$\qquad$

Provide the missing product(s), starting material(s), or reaction conditions for the following transformations. Include stereochemistry when it is known, and otherwise follow the directions.



Question II (32 points)
Name: $\qquad$
A. Provide all of the organic (carbon-containing) products for the following four reactions, which all derive from the same starting material. Include stereochemical outcomes.

B. Upon standing, a certain compound reacts with itself (dimerizes) to produce the following product along with two equivalents of ethanol. What is the structure of the starting compound? Note: the equation is balanced; include stereochemistry.

C. Provide the reaction conditions for the following transformations. If an answer involves a sequence of experimental steps, they need to be correctly numbered.

$$
\text { also } \mathrm{OK}: \begin{array}{ll}
\text { 1) } \mathrm{H}_{2} \mathrm{SO}_{4} & \text { 1) } \mathrm{H}_{2} \mathrm{O}, \mathrm{H}_{2} \mathrm{SO}_{4} \\
\text { 2) } \mathrm{H}_{3} \mathrm{O}^{+} & \text {2) } \mathrm{H}_{3} \mathrm{O}^{+} \\
\text {3) "heat" or show " } \Delta \text { " }
\end{array}
$$



also OK: $\mathrm{LiAlH}_{4}$ alone of the next product is the double alkoxide!

$$
\begin{aligned}
& \text { no partial } \\
& \quad \mathrm{H}_{2} \mathrm{O}, \mathrm{H}_{2} \mathrm{SO}_{4}
\end{aligned}
$$

(may say "heat"

$$
\xrightarrow{\text { or show " } \Delta \text { ") }}
$$

OR: 1) $\mathrm{NaOH} / \mathrm{H}_{2} \mathrm{O}$
2) $\mathrm{H}_{3} \mathrm{O}^{+}, \Delta$
cannot be keto alcohol UNLESS it is deliberaely made in the previous step: make
mixture of stereoisomers 1 excess the ketal, hydrolyze and reduce ester (or just (draw connectivity only)
 4

## Question III (20 points)

Name: $\qquad$
Compound A reacts with benzaldehyde under three different reversible (weak) organic base conditions, each reaction resulting in a different experimental outcome (Org Lett, 2011, 13, 5282).
(a) In the first case, compound A was treated in an aqueous solution with a catalytic amount of the base called DABCO. Under these conditions, an aldol addition reaction outcome with a mixture of four stereoisomers was observed. Draw the connectivity of the product.

(b) In the second case, compound A was treated in an aqueous solution with a catalytic amount of triethylamine (TEA). Under these conditions, an aldol condensation outcome with a mixture of two stereoisomers was observed. Draw one of the stereoisomeric condensation products.

(c) In the third case, compound A was treated in an aqueous solution with a catalytic amount of DBU. Under these conditions, a reaction product known as the Baylis-Hillman outcome was observed. Draw the connectivity of the intermediates in this reaction, as described in words, below.

$\qquad$
(a) There are a number of different methods for preparing anhydrides. Based on the information provided here, what are the structures of the two starting materials in this case?

(b) When the anhydride is treated with pyridine, a cyclic ester (lactone) forms. In the first part of the mechanism, an acyl pyridinium intermediate is formed. Show the curved arrow mechanism for its formation and draw the acyl pyridinium intermediate in the space designated for it. Then, complete the mechanism, which is still under weak base conditions. You may used $\mathrm{H}-\mathrm{B}$ or $\mathrm{B}: \ominus$ for any general Brønsted acid or base you need as you complete the mechanism.

$\qquad$

Provide the missing product(s), starting material(s), or reaction conditions for the following transformations. Include stereochemistry when it is known, and otherwise follow the directions.
(a) / Org Chem, 2000, 65, 7231
no partial

1) LiH (1 equiv.)
2) $\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right]_{2} \mathrm{NLi}$ (1 equiv. LDA)

3) $\mathrm{H}_{3} \mathrm{O}^{\oplus}$


4
(b)


key feature = conj addn
$=2 \mathrm{pts}$
if OK, then getting remaining structure correct $=2$
(2)
4) acidic workup
(c)


1) excess

2) (low temperature)
key feature $=$ new ketone $=2$ pts
if OK , then getting remaining
 structure correct $=2$
3) $\mathrm{H}_{3} \mathrm{O}^{\oplus}$ workup
(d)




| a |  |  |
| :---: | :---: | :---: |
| b |  | $/ 04$ |
| c |  | $/ 04$ |
| c | $:$ | $/ 04$ |
| d | $:$ | $/ 06$ |
|  |  |  |
|  |  |  |

