

Circle one: I wish to have my exam
put in the rack.

I wish to pick up
my exam.

Printed Name Answer Key
(Please print clearly)

Signature _____

CHEMISTRY 262

Exam I
100 Points

February 5, 2013
6:30 – 8:30 PM

This exam has 8 problems on pages 2 through 8.

RULES

1. The use of a calculator and model kits are **not** permitted.
2. This exam is closed book and closed note. No aids other than writing implements are permitted.
3. Answer the questions in the spaces provided on this exam.
4. If you wish to ask a question about procedures or about a problem on the exam, raise your hand.

1. _____

6. _____

2. _____

7. _____

3. _____

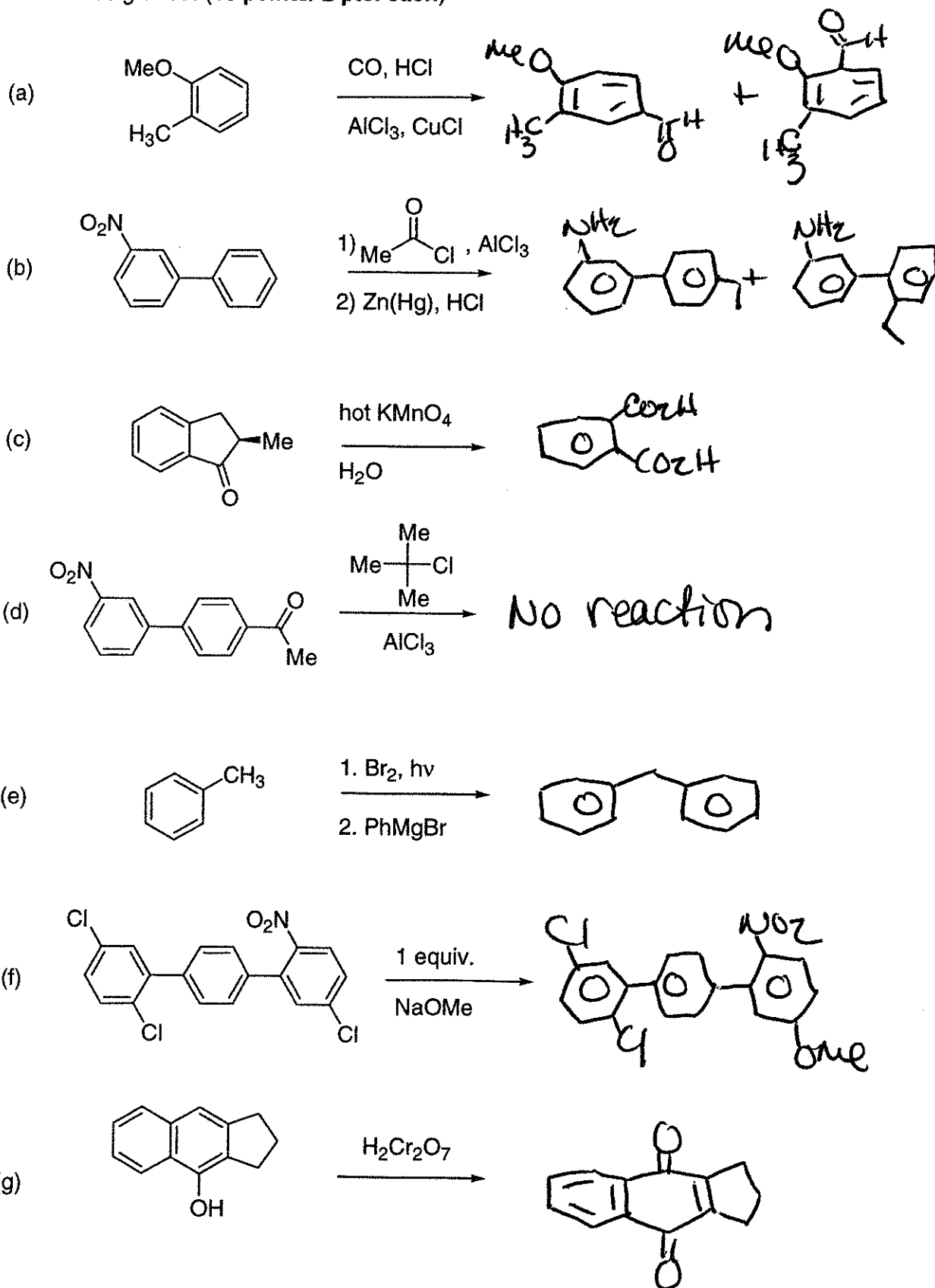
8. _____

4. _____

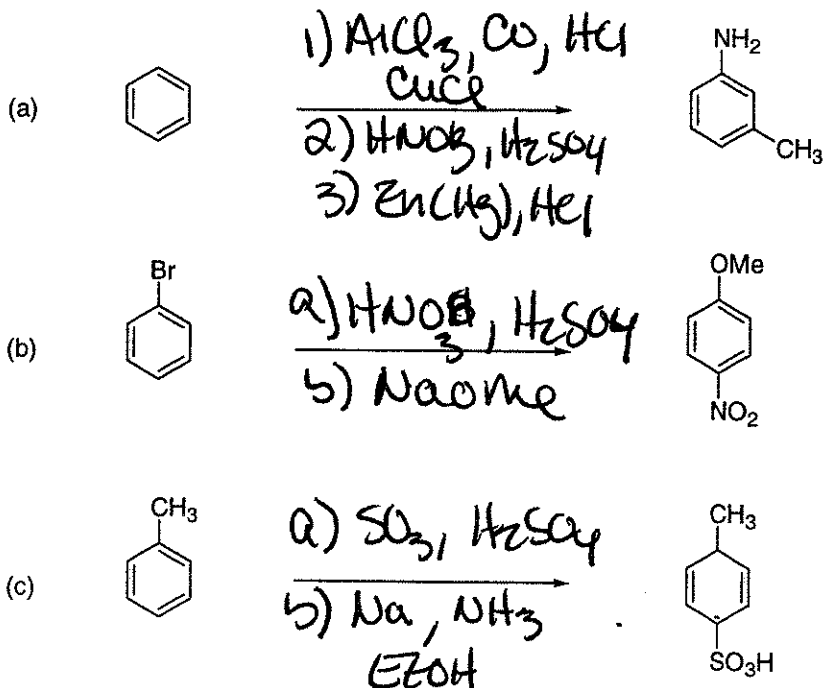
5. _____

TOTAL: /100

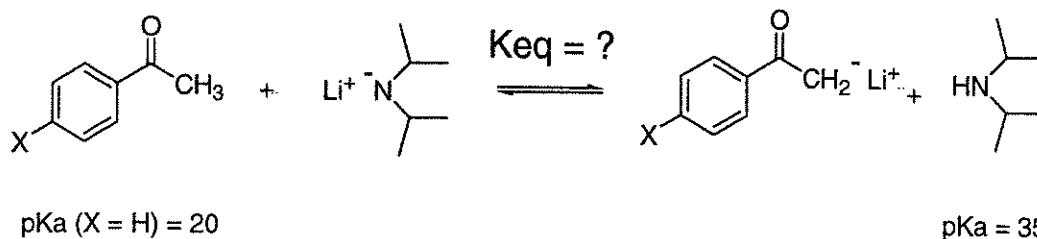
1. Predict the major product or products (be inclusive) that you would expect to be formed in **five** of the following seven reactions. If you feel that no reaction will occur, then answer no reaction. Be sure to answer **only** five problems. If you answer more than five, then *only your first five will be graded*. (10 points/ 2 pts. each)



2. Fill in the reagents needed for accomplishing **two** of the three following transformations. More than one step is required. Remember that the order of the steps in a synthesis is important. Be sure to answer **only two** problems. (6 points/ 3 pts. each)



3. a. What is the equilibrium constant for the following reaction? (5 points)

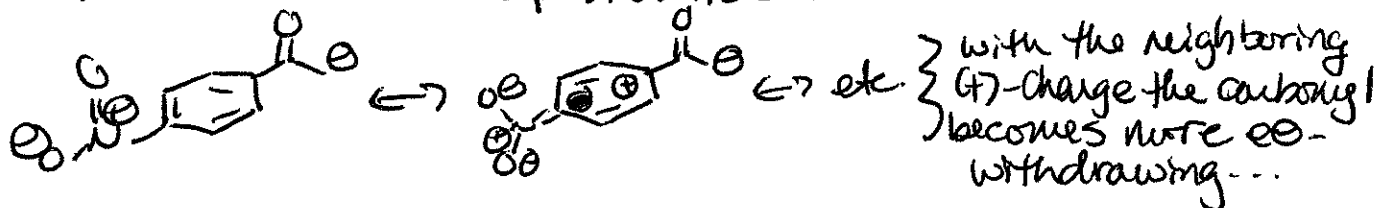


$$\text{pK}_{\text{eq}} = 20 - 35 = -15$$

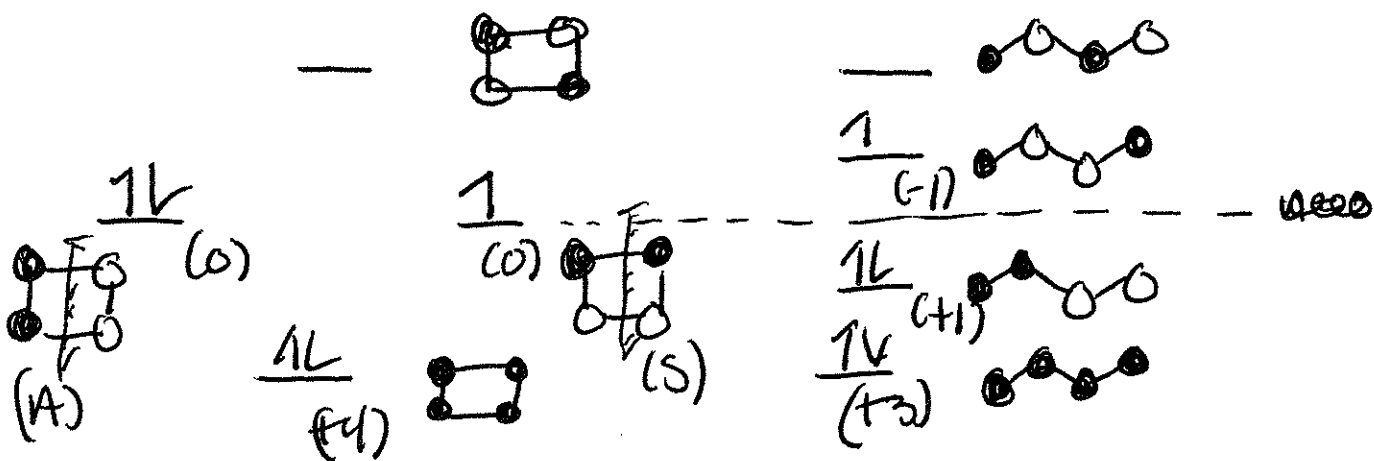
$$\text{K}_{\text{eq}} = 10^{15}$$

- b. The pK_a given for the ketone was for a substrate where $\text{X} = \text{H}$. Would the pK_a of the ketone be higher or lower than 20 if the substituent (X) was a nitro (NO_2) group? Why? (4 points)

Lower. The molecule would be more acidic because the EWG would help stabilize the anion.



4. a. On several of the practice exams, you were asked about what would happen to an aromatic ring if you added or removed an electron from the π -system. Along the same lines, people have wondered what would happen if you added an electron to a system that is anti-aromatic. Does it become an aromatic ring? Show how you would answer this question with a consideration of cyclobutadiene (shown below). (10 points)



$$\text{Bonding} = 4(2) + 0(2) + 0(1)$$

$$= \boxed{8}$$

$$\text{Bonding} = 3(2) + 2(1) + 1(-1)$$

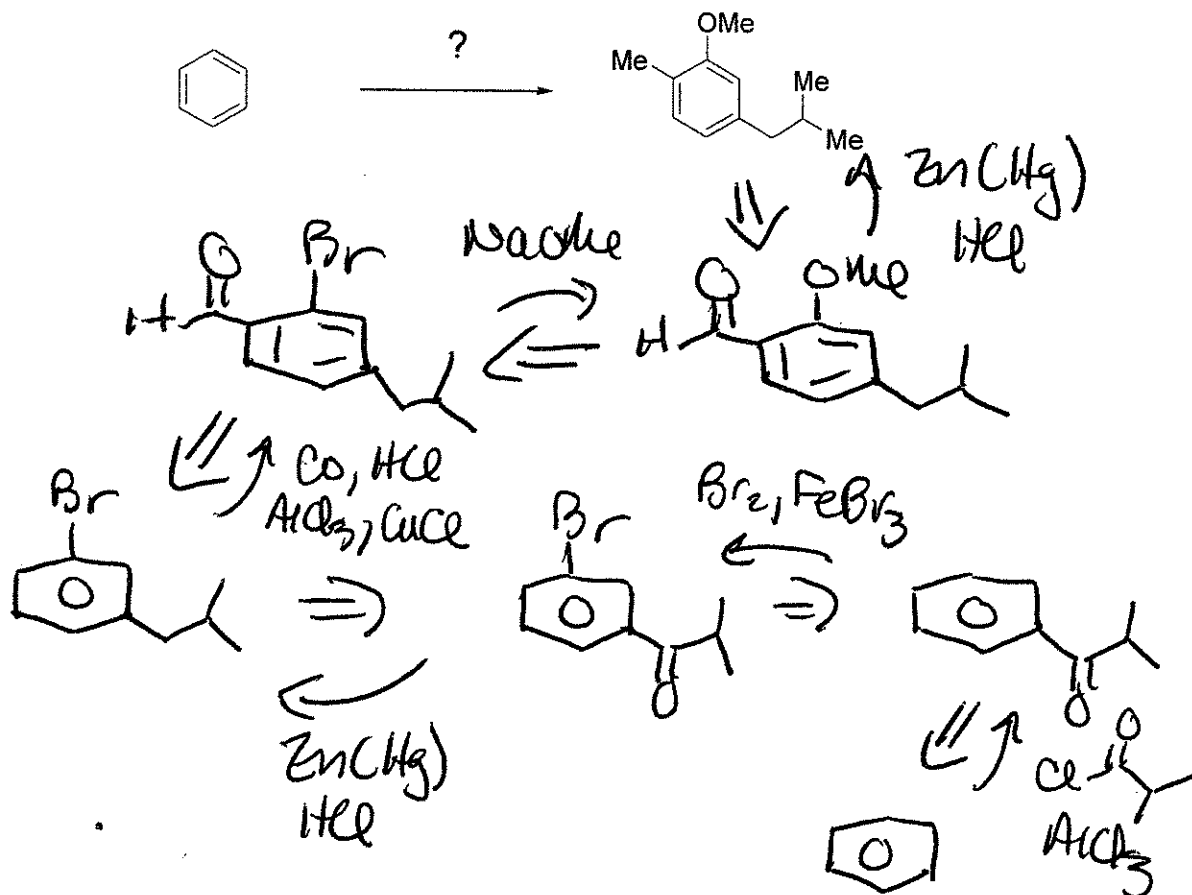
$$= 7$$

The cyclic radical anion is more stable than its acyclic counterpart. It is aromatic! ^{So the answer} is YES.

- b. In part a, cyclobutadiene was pictured as a rectangle. Would the addition of an electron to cyclobutadiene to make the radical anion change this geometry? Why or why not? (5 points)

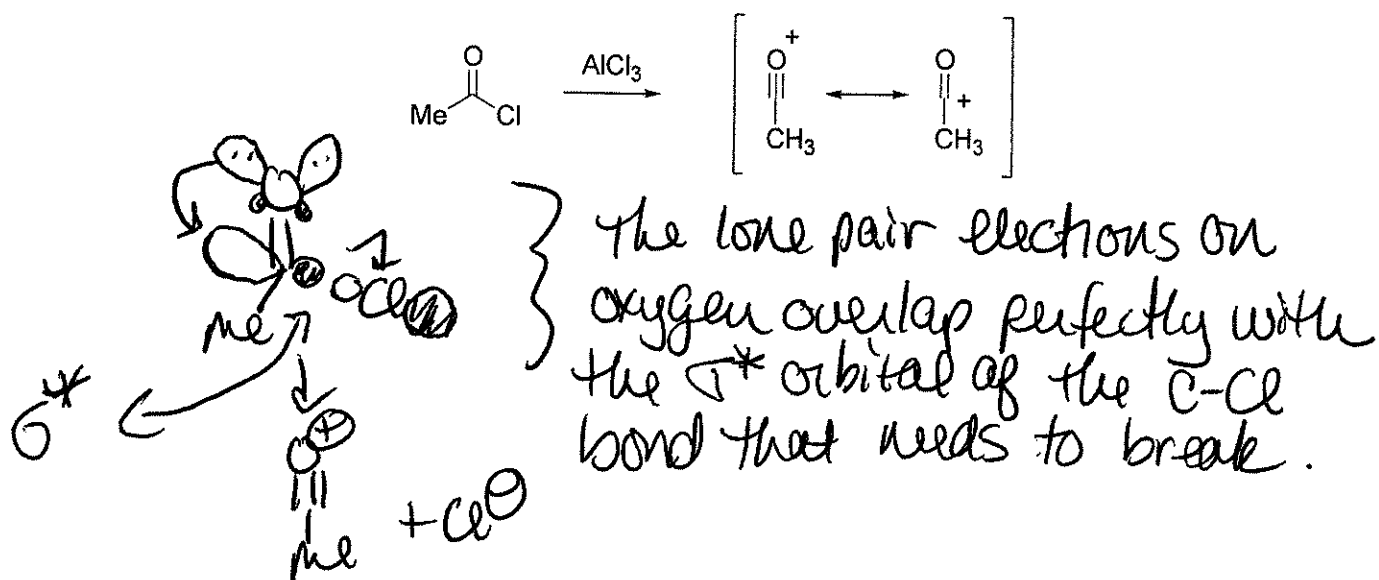
Yes. The geometry becomes symmetrical (a square) because the electrons fully-delocalize. ~~So that~~ ~~the molecule can be aromatic.~~ ~~There is a driving force~~ There is a driving force for the molecule to be aromatic.

5. Suggest a synthetic scheme that would allow you to accomplish the following transformation. Make sure that you show your retrosynthesis – it will help. (10 points)

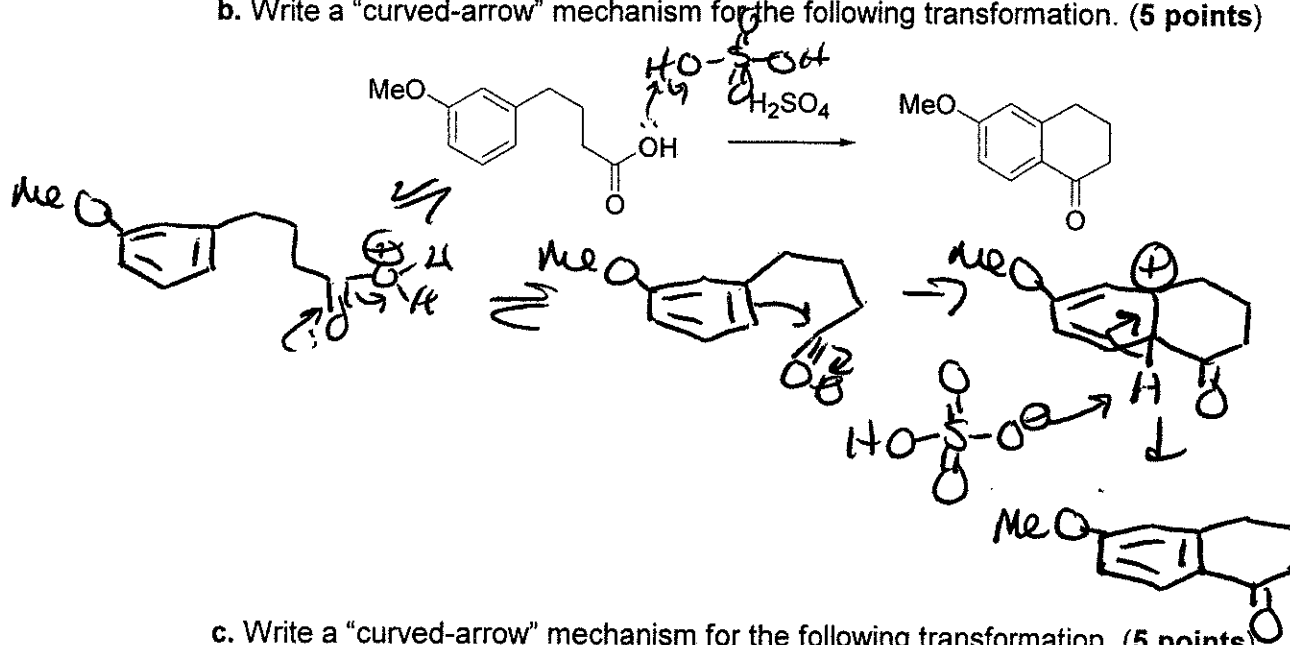


6. Consider each of the following mechanism questions:

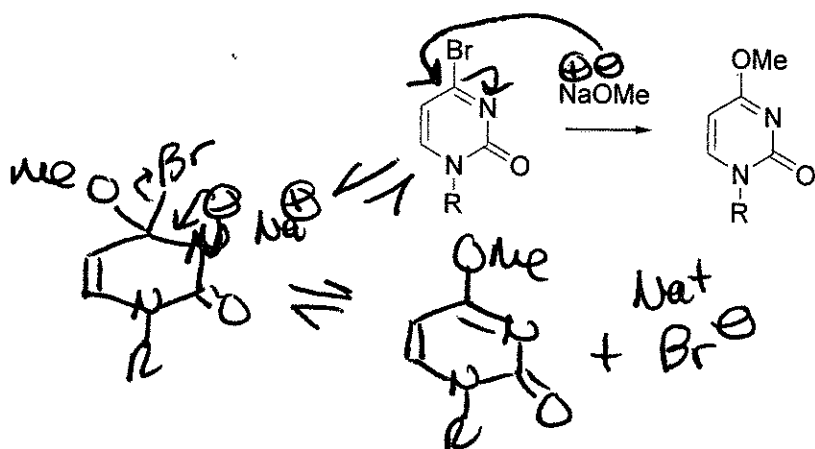
a. Initially, it seems surprising that acylium ions form so easily during a Friedel-Crafts acylation. However, a consideration of orbitals can provide a nice rationale for this observation. With this in mind, draw the σ^* -orbital for the C-Cl bond and use your drawing to illustrate why acylium ions are so easy to generate. (5 points)



b. Write a "curved-arrow" mechanism for the following transformation. (5 points)

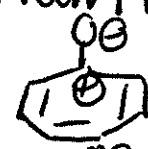



c. Write a "curved-arrow" mechanism for the following transformation. (5 points)



d. Would the equilibrium constant for the reaction illustrated below be less than or greater than one? In other words, which side of the equilibrium would be favored? Why? (5 points)



$K_{eq} > 1$. The equilibrium would lie to the right because  has aromatic character and  anti-aromatic character.

7. Parts a – e. For each series of molecules illustrate below an arrow points to a bond. Rank the wavenumber that would be associated with the bond indicated from the highest (assign the number 1) to the lowest (assign the number 3) value. (10 points)

Answers for part f below:

a.				<div style="border: 1px solid black; padding: 5px; display: inline-block;">1780-1800 cm⁻¹</div>
b.				<div style="border: 1px solid black; padding: 5px; display: inline-block;">2200-2000 cm⁻¹</div>
c.				<div style="border: 1px solid black; padding: 5px; display: inline-block;">~ 3500 cm⁻¹</div>
d.				<div style="border: 1px solid black; padding: 5px; display: inline-block;">3000-3100 cm⁻¹</div>
e.				<div style="border: 1px solid black; padding: 5px; display: inline-block;">1780-1800 cm⁻¹</div>

f. For each molecule that you labeled with a 1 in parts a – e, indicate the region of the IR spectrum (an approximate wave number or range of wave numbers) where you would find the stretch for the bond indicated. Write the number or range of numbers in the right hand margin next to the series above. (5 points)

g. For part e above, which aldehyde would have the most intense signal? Why? (5 points)

