Chem 112B Midterm 3

Instructor: Richmond Sarpong

April 27th 2017

8:10–9:30 am, 100 Lewis

You have **80 minutes** to complete this exam. Please write your answers clearly only on the pages indicated _and be as detailed as possible_. Nothing written outside the numbered pages will be graded. There should be 9 total pages in this exam.
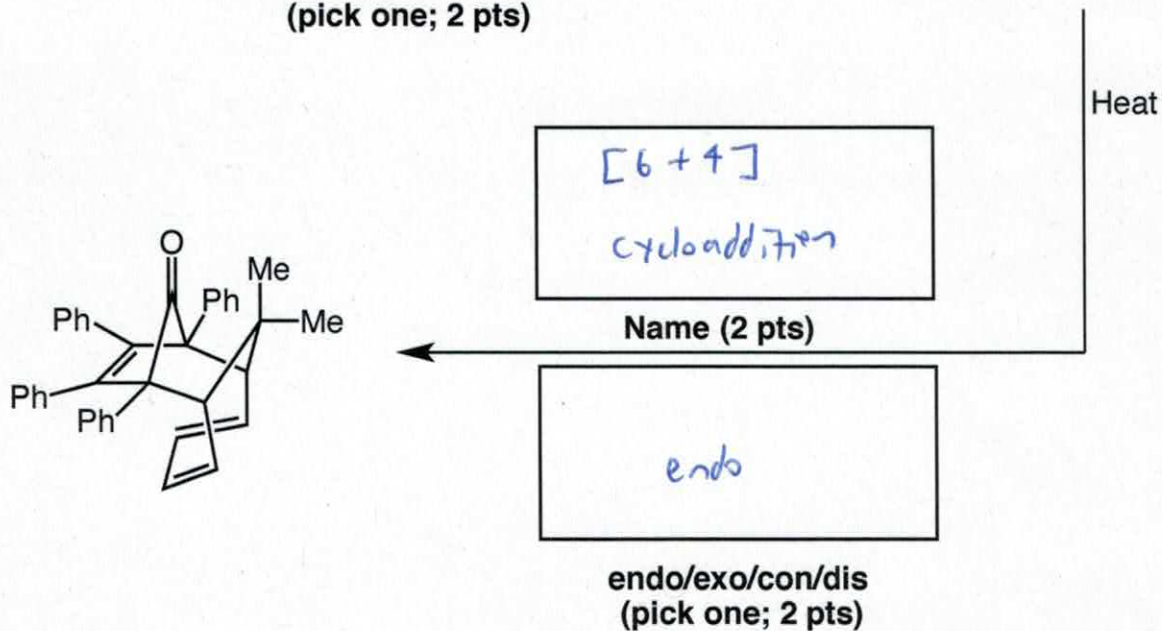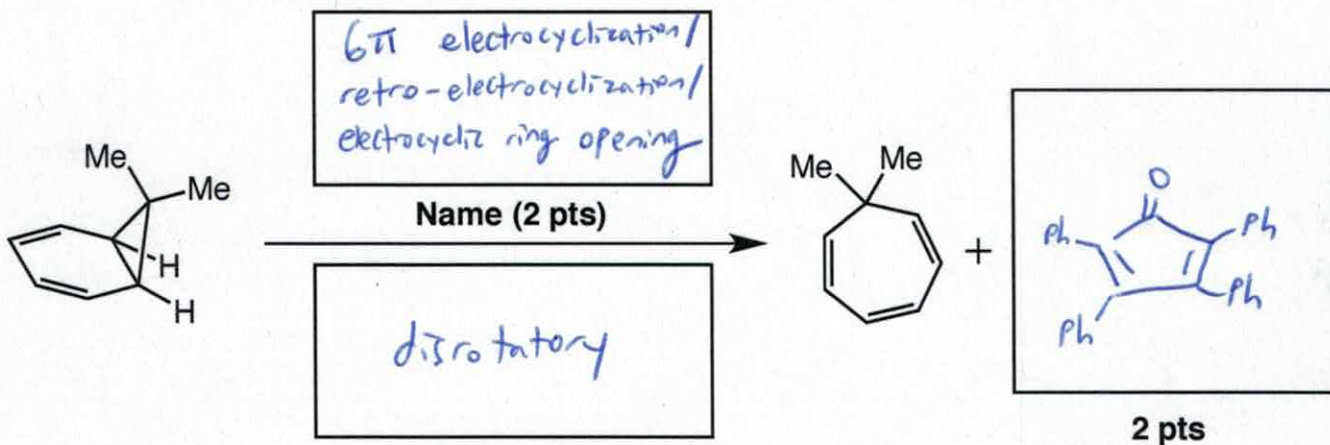
Name:_____KEY_____

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GSI Name:_____

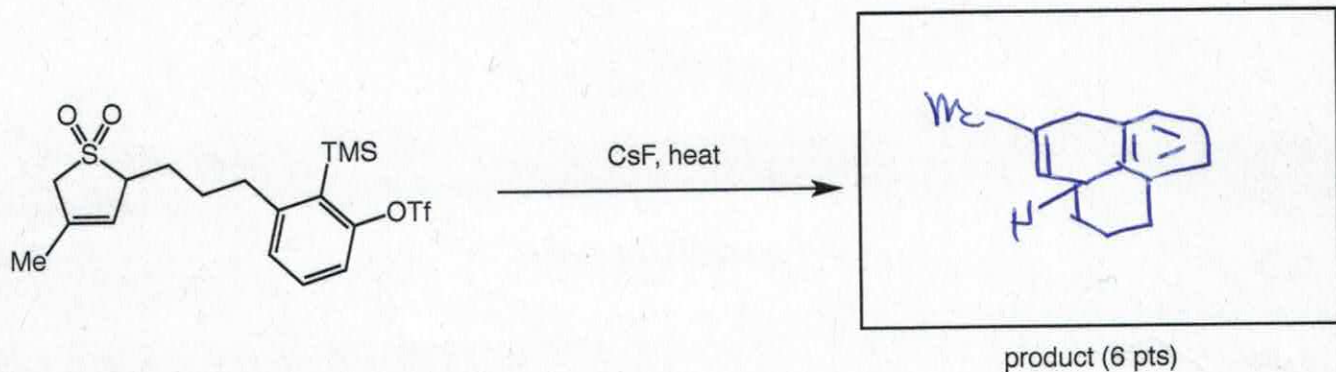| Question	Score
1	_____ (10 points)
2	_____ (12 points)
3	_____ (15 points)
4	_____ (15 points)
5	_____ (16 points)
6	_____ (14 points)
7	_____ (18 points)
Total	_____(100)

Question 1 (10 points):
Fill in the following boxes for the sequence of pericyclic processes that involve only the addition of heat. Be specific with the number of electrons (e.g., [m+n], [x,y], nπ) involved in each process

6π electrocyclization/
retro-electrocyclization/
electrocycliz ring opening

Name (2 pts)

disrotatory

**endo/exo/con/dis
(pick one; 2 pts)**

2 pts

Heat

[6 + 4]

cycloaddition

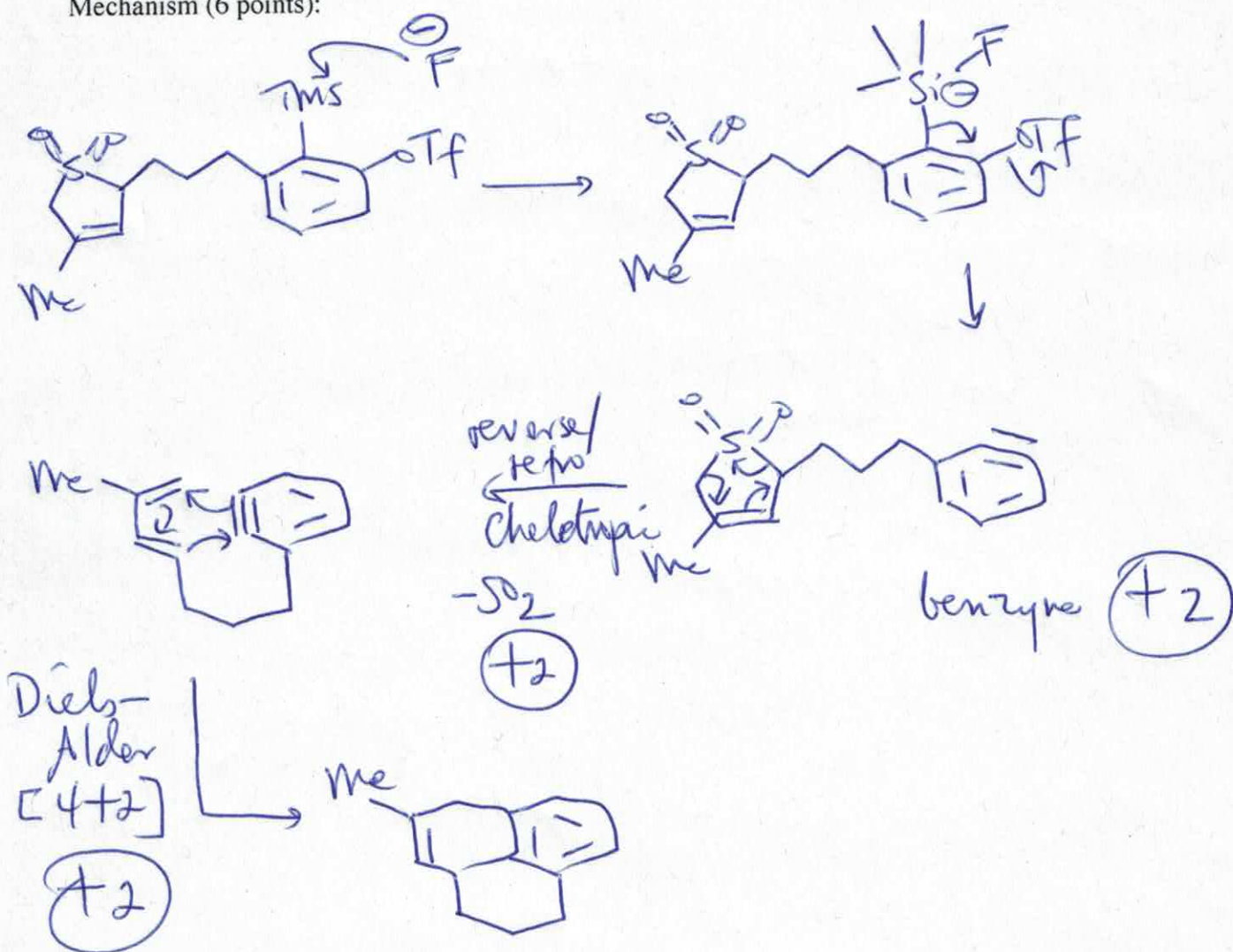**Name (2 pts)**

endo

**endo/exo/con/dis
(pick one; 2 pts)**

2

Question 2 (12 points):

Predict the product of the following reaction and show the mechanism for its formation knowing that it involves a cheletropic reaction. Indicate the cheletropic step in your mechanism and also show byproducts.
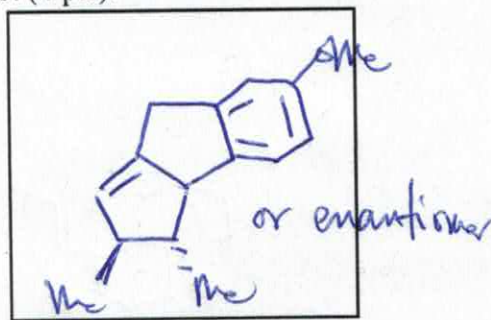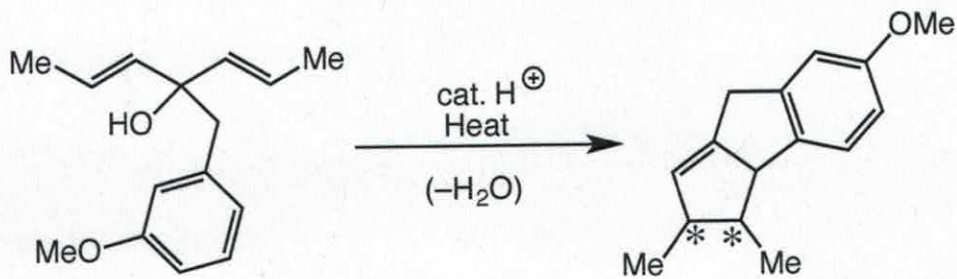

product (6 pts)

Mechanism (6 points):
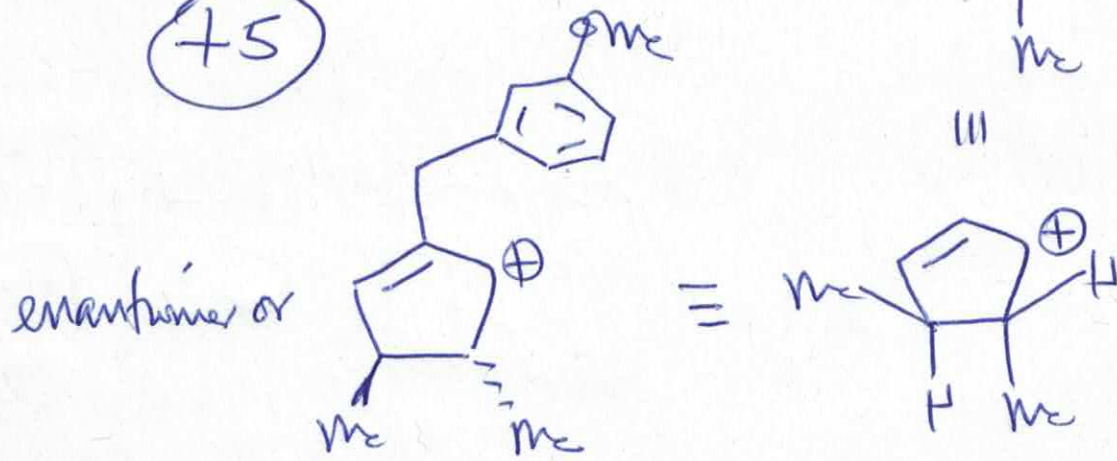
Question 3 (15 points):
(a) Redraw the product shown below, indicating the stereochemistry at the asterisked positions for one enantiomer. This is a Nazarov cyclization/Friedel-Crafts alkylation sequence. (4 pts).

product with stereochem.
(4 pts)

(b) Provide a rationalization for the stereochemistry you indicated in Part (a) using a drawing of the molecular orbital involved and up to 3 additional figures and 3 sentences (11 pts).
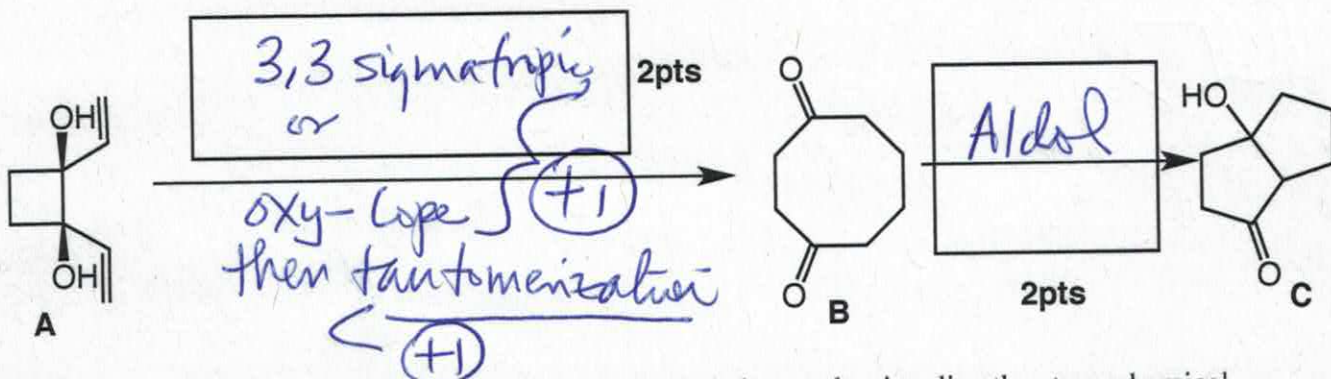

Con rotatory
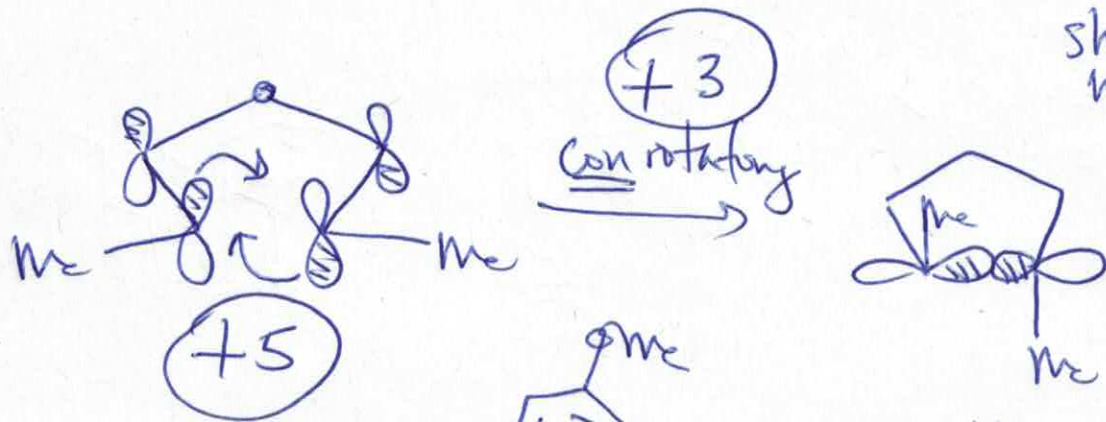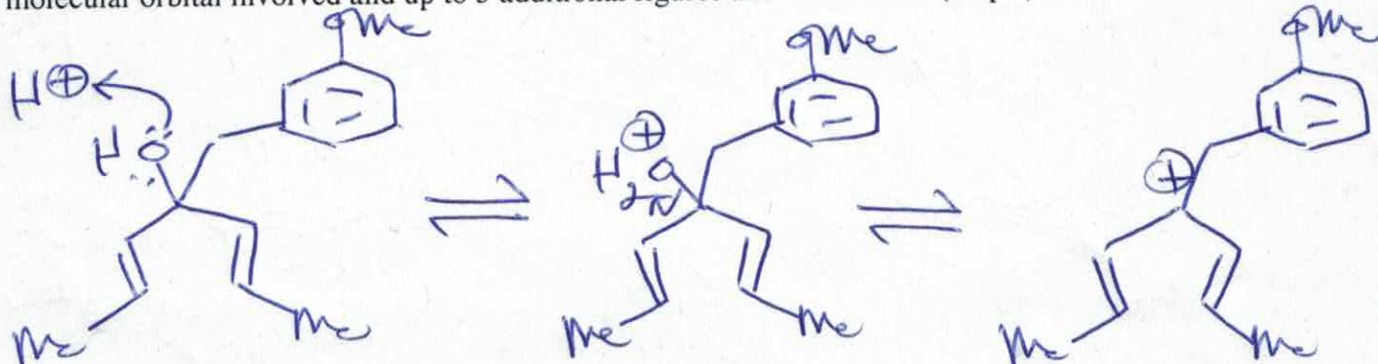
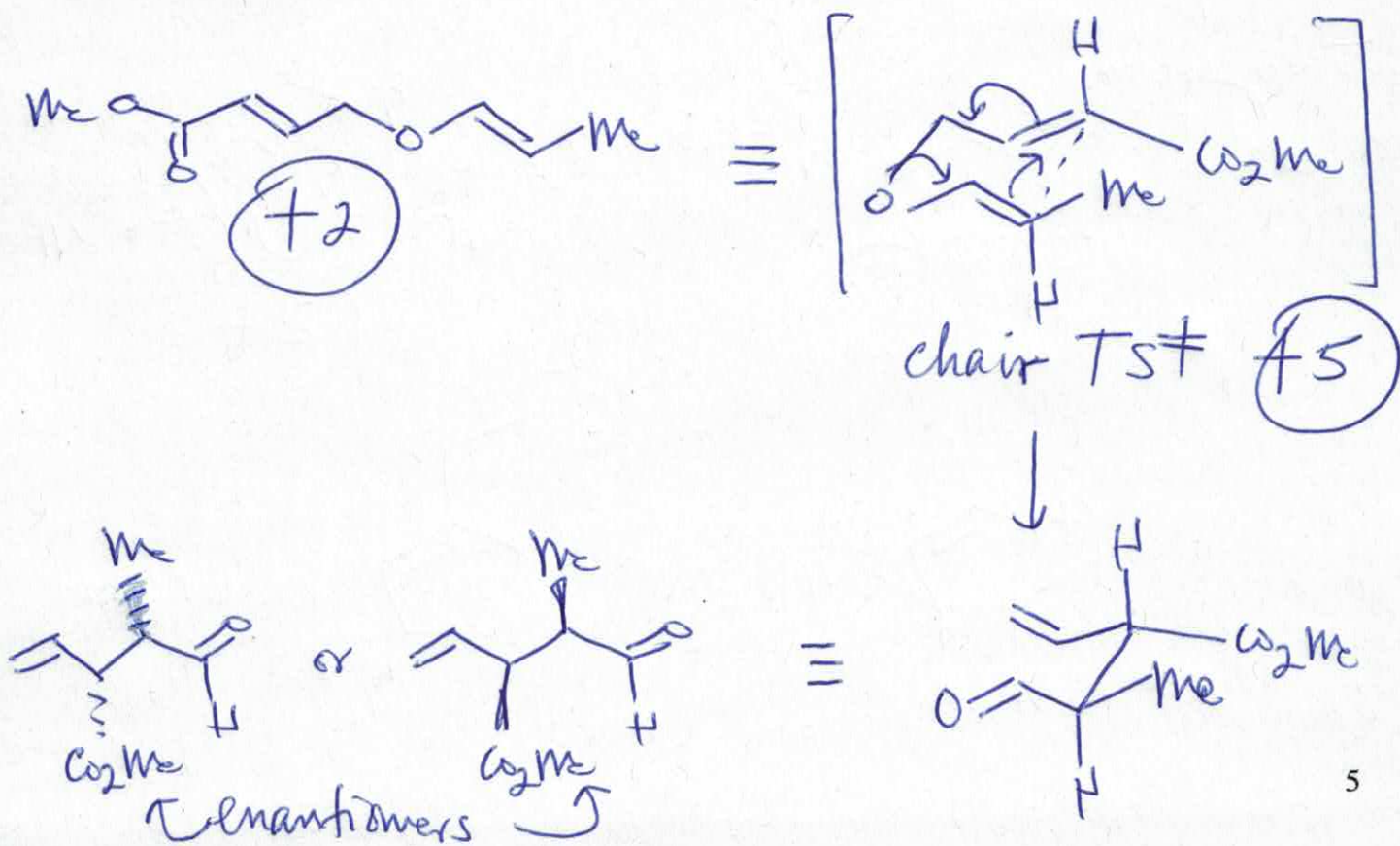only need to show this intermediate
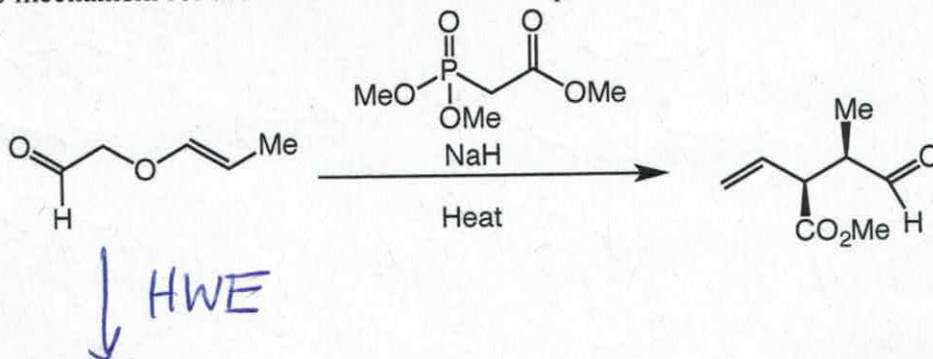
+3

enantiomer or

4

Question 4 (15 Points):

(a) Provide the **names** associated with the two transformations that convert **A** to **B** (upon heating) and then **B** to **C** in the boxes provided below (4 pts).

3,3 sigmatropic
or
oxy-Cope (+1)
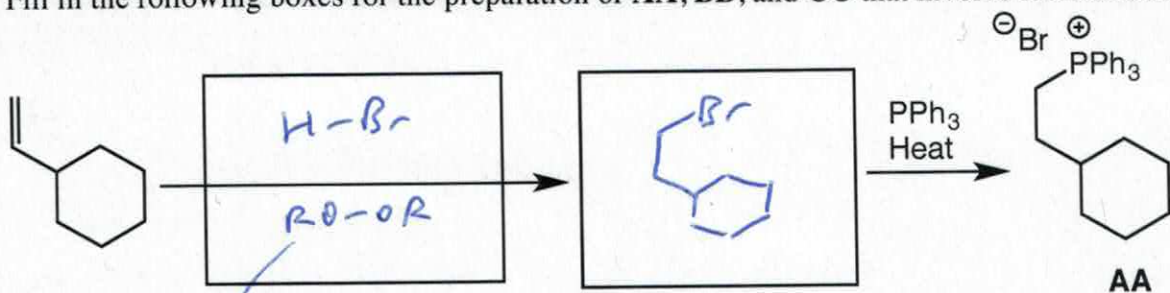then tautomerization
(+1)

2pts

Aldol

2pts

A

B

C

(b) Provide a mechanism for the transformation shown below and rationalize the stereochemical outcome given that the transformation involves a Horner-Wadsworth-Emmons (HWE) reaction (11 pts) (don't show the mechanism for the formation of the HWE product)
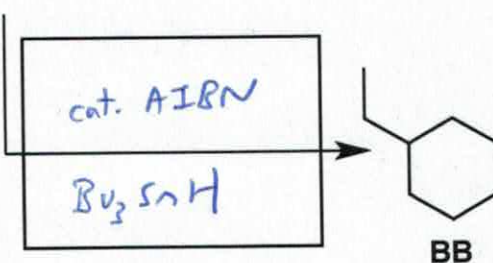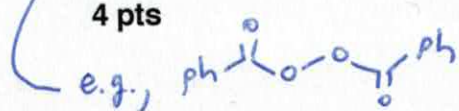
$$MeO-P(=O)(OMe)-CH_2-C(=O)-OMe$$

NaH

Heat

Me

CO_2Me H

HWE

(+2)

=

chair TS‡ (+5)

Me

CO_2Me

or

Me

CO_2Me

enantiomers

=

CO_2Me

Me

5

Question 5 (16 points):
Fill in the following boxes for the preparation of **AA**, **BB**, and **CC** that involve radical reactions.

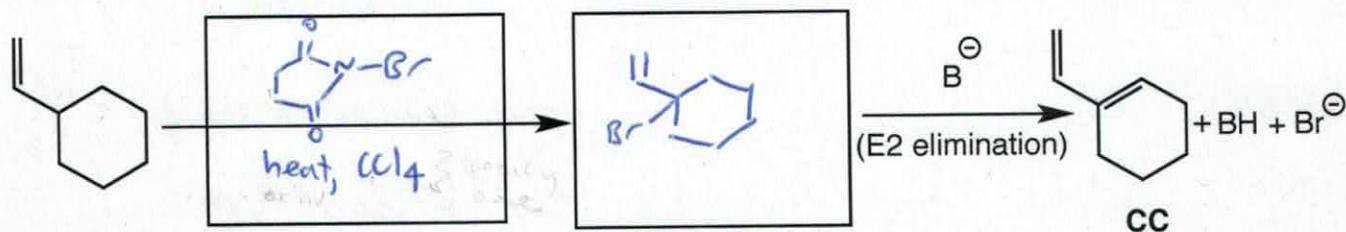Box 1 (4 pts): H—Br, RO—OR, e.g., Ph(C=O)O—O(C=O)Ph

Box 2 (2 pts): [bromide structure]

PPh₃, Heat → **AA** (Br^{-}, PPh_3^{+} structure)

Box 3 (4 pts): cat. AIBN, Bu₃SnH → **BB**

Box 4 (4 pts): N-bromosuccinimide, heat, CCl₄

for just "NBS" (2 pts)

Box 5 (2 pts): [bromocyclohexane structure]

B^{-} (E2 elimination) → **CC** + BH + Br^{-}

Question 6 (14 pts)

(a) Circle the diene that is likely to react fastest with the dienophile that is shown below (2 pts).

Me —— OMe   Me —— OMe (circled)
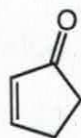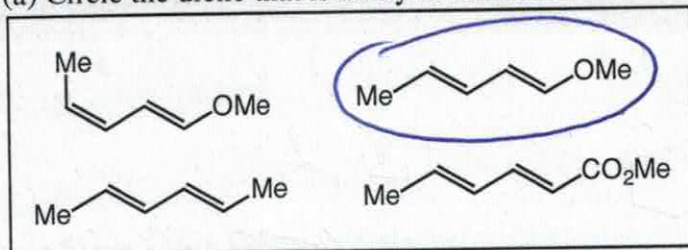
Me —— Me   Me —— CO₂Me   dienophile

(b) Using no more than 4 figures and 4 sentences, provide a rationalization for your answer to Part (a) (4 pts)

+2

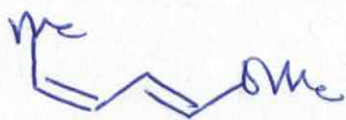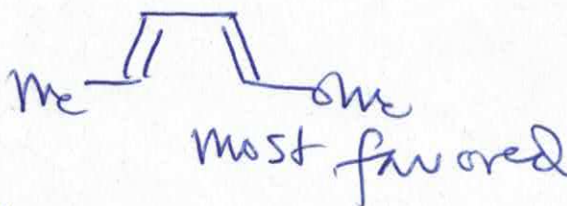Me $\diagdown$ CO₂Me   electron-poor; least reactive

Me $\diagdown$ Me   electron neutral

+2

Me $\diagdown$ OMe   Me $\diagdown$ OMe

S-cis form
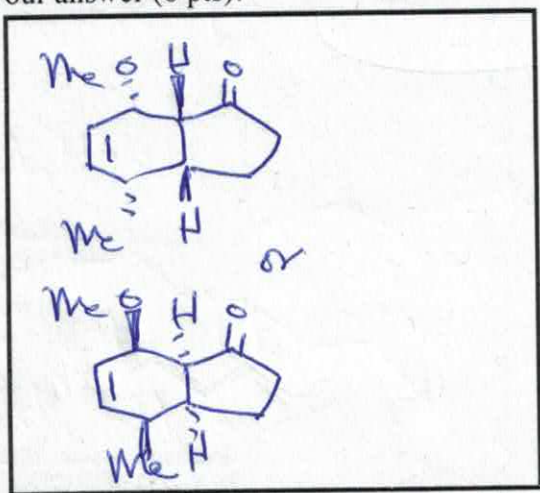
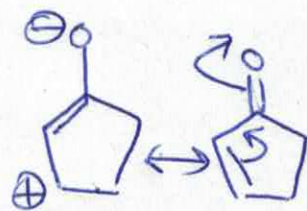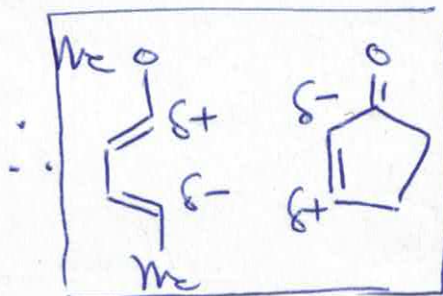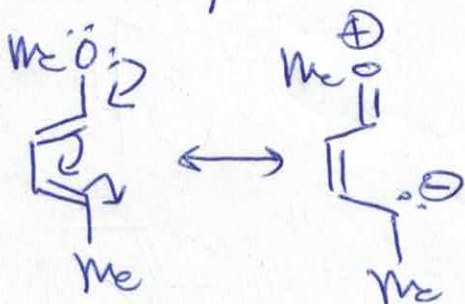Me $\diagdown$ OMe   sterics unfavorable   Me $\diagdown$ OMe   most favored

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(c) Show the kinetic product that is formed in Part 6(a) in the box below (2pts). Using no more than 4 sentences and 4 figures, provide a rationalization for the stereochemical and regiochemical outcome of your answer (6 pts).
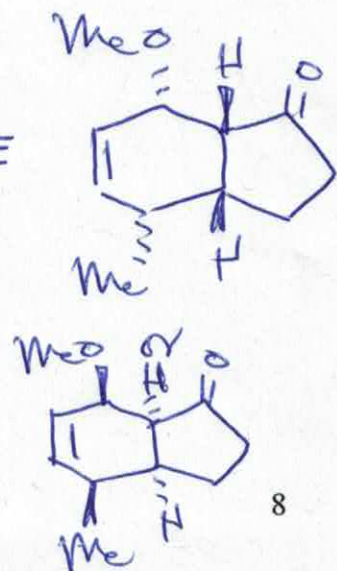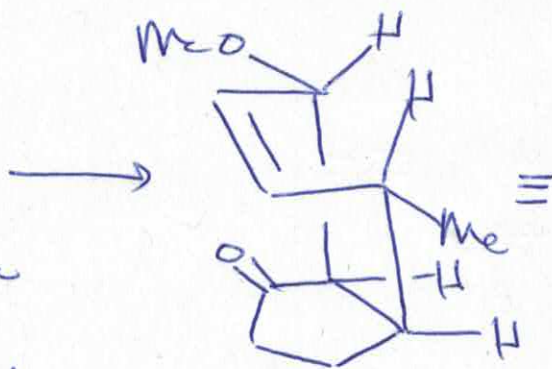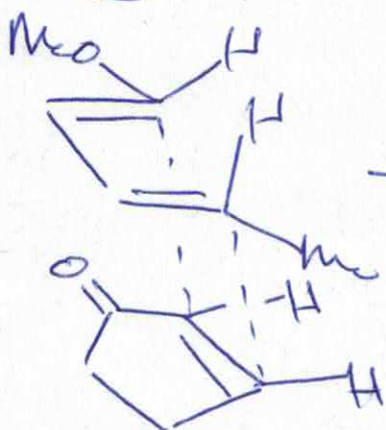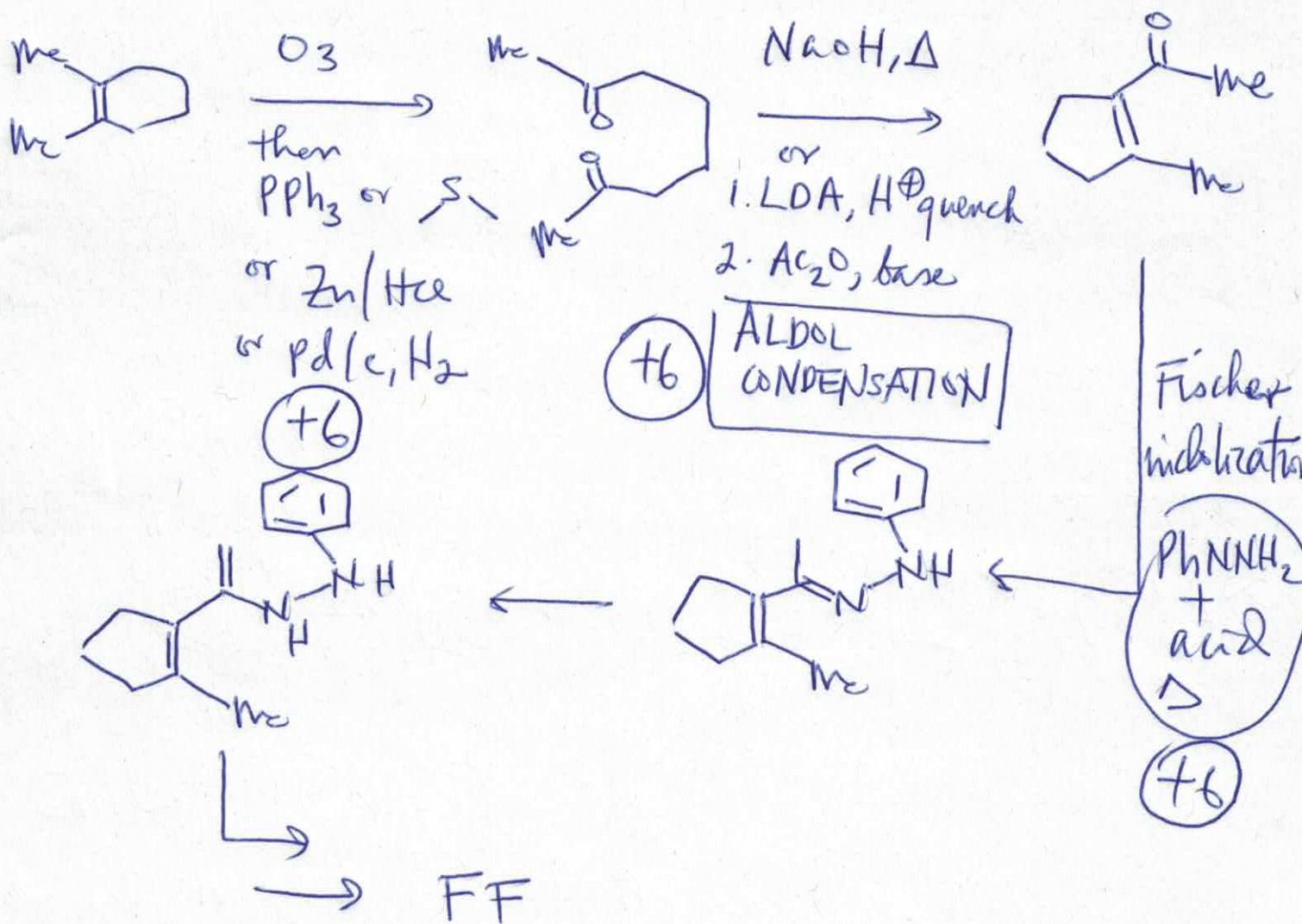

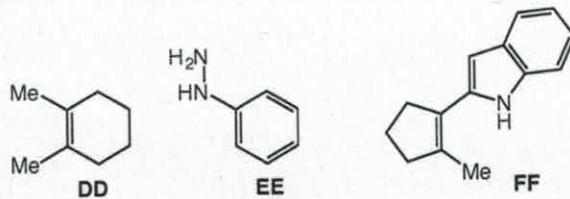product with stereochem.
(2 pts)

Regiochemistry: (+2)

Endo (+4)

8

Question 7 (18 points):
Provide a synthesis of **FF** given **DD** and **EE** as starting materials. (Hint: a Fischer indolization is involved).

Me—⟨ ⟩ (DD)   H₂N HN—⟨ ⟩ (EE)   ⟨indole with Me⟩ (FF)

Me,Me-cyclohexene →O₃, then PPh₃ or S, or Zn/HCl or Pd(c,H₂) **(+6)** → Me,Me-diketone →NaOH,Δ or 1. LDA, H⊕ quench 2. Ac₂O, base **(+6)** [ALDOL CONDENSATION] → cyclopentene-C(=O)-Me

(+6) hydrazone-NH product →Fischer indolization → imine-NH intermediate ← PhNNH₂ + acid Δ **(+6)**

→ FF

The End

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