
a)

cat. NaOEt
b)

(6 points) Aldol Reactions. The following molecule was one of several different structures isolated from an aldol condensation reaction. What were the starting materials?

(2 points). How many different aldol condensation products (as $\beta$-hydroxy aldehydes) are possible from the following mix of aldehydes, even if expected to be a minor product? Put your answer (a whole number) in the box.






(24 points). Aldol reactions. Show all the possible aldol products (as $\beta$-hydroxy carbonyl compounds) from the following reaction mixture:


Dehydrate the above products and show the corresponding $\alpha, \beta$-unsaturated compounds. (There's additional space on the next page).

No question this page.

*Lanthanide series

| 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| 140.12 | 0.907 | 144.24 | (145) | 150.4 | 151.96 | 157.25 | 8.92 | 162.50 | 64.9304 | 167.26 | 168.9342 | 173.04 | 174.967 |


(3 points). Claisen and Diekmann Reactions. Draw the major products(s) expected from the following reaction.

a) NaOEt
b) $\mathrm{H}_{2} \mathrm{O}, \mathrm{HCl}$ (work-up)
(16 points). Claisen and Diekmann Reactions. Draw the four major products(s) expected from the following reaction.
C

a) NaOEt
$\longrightarrow$
b) $\mathrm{H}_{2} \mathrm{O}, \mathrm{HCl}$ (work-up)
(4 points). Claisen and Diekmann Reactions. Draw both products expected from the following Diekmann reaction.

( 9 points). The following Stork enamine synthesis was used to make compound $\mathbf{E}$. Show the structure of $\mathbf{C}$, the salt $\mathbf{D}$ and product $\mathbf{E}$.

(4 points). The product $\mathbf{E}$ on the preceding page can also be prepared by the acetoacetic ester synthesis. Show all the reagents and steps necessary for its synthesis.
(4 points). Show how to synthesize the following compounds using either the malonic ester synthesis or the acetoacetic ester synthesis by providing the necessary reagents and conditions. Show all required steps.

(6 points). Synthesis. Propose a synthesis of the following compound using any reagents you like with the only restriction that they can only add four carbons or less to the target molecule.


