Chemistry 3B – Exam #1

Student Name: Pete's Key

Student ID Number: _____

Student Averages.

Point Breakdown

Problem 1	13.5	/ 18
Problem 2	7.5	/ 17
Problem 3	11.7	/ 15
Problem 4	11.5	/ 15
	11	/ 14
Problem 5	13.4	/ 20
Problem 6	8.9	/ 18
Problem 7	6.4	/ 12
	15	/ 21
Total	98.8	/ 150

stdev = 26/150

Average 65.9%

Median: $\frac{102.5}{150} = 68.3\%$

Check that you have 10 pages.

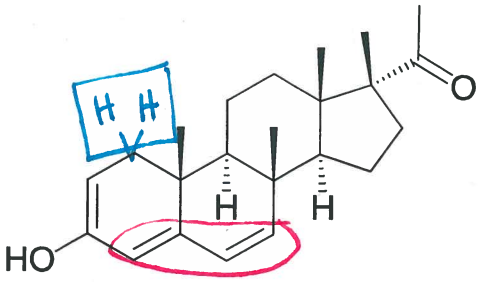
You will have 120 minutes for this exam.

Remember: Resonance, orbital overlap, and lone pair hybridization. Also, puppies. We must never forget puppies.

1. A. Medrogestone is a synthetic analog of progestrone, a hormone. On the structure below, circle the s-trans diene. (2 points)

1. B. How many allylic carbons are present in Medrogestone? Place your answer in the appropriate box below. (2 points)

1. C. Specifically draw in each allylic hydrogen atom on the structure of Medrogestone and draw a box around it. (2 points)



Medrogestone

1.A. Circle *s-trans* diene.

1.B. Number of allylic carbons.

3

1.C. Draw and box the allylic H atoms.

4.7/6

1. D. In a Diels-Alder reaction, which orientation of the dieneophile is preferred when secondary orbital overlap is present? (2 points) endo

1.6/2

1. E. Will the simple Diels-Alder reaction below be endothermic or exothermic? Why? (4 points)

The above reaction will be exo thermic because:

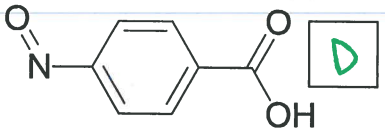
trading 2 weak π bonds for 2 strong σ bonds.

15 words or fewer

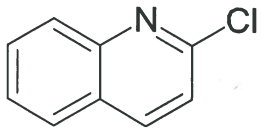
1.8/4

1. F. Match the name to the structure. Place the letter of the name in the box of the corresponding structure. Some names will not be used. (6 points)

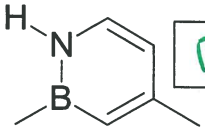
A *ortho*-Chloroquinoline
B *meta*-dimethylborazine
C *ortho*-Chloroaniline
D *para*-Nitrosobenzoic acid
E *ortho*-dimethylborazine
F *para*-Nitrosobenzaldehyde



D



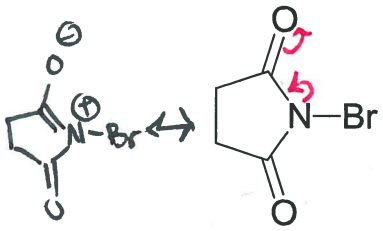
A



B or E

5.4/6

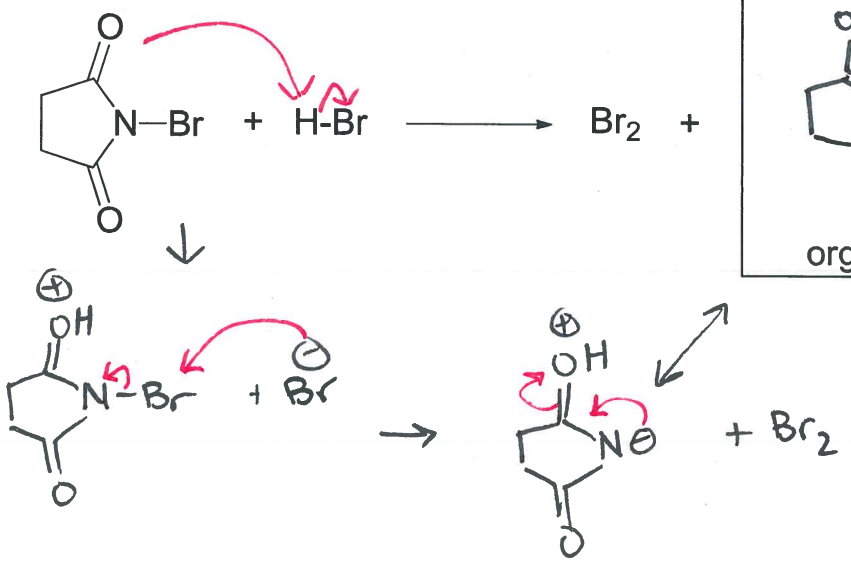
2. A. Which atom in *N*-Bromosuccinimide is most basic? Explain in 15 words or fewer. (4 points)



The oxygen atom is most basic because: resonance puts δ⁻ on the O.

1.5/4

2. B. Show the mechanism of formation of Br_2 from NBS and HBr. Also draw the **immediate organic byproduct after Br_2 is released**. (8 points)



3.9/8

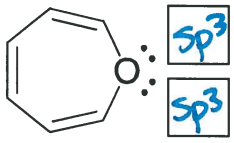
2. C. In 15 or fewer words, describe why NBS is considered a "slow release" source of Br_2 in an allylic bromination reaction? *Hint: what are the products of a radical bromination?* (5 points)

NBS is a slow-release source of Br_2 in an allylic bromination reaction because: it requires HBr to form Br_2, and HBr is only released after Br_2 is used in the radical reaction.

2/5

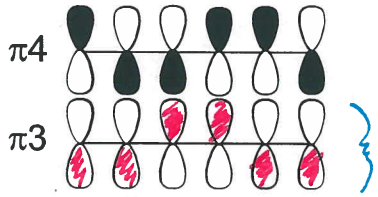
3. A. The following molecule is non-aromatic. What orbitals do the lone pairs on oxygen occupy? (2 points)

not planar.



0.6/2

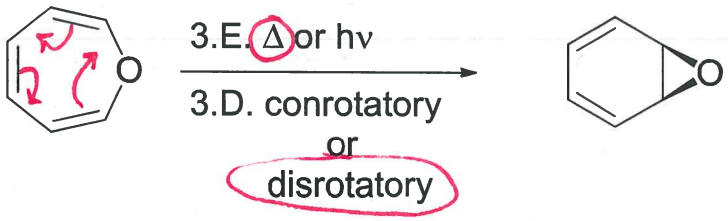
3. B. The LUMO of the pi system for the above molecule is shown below. Fill in the next lowest pi energy orbital diagram by shading the appropriate orbitals. (2 points)



reverse shading also fine.

2/2 ☺

3. C. Add electron-pushing arrows to the reaction below. (3 points)



6.4/7

3. D. Was the above electrocyclization conrotatory or disrotatory? Circle the answer above. (2 points)

3. E. Was the energy source for the above electrocyclization light or heat? Circle the answer above. (2 points)

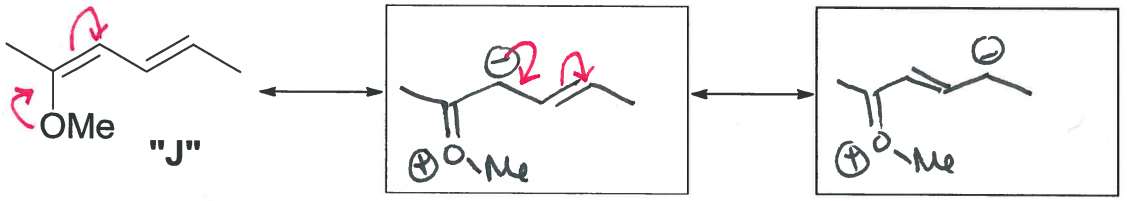
3. F. Why is the reaction with opposite rotation not observed? Explain using 15 words or fewer. (4 points)

Reaction with opposite rotation is not observed because:
that would lead to a trans epoxide which has too much ring strain.

15 words or fewer

2.7/4

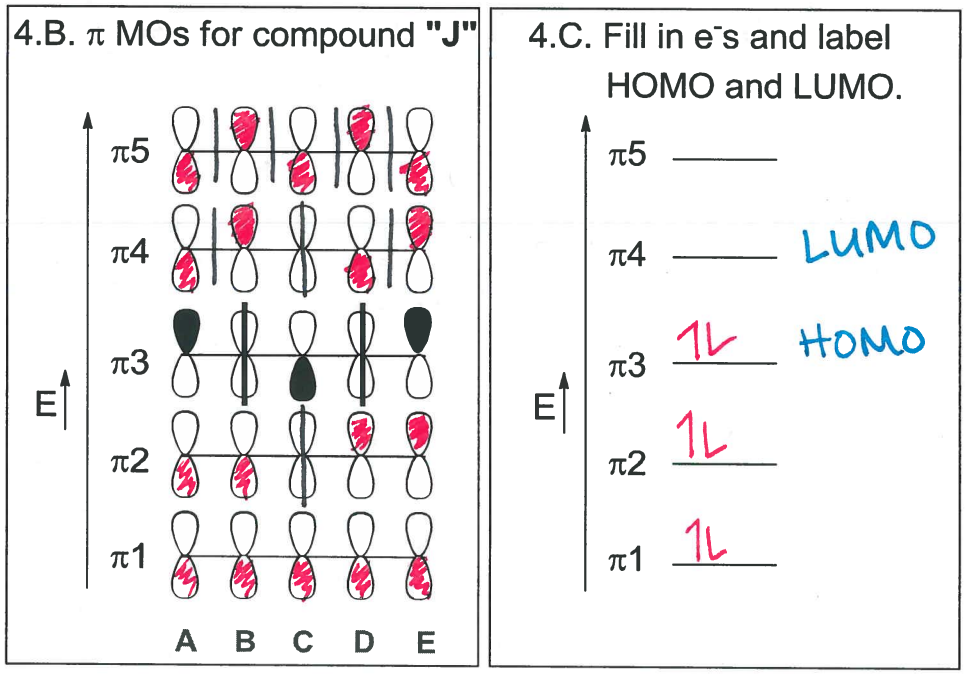
4. A. Draw two more resonance contributors of molecule **"J"** below. Each contributor must have a filled octet. (6 points)



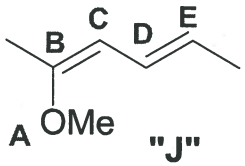
4.4 / 6

4. B. Shade in the pi MOs for compound "J" in the space provided below. Include a vertical line for each node. The third pi energy level has been completed for you. (4 points)

4. C. Fill in the electrons into the pi energy levels and label the HOMO and the LUMO. (2 points)



5.6 / 6

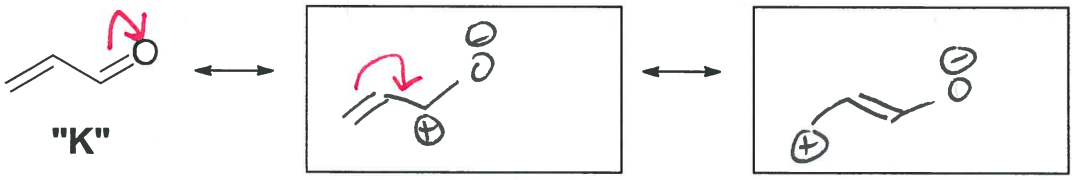


4. D. Explain why compound "J" cannot undergo a concerted cycloaddition with its highest occupied pi molecular orbital. (3 points)

1.5 / 3

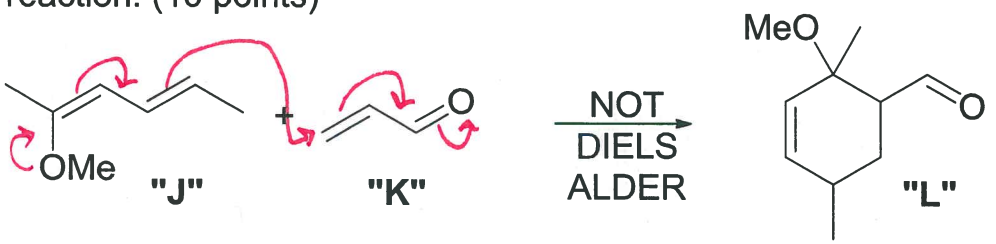
"J" cannot undergo a concerted cycloaddition with its highest occupied pi MO because: there are nodes on the carbons that might react.

4. E. Acrolein, compound "K", is a good dieneophile and a good electrophile. Draw two resonance contributors that clearly show where "K" is electrophilic. Filled octets are not necessary. (4 points)

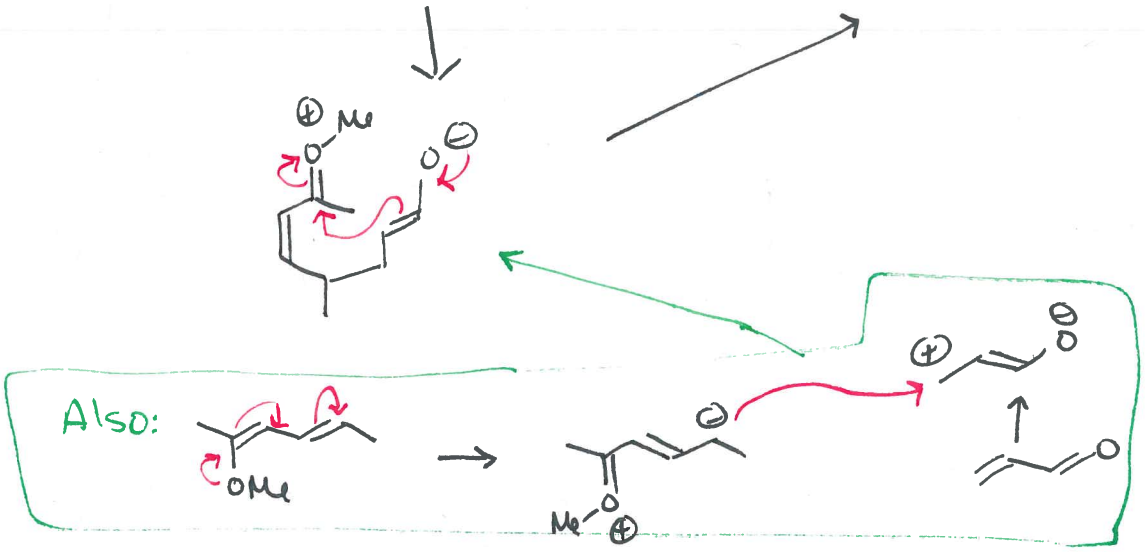


3.5/4

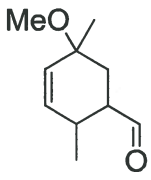
4. F. Compounds "J" and "K" do react to yield a product that appears to be from a concerted Diels-Alder reaction. However, it goes through a different mechanism. Provide a STEP-WISE mechanism for the reaction. (10 points)



6/10



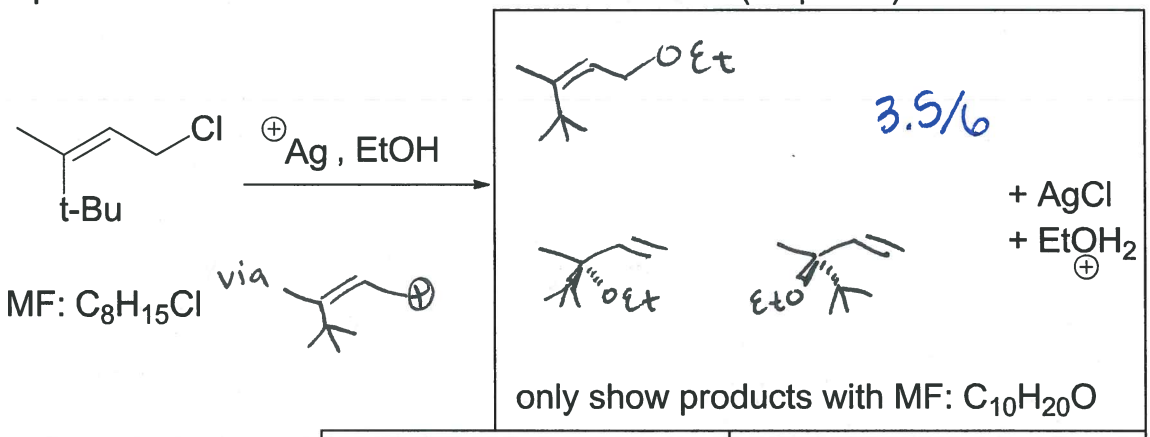
Extra Credit: Why is the following product not seen when "J" and "K" react?

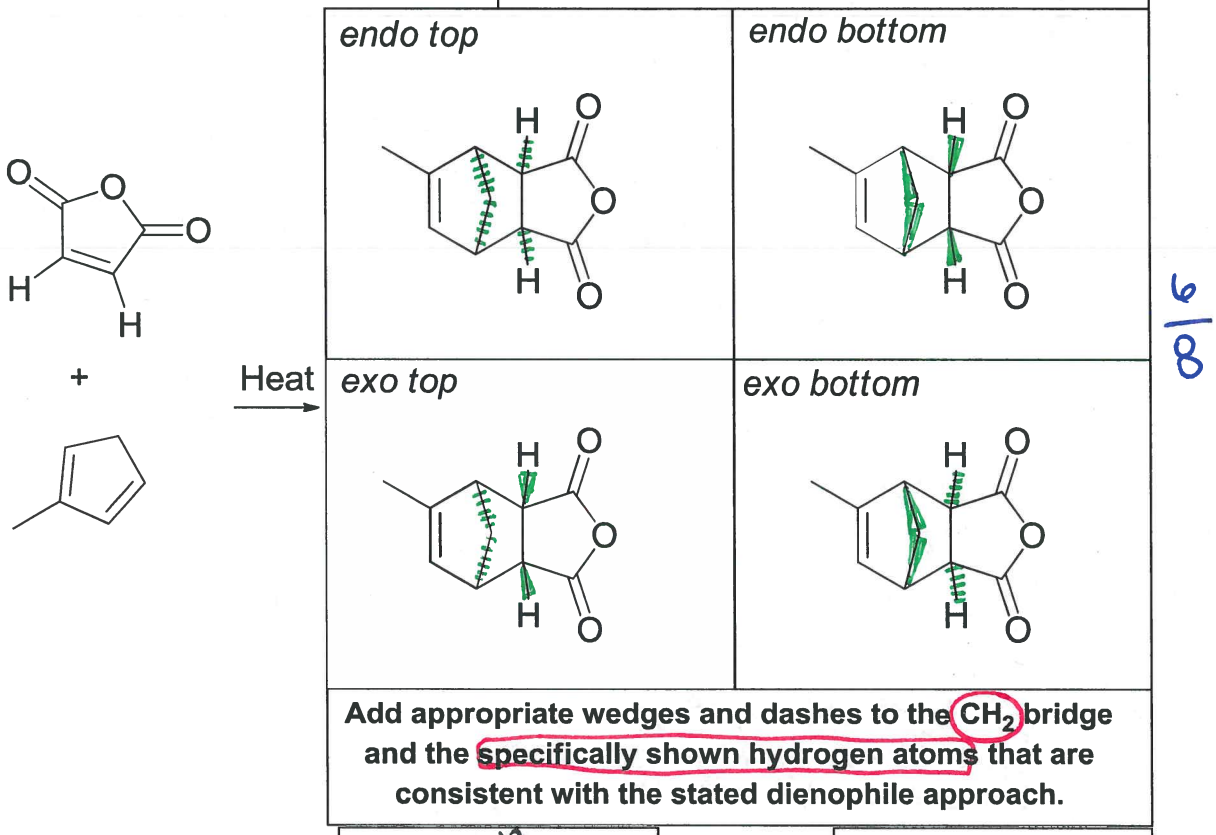


The resonance puts the nucleophilic + electrophilic ~~carbons~~ sites on specific carbons.

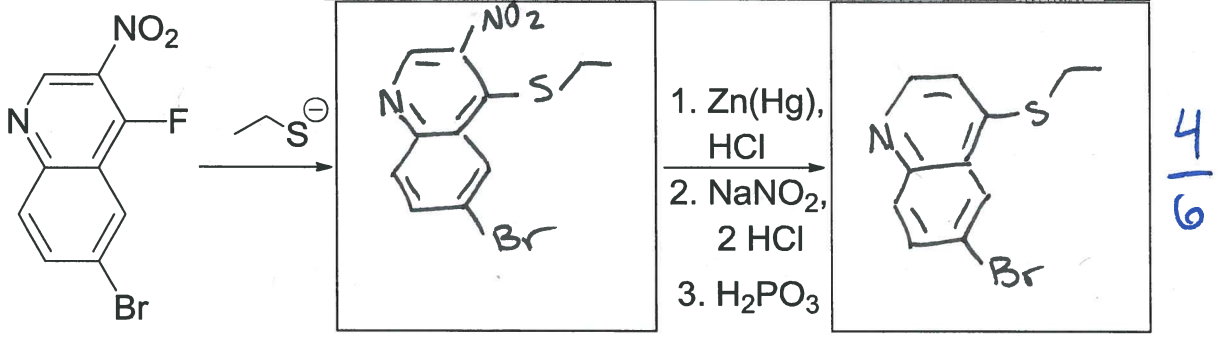
1.4/possib 5EC points

5. Predict the ORGANIC products of the following reactions, including stereoisomers. Pay close attention to any special instructions in each box. Repeat answers will cancel out correct answers. (20 points)

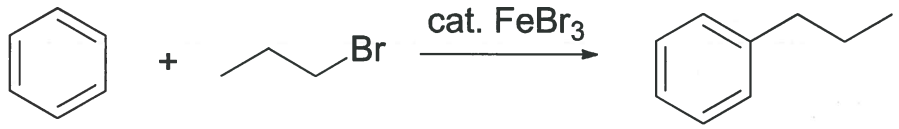




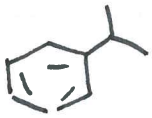
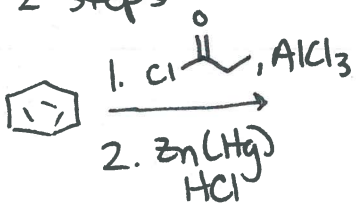
Add appropriate wedges and dashes to the CH_2 bridge and the specifically shown hydrogen atoms that are consistent with the stated dienophile approach.



6. A. A student proposes the following synthesis. It will not yield the desired product. Indicate the problem, provide the actual products, and suggest a change to the synthesis which will make it work. (9 pts)

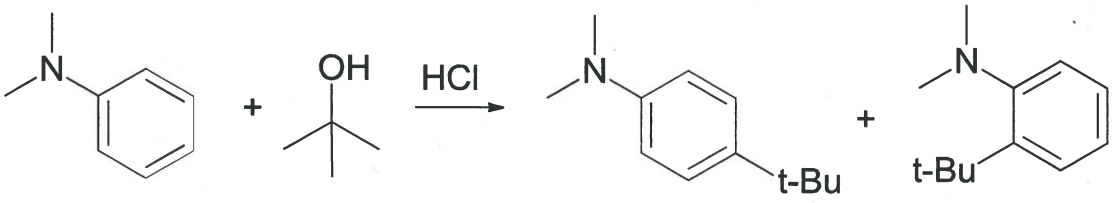


Desired Product

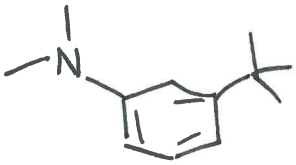
Problem:	Actual Products:	Proposed Change:
carbo-cation rearranges		2 steps  1. Cl, AlCl3 2. Zn(Hg) HCl Acylate then reduce

6.7/9

6. B. A student proposes the following synthesis. It will not yield the desired product. Indicate the problem, provide the actual products, and suggest a change to the synthesis which will make it work. (9 pts)

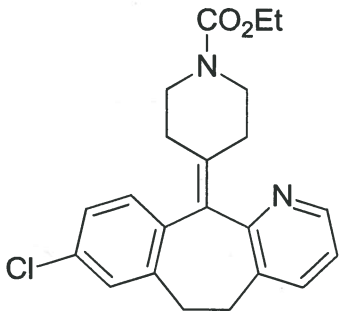


Desired Products

Problem:	Actual Products:	Proposed Change:
Nitrogen is basic. Becomes protonated and a meta director		use a non-Bronsted Acid method of generating the E⊕. → Cl, AlCl3, for example

2.3/9

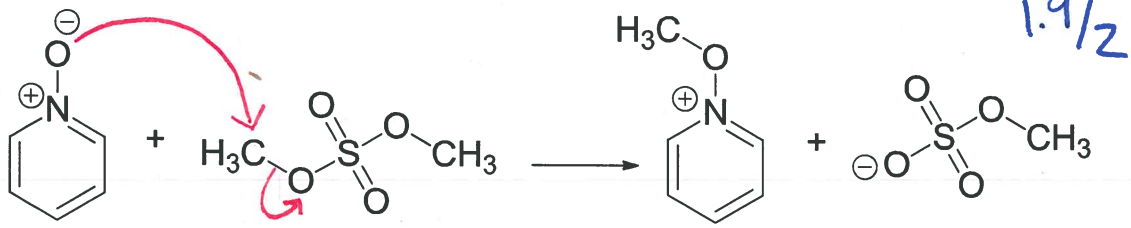
7. The active ingredient in Claritin is Loratidine, shown below. A lot of work has been done in making analogs of Loratidine to increase its pharmacological effects.



Loratidine

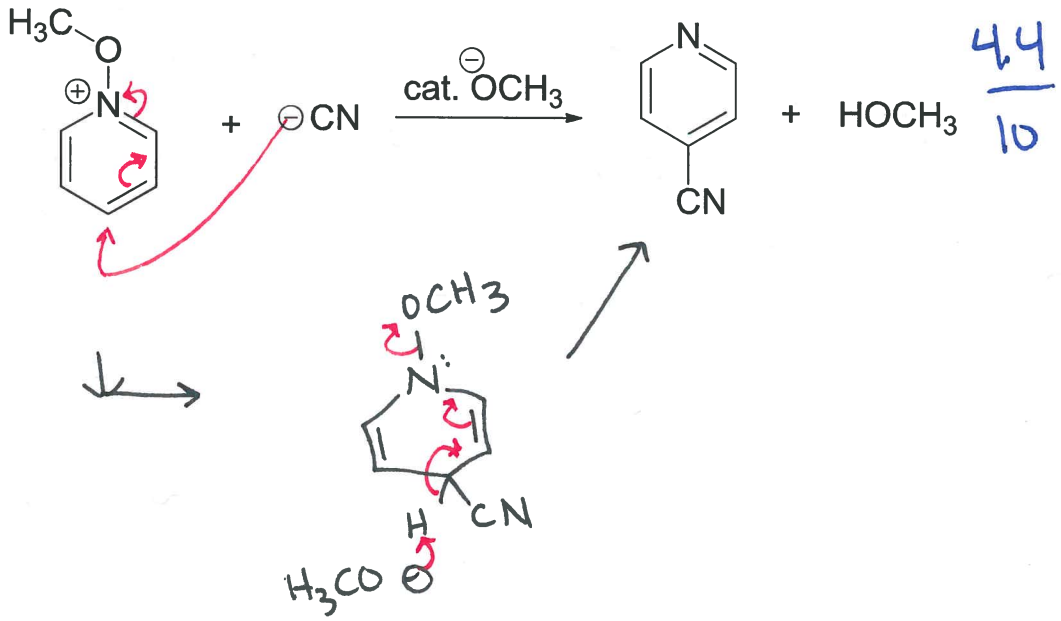
7. A. Add electron pushing arrows to the reagents below that would yield the products. (2 points)

1.9/2

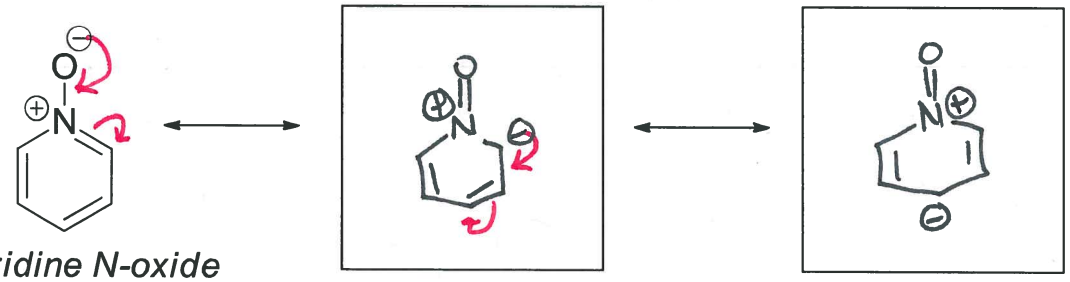


7. B. Provide a mechanism for the following transformation. (10 points)

4.4/10



7. C. Pyridine N-oxide can undergo electrophilic aromatic substitution. Show two more resonance contributors that identify the nucleophilic carbons of the aromatic ring. (6 points)



pyridine N-oxide

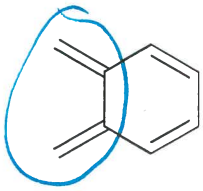
4.2/6

7. D. Will pyridine N-oxide add a super electrophile ortho/para or meta? Circle your choice and explain in 15 words or fewer. (5 points)

Pyridine N-Oxide adds **ortho/para** **meta** because:
The o/p carbons are nucleophilic

4/5

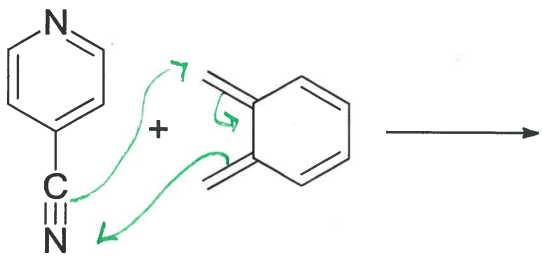
7. E. The molecule below can act as a diene in a Diels Alder reaction. On the molecule, circle the s-cis diene that will most likely react. Explain your choice in 15 words or fewer. (6 points)

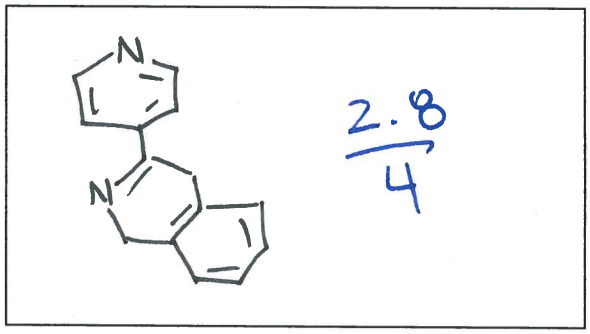


The circled diene will preferentially react because:
the D.A. product will have an aromatic ring.

3.9/6

7. F. The cyano group can act as a dieneophile in a Diels Alder reaction. Predict the product(s) of the following reaction. (4 points)





2.8/4