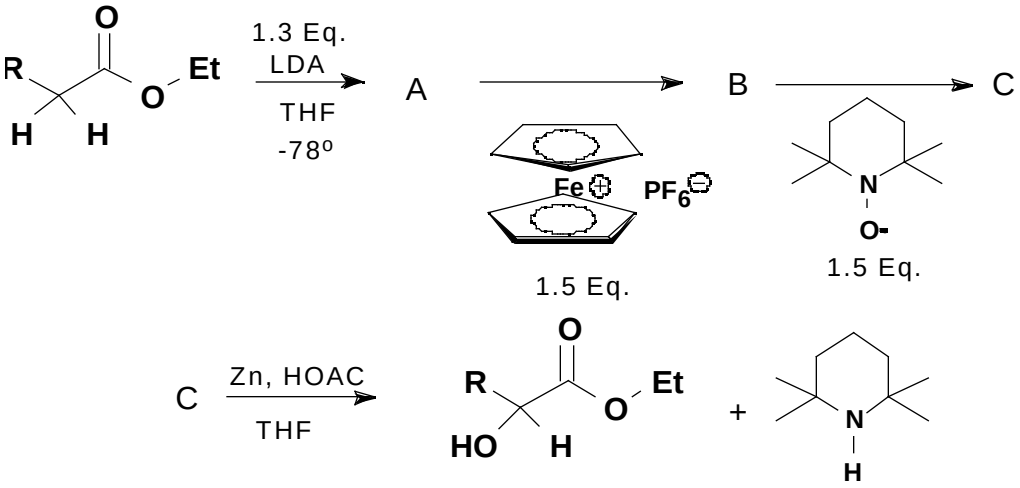
ORGANIC CUMULATIVE EXAMINATION
December 5, 1998

Name_____

1. (JOC ***63*** #21, 7130-7131) Jahn reports the following procedure for introducing a hydroxy group at the α-position of an ester.



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(15) Give the structures of each intermediate A-C along with appropriate (but brief) rationale for your choice. (A and B are not isolated).

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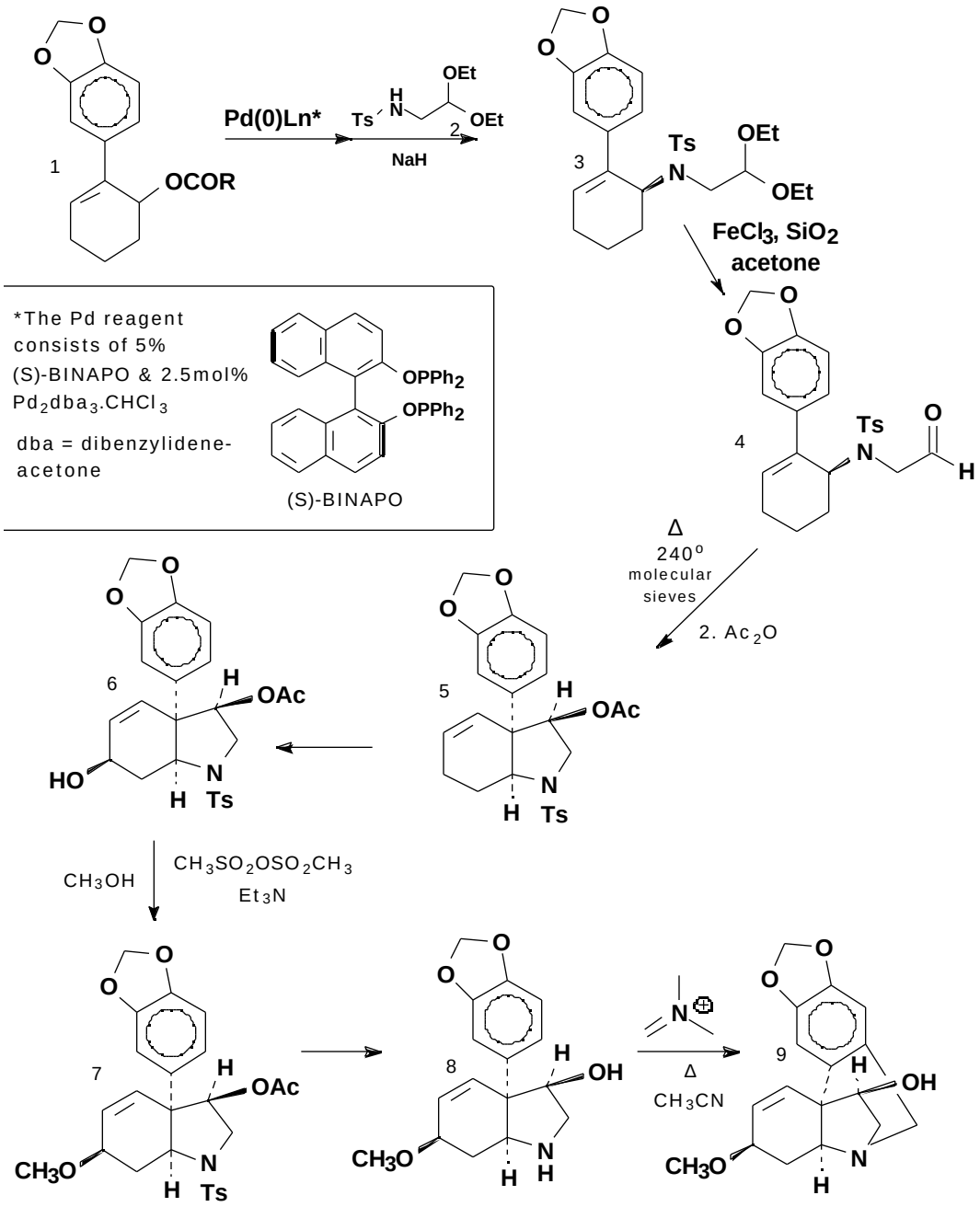
2. Nishimata and Mori (JOC ***63*** # 22, 7586-7587) report an asymmetric synthesis of several ***Amaryllidaceae*** alkaloids. The synthetic strategy contains several interesting transformations. The synthesis of (+) crinamine **9** (Scheme 1) is achieved in 20% yield and is identical to the natural product in all respects.

Notes: Compound **3** is obtained in 59% yield and 74% ee. Upon recrystalization of this material, the racemate crystallized out and the mother liquor contained (-) **3** in 99% ee which was used in the succeeding synthetic steps.

Scheme 1



Answer the following questions.

A. (5) There are other leaving groups and procedures to accomplish the transformation **1 + 2** → **3**.

(1) Mechanistically what is the purpose of the Pd reagent?

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(1) (5) What is the function of (***S***)-BINAPO?

(3) (5) Show the specific reaction involving NaH and explain why it is used.

B. (15) Using arrows, give a plausible mechanistic rationale for the thermal rearrangement which converts **4** → **5**.

C. (12) Describe in some detail an experimental method or methods for determining the relative stereochemistry of the ring fusion and the acetate in **5.**

D. (6) Give a reagent or a set of reagents which could be used to convert **5** to **6.**

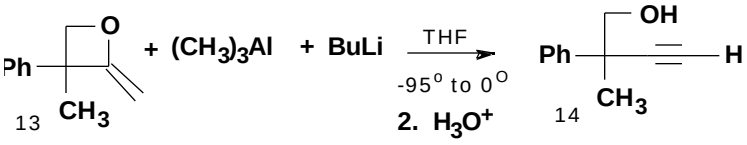
E. (6) Give a reagent or reagents which could be used to remove the protecting tosylate (Ts) and acetate groups (**7** → **8**).

F. (12) Give a mechanism for the cyclization **8** → **9**.

3. (7) In a communication (Collman et al., JOC ***63*** # 23 8084) describe a “biomimetic synthesis” of a heme models. What does the term biomimetic synthesis mean?

4. Dollinger and Howell (JOC ***63*** #20, 6782) describe the transformation shown in Scheme 2 as a superior method for the synthesis of homopropargylic alcohols.

Scheme 2



(12) Give a plausible mechanism for this reaction.