Chemistry 3B – Exam #1

Student Name: Pete's Key SID: _____

Points Breakdown

Question 1 Page 2 : 15 pts	**Question 3** Page 4 : 13 pts Page 5 : 11 pts Page 6 : 21 pts	**Question 5** Page 8 : 12 pts Page 9 : 13 pts Page 10 : 13 pts
Question 2 Page 3 : 18 pts	**Question 4** Page 7 : 19 pts	**Question 6** Page 11 : 21 pts

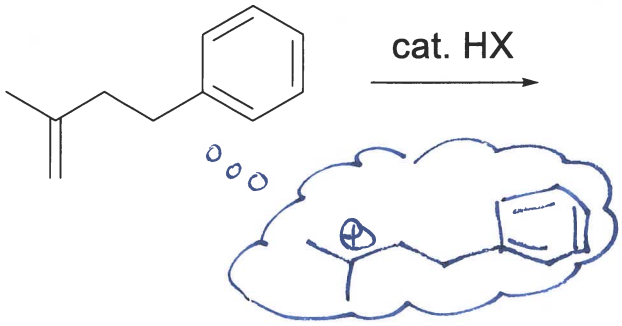
Notice: There are 156 possible points. You can earn over 100% on this exam.

Remember: Number your carbons. Thought bubbles are a valid method of working out ideas. Mechanisms can help you with predicting products. Take your time. Please make sure you write your name at the top of each page.

Y'all need to remember that you're amazing and have studied hard. Trust yourselves! ~Pete

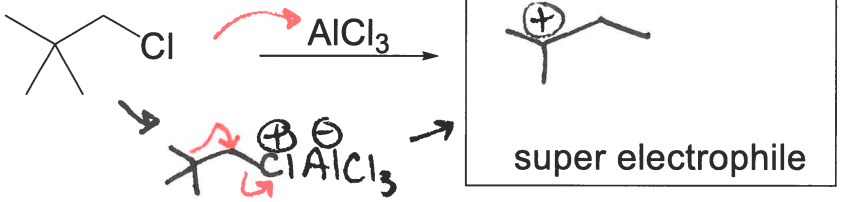
Here are some jacobins, the most fabulous of pigeons

1.A. Predict the product of the intramolecular EAS reaction below. (3 pts)



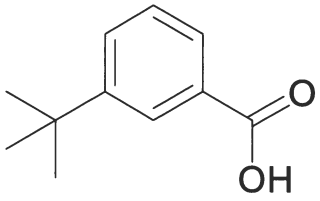
product of intramolecular EAS reaction

1.B. What is the super electrophile generated from the following reaction? (3 pts)



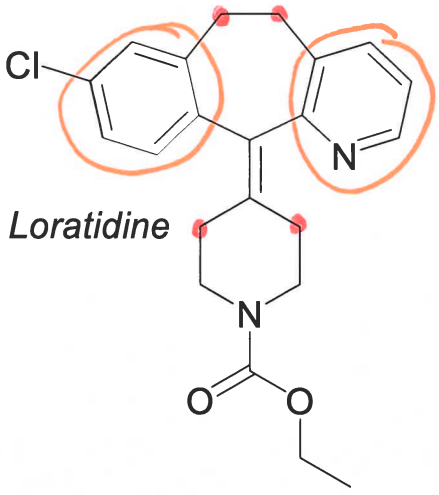
super electrophile

1.C. Provide a name for the following molecule using the conventions from lecture. (3 pts)



meta-tert butyl-benzoic acid.

Loratidine (Claritin) is great for fighting allergies.



Loratidine

1.D. Circle each aromatic ring of loratidine on the structure to the left. (2 pts)

1.E. How many allylic **carbons** are present in loratidine? (2 pts)

4

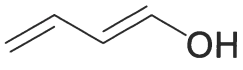
1.F. How many allylic **hydrogens** are present in loratidine? (2 pts)

8

Quiz Redemption

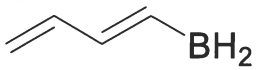
2.A. For each compound below, choose the number of e⁻s in the pi system. (3 pts)

A



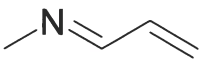
○ 2
○ 4
● 6

B



○ 2
● 4
○ 6

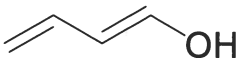
C



○ 2
● 4
○ 6

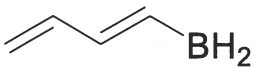
2.B. For each compound below, choose the number of pi molecular orbitals. (3 pts)

A



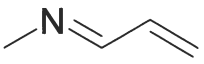
○ 3
○ 4
● 5

B



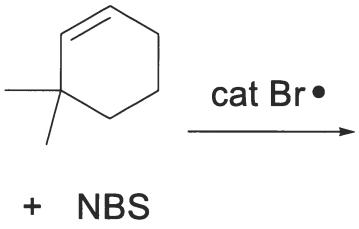
○ 3
○ 4
● 5

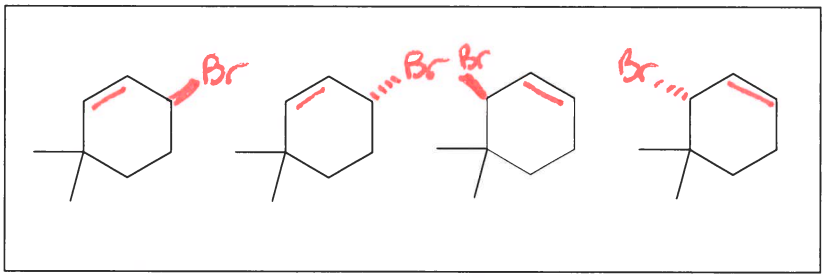
C



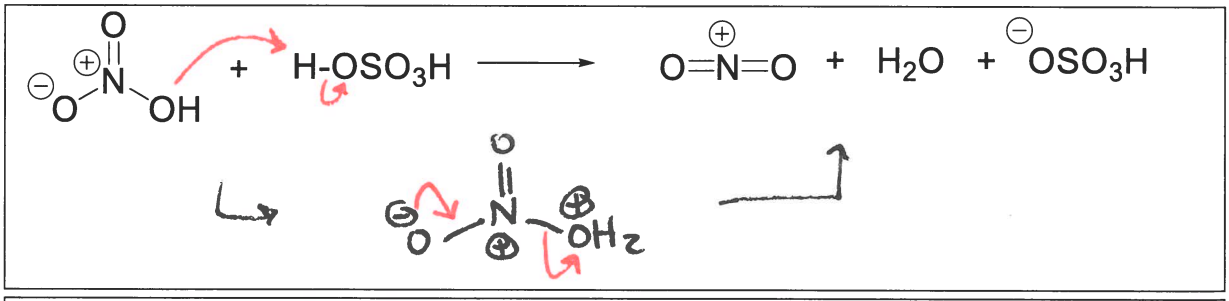
○ 3
● 4
○ 5

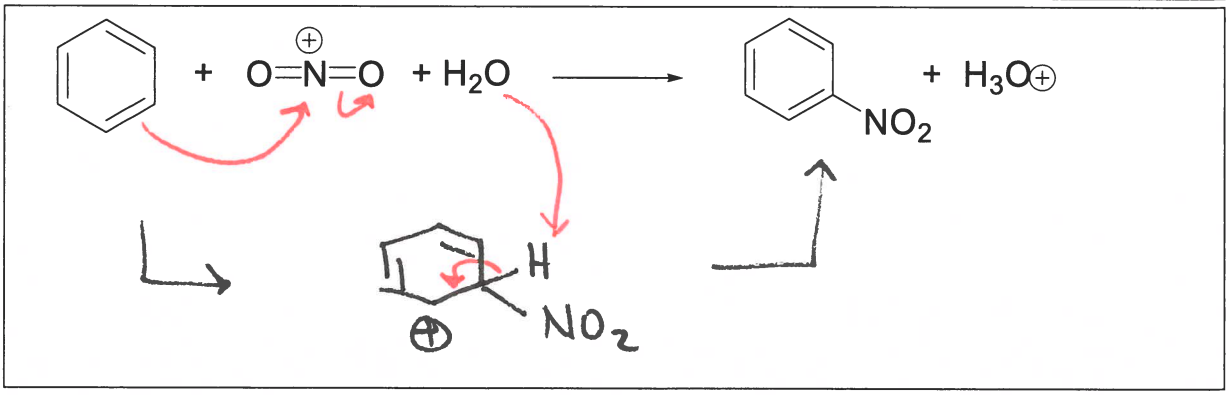
2.C. Predict the products of the following reaction. Fill in the missing bromine atoms with appropriate stereochemistry and pi bond(s). (4 pts)



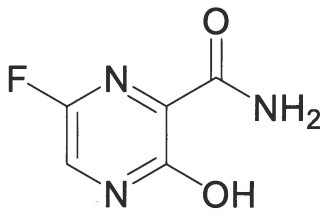


2.D. Provide a curved arrow mechanism for the reaction below. (8 pts)



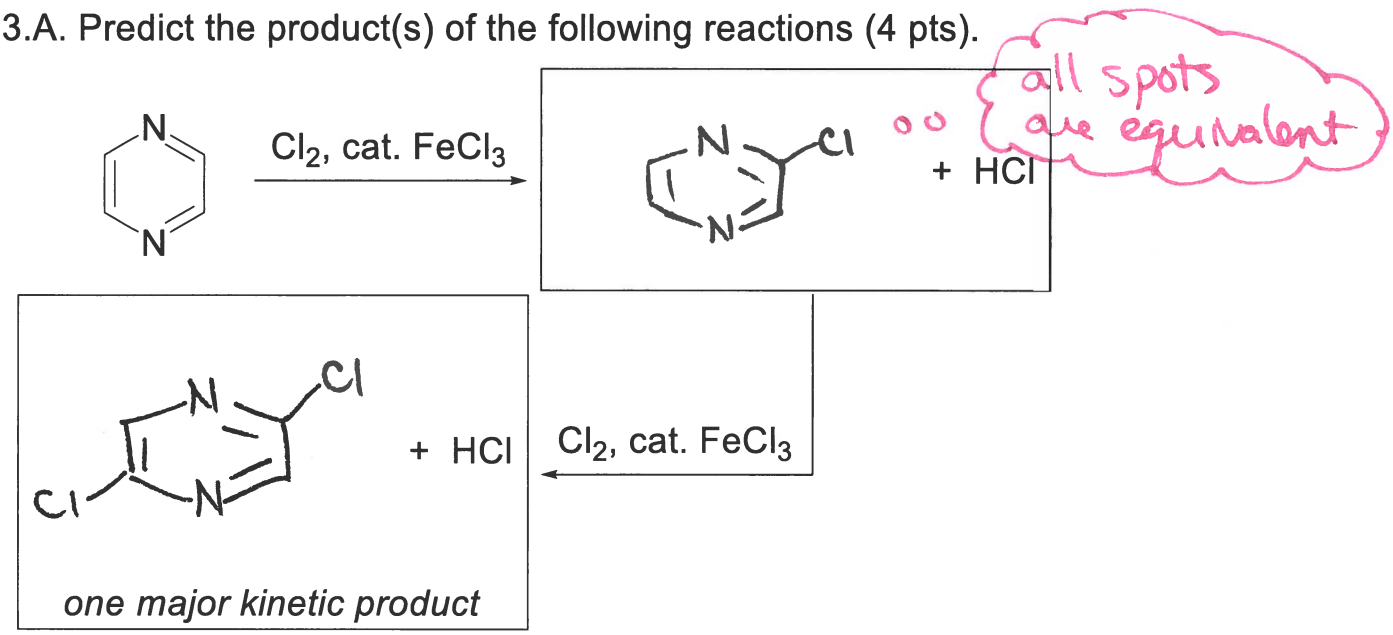


3. Favipiravir is an experimental drug that was somewhat effective in fighting ebola.

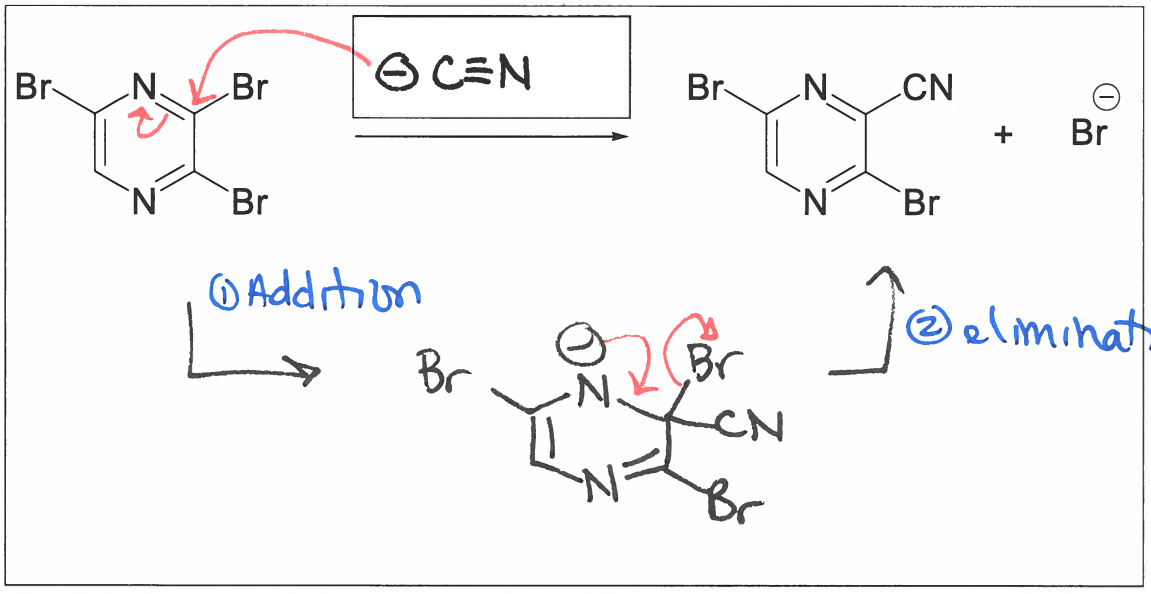


Favipiravir

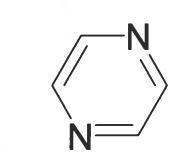
3.A. Predict the product(s) of the following reactions (4 pts).



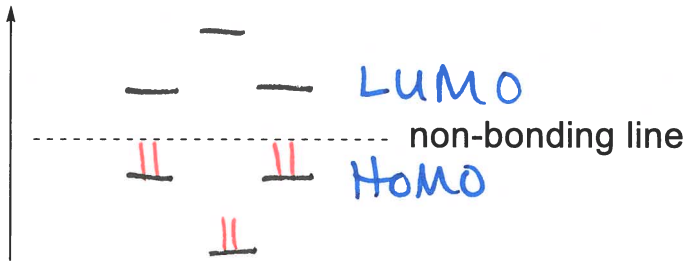
3.B. Fill in the missing reagent for the following reaction. Also, show the mechanism leading to the product.
(3 pts for reagent, 6 pts for mechanism)



3.C. Draw the pi MO energy levels for the pyrazine core of Favipiravir using a Frost Diagram. Add the correct number of e⁻s and label the HOMO and LUMO. (4 pts)

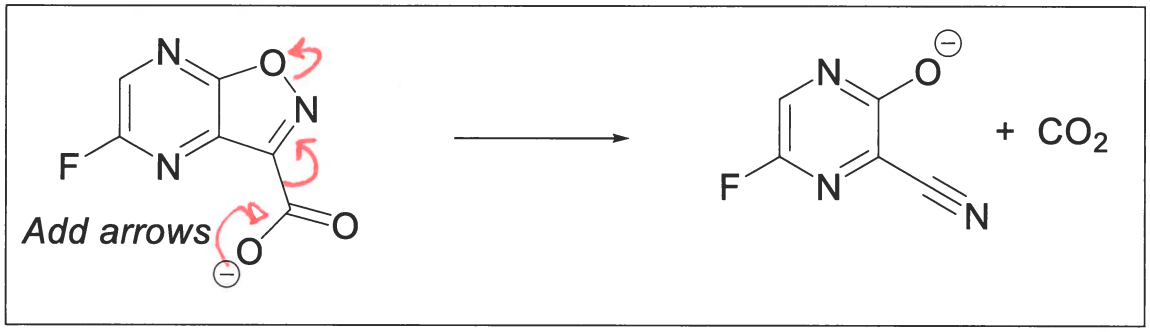


pyrazine

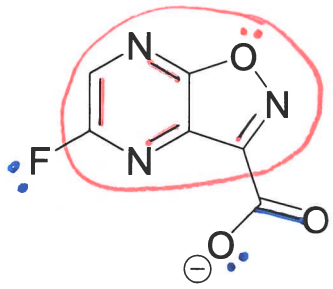


3.D. To study the efficacy of this drug, it needs to be labeled with a radioactive fluorine atom. This requires a synthesis that takes no more than 30 minutes.

Add curved arrows to the following intermediate to show how it becomes the product. (3 pts)



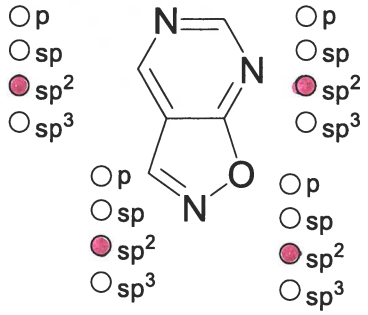
3.E. The ring core of the material below is a kind of pyrisoxazole. How many electrons are in the aromatic system? How many electrons are in the pi system (don't forget the halogen)? (4 pts)



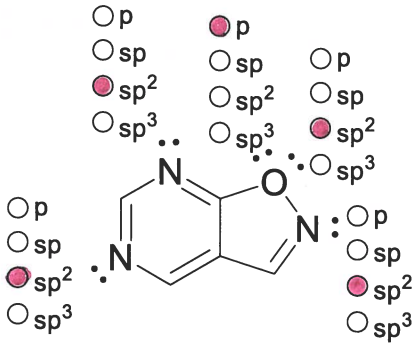
Number of electrons in the aromatic system: 10

Number of electrons in the entire pi system: 16

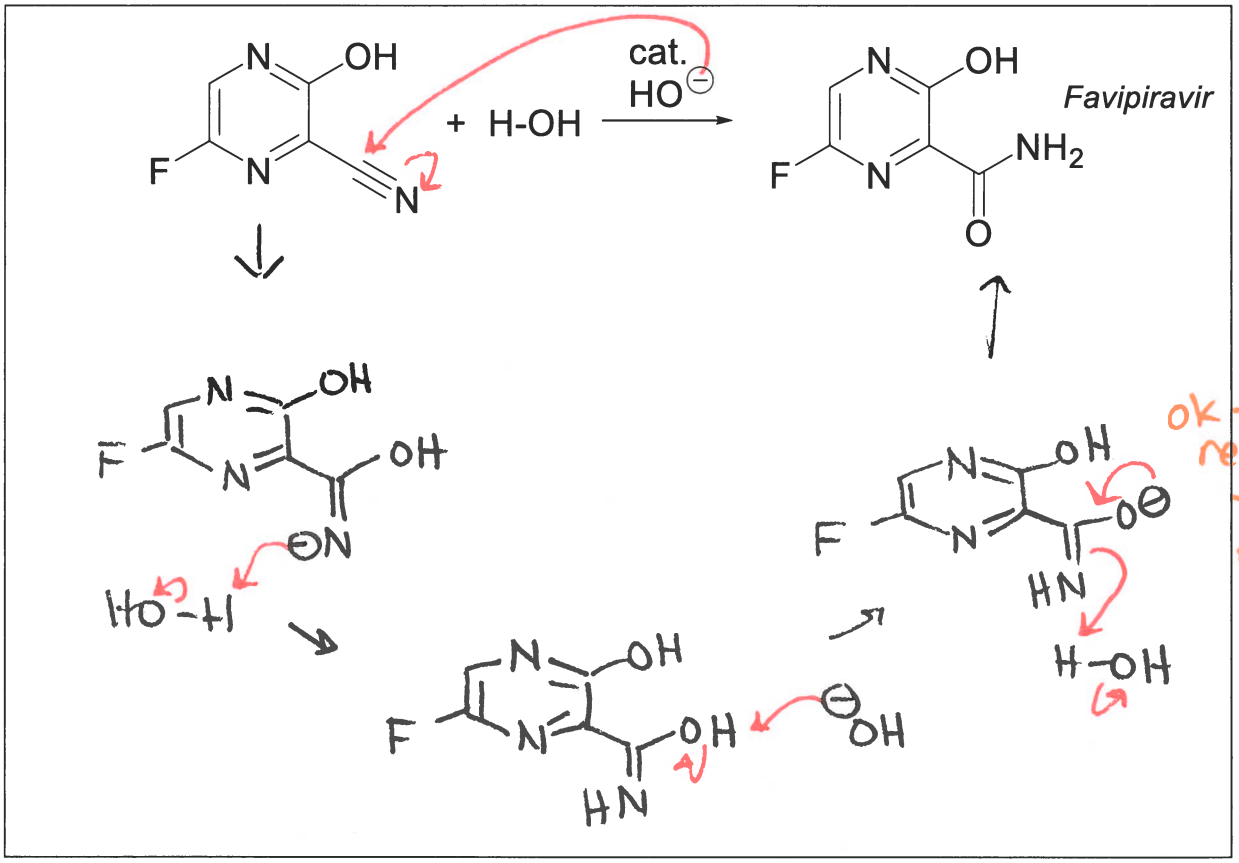
3.F. Indicate the hybridization of each **heteroatom**. (2 pts)



3.G. Indicate the atomic orbital of the **lone pairs**. (2 pts)



3.H. Show a mechanism for the following conversion of the nitrile to an amide. *Hint: The first step is the hydroxide attacking the nitrile. The rest of the steps are a combination of acid/base and resonance.* (12 pts)

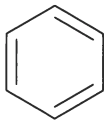


3.I. The pK_a range for the OH hydrogen of Favipiravir is 5-10. Explain why the range makes sense. (5 pts)

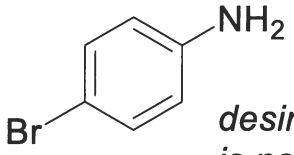
Relevant fxnl grp with pK_a 5	Relevant fxnl grp with pK_a 10	Hydrogen is more acidic than pKa 10 because: EN(N) > EN(C) or inductive effect Hydrogen is less acidic than pKa 5 because: EN(N) < EN(O) or inductive effect.
Carboxylic Acid or RCO_2H	phenol or PhOH	

4.A. Pete attempted the following synthesis, but the desired product was not formed. (9 pts)

(1) Indicate the problem with the synthesis with 15 or fewer words.
(2) Draw the actual product that would form under these conditions.
(3) Propose a new synthesis leading to the desired product without changing your aromatic starting material.



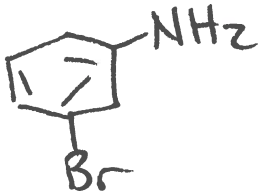
1. HNO_3, H_2SO_4
2. Br_2, cat. $AlBr_3$
3. Zn(Hg), HCl



desired product is not obtained

Problem(s):
Nitro grp is added 1st and directs to the meta position.

Actual Product



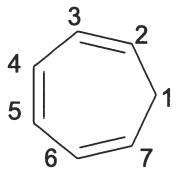
New Synthesis

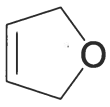
option ①
1. HNO_3, H_2SO_4
2. Zn(Hg), HCl
3. Br_2, cat $AlBr_3$

OPTION ②
1. Br_2, cat $AlBr_3$
2. HNO_3, H_2SO_4
3. Zn(Hg), HCl

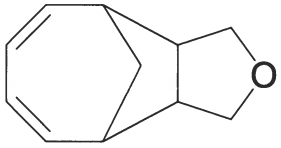
4.B. Pete attempted the following synthesis, but the desired product was not formed. (10 pts)

(1) Indicate the problem with the proposed cycloaddition with 10 words or fewer and a comparison of both HOMOs and LUMOs.
(2) Show the actual diels alder product that formed.

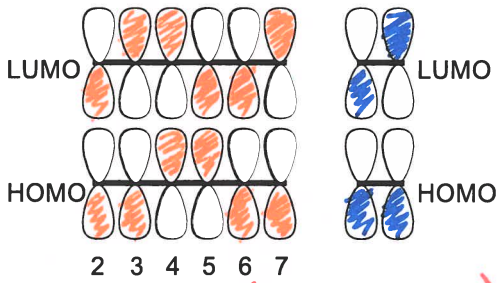




cycloaddition →

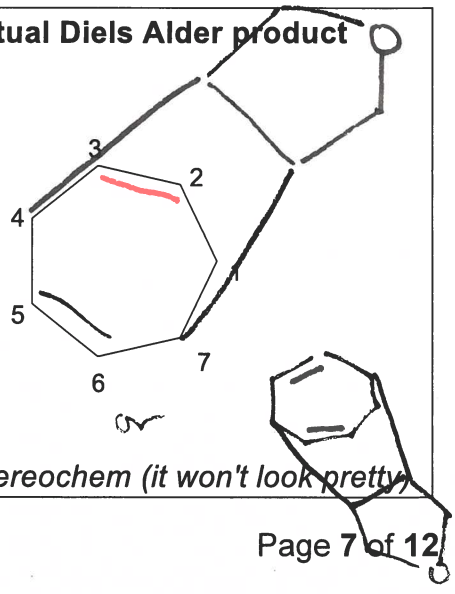


desired compound not formed



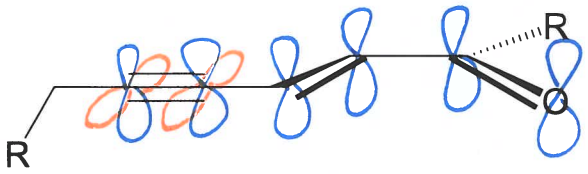
Problem(s): It's impossible to get constructive overlap b/w HOMO/LUMO

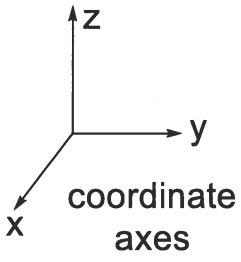
Actual Diels Alder product



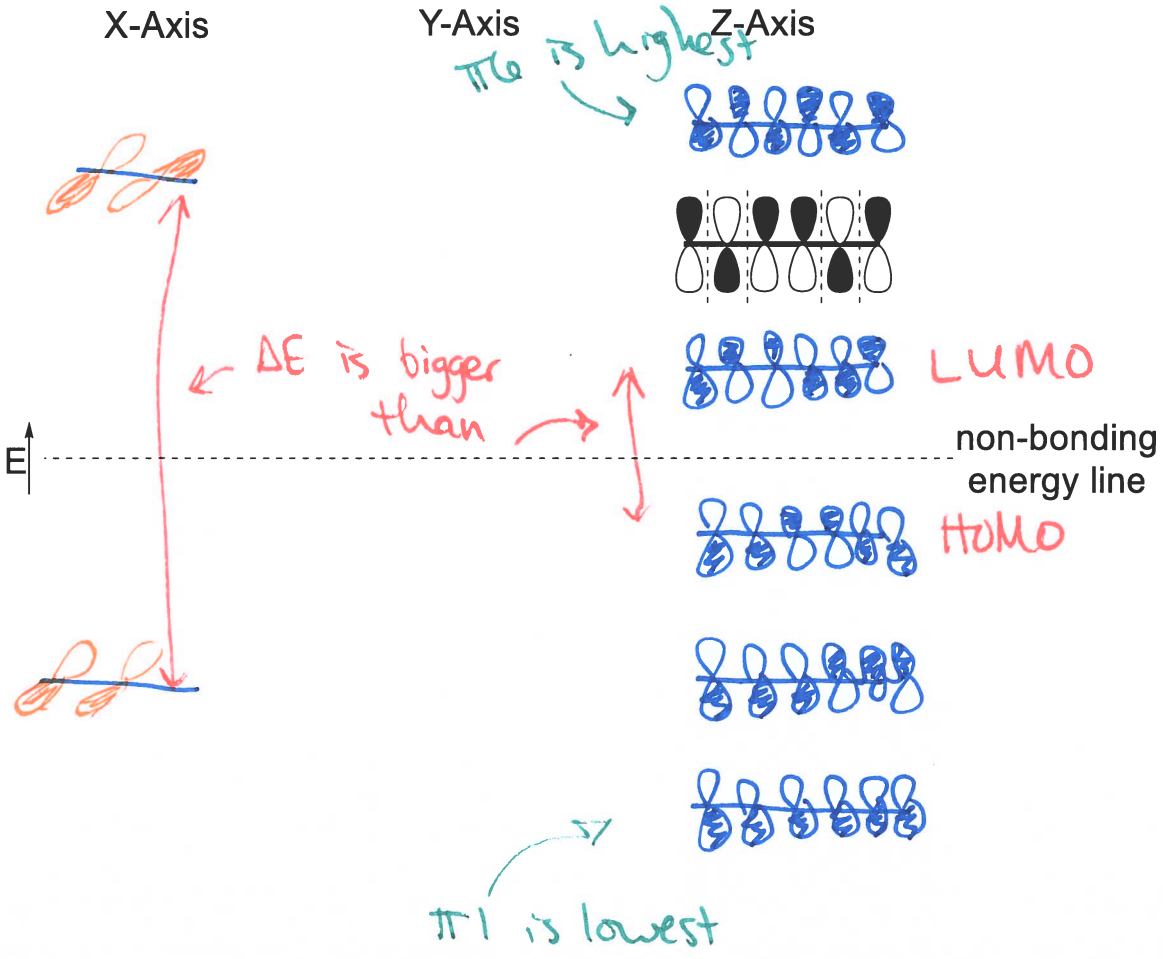
ignore stereochem (it won't look pretty)

5.A. Ynenones are a very versatile motif in generating heterocycles. Add p-orbitals with appropriate 3-dimensional representations on the ynenone below. (4 pts)

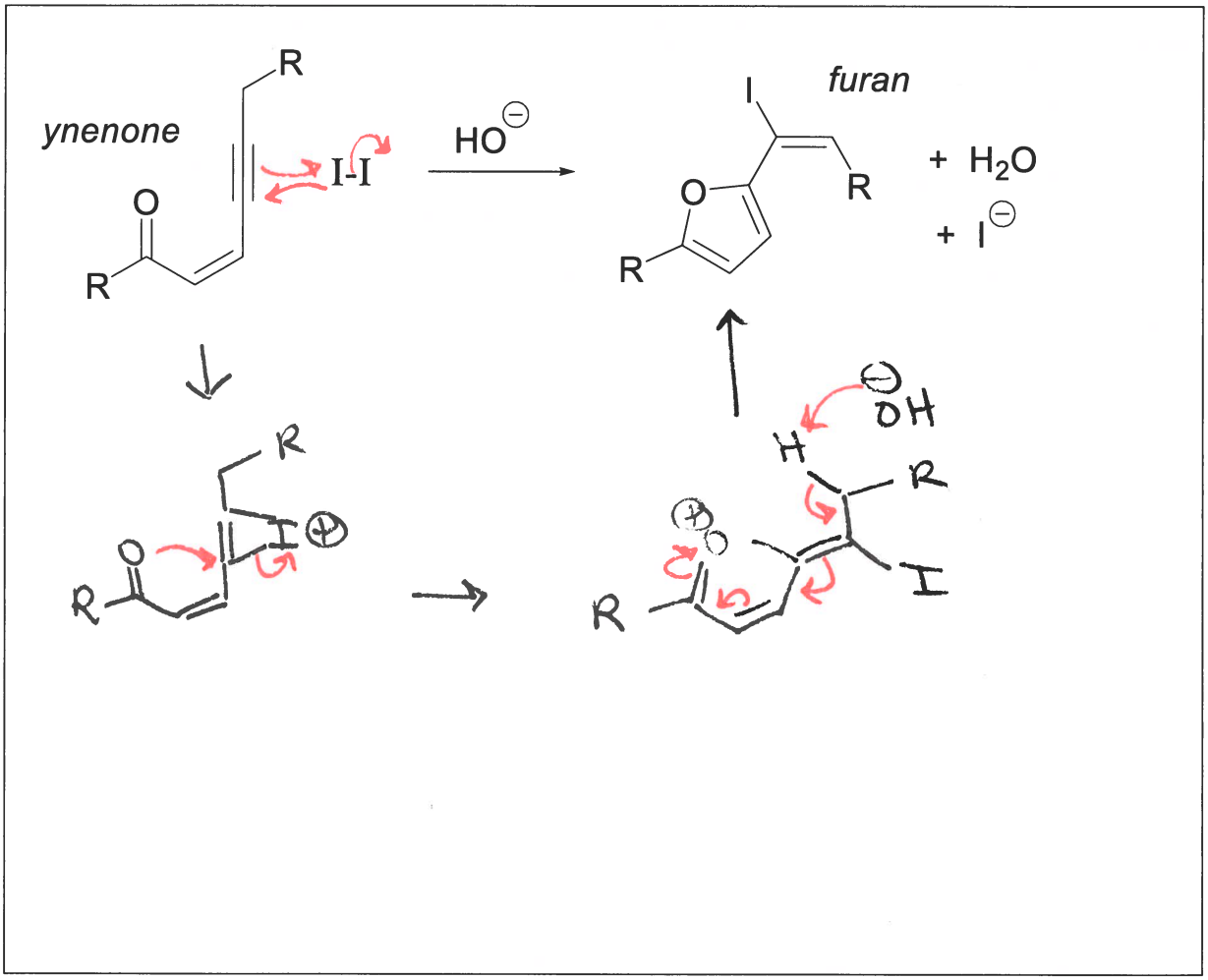




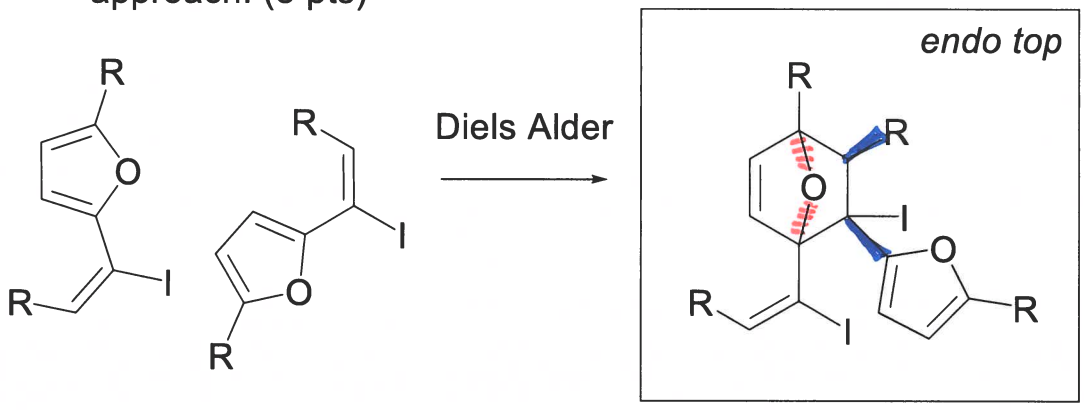
5.B. Two of the three axes (x, y and z) have p-orbitals in this ynenone.
(1) In the appropriate column, add the pi molecular orbital diagrams.
(2) Include shading, vertical nodes, as well as correct 3-D orientation according to the given corrdinate axes above.
(3) Make sure that your energy gaps are consistent, even if the absolute energies aren't perfect.
(4) Label the HOMO and LUMO of this molecule.
Hint: one of these levels has been done for you. (8 pts)



5.C. Provide a mechanism for the following transformation. (10 pts)
Hint: First step is formation of an iodonium ion with the alkyne.
Hint: Last step is acid/base with an allylic hydrogen.



5.D. Given: The furan above undergoes Diels Alder dimerization exlusively via an endo approach.
Question: Add wedges and dashes to the "IN" and "TOWARDS" substituents on the product below consistent with an **endo top** approach. (3 pts)

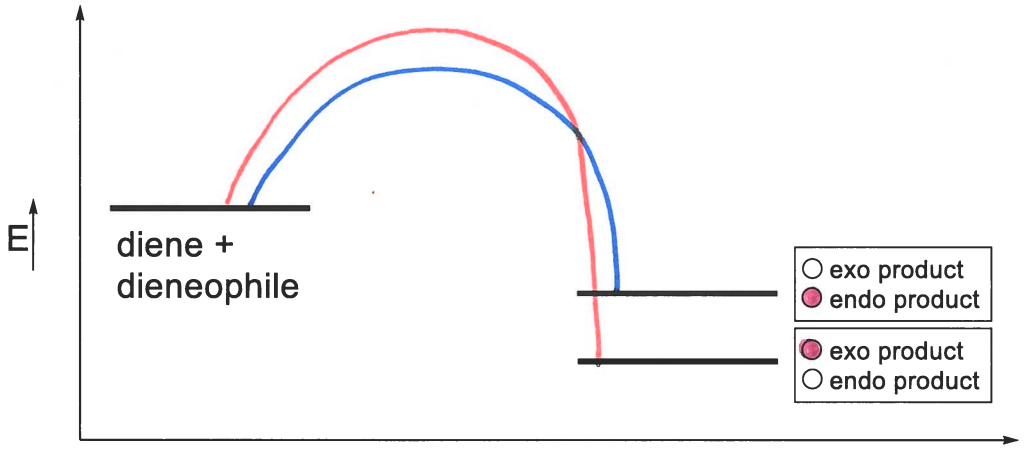


5.E. What aspect of the endo approach leads to a faster reaction rate? (2 pts)

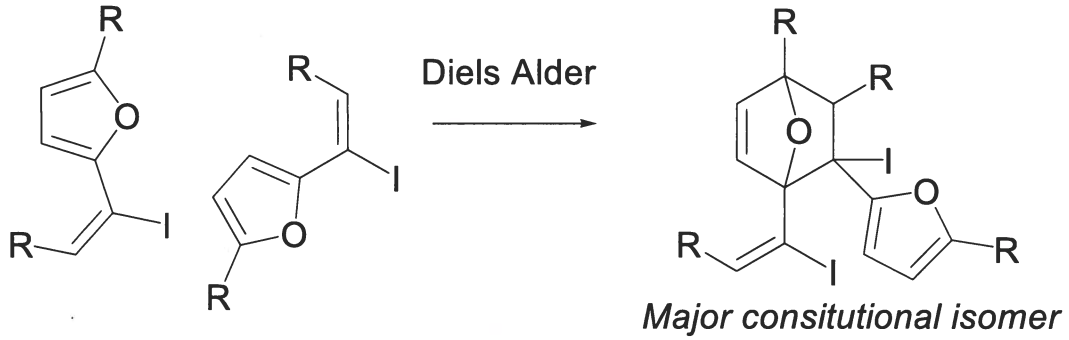
- ○ diene orientation
- ● secondary orbital overlap
- ○ electronic effects
- ○ ground state destabilization

5.F. Finish the energy diagram to make it consistent with the following data. (6 pts)

1) The endo approach has a faster rate.
2) The exo approach leads to a more stabilized product.



5.G. Explain why this consitutional isomer is the major product observed. To receive full credit, describe the specific interaction only possible for this isomer and not the other possible constitutional isomer. (5 pts)

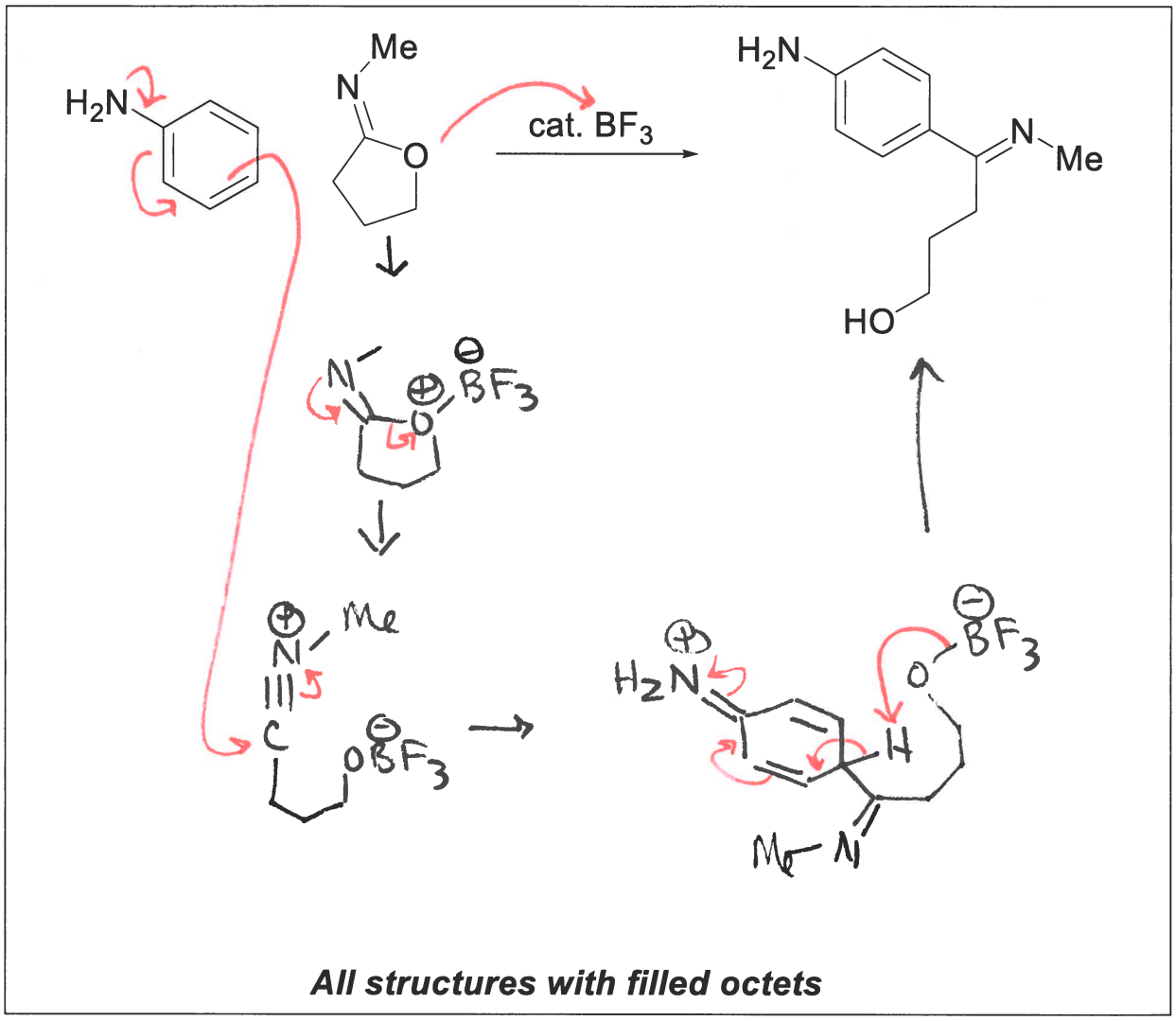


Major consitutional isomer

This is the major consitutional isomer because: the aromatic ring of the dienophile has extra secondary orbital overlap w/ the π bond of the diene.

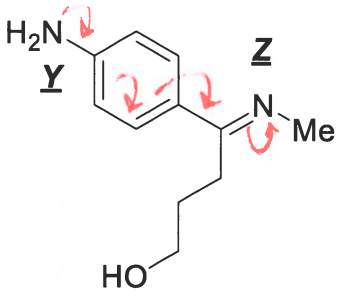
25 words or fewer

6.A. Provide a mechanism for the following reaction. It is similar to an acylation. ***The first step*** is a Lewis Acid/Base reaction between the oxygen and the boron. Make sure that **all structures have filled octets**. (15 pts)

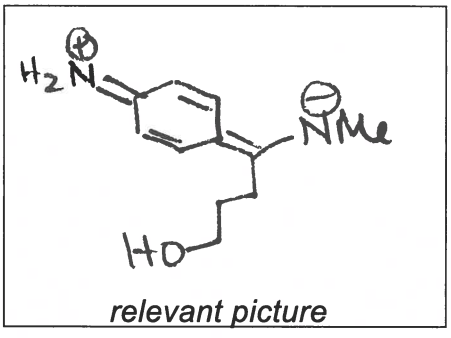


All structures with filled octets

6.B. Which nitrogen of the product is more basic? Explain with 15 words or fewer and a relevant picture. (6 pts)



Nitrogen ○ Y / ◉ Z is more basic because:

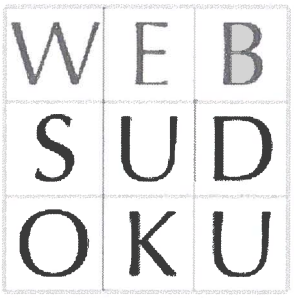


relevant picture

resonance makes it ⊖.

15 words or fewer

Here's a Sudoku for you to try while waiting for the exam. Or if you need a brain break in the middle of the exam.



Medium Puzzle 9,346,648,875

8	1	2	7	9	3	4	5	6
9	6	7	5	2	4	3	8	1
5	3	4	1	8	6	9	7	2
1	2	6	8	4	5	7	9	3
4	5	3	9	6	7	2	1	8
7	8	9	3	1	2	5	6	4
6	4	1	2	7	9	8	3	5
3	7	8	4	5	1	6	2	9
2	9	5	6	3	8	1	4	7