KEY

Chemistry 112B: Midterm 2, Thursday March 1, 2012

Name: _____.

UCSID: _____ *GSI:*_____

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Question 1 _____ (10 points)

Question 2 _____ (15 points)

Question 3 _____ (25 points)

Question 4 _____ (25 points)

Question 5 _____ (24 points)

Question 6 _____ (10 points)

Question 7 _____ (30 points)

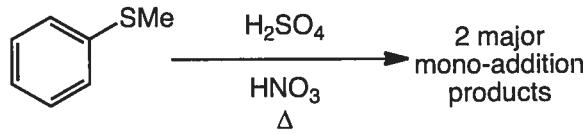
Question 8 _____ (36 points)

Total _____/175 points

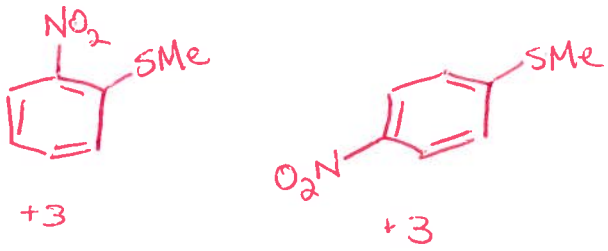
Question 1

Predict the *major* products of the following reactions.

(a)

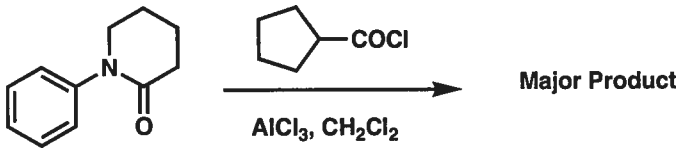


(6 points)

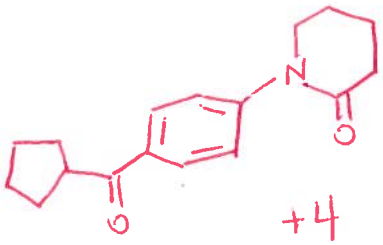


ortho/para director

(b)



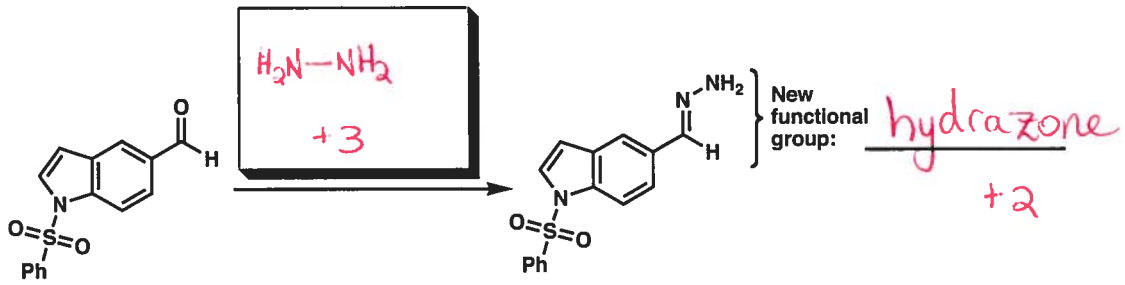
(4 points)



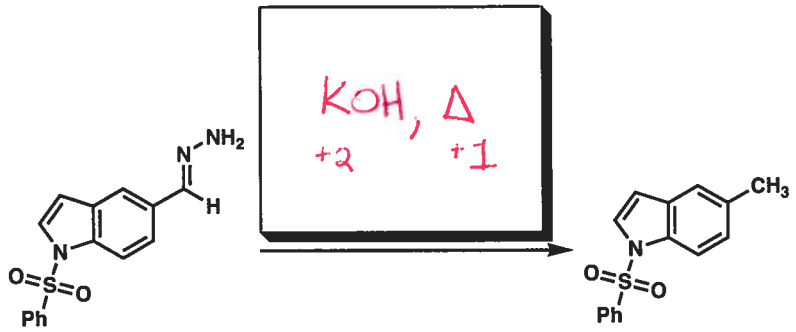
ortho/para director, para = major product due to sterics

Question 2

(a) Propose reagents and reaction conditions for the following transformation, and a name for the functional group in the product. (5 points)



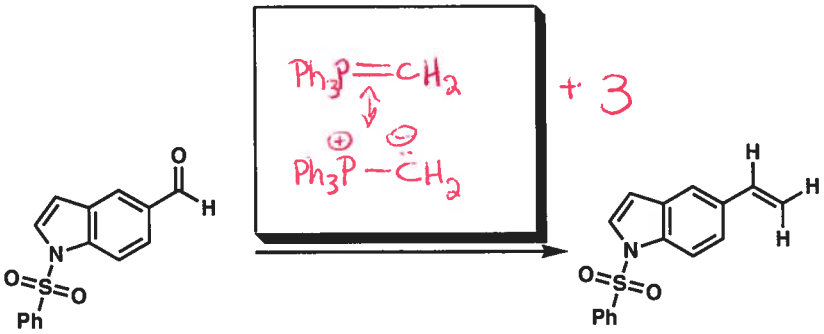
(b) Propose reagents for the following transformation and a name for this type of reaction. (5 points)



Name: Wolff-Kishner

+2

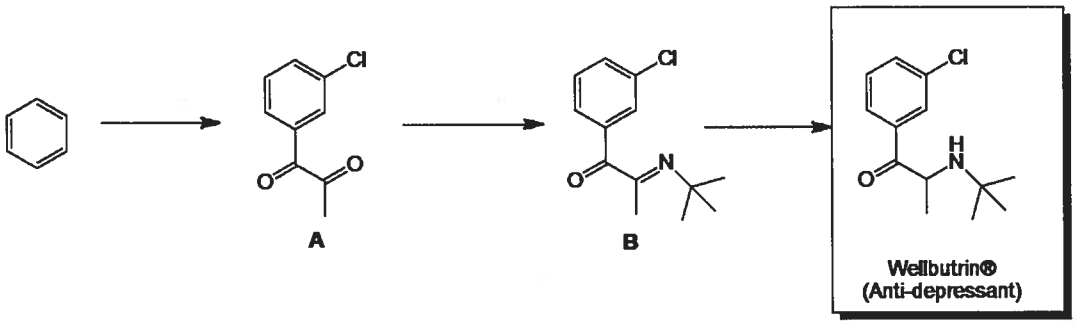
(c) Propose reagents for the following transformation and a name for this type of reaction. (5 points)



Name Wittig Rxn + 2

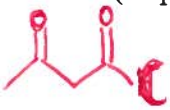
Question 3

Wellbutrin®, an anti-depressant manufactured by GlaxoSmithKline, may be prepared from benzene as shown below.



(a) Propose a synthesis of intermediate compound **A** from benzene and any other reagents three carbons or less. (15 points)

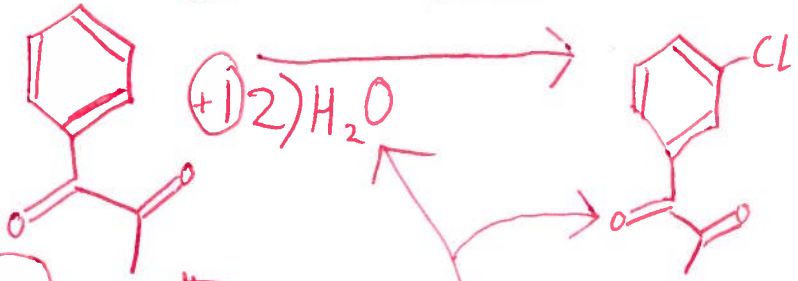
because of the extra carbonyl

(+3) 1)  , $AlCl_3$

(+2) 2) H_2O

(+4) 1) Cl_2, $AlCl_3$ (excess)

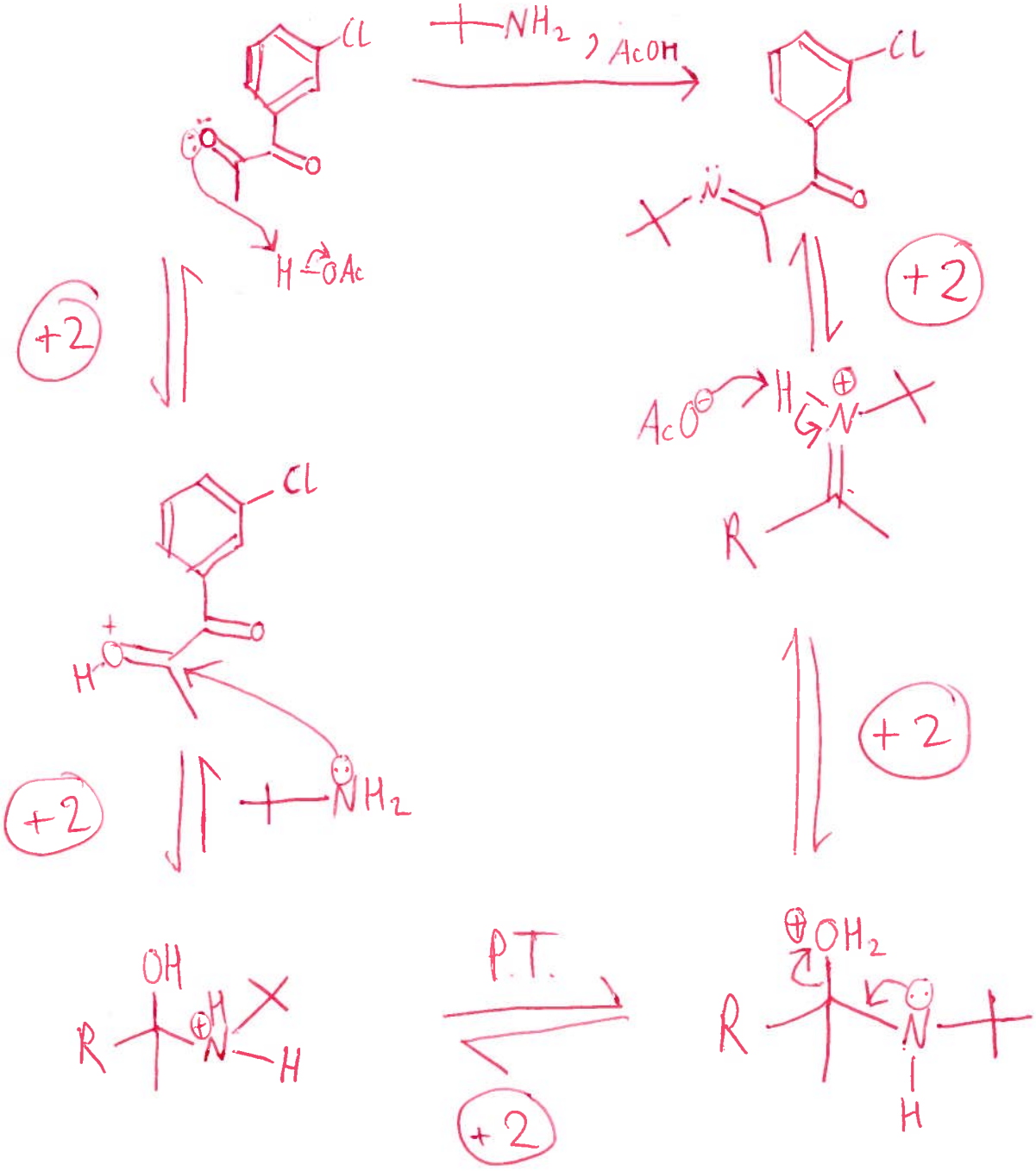
(+1) 2) H_2O



(+5) for getting correct order and regioselectivity.

Water necessary to hydrolyze Fe or Al complex with the extraneous carbonyl

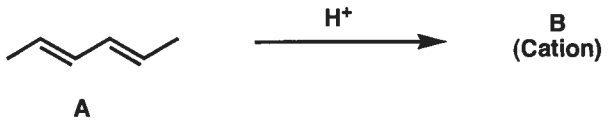
(b) Propose reagents an acid-catalyzed mechanism for the conversion of **A** to **B.** (10 points)



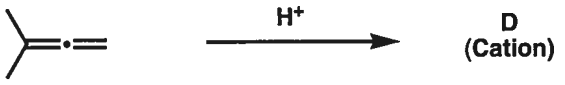
Points taken off for missing ⇌ arrows, bad arrows, missing charges, incorrect P.T. usage, too many arrows/action in a step, and for deprotonating nitrogen or having an $N^{\ominus}$

Question 4

(a) The following compounds **A** and **C** undergo protonation to form cations **B** and **D**, respectively. Show the corresponding cations and explain why they are preferentially formed over other cations in 25 words or less with appropriate figures. (10 points).



A



C

B

+3

*resonance stabilization +2

D

+3

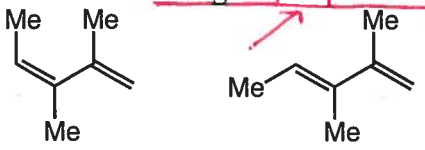
*resonance stabilization +2

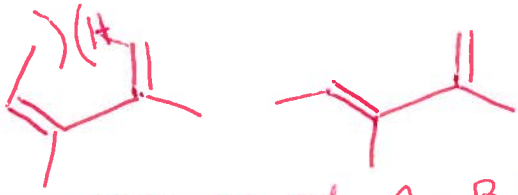
(-1) for improper olefin geometry (ex.)

(-2) for dropping atoms (ex)

(-1) for implying resonance but not stating it

(b) Which of the following dienes reacts faster in a Diels-Alder reaction? Explain your answer with no more than **two** figures and **two** sentences. (5 points)



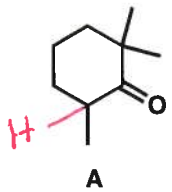


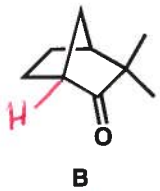
(+2) for drawing s-cis

* steric hindrance of A, B reacts faster (+3)

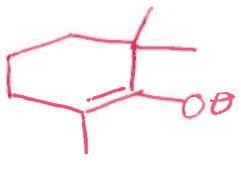
(-1) for not stating explicitly (but implying)

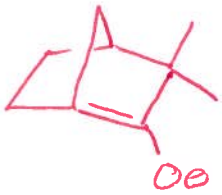
(c) Which of the following is more acidic? Explain your answer with no more than **two** figures and **two** sentences. (10 points)





(+2) for indicating acidic protons





ring strain
poor orbital overlap.

* A is more acidic (+8)

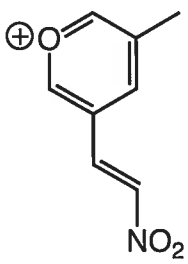
(-1 to 6) depending on incompleteness of explaination

(-6) for inverting charges but explaination is essentially correct.

(-1) if no figures but text perfect

Question 5

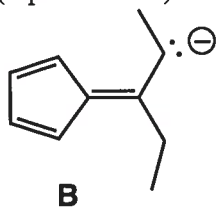
State whether the following compounds are aromatic, antiaromatic or neither. Explain your rationale using resonance structures or conformational depictions where appropriate to support your answer. (6 points each).



A

Aromatic

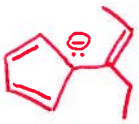
$(4n+2)=6$

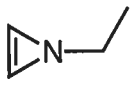


B

Aromatic

$(4n+2)=6$





C

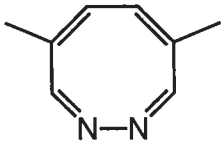
Antiaromatic if

in P orbital

neither if

if in sp^3 orbital

$4n$ $n=1$



(flat)

D

Antiaromatic

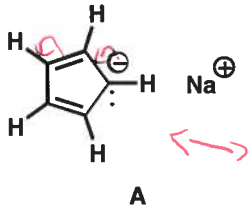
$4n = 8$

$n=2$

Question 6

(From Loudon; Problem 16.36)

(a) The ^{1}H NMR spectrum of the sodium salt of cyclopentadiene (**A**) consists of a singlet, why? (5 points)

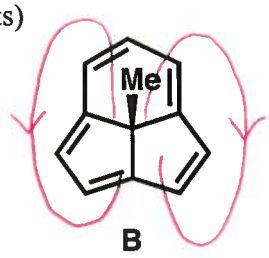


A

all protons are equivalent by resonance

etc.

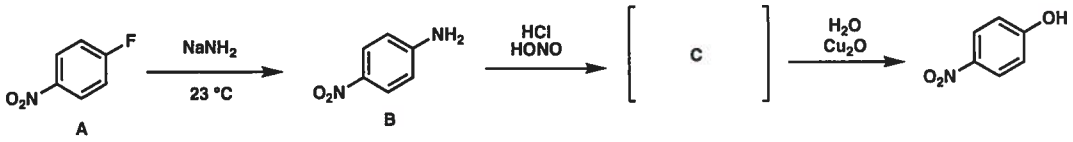
(b) The methyl group in the following compound (**B**) has an unusual ^{1}H chemical shift of δ (-1.67), about 4 ppm lower than the chemical shift of a typical allylic methyl group, why? (5 points)



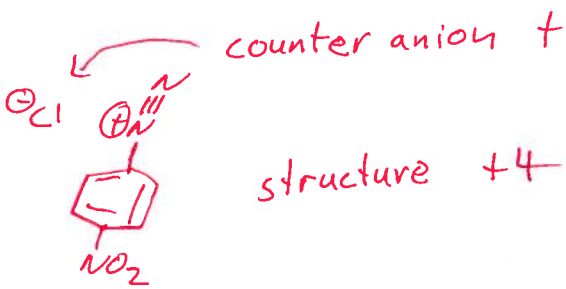
B

Methyl group is shielded by magnetic field generated from aromatic system.

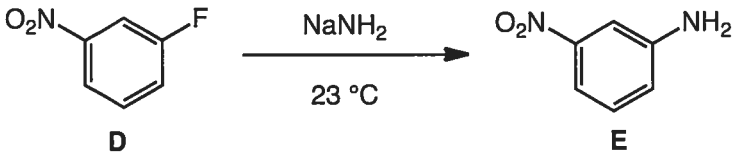
Question 7

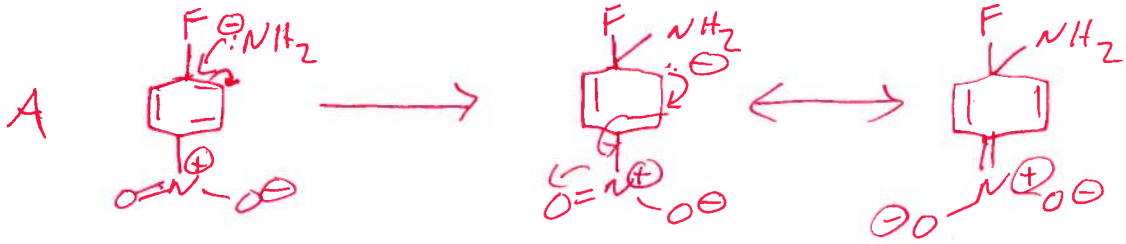


(a) Propose a structure for ~~C~~ (5 points)

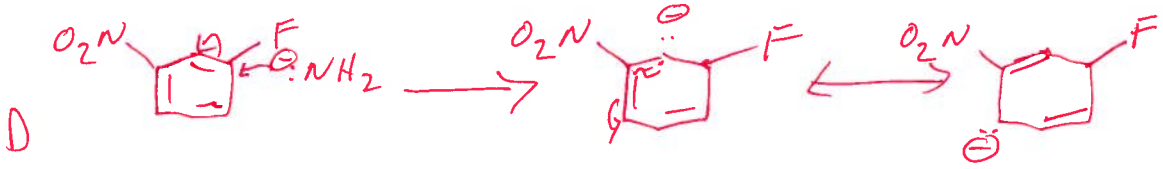


(b) Why would the conversion **D** to **E** be slower than **A** to **B**? Explain your answer with no more than **two** figures and **two** sentences (10 points)





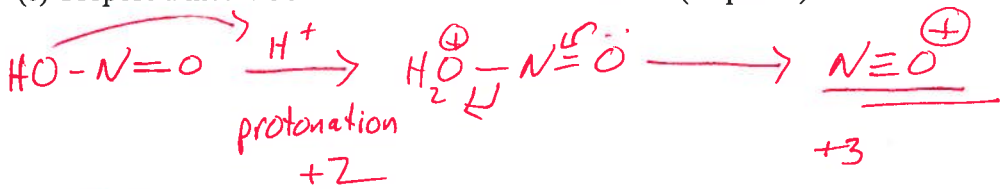
resonance stabilization on nitro group



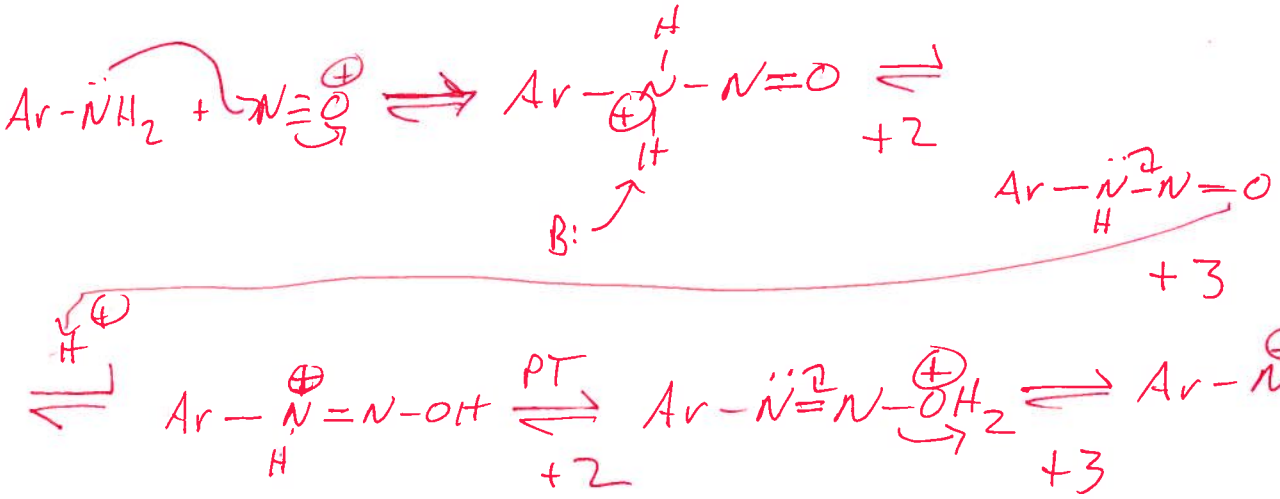
no resonance stabilization on nitro group

Must discuss both rxn A → B + D → E for full credit

(c) Propose a mechanism for the conversion of **B** to **C**. (15 points)

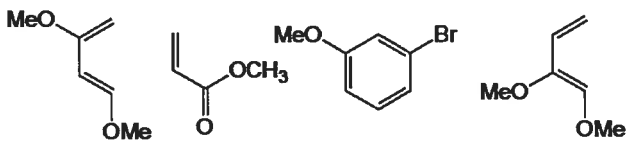


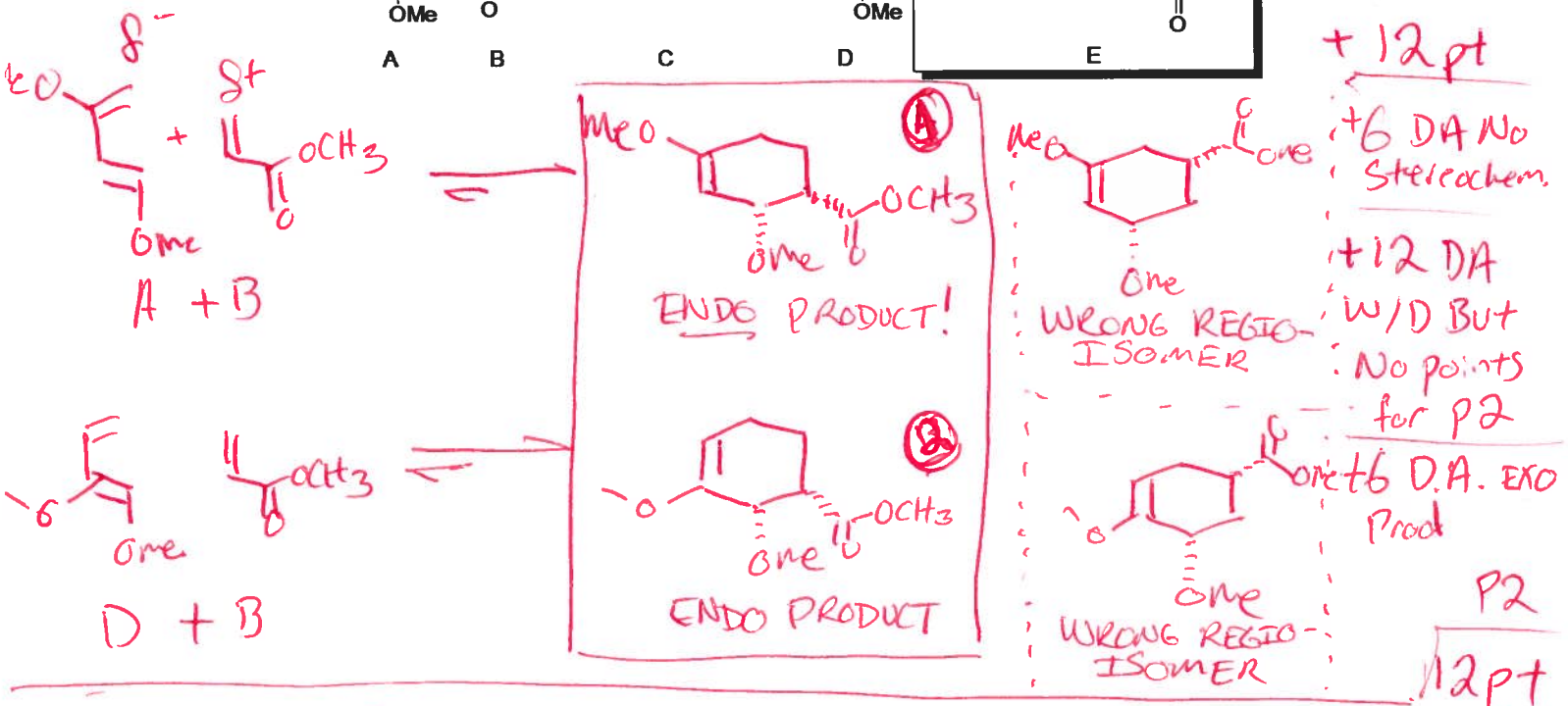
Ar=



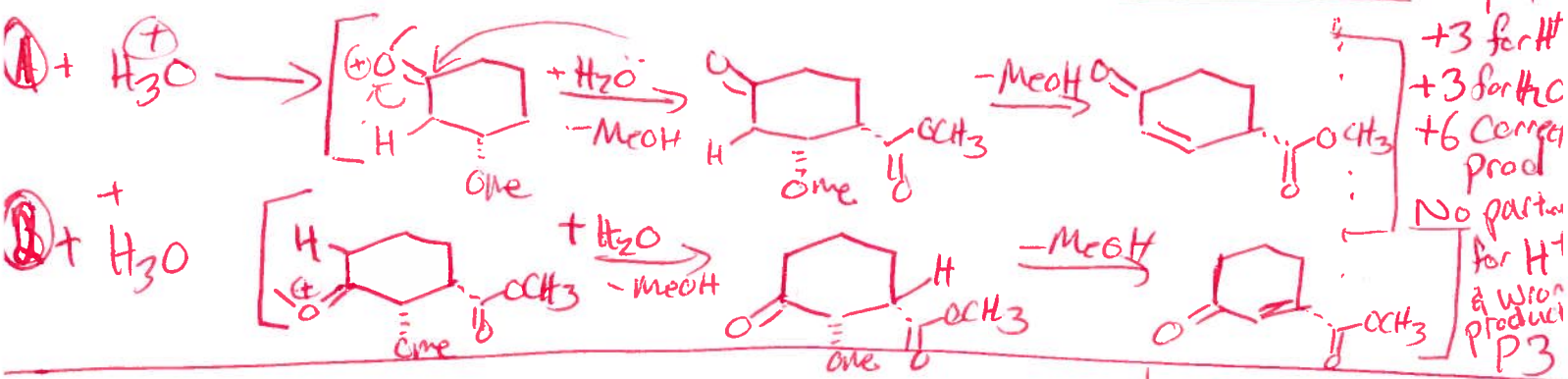
Question 8

Provide reagents and a synthesis for **E** given that it begins with a Diels Alder reaction. Other steps could include an acid-catalyzed enol hydrolysis (i.e., loss of two equivalents of methanol), and an irreversible 1, 2- addition. Alternatively, you may also propose a synthesis of **E** from any starting material four carbons or less. *Show stereochemistry of the initial Diels Alder product.* (36 points)





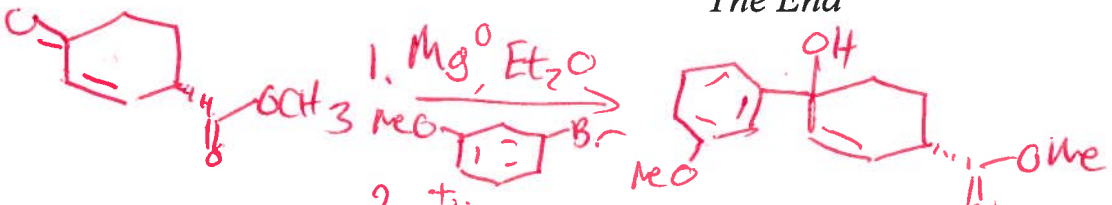
P1
+12 pt
+6 DA No Stereochem.
+12 DA W/D But No points for P2
+6 D.A. EXO Prod



P2
12pt
+3 for H+
+3 for H2O
+6 Correct Prod
No partial for H+ & Wrong product

P3

The End



+6 for Grignard formation
+4 for Grignard Addition
+2 for Workup.
12pt

* We ignored Protection groups on the ester. Can't do acetal protection on esters...