* Answers to lab questions not provided since not relevant to this year *

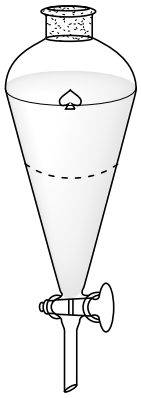
Lab questions. Provide all answers in the spaces provided.

1) In Experiment 1, a Grignard reagent was prepared from magnesium metal and 1-bromobutane. Before combining the reagents, the magnesium metal was ground in a mortar and pestle to scratch its surface. What was the purpose of this step? (1 point)

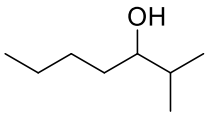
_____

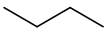
_____

2) The alcohol prepared in Experiment 1 (2-methyl-3-heptanol) was separated from the reaction mixture by extraction. After pouring the contents of the reaction flask into a beaker containing sulfuric acid and ice, the mixture was transferred to a separatory funnel. Diethyl ether was used to facilitate the transfer. At this point in the extraction, several chemical species were present in the biphasic mixture. Use the diagram below to indicate where each species could be found in the separatory funnel by placing the appropriate letter in either the top or bottom layer. (5 points)



A: Et_2O **B**: H_2O **C**: H_2SO_4

D: 

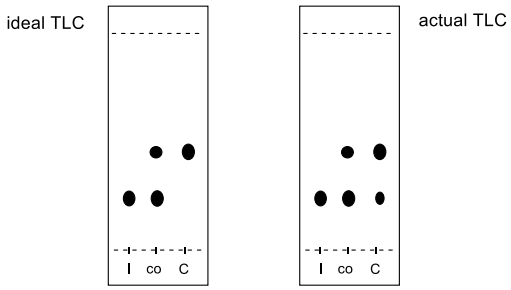
E: 

3) In both Experiment 1 (synthesis of 2-methyl-3-heptanol) and Experiment 5 (synthesis of 4-methylacetanilide), a glass tube filled with $CaCl_2$ was added to the top of the reflux condenser during the reaction. What was the purpose of this glassware? (1 point)

_____

Provide chemical equations in the space below to show the specific reactions that could have taken place if this piece of glassware had not been used. (4 points)

4) Experiment 3 involved the oxidation of isoborneol to camphor. The purity of the crude product was evaluated by TLC. Ideally, this TLC should have looked like the sketch on the left; unfortunately, most students' TLCs looked like the one on the right. With reference to these sketches, answer the questions which follow. (4 points)



a) What is the purpose of the "co spot" in the middle lane?

_____

_____

b) What does the TLC on the right tell us about the product?

_____

c) Suppose you had the chance to try the experiment again. Suggest two modifications you would make to the procedure to try and get the TLC to look like the one on the left.

_____

_____

5) A student needs to recrystallize an unknown compound, compound **X**. Below is a table of solubility data obtained by the student, as well the results of their solvent miscibility tests. Use this data and answer the questions which follow. (5 points)

Solvent	Boiling point (bp)	Solubility of X at 20 ºC	Solubility of X at bp
Water	100 ºC	Highly soluble	Highly soluble
Methanol	65 ºC	Highly soluble	Highly soluble
Diethyl ether	35 ºC	Insoluble	Insoluble

- Water and methanol are miscible
- Methanol and diethyl ether are miscible
- Water and diethyl ether are immiscible

a) Is a 1-solvent recrystallization possible? If yes, what solvent should be selected?

_____

b) Is a 2-solvent recrystallization possible? If yes, what TWO solvents should be selected?

_____

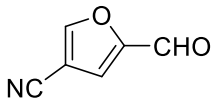
c) Is compound X best classified as a polar or non-polar substance? _____

Multiple choice questions: Transfer all answers to the tables below. (8 points; 1 point per question)

Question	A	B	C	D	E	F
1						
2						
3						
4						

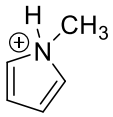
Question	A	B	C	D	E	F
5						
6						
7						
8						

1) How many degrees of unsaturation does the molecule below have?



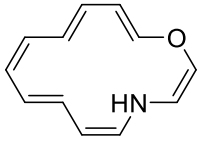
a. three
b. four
c. five
d. six
e. seven

2) The compound below can NOT be classified as aromatic. Identify the reason(s) why.



a. Not all atoms in the ring lie in the same plane.
b. Not all atoms in the ring have a p orbital.
c. There are not [4n+2] *pi* electrons in the ring.
d. All of the above.
e. Both a and b above.
f. Both b and c above.

3) The compound below can NOT be classified as aromatic. Identify the reason(s) why.

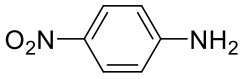


a. Not all atoms in the ring lie in the same plane.
b. Not all atoms in the ring have a p orbital.
c. There are not [4n+2] *pi* electrons in the ring.
d. All of the above.
e. Both a and b above.
f. Both b and c above.

4) Which compound would react the fastest with SO_3/H_2SO_4?
   a. Phenol
   b. Toluene
   c. Pyridine
   d. Nitrobenzene
   e. Chlorobenzene

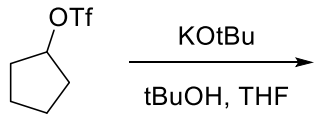
5) Which compound would react the fastest with NaOMe in methanol?
   a. 2,3-dichlorofuran
   b. 1,4-dichlorobenzene
   c. 2,3-dichloropyridine
   d. 2-chloro-3-nitropyridine
   e. 1-chloro-4-nitrobenzene

6) Select the INCORRECT statement about the ^{13}C NMR of *para*-nitroaniline, shown below.



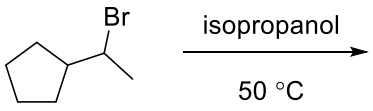
   a. There are 4 signals.
   b. The most shielded carbons are ortho to the nitro group.
   c. The most deshielded carbon is attached to a nitrogen atom.
   d. All signals appear as singlets in the spectrum.

7) Select the most likely mechanism(s) for the reaction below:



   a. S_N1
   b. S_N2
   c. E1
   d. E2
   e. Mixture of S_N1 and E1

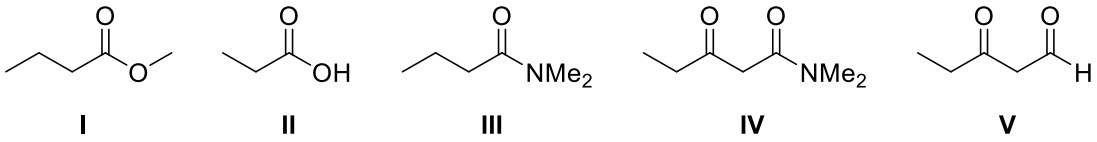
8) Select the most likely mechanism(s) for the reaction below:



   a. S_N1
   b. S_N2
   c. E1
   d. E2
   e. Mixture of S_N1 and E1

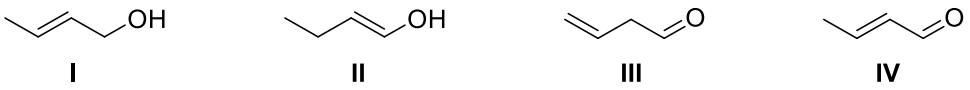
Short Answer Questions. Provide all answers in the spaces provided.

1) Rank the following compounds in order of increasing acidity. (2 points)



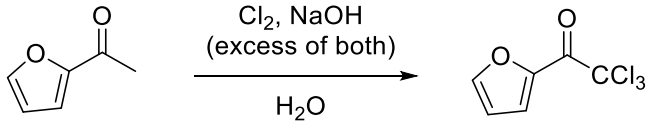
(least acidic) III < I < IV < V < II (most acidic)

2) Rank the following compounds in order of increasing C-O bond length. (2 points)

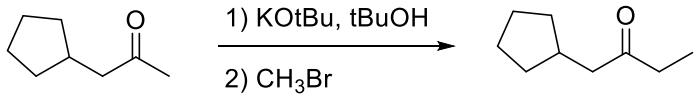


(shortest) III < IV < II < I (longest)

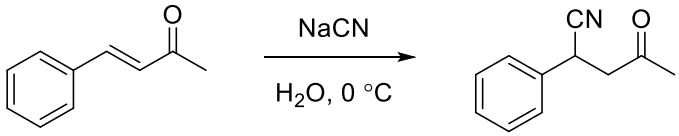
3) The following reactions do not work well as shown. For each reaction, provide a brief explanation for why it doesn't work as written. (6 points)



a) CCl_3 is a good leaving group; the hydroxide will react again making a carboxylate group instead.

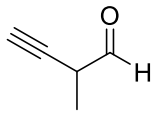


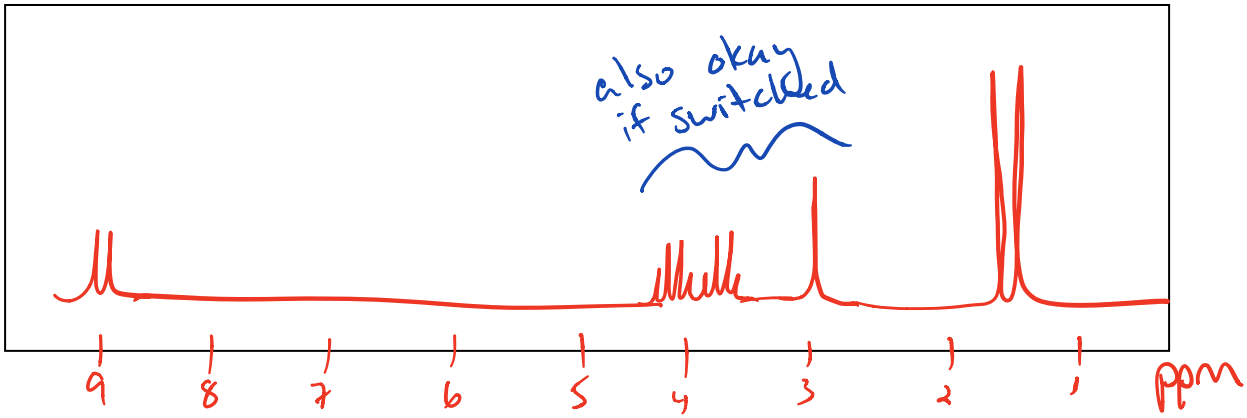
b) The base is not strong enough to fully deprotonate in the first step. Result could be competing aldol reaction OR alkylation on the other side due to thermodynamic enolate forming under the equilibrium conditions.



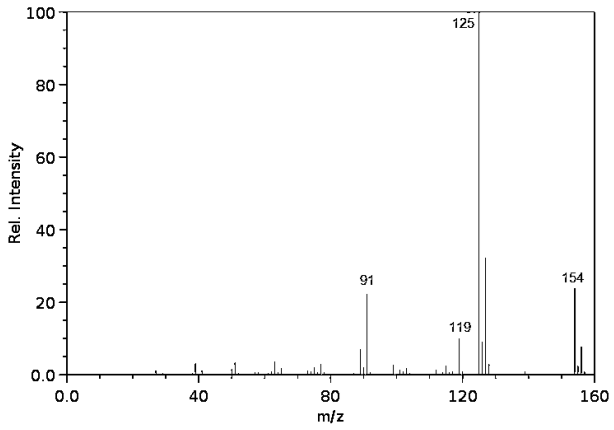
c) The nucleophile is not soft enough to do conjugate addition unless temperatures are elevated. Likely product would be cyanohydrin from direct addition.

4) Sketch the expected ^{1}H NMR for the following compound. Your drawing should accurately represent the number of signals, their *approximate* chemical shifts (don't forget the ppm scale) and the expected splitting patterns. Do not worry about accurately representing the integration of each signal. (4 points)



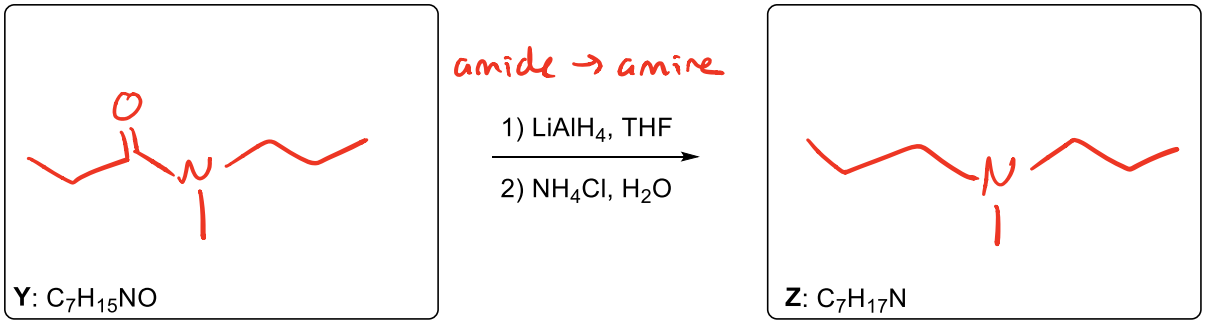


5) The mass spectrum of compound **W** is provided below. Use the table below to list key information about the structure of **W** that can be obtained from its mass spectrum. For each piece of information, provide a brief explanation. (4 points)

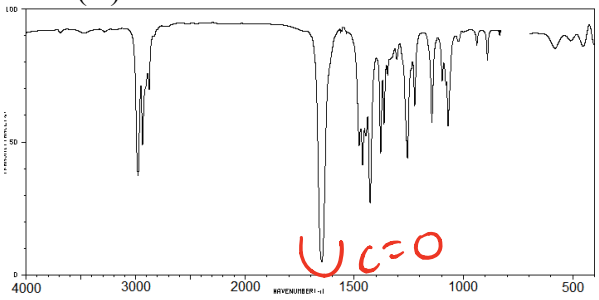


Structural Element	Rationale (Be brief! I will only read the first 10 words!)
Molar mass = 154	M+ peak is at 154 m/z
Cl present	Ratio or M+ to M+2 is roughly 1:3 suggesting isotope signature of chlorine
Ph-CH_2- fragment	Peak at 91 m/z suggests a benzylic carbocation
Either aldehyde or ethyl group	Loss of 29 (154-125) suggests loss of either -CH_2CH_3 or O≡C-H (from aldehyde)

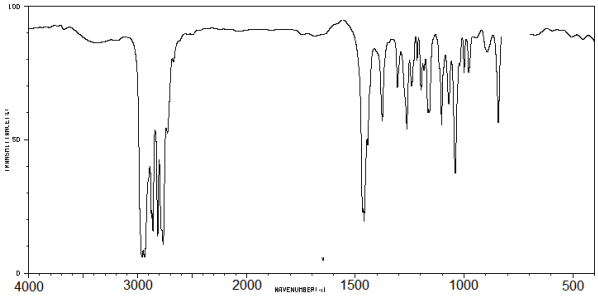
6) Compound **Y** is reacted with $LiAlH_4$ to give compound **Z**. Spectral data for both compounds is provided below. Use the data provided to determine the structures of **Y** and **Z**. For full marks, you must adequately annotate your spectra to support the structures. (12 points)



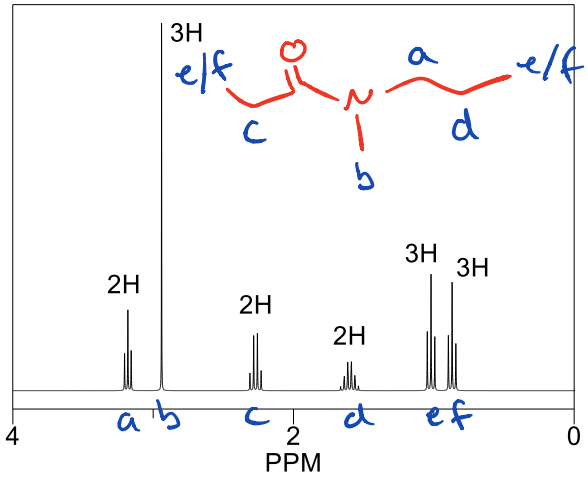
IR (**Y**):



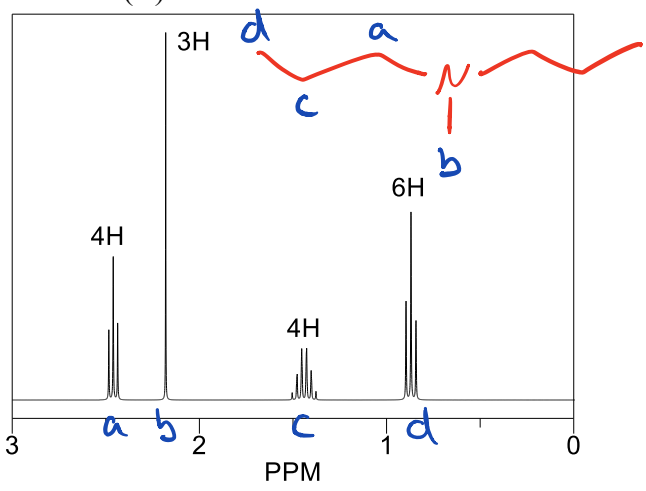
IR (**Z**):



^{1}H NMR (**Y**):



^{1}H NMR (**Z**):

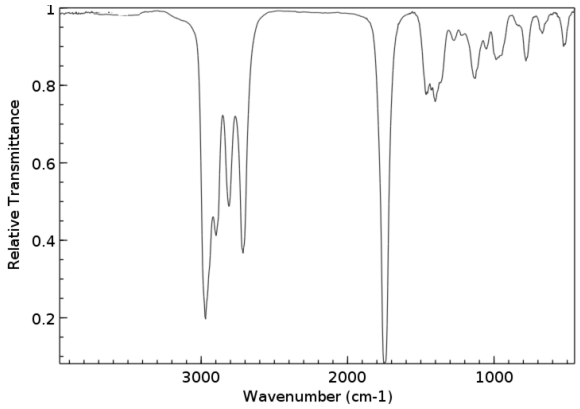


^{13}C NMR (**Y**):
172.0, 54.0, 32.5, 26.0, 20.6, 11.5, 10.3

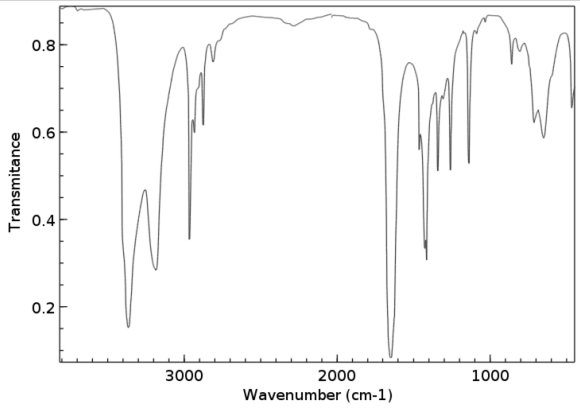
^{13}C NMR (**Z**):
61.6, 47.2, 21.1, 11.8

7) Assign one of the compounds below to each of the IR spectra which follow. (4 points)

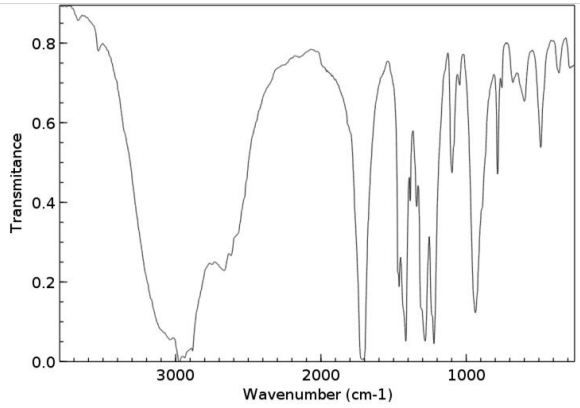
E



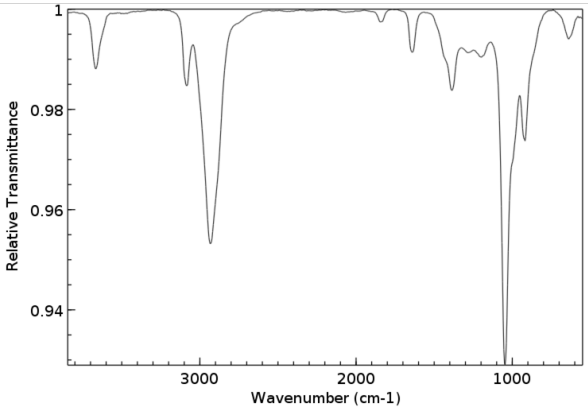
B



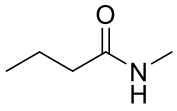
C



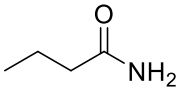
G



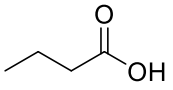
A



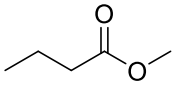
B



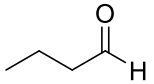
C



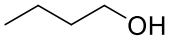
D



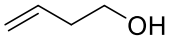
E



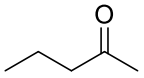
F



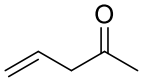
G



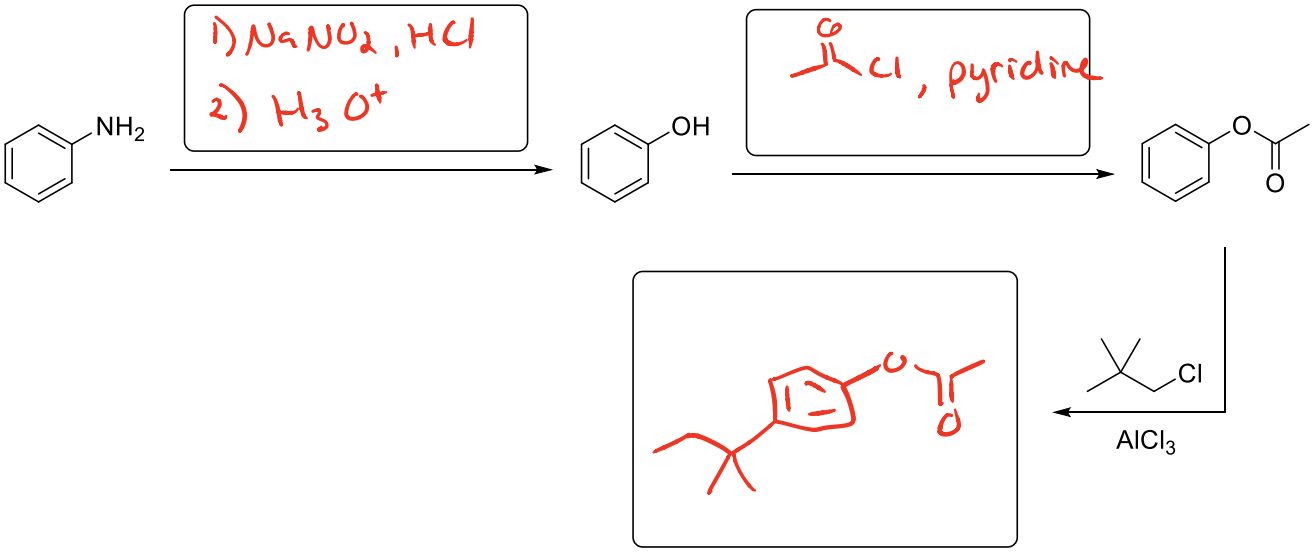
H

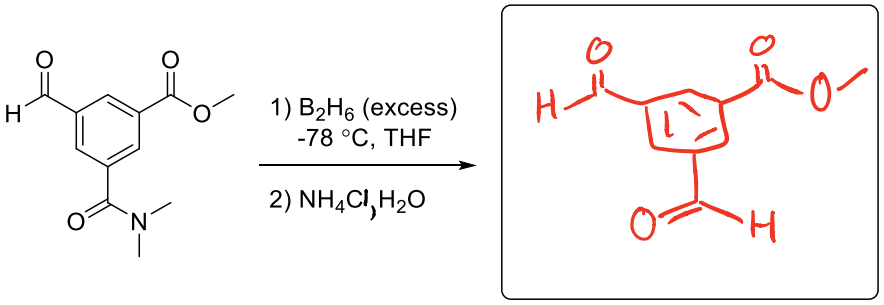


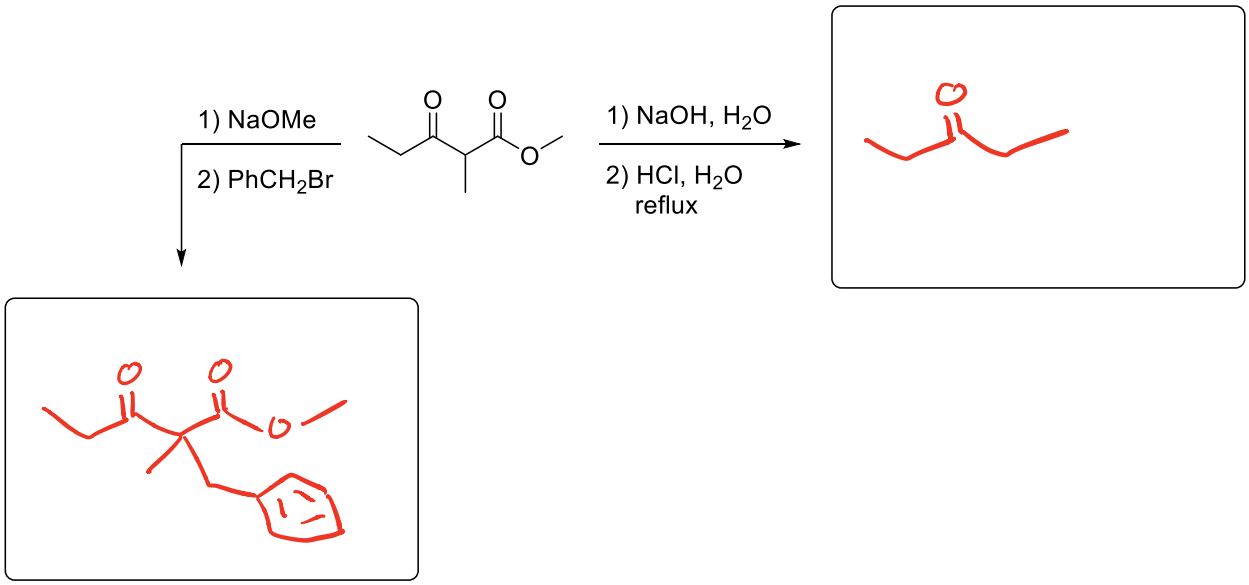
I

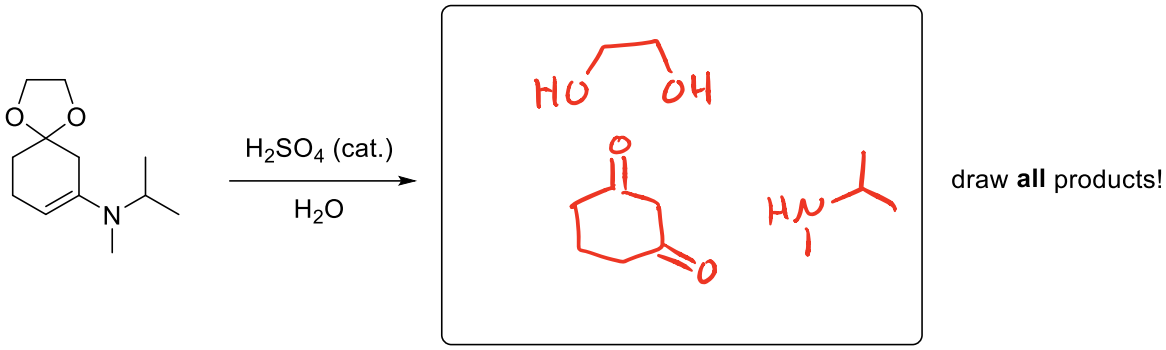


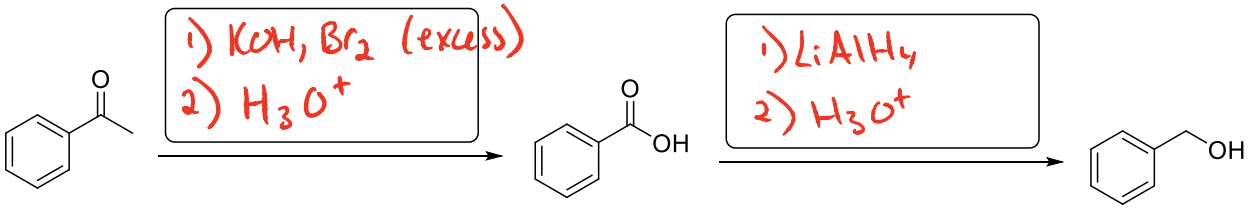
8) Fill in the missing reagents and/or structures for each of the following transformations. Unless otherwise instructed, show **only the major product**. (46 points, 2 points per box).

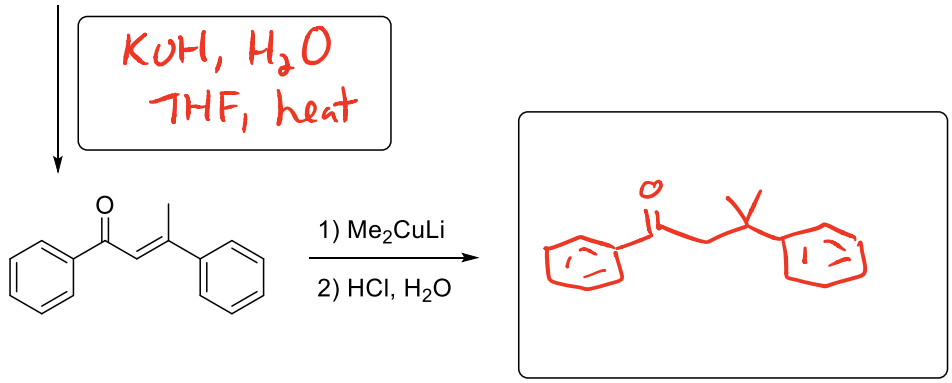


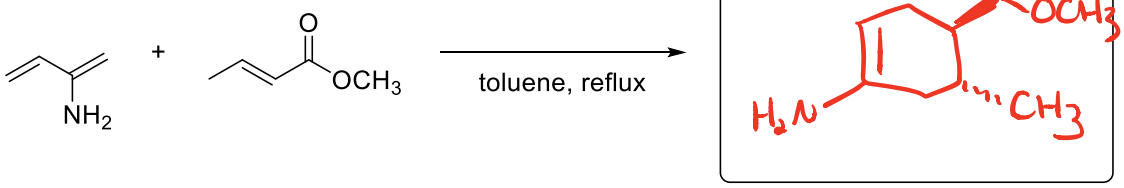




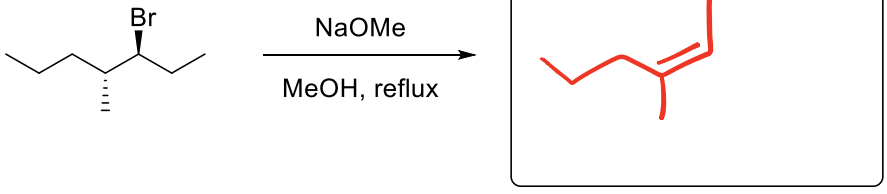

H_2SO_4 (cat.)
H_2O
HO
OH
draw **all** products!

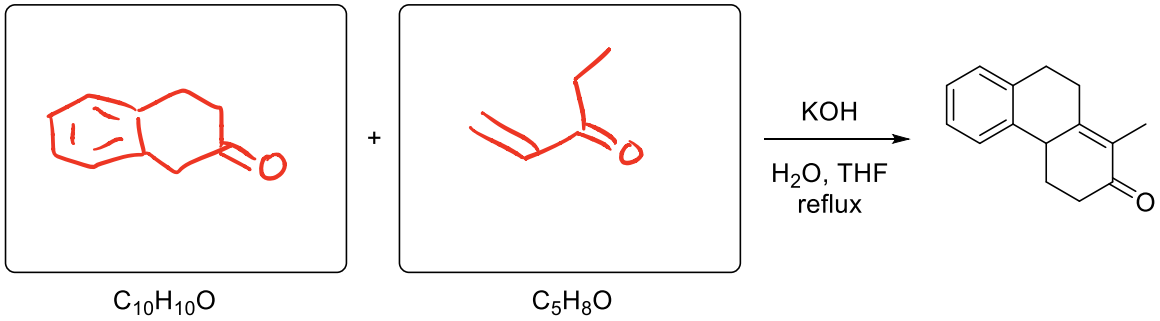

1) KOH, Br_2 (excess)
2) H_3O^+
1) $LiAlH_4$
2) H_3O^+
OH
OH


KOH, H_2O
THF, heat
1) Me_2CuLi
2) HCl, H_2O

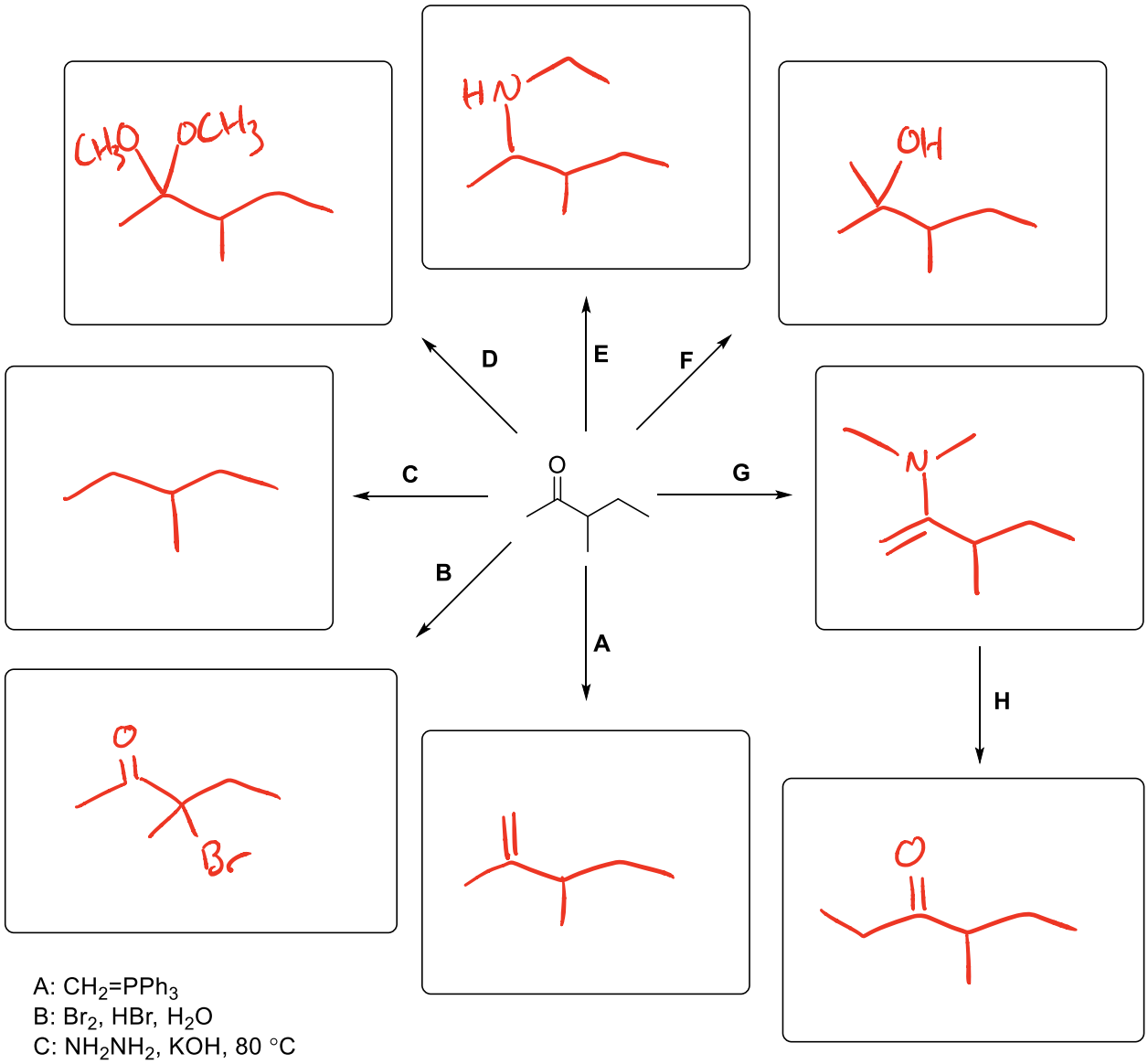

NH_2
+
OCH_3
toluene, reflux
OCH_3
H_2N
CH_3

$C_8H_{13}NO_2$


Br
NaOMe
MeOH, reflux

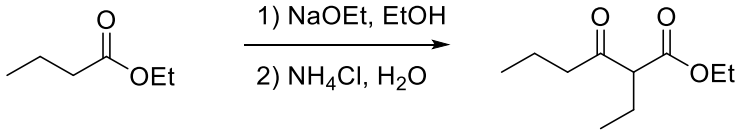


$C_{10}H_{10}O$ C_5H_8O

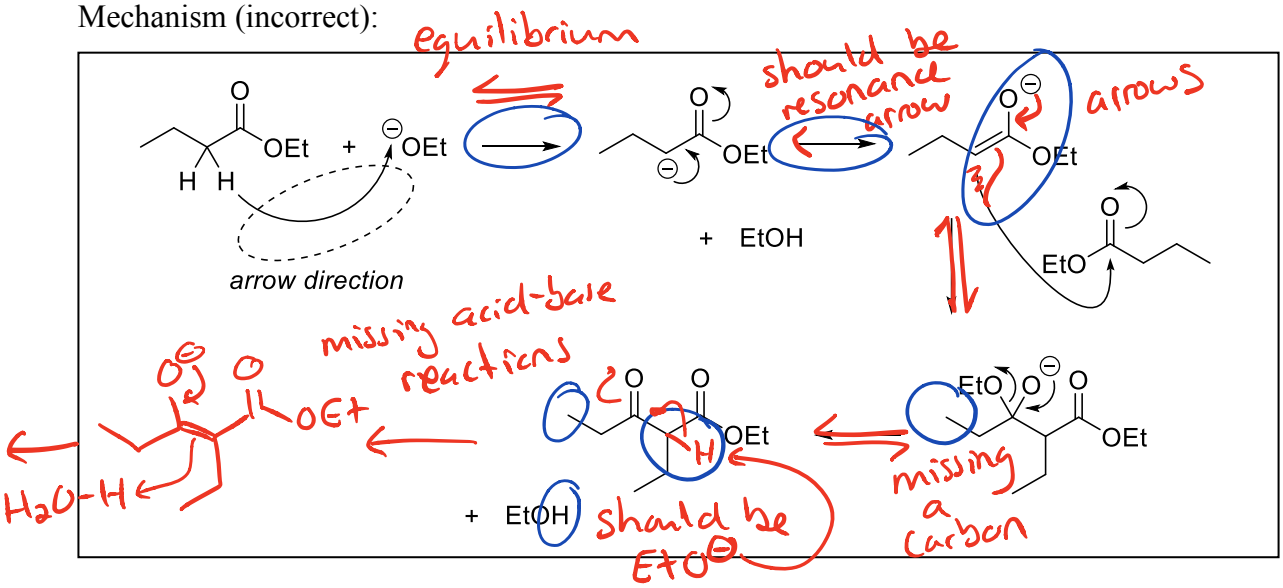


A: $CH_2{=}PPh_3$
B: Br_2, HBr, H_2O
C: NH_2NH_2, KOH, 80 °C
D: H_2SO_4 (cat.), methanol
E: $CH_3CH_2NH_2$, $NaBH_3CN$, pH 5
F: CH_3MgBr, followed by HCl/H_2O
G: $(CH_3)_2NH$, acetic acid
H: CH_3Br, followed by H_3O^+

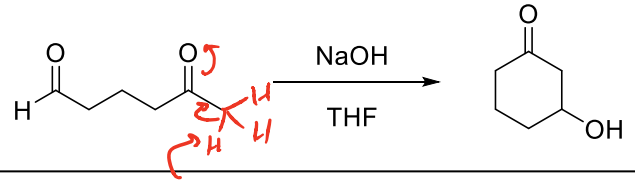
9) Identify the errors in the mechanism below. For each error, provide a 2-3 word description of the error. The first mistake has been highlighted for you as an example. (6 points)



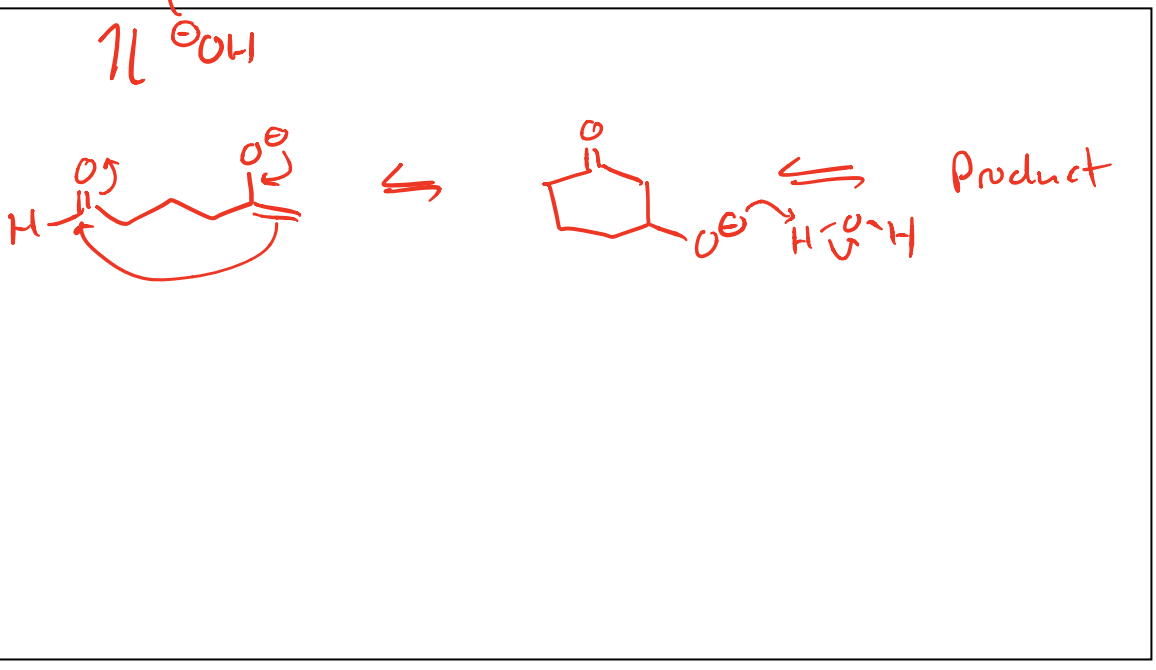
Mechanism (incorrect):



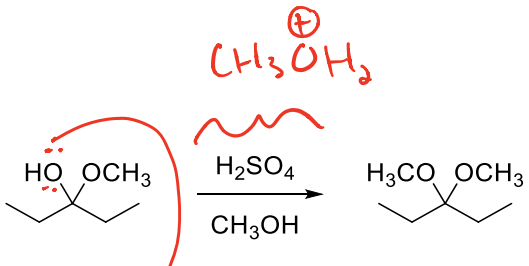
10) Provide detailed stepwise mechanisms for all steps in the following reactions.

a. 

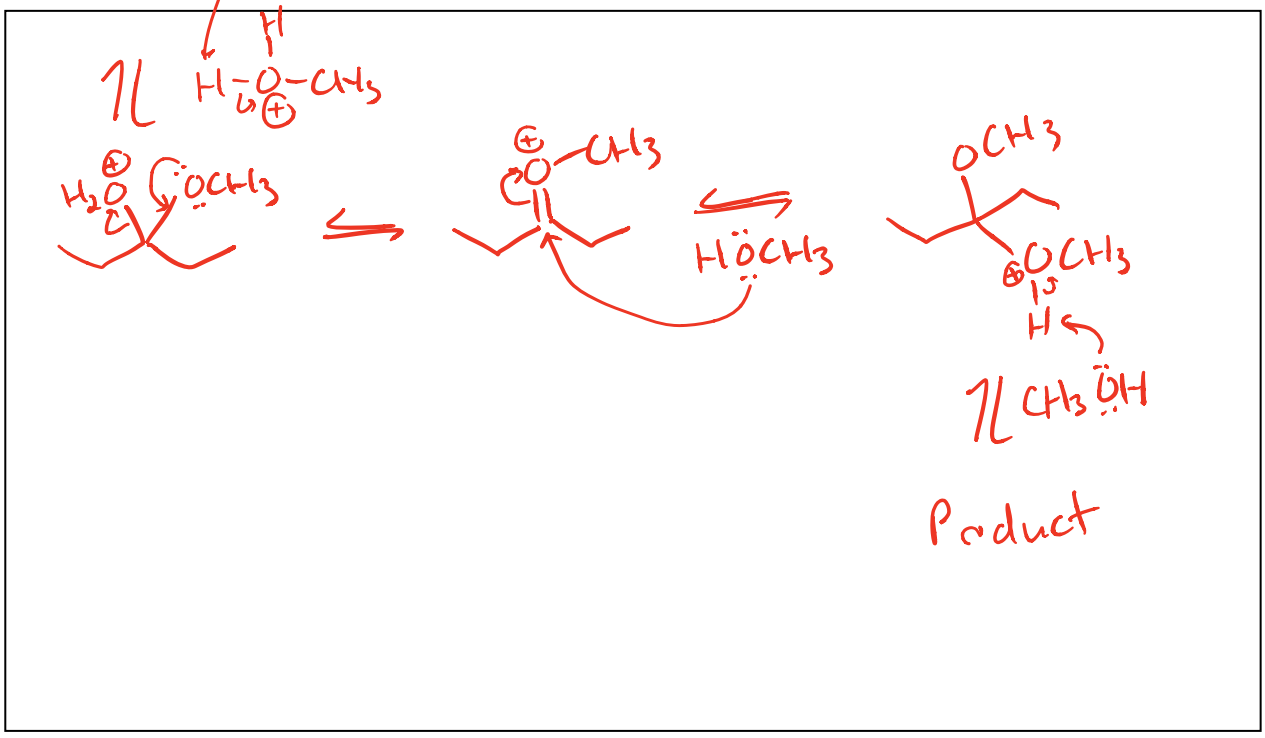
(5 points)



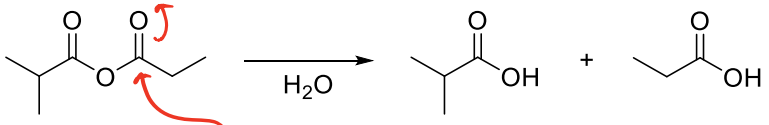
b.



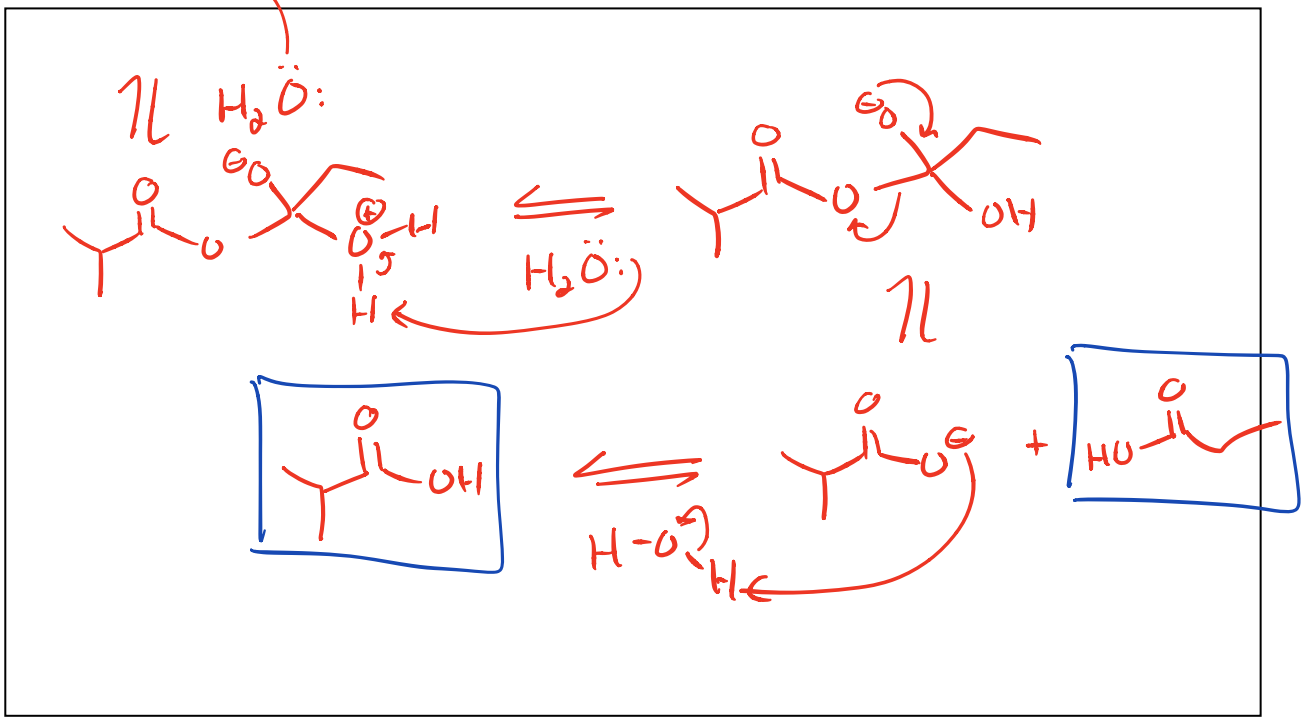
(7 points)

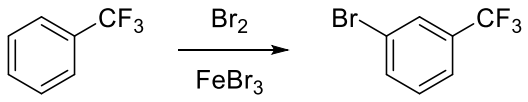


c.



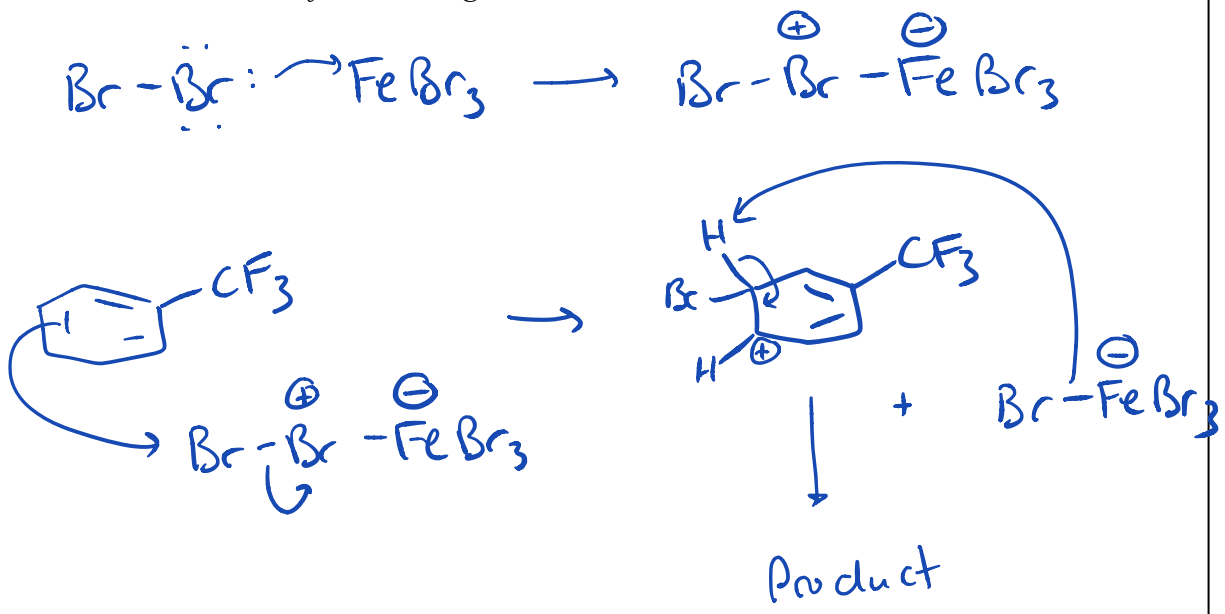
(7 points)



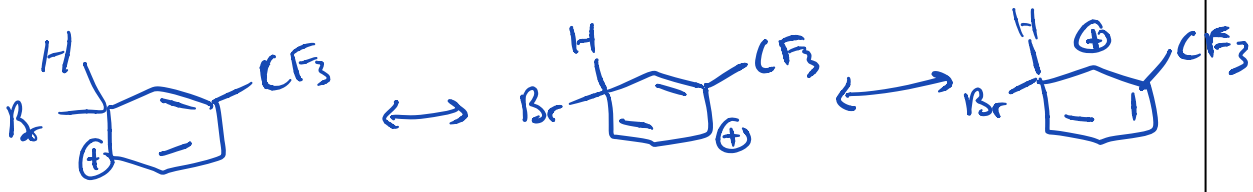
d. 

(7 points)

NOTE: For full points, you must i) show the formation of the reactive electrophile, and ii) include all resonance contributors for the charged intermediate.

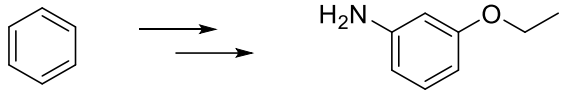


Resonance

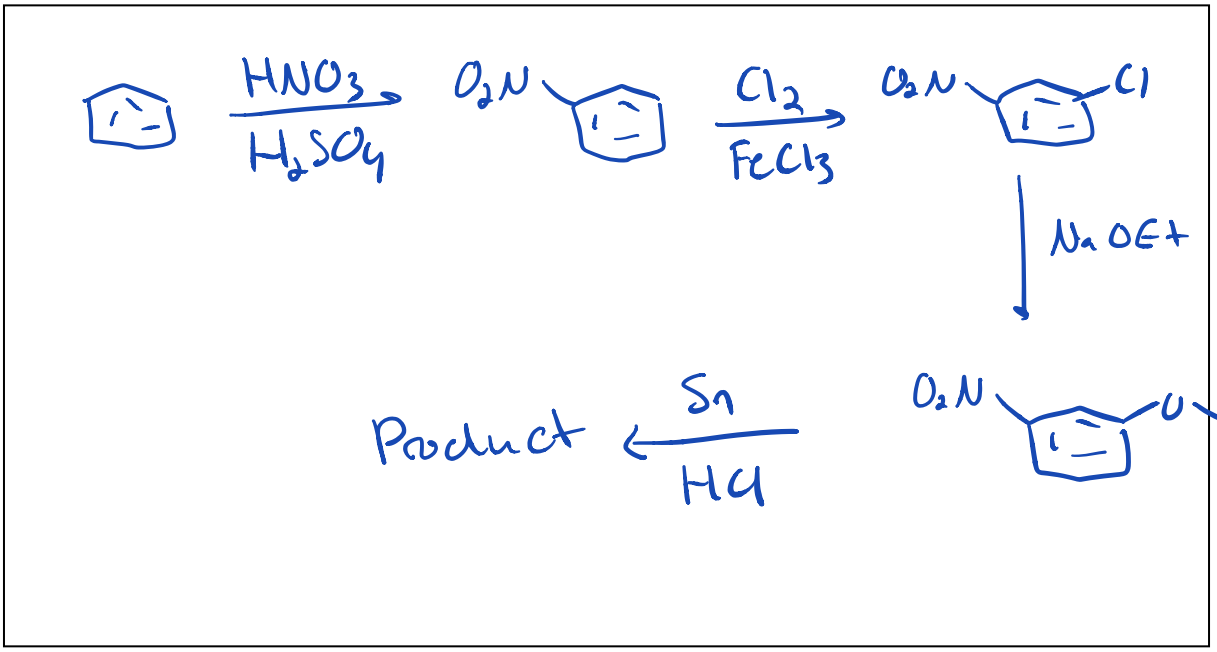


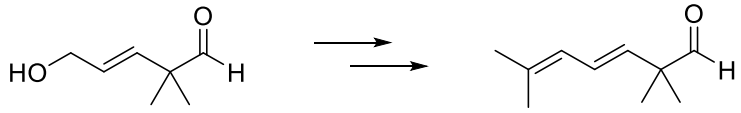
* Other routes possible for these *

11) For each of the multistep syntheses which follow, propose a series of reagents that could be used to carry out the transformation. Note that you do NOT need to show any mechanisms or retrosynthetic analysis. Unless otherwise indicated, you can use any reagents you wish.

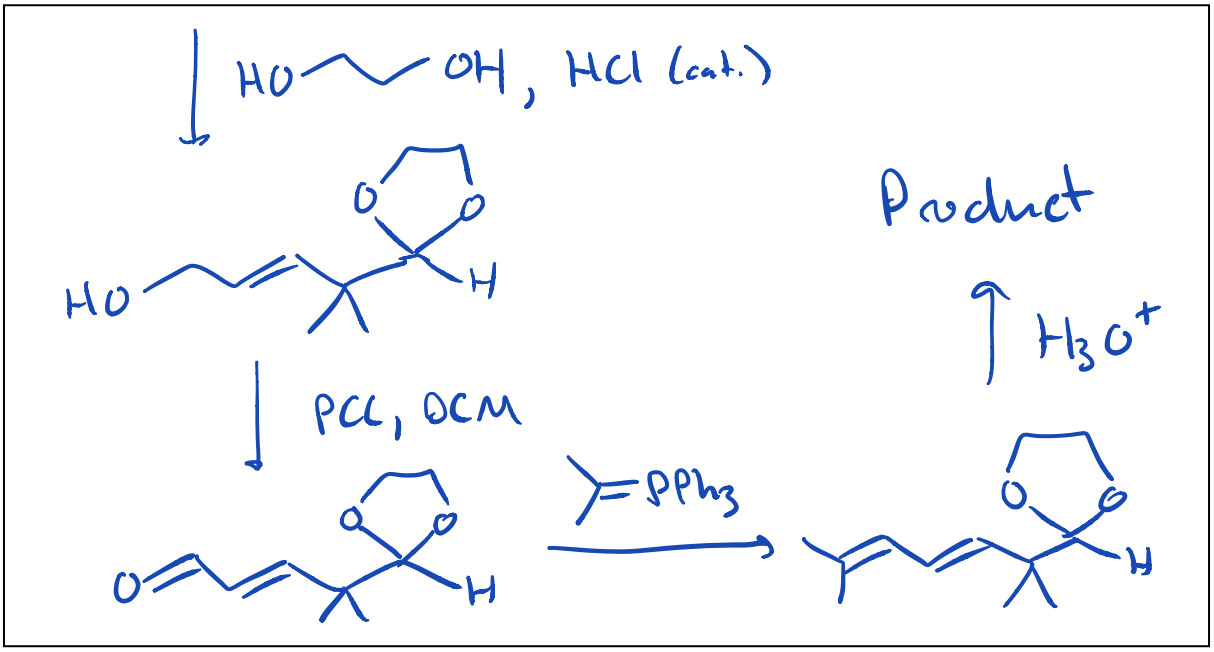
a. 

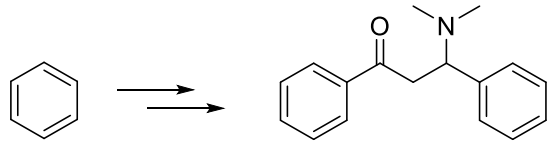
(5 points)



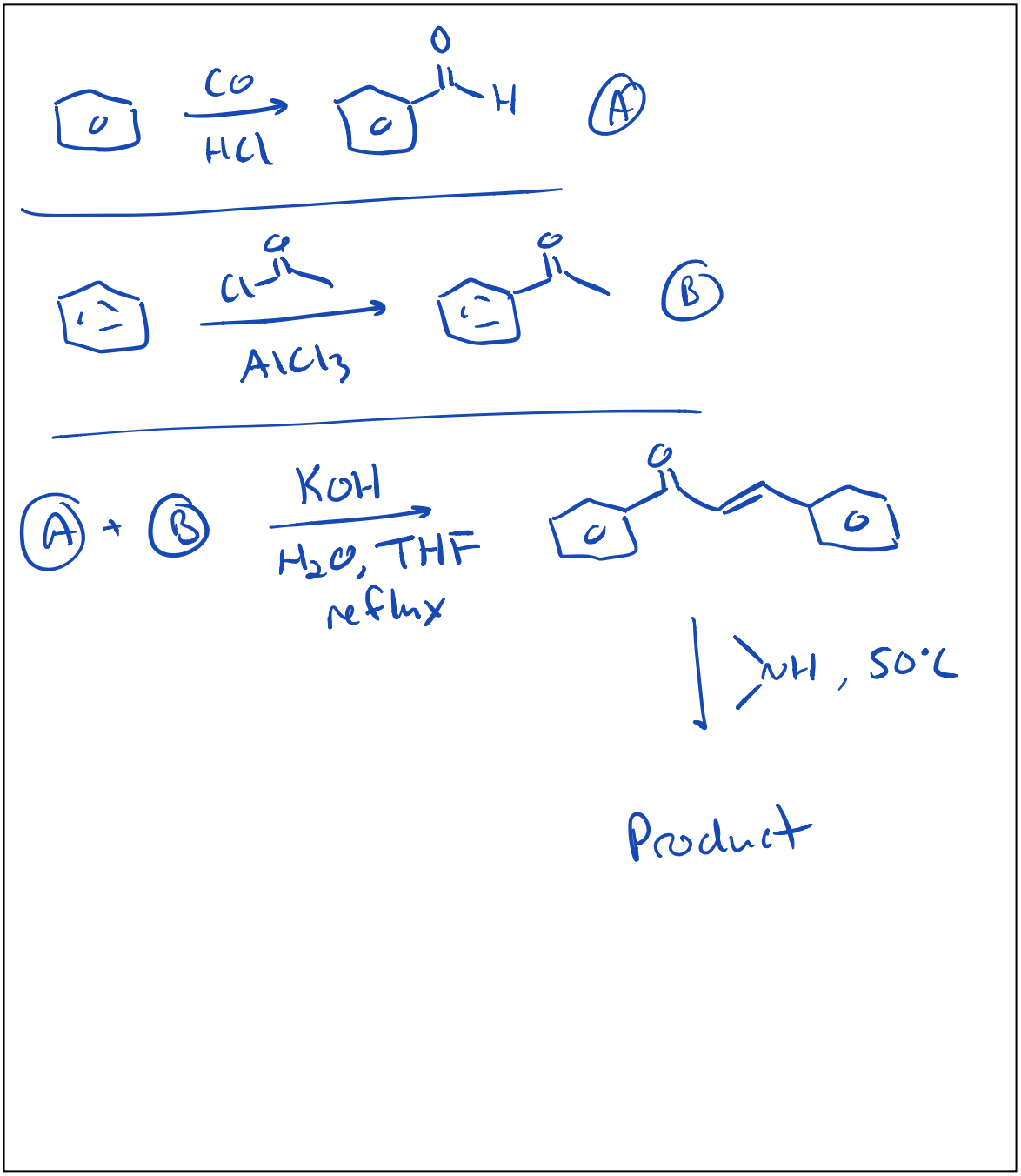
b. 

(5 points)



c.  (5 points)

No reagent/reactant used can have more than 6 carbon atoms



** End of Exam **
(Enjoy the last two weeks of summer!)