

# Chem 30C, Spring 2006

## Final Exam

Prof. Ohyun Kwon, UCLA

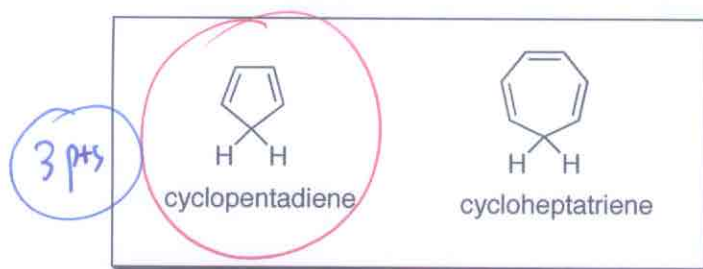
Answer Key

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Your Name (Please Print)

Question	Your points
1 (17 points)	17
2 (16 points)	16
3 (8 points)	8
4 (20 points)	20
5 (17 points)	17
6 (8 points)	8
7 (27 points)	27
8 (10 points)	10
9 (16 points)	16
10 (16 points)	16
11 (12 points)	12
12 (16 points)	16
13 (17 points)	17
Total (200 points)	200

1. (a) (9 points) Which of the following is a stronger acid? Explain why.



6 $\pi$  electrons  $\rightarrow$  aromatic  $\rightarrow$  stable

3 pts



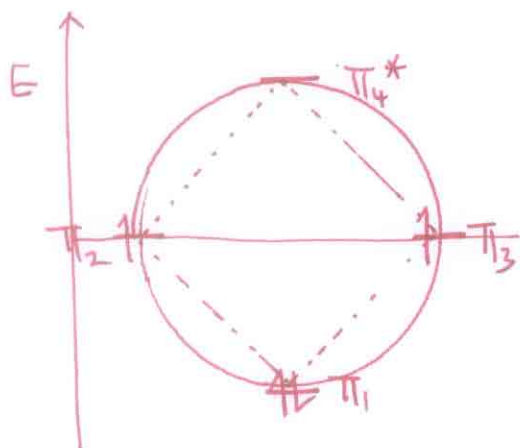
8 $\pi$  electrons  $\rightarrow$  antiaromatic  $\rightarrow$  unstable  
(if planar)

3 pts

$\therefore$  likely to be nonaromatic

and no extra stabilization

(b) (8 points) Draw the pi molecular orbital (MO) energy diagram of cyclobutadiene. Indicate in which  $\pi$  MO's the electrons are located and predict the stability of cyclobutadiene in a very short sentence.



4 pts

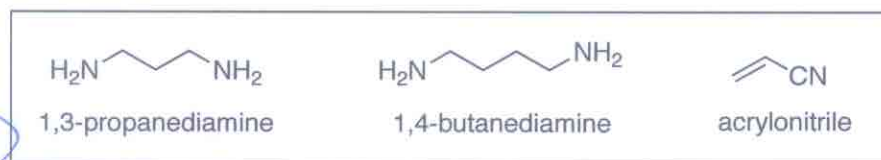
The two unpaired electrons in  $\pi_2$  and  $\pi_3$  non-bonding MOs make cyclobutadiene unstable and reactive (like a (di)radical).

$\rightarrow$  antiaromatic

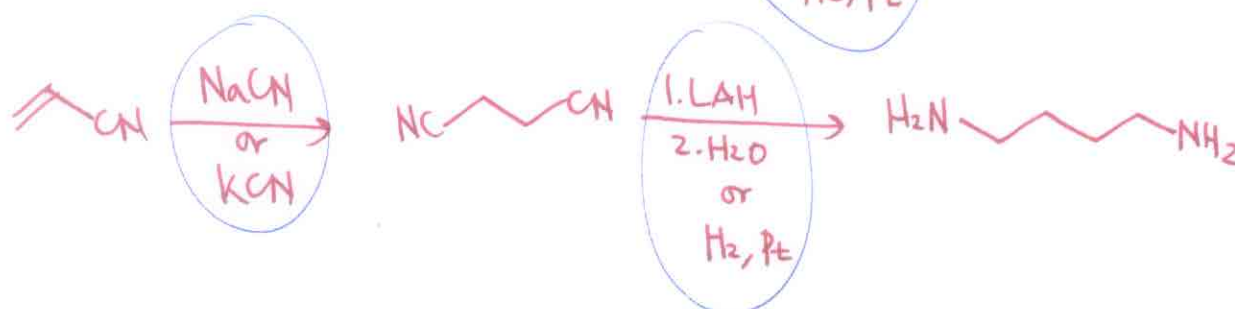
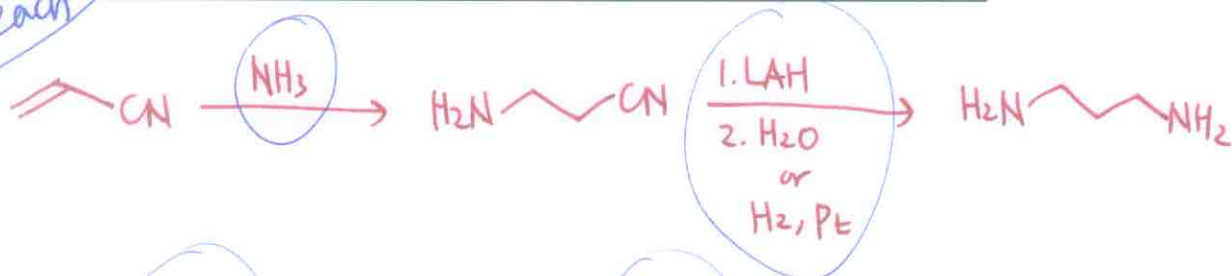
4 pts

or

2. (a) (8 points) Several diamines are common building blocks for the synthesis of pharmaceutical drugs and agrochemicals. Show how 1,3-propanediamine and 1,4-butanediamine can be prepared from acrylonitrile.



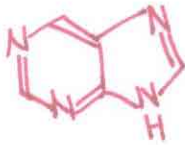



2 pts each



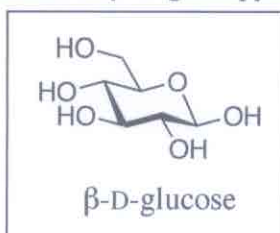
(b) (8 points) Draw structural formulas for the following heterocyclic aromatic compounds.

2 pts each

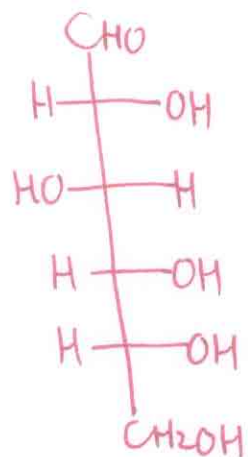
			
Imidazole	indole	purine	pyrimidine

3. (8 points) Write Fisher projections of D-glucose and L-glucose.

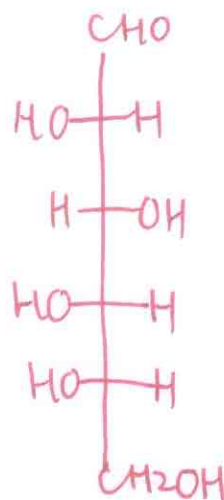
Hint: The following is the structure of  $\beta$ -D-glucopyranose ( $\beta$ -D-glucose).



4 pts each

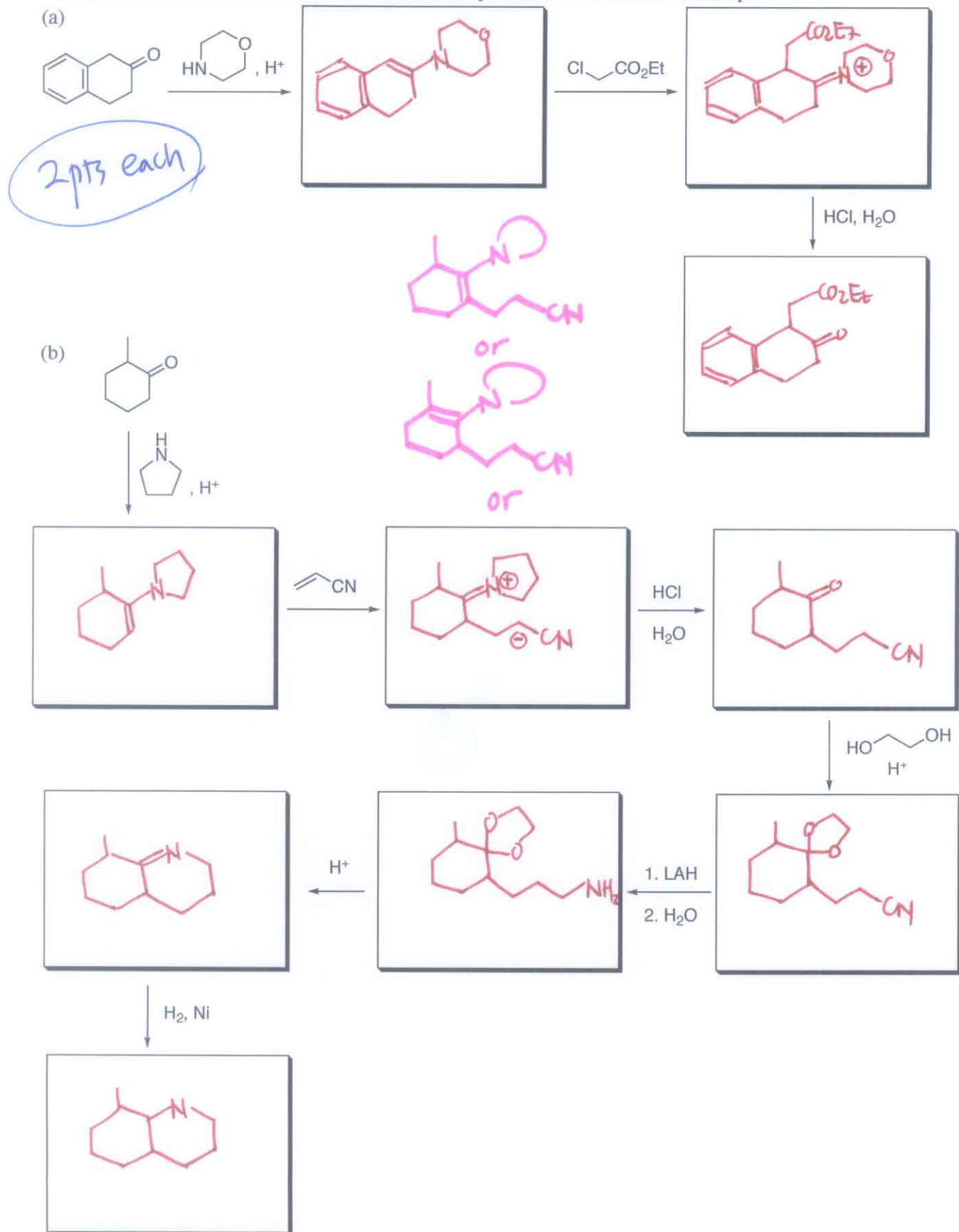


D-glucose

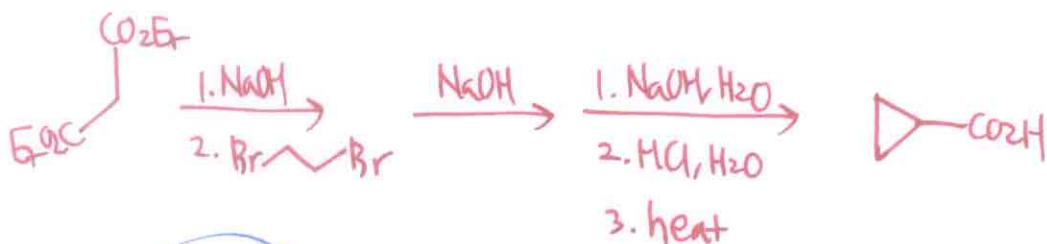


L-glucose

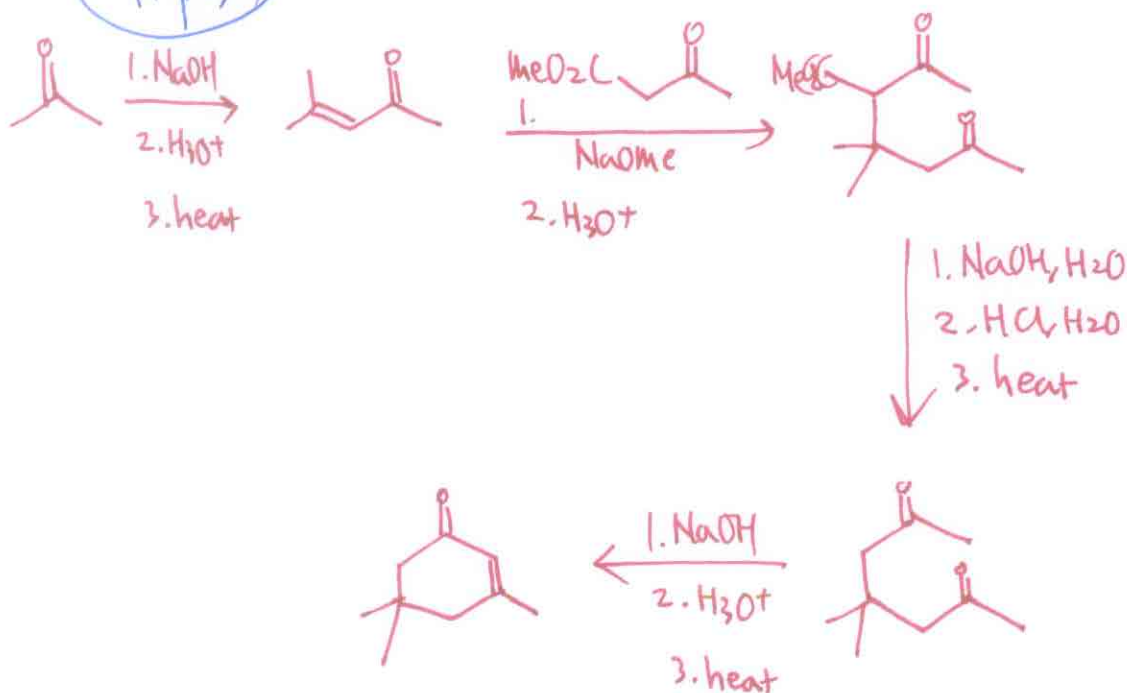
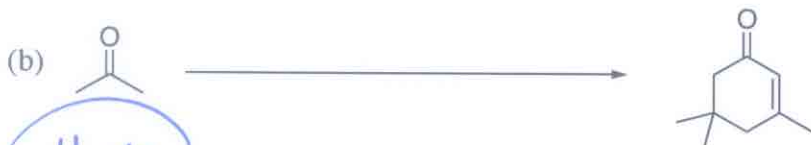
4. (20 points) Provide structural formulas for the products of each reaction step.



5. (17 points) Show how to synthesize the following products from the given starting materials using either the malonic ester synthesis or the acetoacetic ester synthesis.

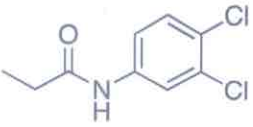
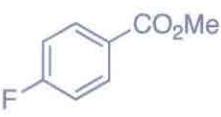
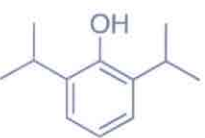
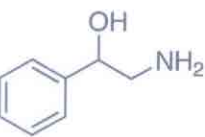


6 pts



6. (8 points) Name the following molecules.

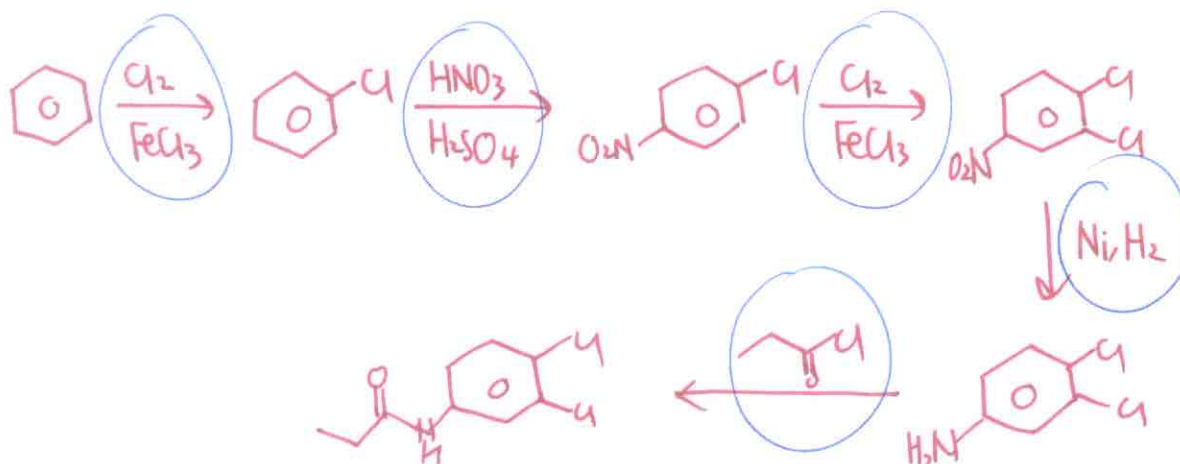
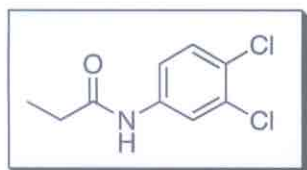
2 pts each

	propan-3,4-dichloroanilide propion-3,4-dichloroanilide
	methyl 4-fluorobenzoate
	2,6-diisopropylphenol
	2-amino-1-phenylethanol

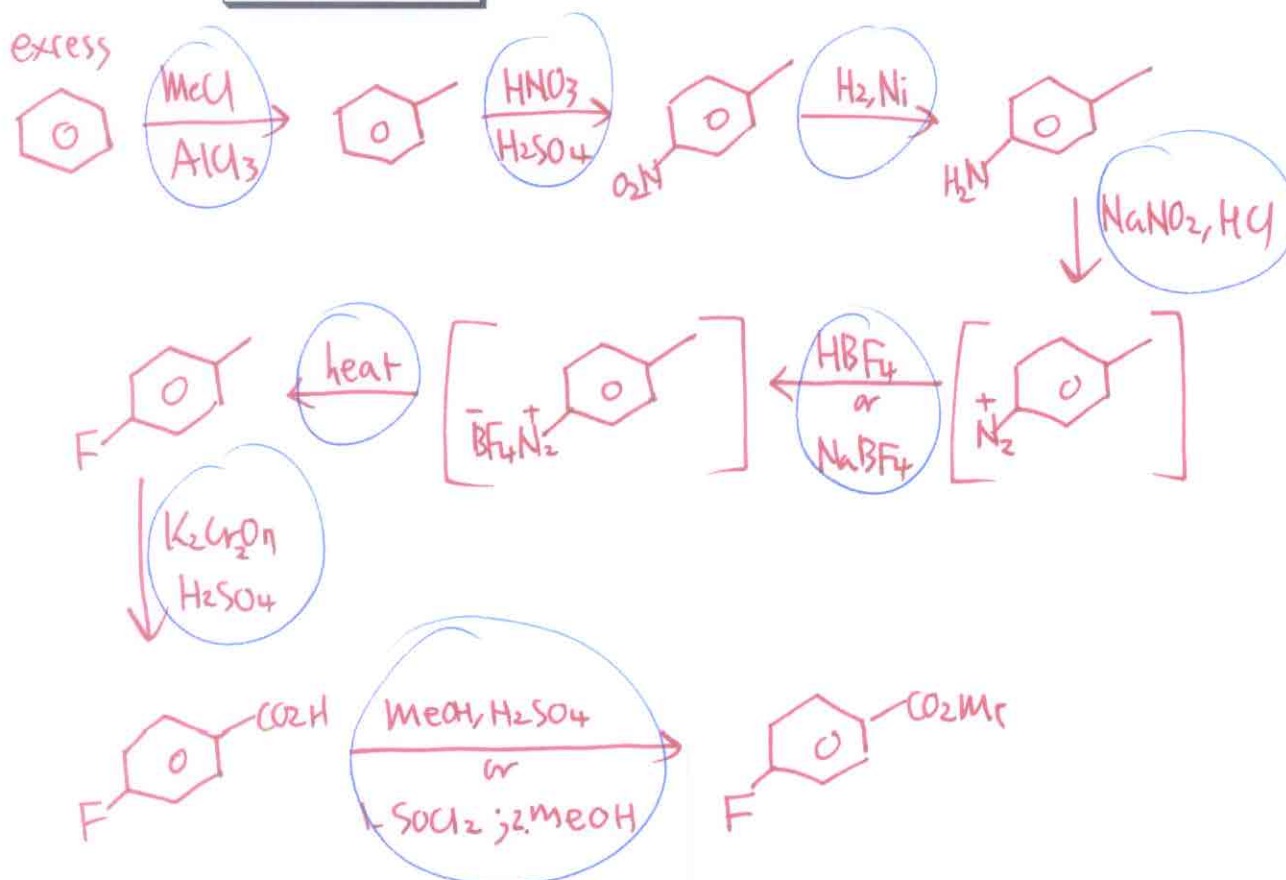
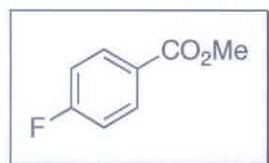
7. Show how each of the following compounds can be synthesized from benzene.

1 pt each

(a) (5 points)



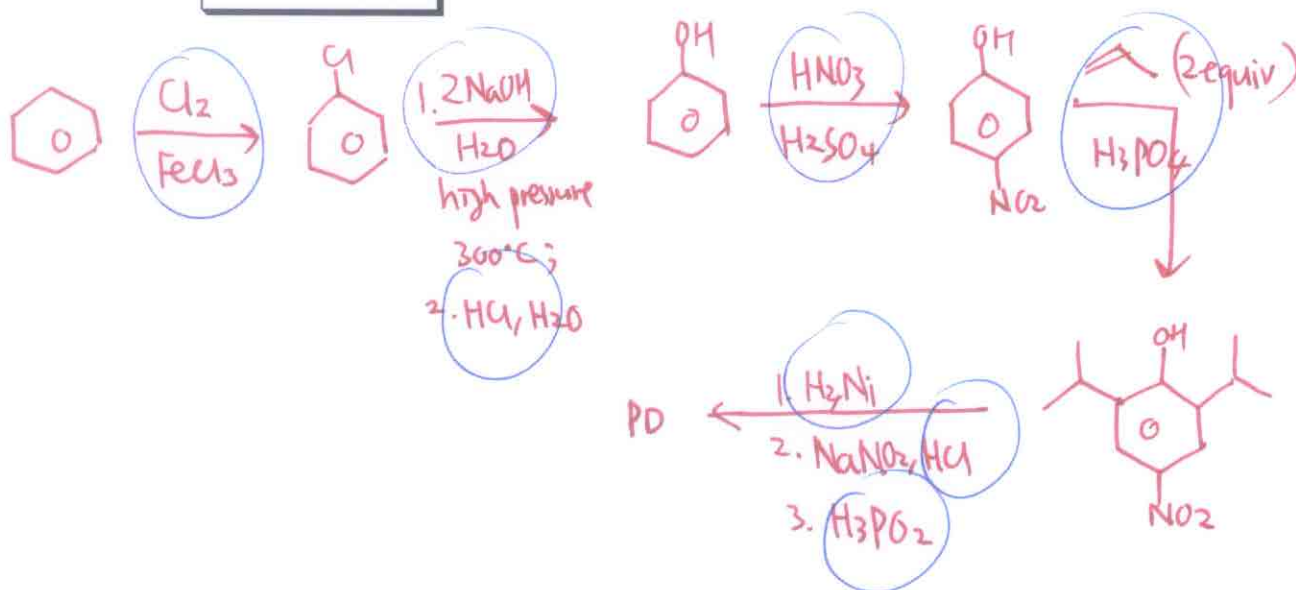
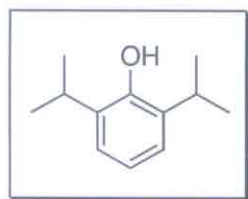
(b) (8 points)



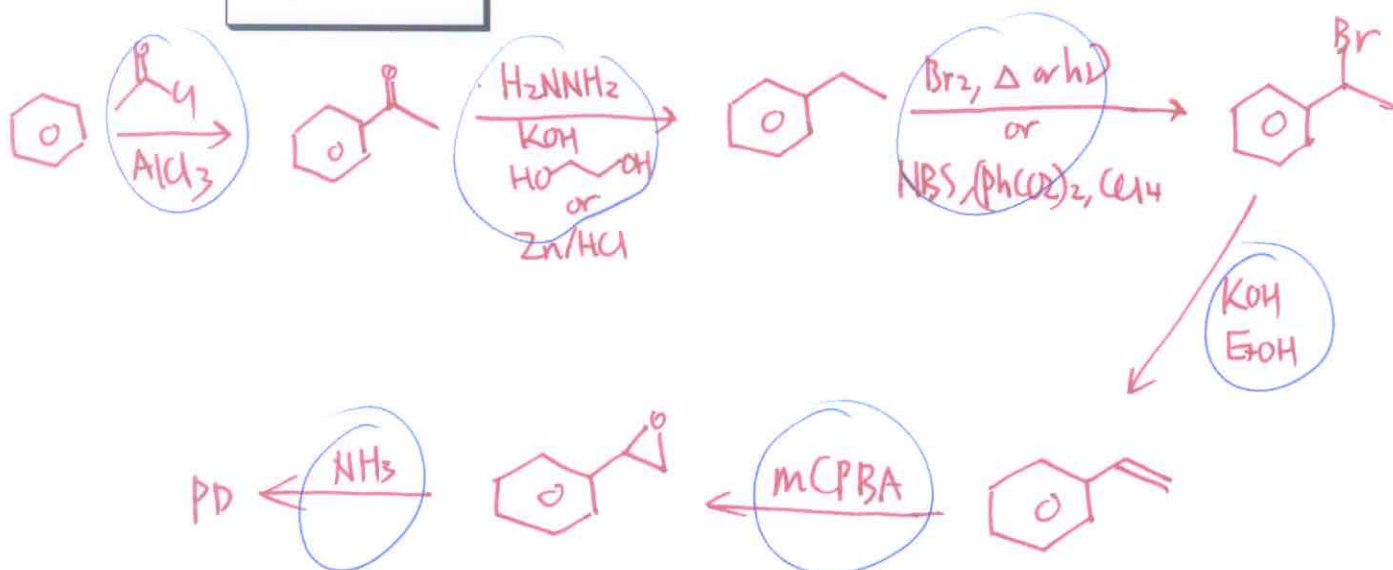
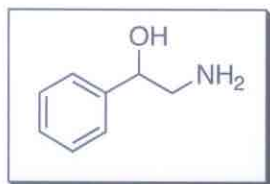


7. Continued.

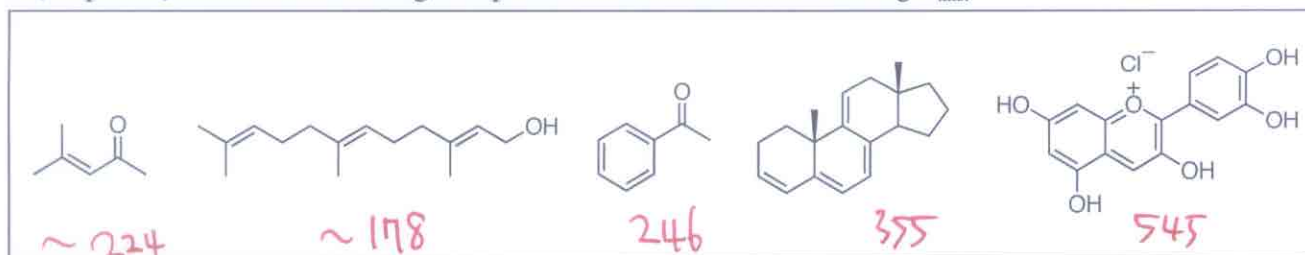
(c) (8 points)





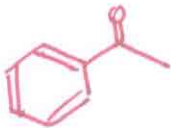
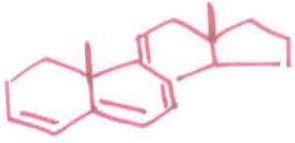
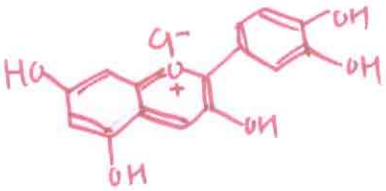
(d) (6 points)



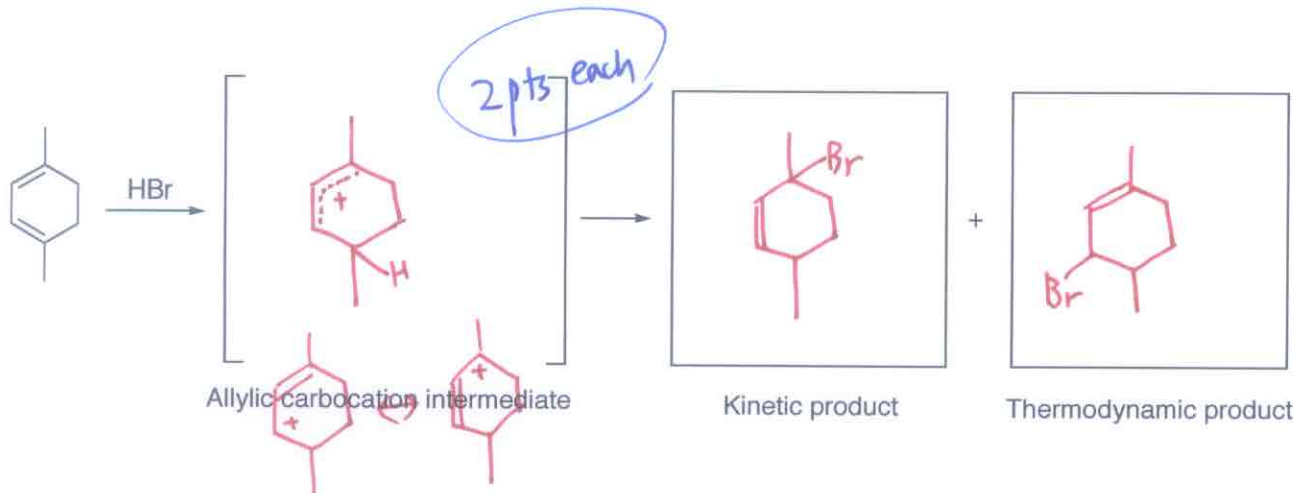
8. (10 points) Rank the following compounds in the order of increasing  $\lambda_{\max}$ .



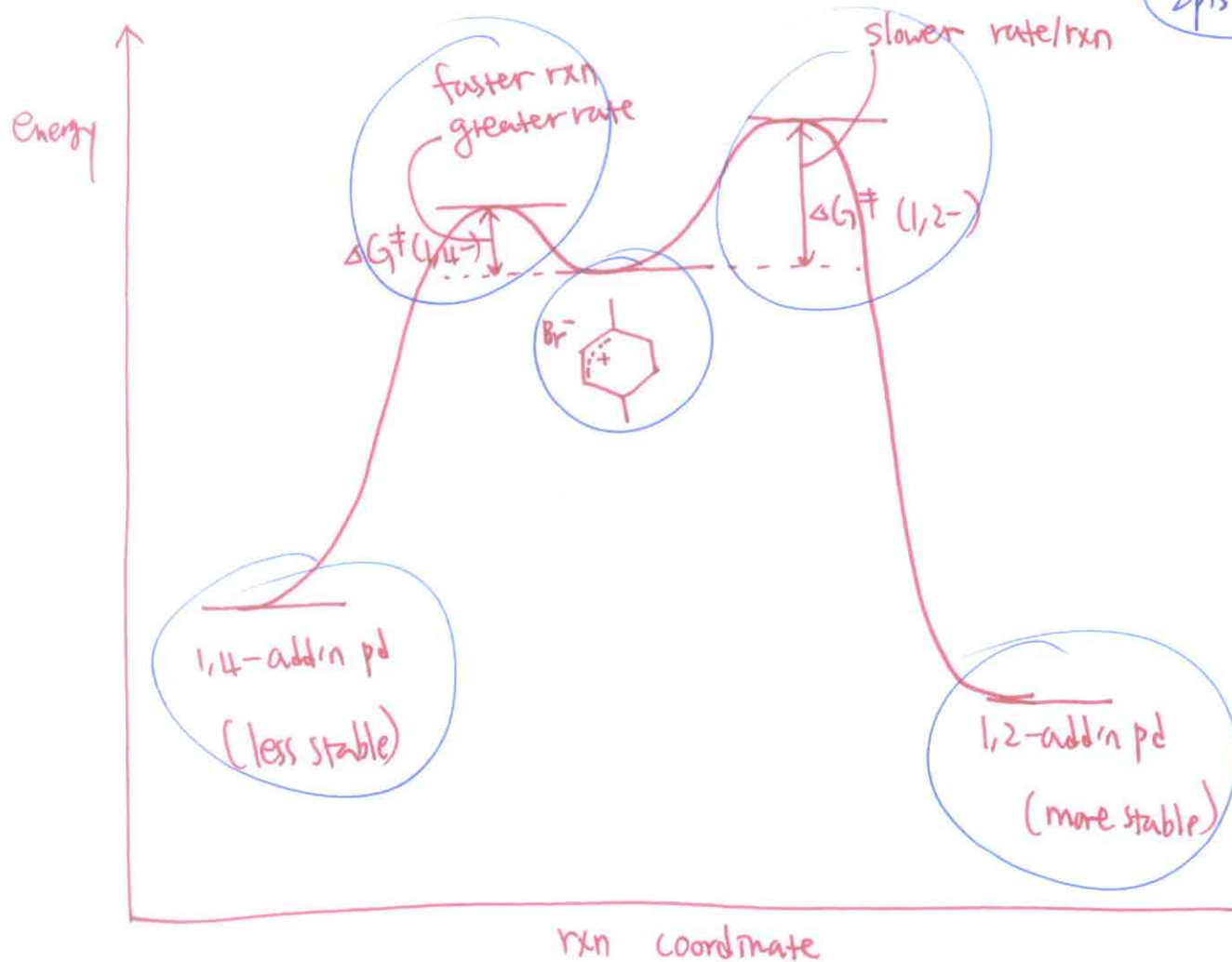
Cyanidine chloride

Smallest $\lambda_{\max}$		2 pts each
↓		
↓		
↓		
Largest $\lambda_{\max}$		

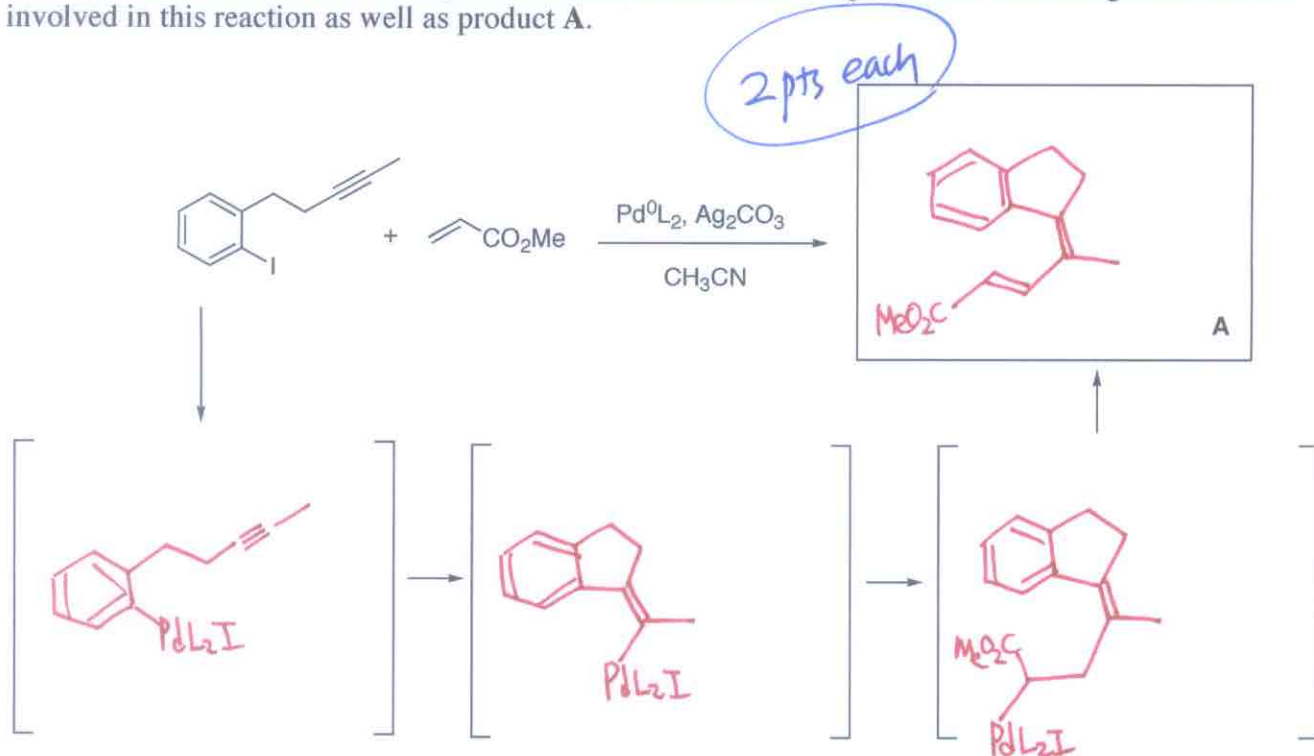
9. (a) (6 points) Predict the structures of the expected kinetic and thermodynamic products from addition of one mole of HBr to 1,4-dimethyl-1,3-cyclohexadiene.



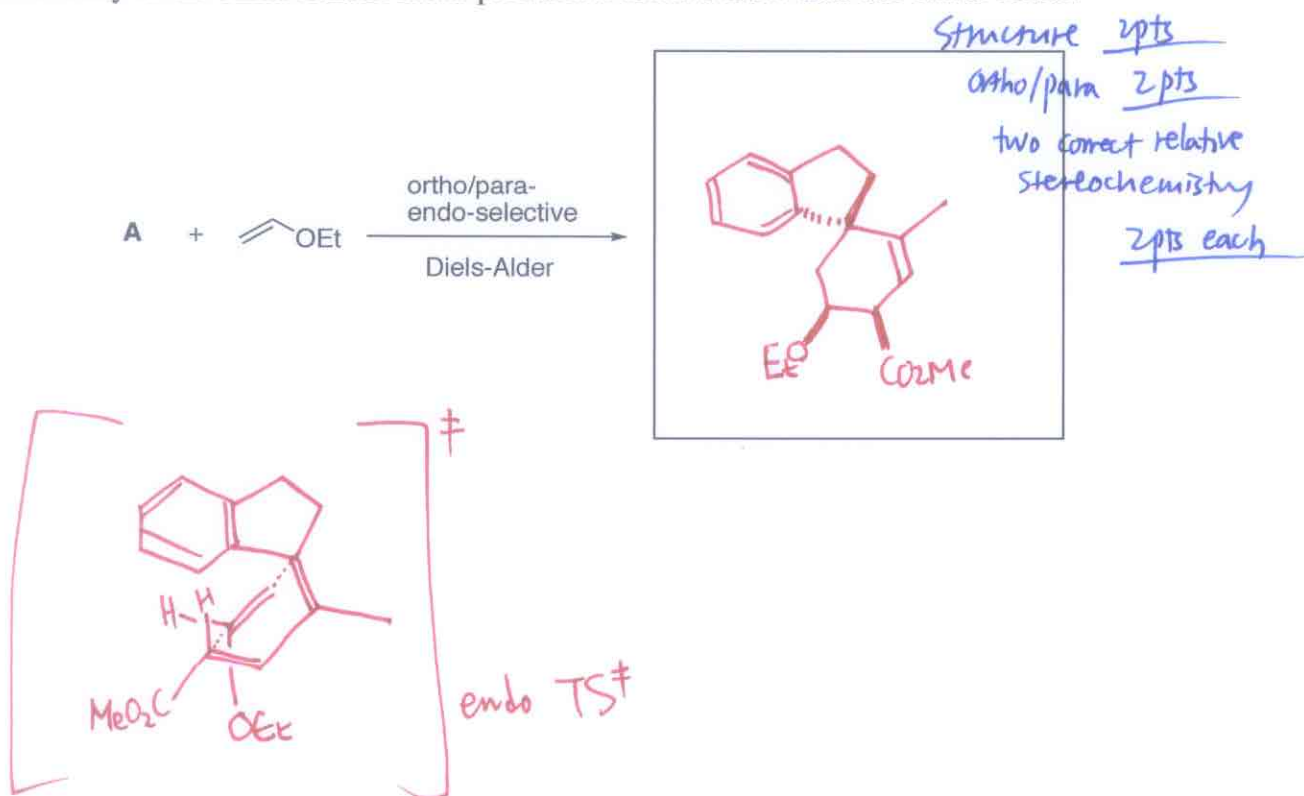
(b) (10 points) Draw a plot of Gibbs free energy versus reaction coordinate for the reaction of bromide ion with the allylic carbocation intermediate in the above electrophilic addition of HBr to 1,4-dimethyl-1,3-cyclohexadiene. Clearly indicate relative energies of the allylic carbocation intermediate, 1,2-addition product and 1,4-addition product as well as the activation energies for the formation of the 1,2-addition product and the 1,4-addition product.



10. (a) (8 points) The following conversion involves an intramolecular Heck reaction followed by an intermolecular Heck reaction. Propose structural formulas for the palladium-containing intermediates involved in this reaction as well as product A.

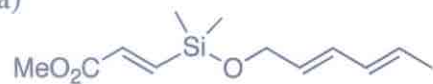


(b) (8 points) Predict the structure of the product of the ortho/para and endo selective Diels-Alder reaction between A (product from the Heck reaction above) and ethyl vinyl ether. Specify the relative stereochemistry of the chiral centers in the products if there is more than one chiral center.

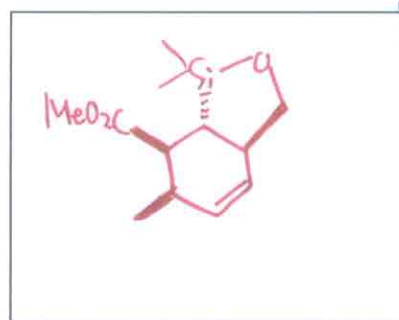


11. (12 points) Predict the structures of the products of the reactions shown below. Specify the relative stereochemistry of the chiral centers in the products if there is more than one chiral center.

(a)



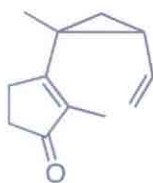
160 °C



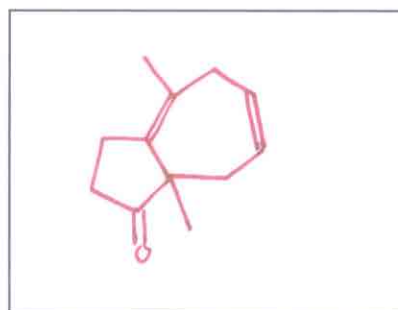
3 pts each

endo product

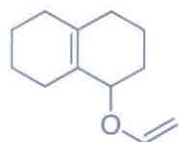
(b)



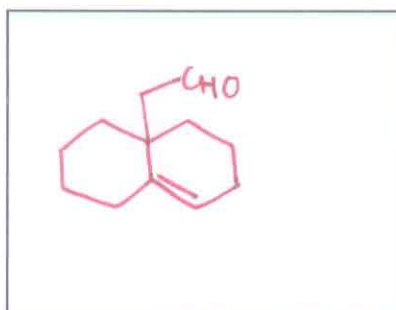
98 °C



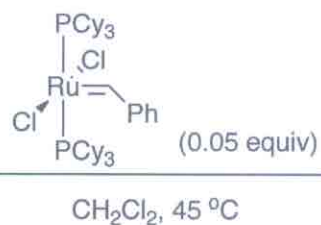
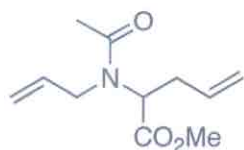
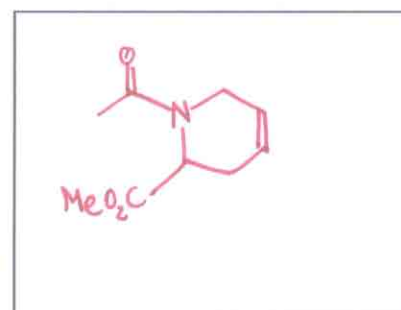
(c)



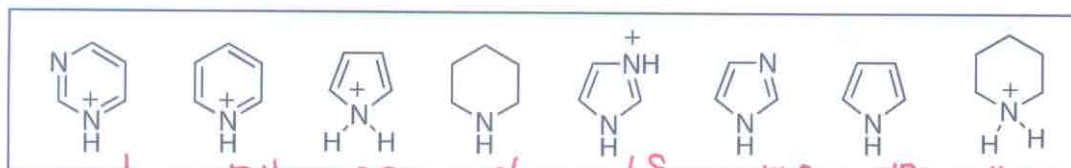
195 °C











(d)

CH<sub>2</sub>Cl<sub>2</sub>, 45 °C

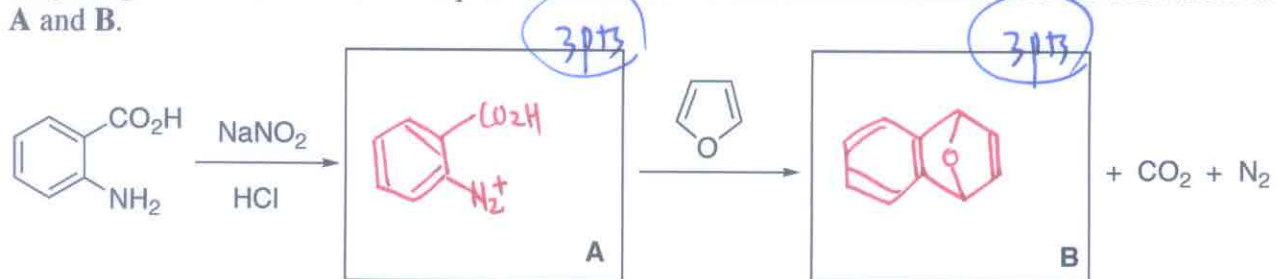
12. (16 points) List the following compounds in order of decreasing acidity.



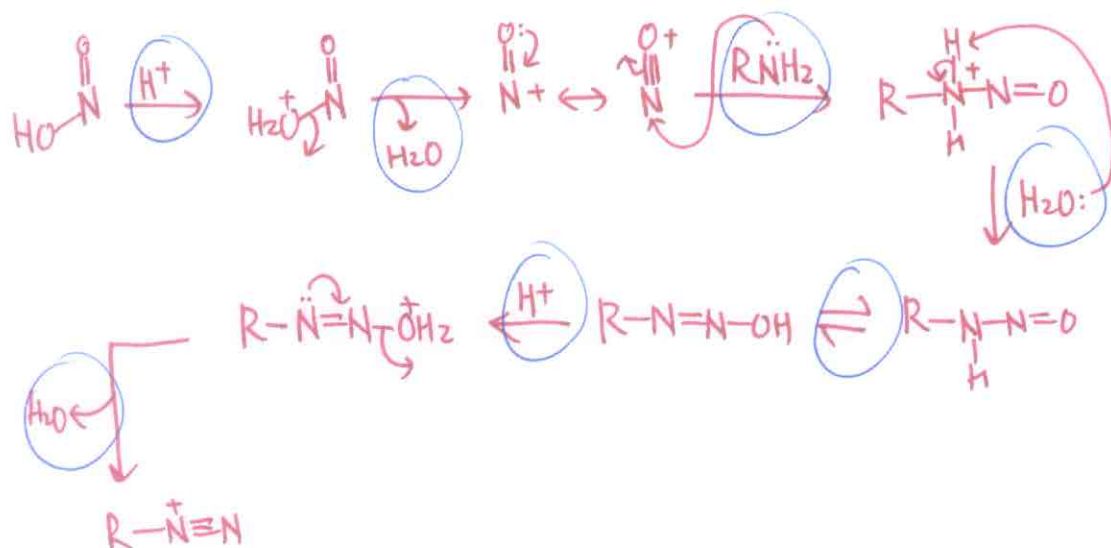
Most acidic		-3.8
↓		1
↓		5.16
↓		6.8
↓		11.2
↓		14.7
↓		17
Least acidic		36

2pts each

13. (17 points) Treatment of anthranilic acid with sodium nitrite and HCl provides an intermediate, **A**, that contains a diazonium ion and a carboxyl group. When **A** is heated in the presence of furan, a tricyclic product, **B**, is formed. Propose structures for **A** and **B** and mechanism for the formation of **A** and **B**.

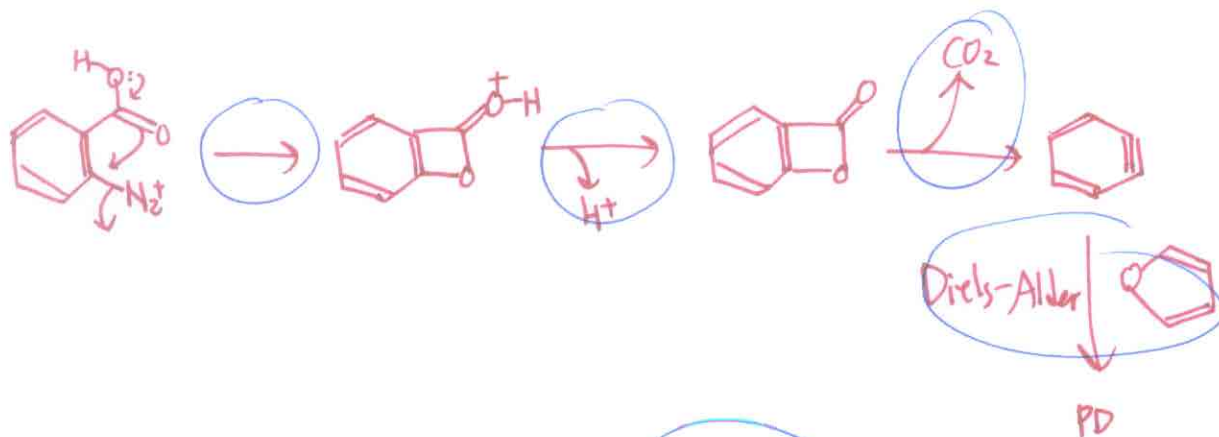


Mechanism for the formation of **A**



2 pts

Mechanism for the formation of **B**



4 pts