Chemistry 342-75
Spring 2015
Final Exam
Dr. Richter

Name KEY

Signature _____

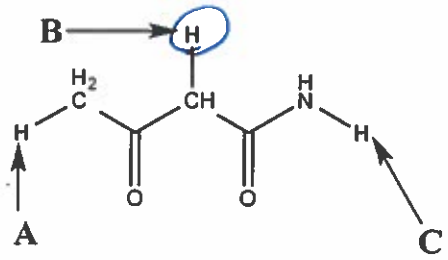
You are required to answer all question sets. Please note that some of the question sets offer you a choice of questions - do only the number of questions asked for. Please write legibly and draw clearly. Points will be deducted for illegible and unclear answers. The point total for this exam is 210 and the value of each question set is shown in parenthesis beside that set. ***READ ALL QUESTIONS CAREFULLY AND APPORTION YOUR TIME ACCORDINGLY***.

## I. NEW MATERIAL (100 Points Total)

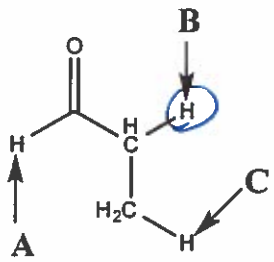
### PART ONE: STRUCTURE, REACTIVITY, MECHANISM (45 points)

For **1-3**, indicate which proton A, B, or C has the lowest pKa. *Circle your answer.* **(9)**

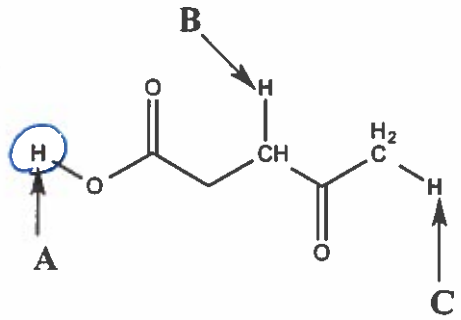
1.



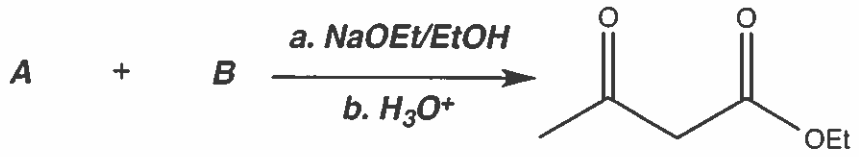

2.




3.



The product below was obtained using enolate chemistry.




For questions 4-7 indicate if the statement is **TRUE or FALSE** regarding the above reaction. *Circle your answer.* **(8)**

4. The organic reaction product is more acidic than either one of the organic starting materials.

**TRUE** **FALSE**

5. The enolate could have been generated from a ketone.

**TRUE** **FALSE**

6. The organic reaction product could form a conjugated carbonyl if heated.

**TRUE** **FALSE**

7. The electrophile must have had a leaving group.

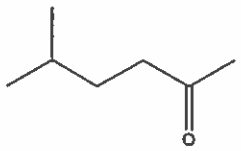
**TRUE** **FALSE**

8. Circle **all TRUE** statements regarding enolates. **(6)**

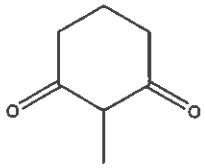
A. An enolate contains a nucleophilic carbon.
B. Enolates are resonance-stabilized anions.
C. In general, enolates of amides are more stable than enolates of esters.
D. If NaOEt is used to deprotonate an α-carbon, nearly 100% of the corresponding enolate will be formed.
E. When dealing with an asymmetric ketone, the formation of the kinetic versus the thermodynamic enolate can be controlled by both the temperature and choice of base.

9. Draw the **major** enolate that would form if the following compound was treated with NaOMe in methanol at 25°C. **(8)**

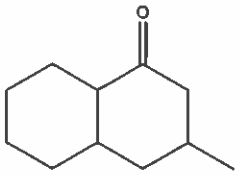
A



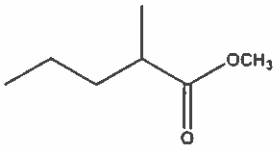
B

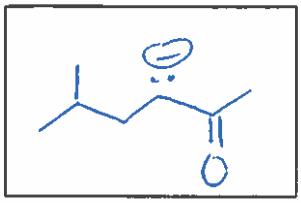


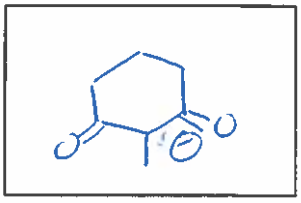
C

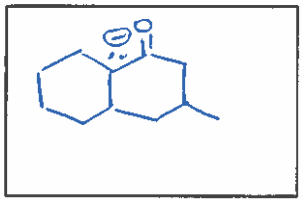


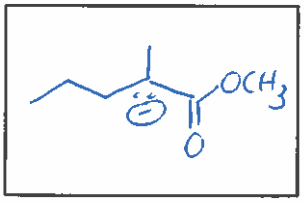
D



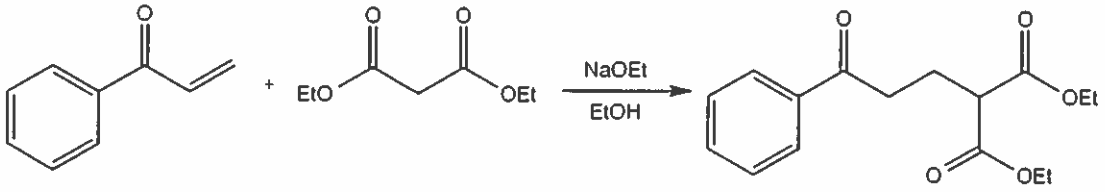



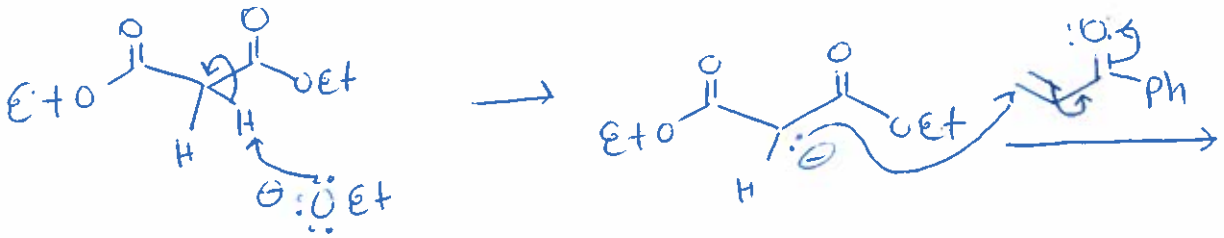


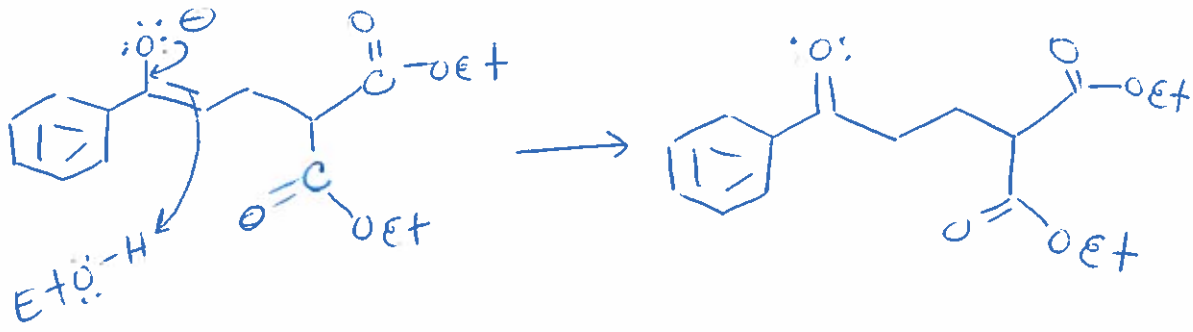





10. Draw the stepwise mechanism for the following reaction using mechanistic arrows to indicate electron movement. ***If you need additional space, please use the back of the page.*** **(14)**

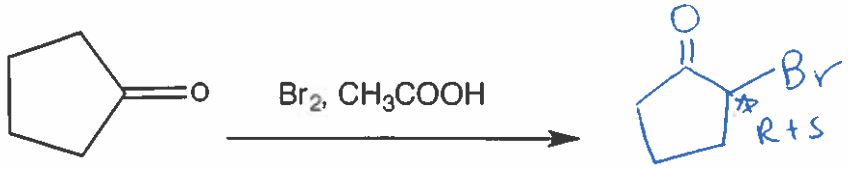


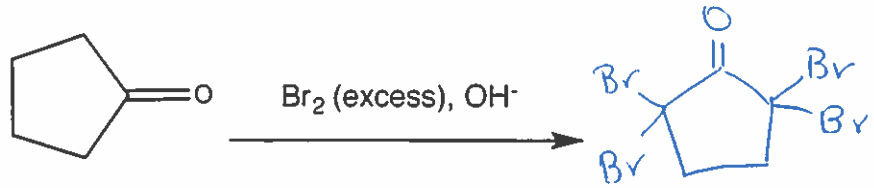



**PART TWO: PREDICT THE PRODUCT** - For *each* of the following questions 11-16 predict the ***major*** organic product(s) showing stereochemistry where appropriate. **(36 points total; 6 points each)**

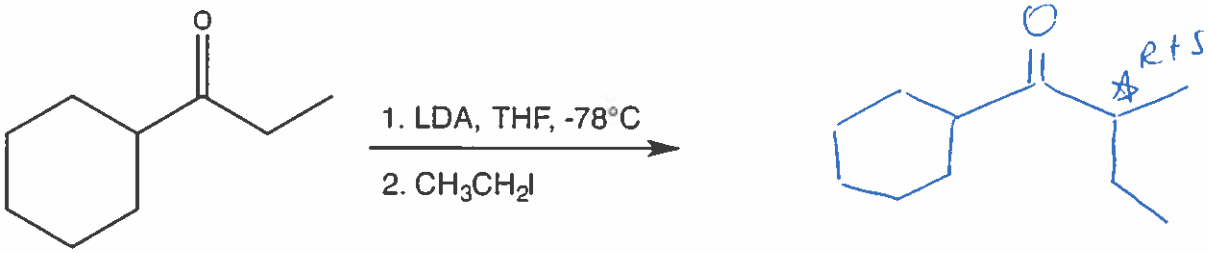
**11.**



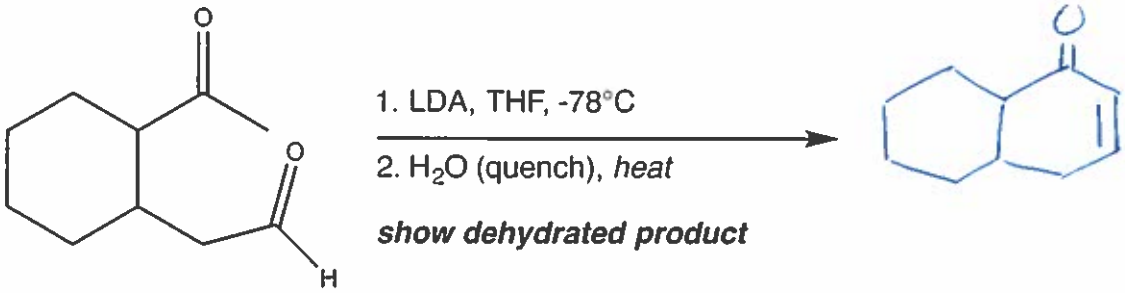

**12.**



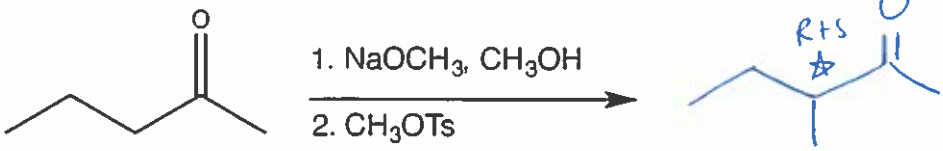

**13.**



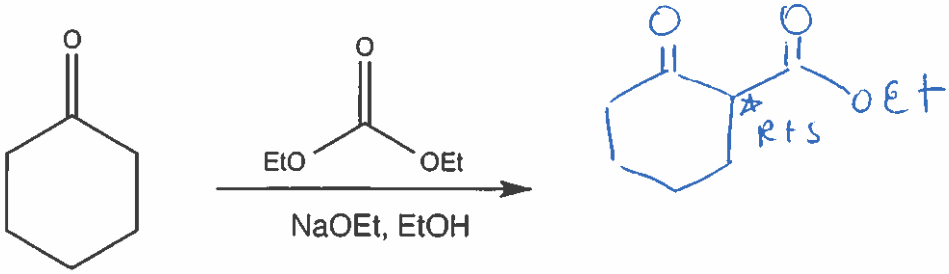

**14.**




**15.**

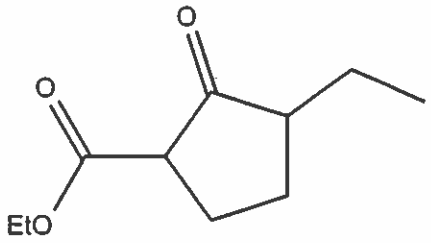


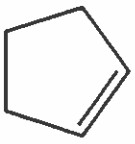

**16.**



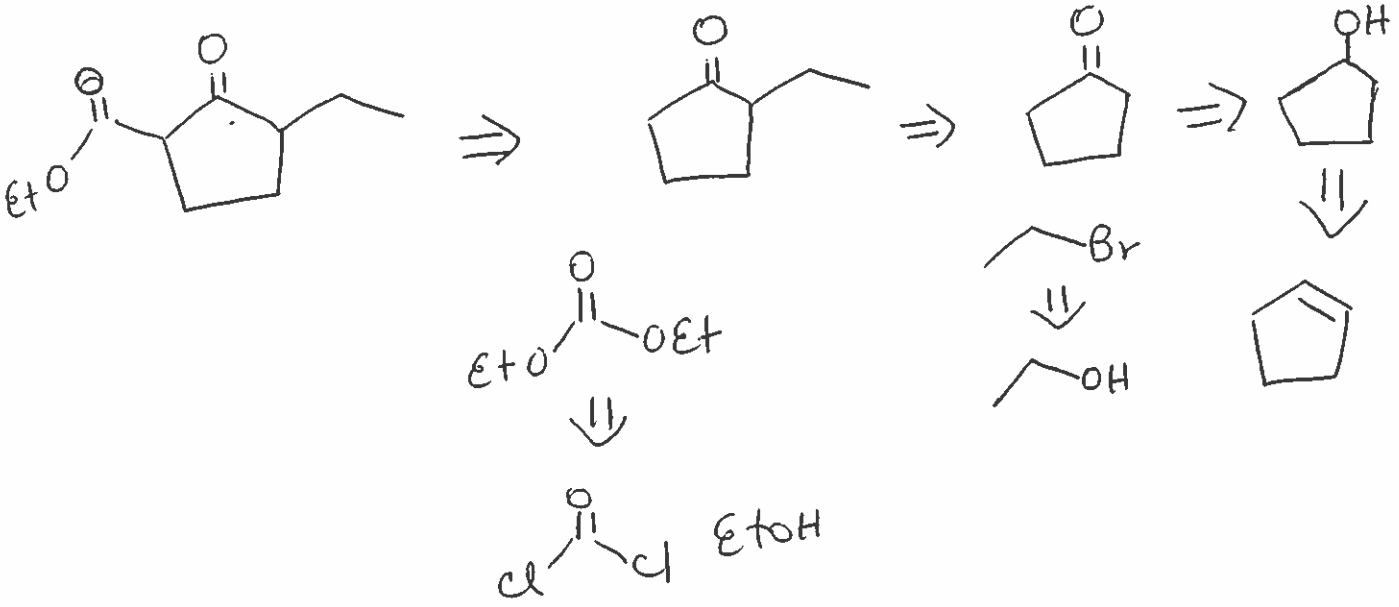
**PART THREE: SYNTHESIS**

**17.** Propose a reasonable synthesis for the structure below. You must start from the indicated organic substrates, but you may use any inorganic reagents you need. Of course you may also use an organic oxidizing agents, reducing agents, acids, and bases that you may find necessary. **(19)**




from  and ethanol + any 1-carbon substrates

Retrosynthesis :

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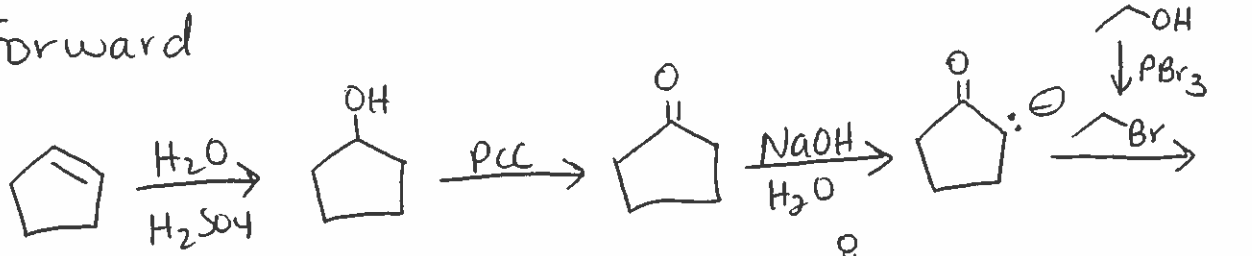
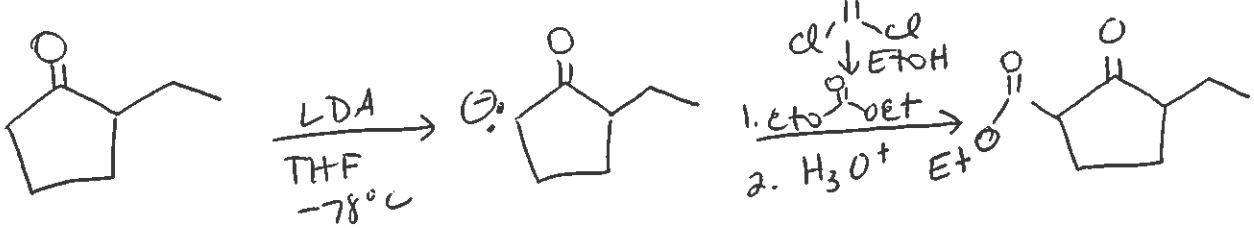
Forward



## II. OLD MATERIAL (110 Points Total)

### PART ONE: STRUCTURE, REACTIVITY, MECHANISM (26 points)

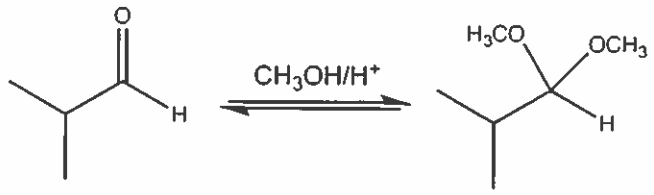
**18.** Consider the five equilibria (A-E) below. Think about which reaction would be the most favorable in the forward direction and which would be most favorable in the reverse direction... Rank the equilibria accordingly. **(5)**

D B A C E

**lies furthest to the left (most favors reactants)**

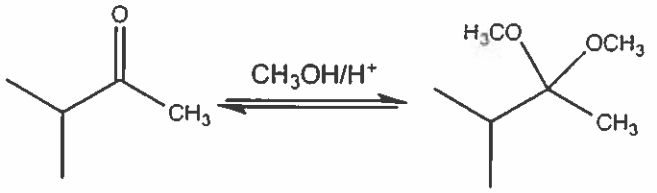
**lies furthest to the right (most favors products)**

**A**



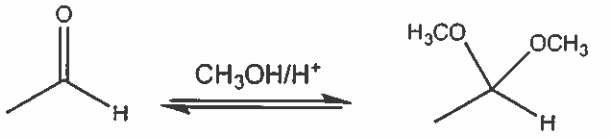

3rd most favorable (forward)

**B**



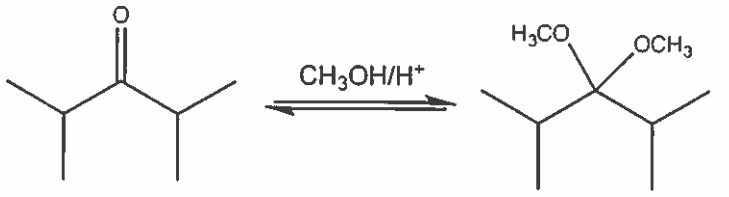

4th most favorable (forward)

**C**



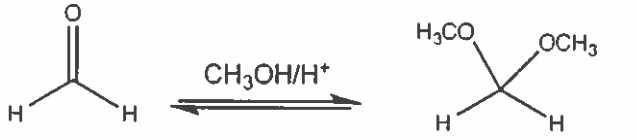

2nd most favorable (forward)

**D**



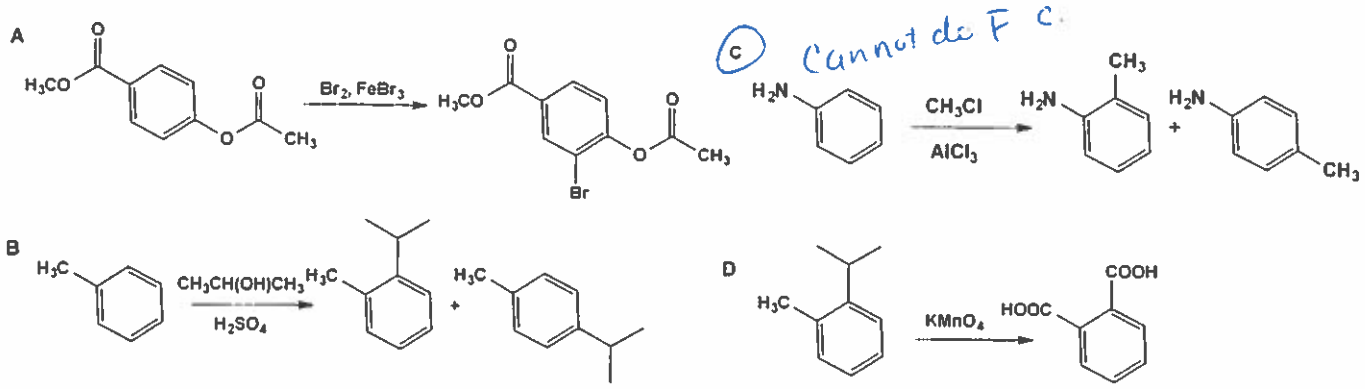

least favorable (forward)

**E**

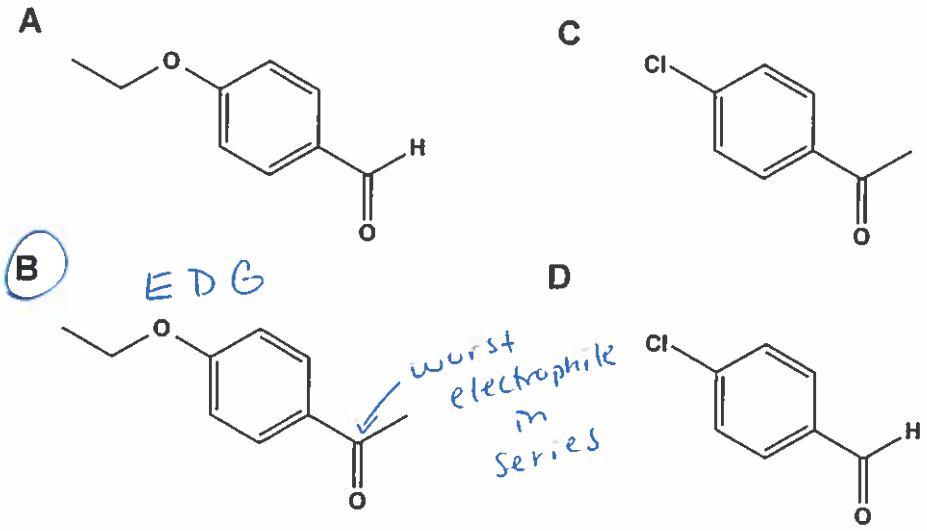



most favorable (forward)

**19.** Circle the reaction (A-D) that **would not** yield the major organic product(s) as indicated. **(5)**



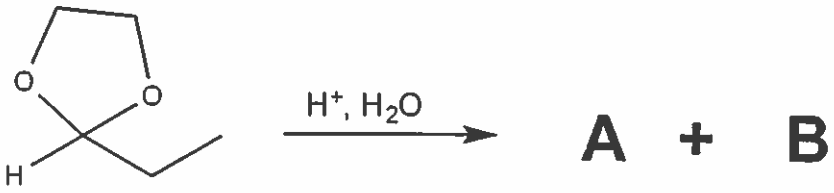

**20.** Which of the following carbonyl substrates would react the slowest with $CH_3Li$? *Circle your answer.* **(5)**




**21.** Consider the reaction below. Which of the statement(s) **A-E** regarding this reaction is/are FALSE? *Circle all that apply.* **(6)**


A. The reaction was performed at a low temperature.
B. The product of the reaction is racemic.
C. The reaction goes through a radical intermediate.
D. The reaction mechanism involves a carbocation rearrangement.
E. The reaction proceeds through a halonium ion.

**22.** Consider the reaction below. **(5)**

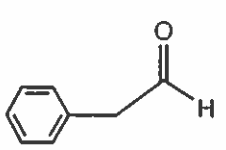



One of the statements below regarding the above reaction is FALSE. Circle the FALSE statement.

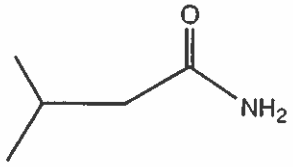
A. One of the organic products of the reaction (A or B) must be an aldehyde. ✓
B. One of the organic products of the reaction (A or B) must be a 1,2-diol. ✓
C. The reaction is reversible. ✓
D. Water acts as a leaving group in the reaction. Nucleophile
E. The first step of this reaction is a protonation. ✓

**PART TWO: SPECTROSCOPY (24 points)**

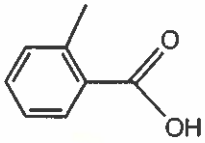
**23.** Shown below are the IR spectra of some carbonyl compounds labeled Figure 1-Figure 4. Match them with the structures below. ***Write your answers in the blanks underneath the structures.*** **(12)**



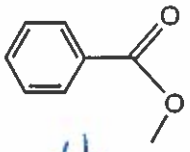

2




3




1




4

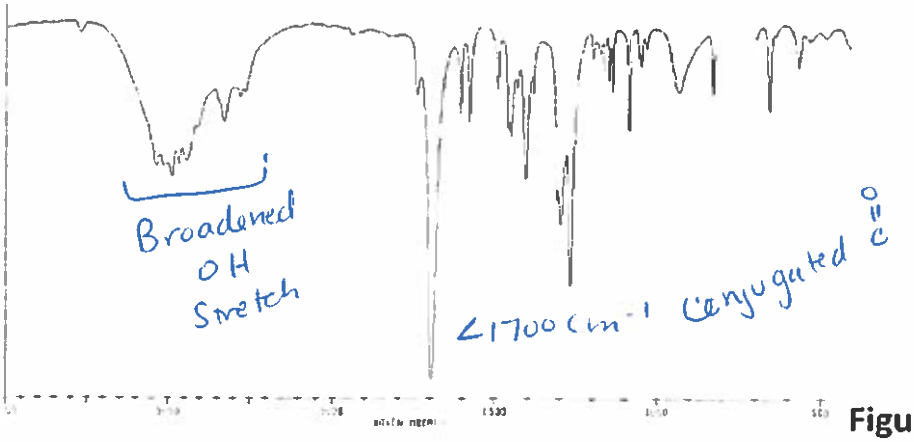



**Figure 1**

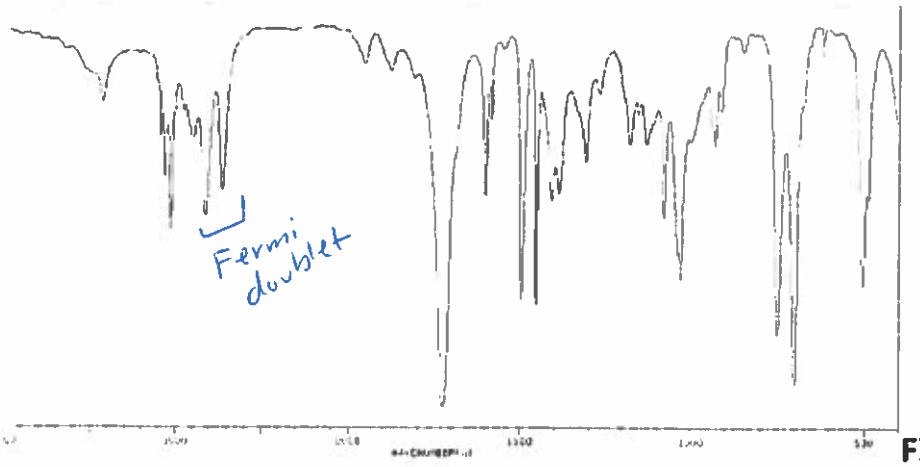



**Figure 2**

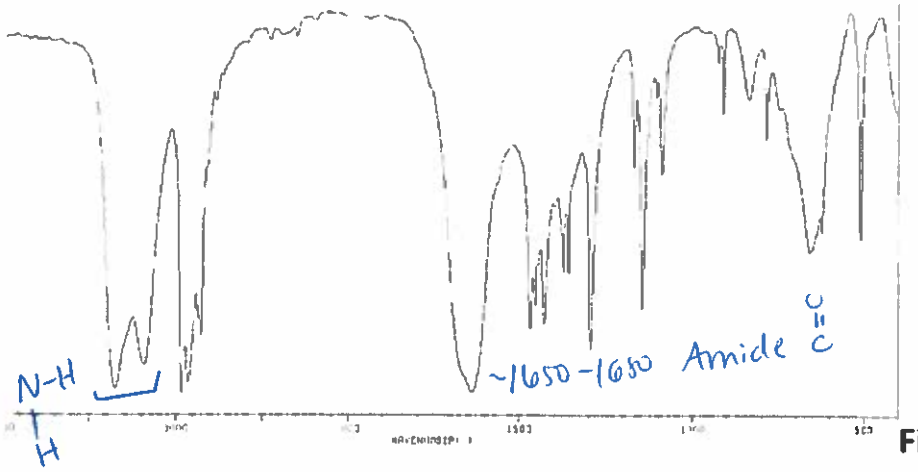



**Figure 3**

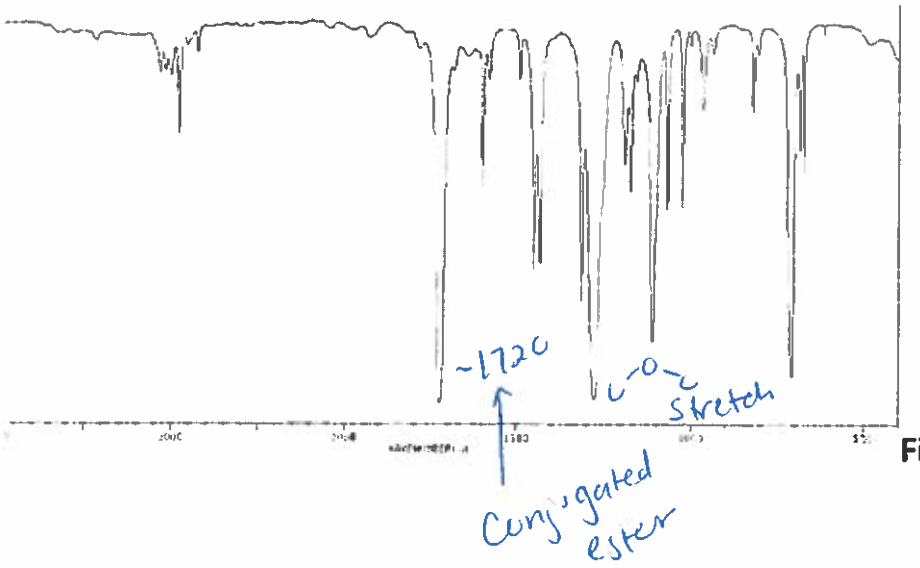
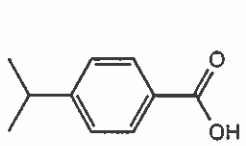
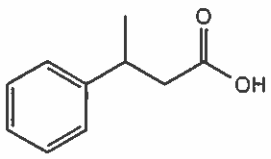



**Figure 4**

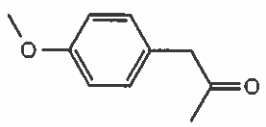
**24.** Match each of the four structures (1-4) below with an proton NMR spectrum (I-IV). **(12)**



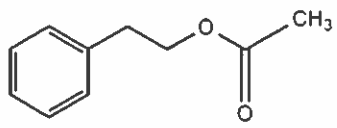

1




2

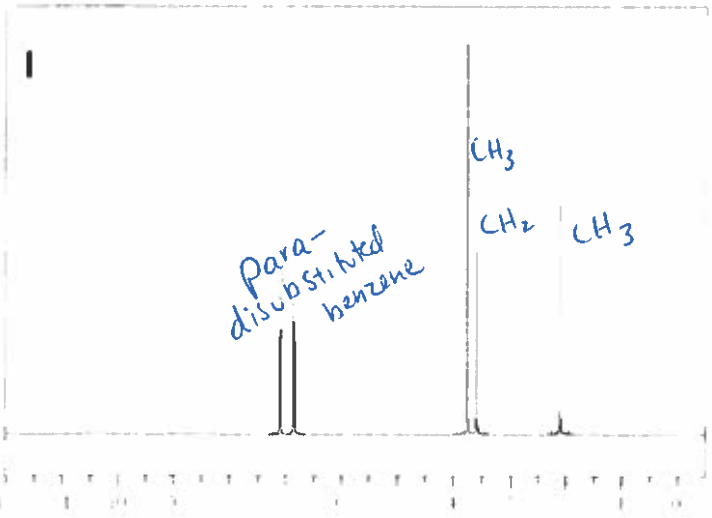



3



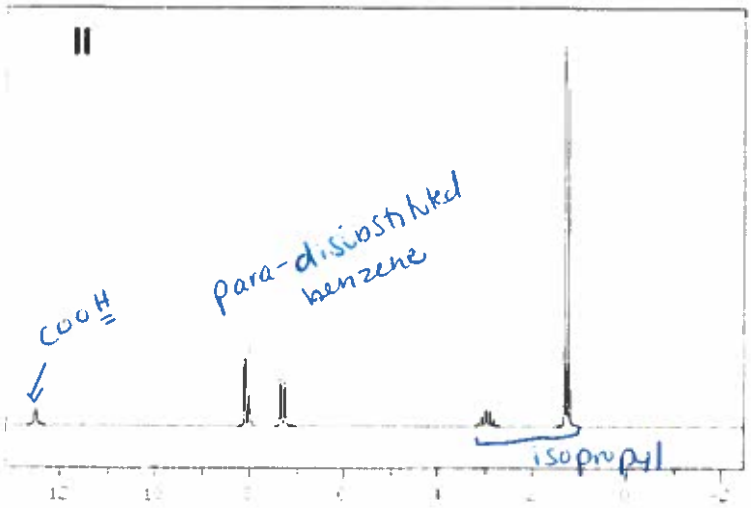

4

I



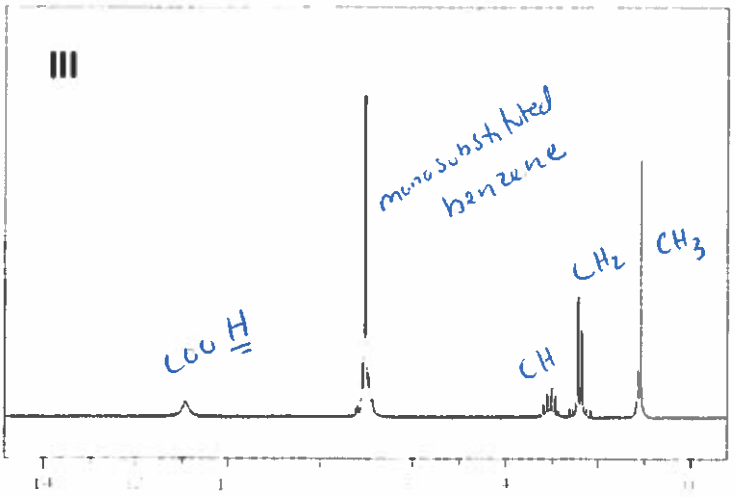

ANSWER 3

II



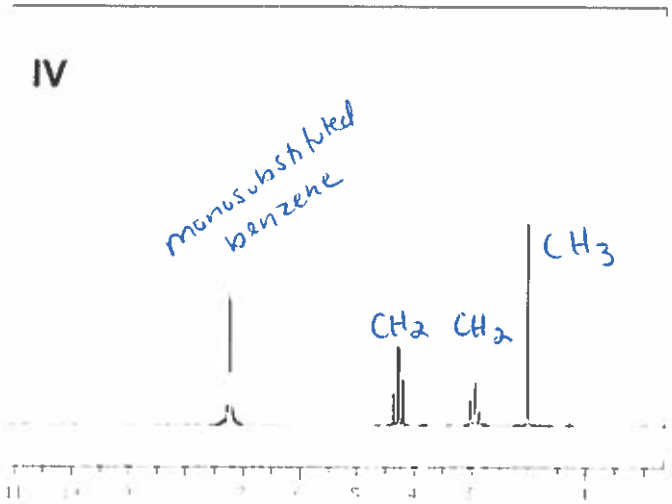

ANSWER 1

III




ANSWER 2

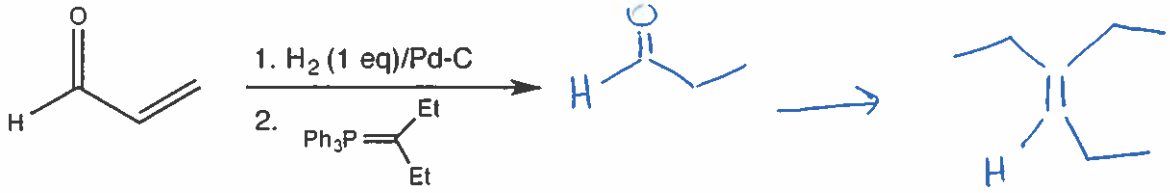
IV



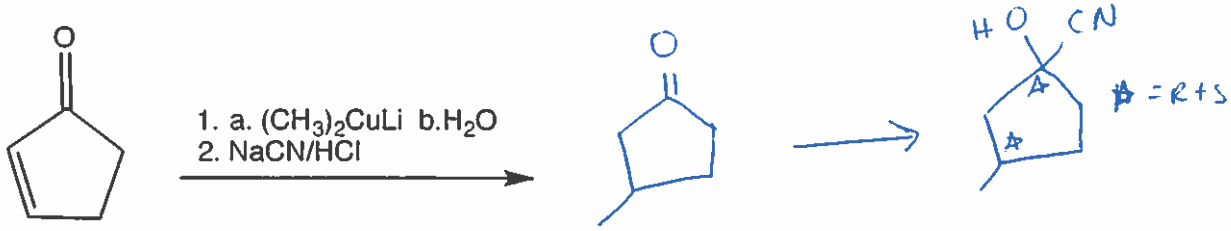

ANSWER 4

**PART THREE: PREDICT THE PRODUCT** - For ***each*** of the following questions **25-29** predict the ***major*** organic product(s) showing stereochemistry where appropriate. **(30 points total; 6 points each)**

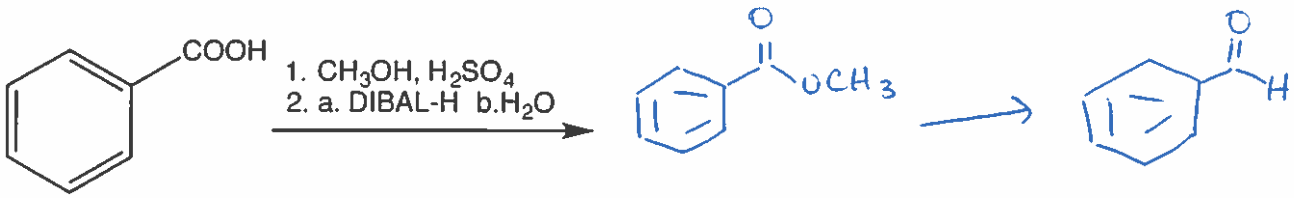
**25.**



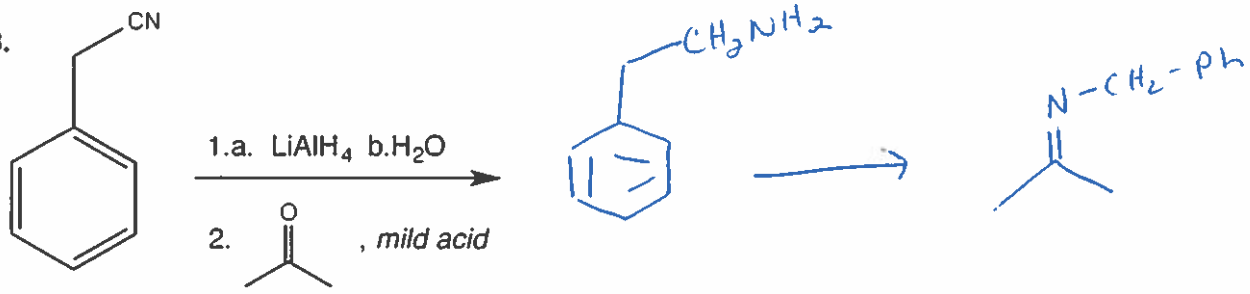

**26.**



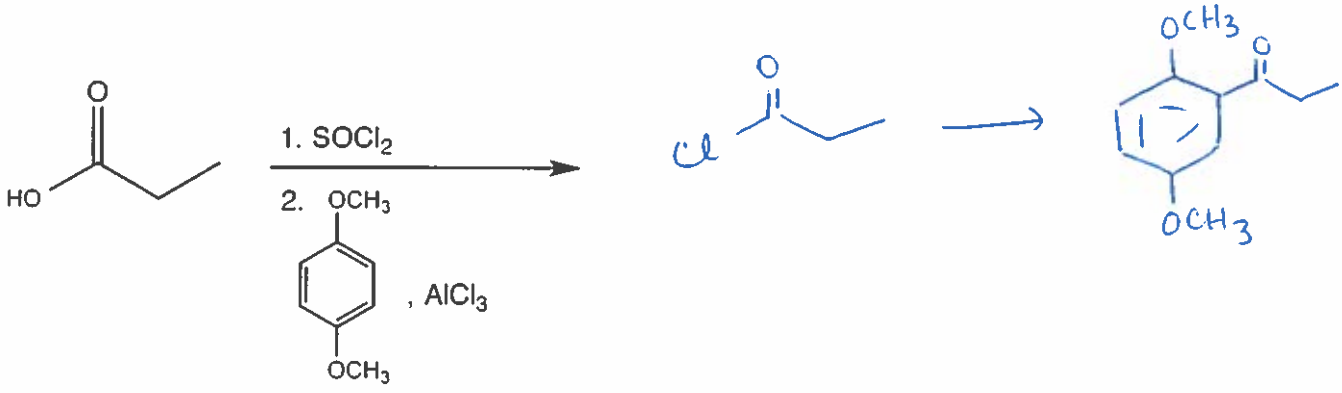

**27.**




**28.**

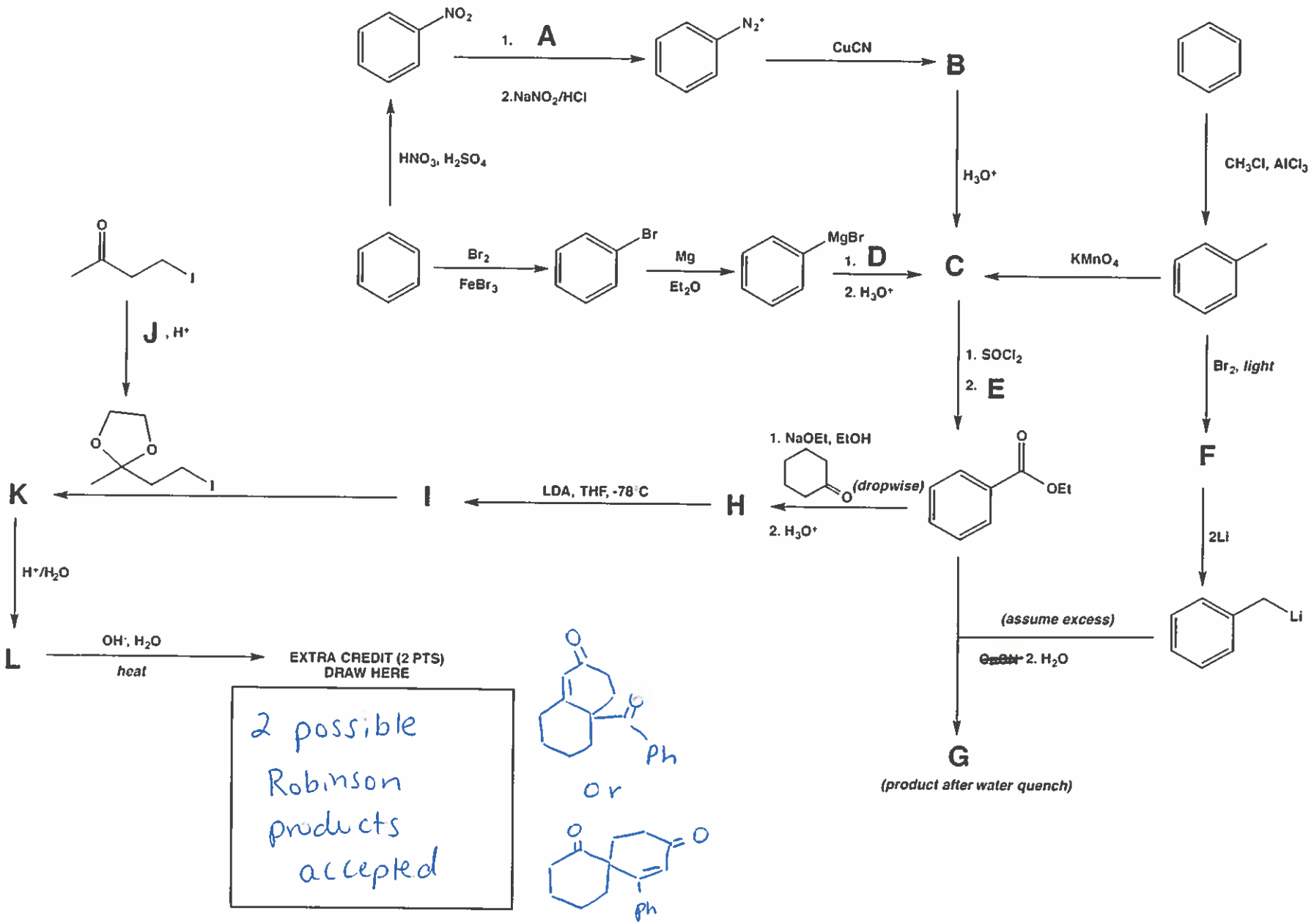


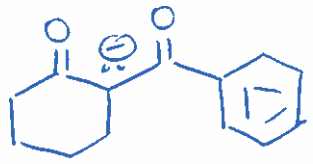
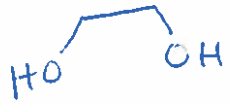
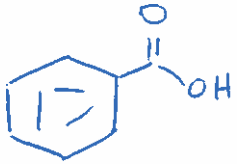
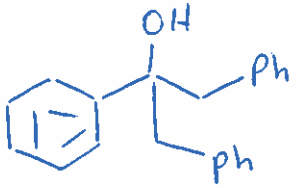
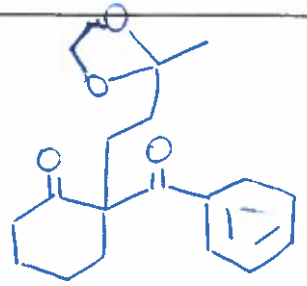
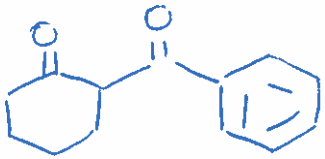
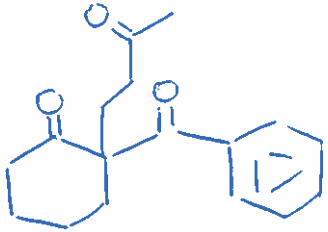

**29.**



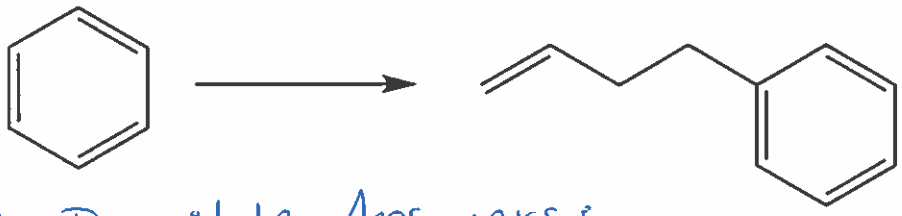
**PART FOUR: SYNTHESIS** (*may consist of "New" and "Old" Material*) **(30 points)**

**30.** Fill in the missing reagents and/or products in the synthetic scheme outlined below. Place your answers in the table provided on the next page. **(12)**



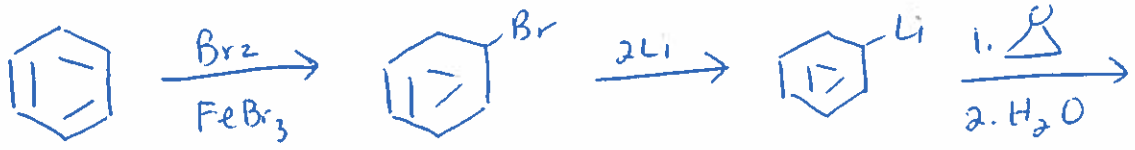
| | MISSING REAGENT/PRODUCT | | MISSING REAGENT/PRODUCT | | MISSING REAGENT/PRODUCT |
|---|---|---|---|---|---|
| A | $H_2$ / Pd-C | E | EtOH / pyridine | I |  |
| B |  | F |  | J |  |
| C |  | G |  | K |  |
| D | $CO_2$ | H |  | L |  |

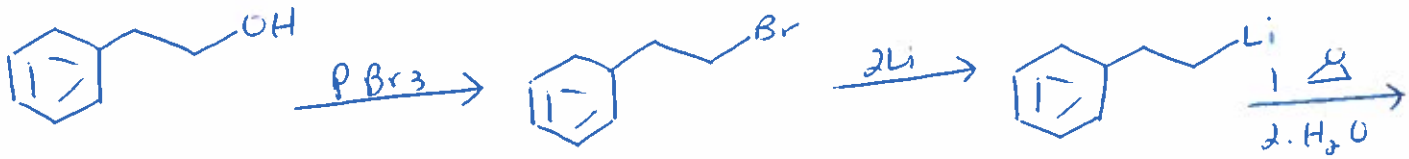
**31.** Indicate **three** possible synthetic routes to perform the conversion shown below. You may use any reagent(s) that you would like. **(9)**

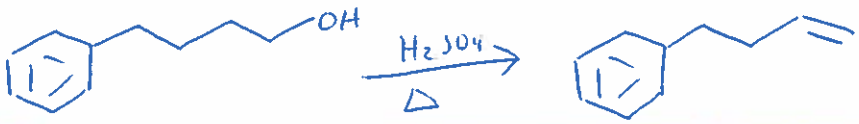


3 Possible Answers:

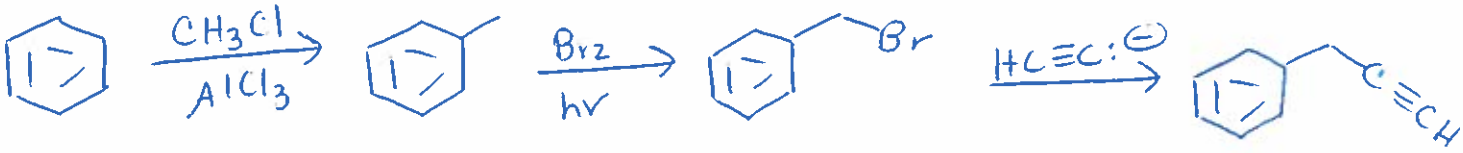
**Route 1:**

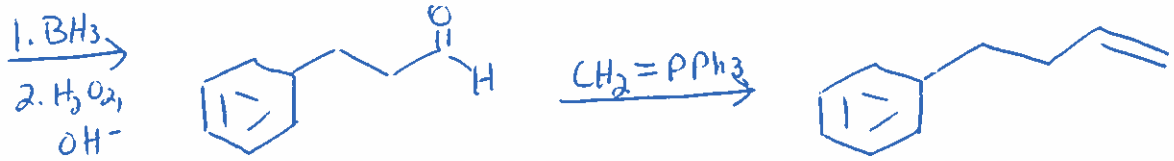


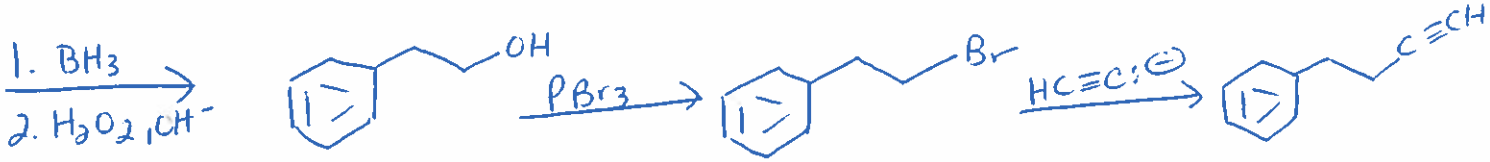




**Route 2:**



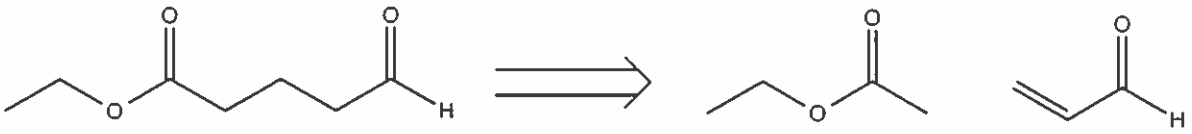




**Route 3:**

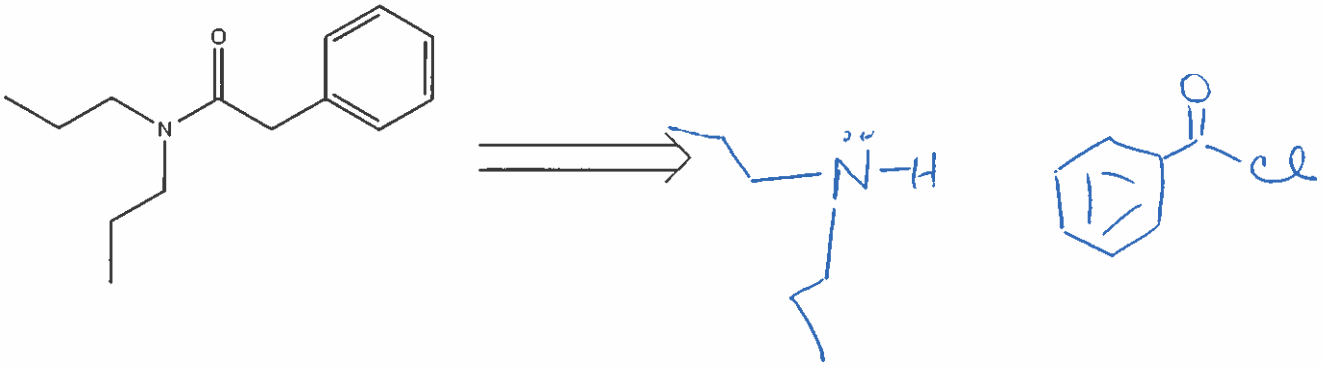




32. **Retrosynthetic Analysis:** For each structure (a-c) below, draw the ***organic reactants*** that would yield the indicated product in **one synthetic step**. Remember, multiple answers are often possible, but try to use the one that seems "the best." **ONE RULE:** for ***full credit*** you must break the desired product into ***at least 2 organic fragments***! **(9)**

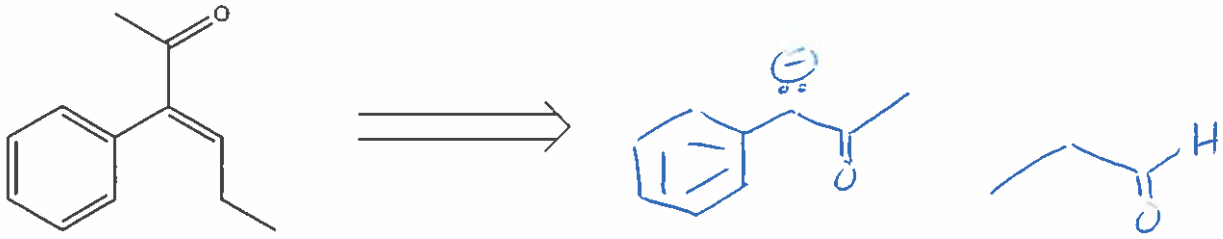
**Example:**



a.



b.



c.