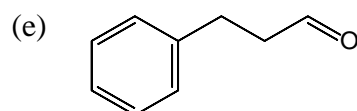
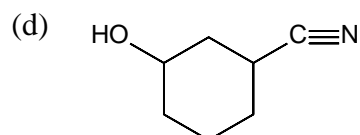
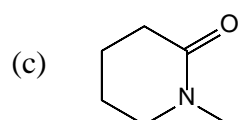
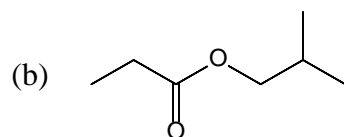
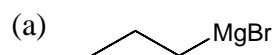
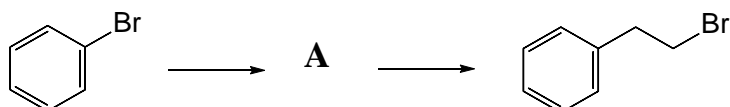


Total 100 points. Write your answers in the space provided. If you need more space, write on the back.

1. [5 x 2 pts] Give the systematic name for each of the following compounds.



2. [10 pts] Of the following 2-step synthesis, the first step is the reaction utilizing organometallic compounds, and the second step is a radical reaction. Answer the following questions.



(a) [2 pts] What should be the compound A? No need to explain; just draw the structure.

(b) [3 x 2 pts] There can be three [3] methods for the first step. Show the reagents needed for each method.

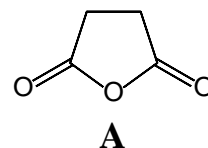
(1)

(2)

(3)

(c) [2 pts] Show the reagents needed for the second step, the radical reaction.

3. [25 points] When the compound **A** on the right is heated in methanol [CH_3OH], the compound **B** is formed: Reaction 1. When the compound **A** is heated in methanol in the presence of a catalytic amount of HCl , the compound **C** is formed: Reaction 2. Answer the following questions.



- (a) [3 pts] Give the name of the compound **A**, **B**, and **C**.

A _____

B _____

C _____

- (b) [4 pts] Show the structure of the compound **B** and **C**.

compound **B**

compound **C**

- (c) [4 pts] What is the name or nature of the reaction 1 and 2, respectively?

1 _____

2 _____

- (d) [4 pts] Explain why different products are formed in the two reactions.

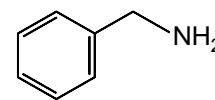
- (e) [3 pts] Would the MS spectra of the compound **B** and **C** be markedly distinguishable? Explain your answer, either yes or no.

- (f) [3 pts] How would you discern the IR spectra of the compound **B** and **C**?

- (g) [4 pts] How would the NMR spectrum of the compound **B** is different from that of **C**? Discuss in terms of number, position, and splitting of the signals.

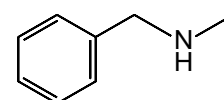
4. [16 pts] Answer the following questions.

- (a) [4 pts] Show the synthetic steps for the preparation of benzylamine through Gabriel synthesis.

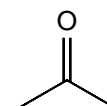


- (b) [3 pts] Show why this method is advantageous over the direct substitution of benzyl halide with ammonia.

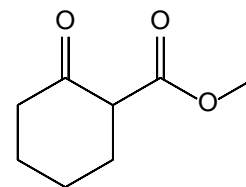
- (c) [3 pts] Show the synthetic steps for the preparation of the compound on the right from benzylamine and a carbonyl compound.



- (d) [6 pts] Show the mechanism for the reaction of the product of (c) above and acetone.



5. [15 points] For the reduction of the β -keto ester on the right, answer the following questions.



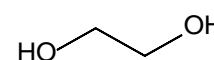
- (a) [2 + 3 pts] If you want to reduce both of the carbonyl groups what reagent would you use? What would be the product in that case?

reducing agent _____

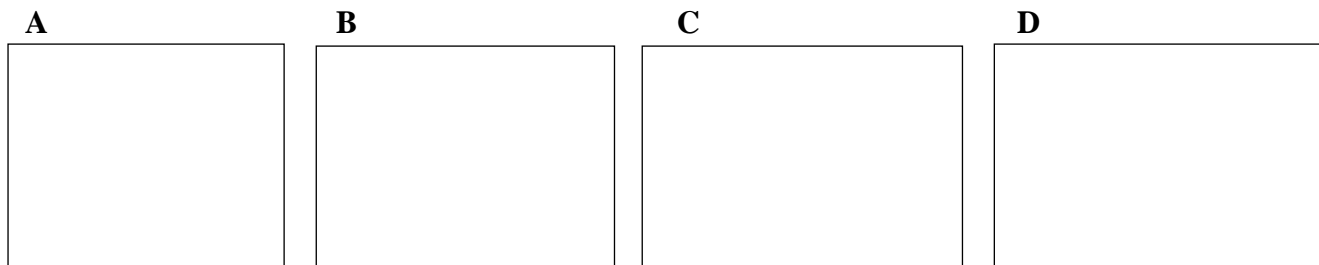
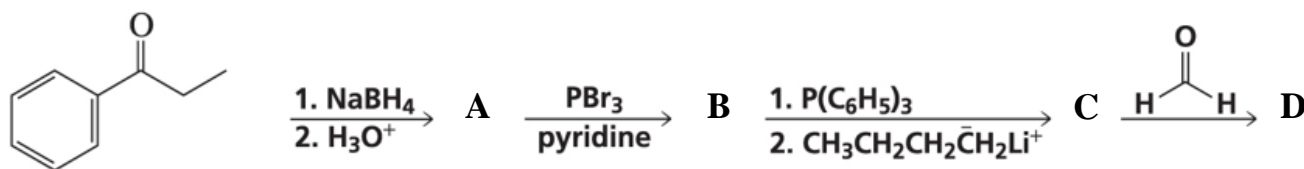
structure of product

- (b) [2 pts] If you want to reduce only the keto group, what reagent would you use? _____

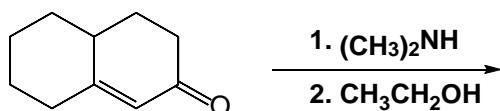
- (c) [8 pts] If you want to reduce only the ester group, you have to convert the keto group to a protecting group like cyclic acetal group. Using 1,2-ethanediol [$\text{HOCH}_2\text{CH}_2\text{OH}$] as the reagent and HCl as the catalyst, show the detailed mechanism for the protection reaction. (Hint: There needs 7 steps.)



6. [4 x 3 pts] Draw the structure of A – D. No need to explain.



7. [12 pts] For the reaction of an α,β -unsaturated ketone below, answer the following questions.



(a) [4 pts] Draw the structure of the kinetic and thermodynamic products.

kinetic product

thermodynamic product

(b) [4 pts] Explain your answer to (a); why one is the kinetic and the other the thermodynamic product. You may discuss the transition states and the intermediates.

(c) [4 pts] If you find that the two products are formed in the same amount (50/50), how would you explain the result?

Table 13.4 Frequencies of Important IR Stretching Vibrations


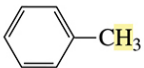
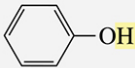
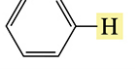
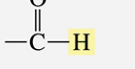
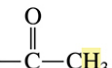
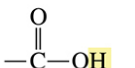
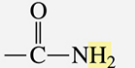
Type of bond	Wavenumber (cm ⁻¹)	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium

Table 14.1 Approximate Values of Chemical Shifts (ppm) for ¹H NMR*

Type of proton	ppm	Type of proton	ppm	Type of proton	ppm	Type of proton	ppm
—CH ₃	0.85		2.3	I—C—H	2.5–4	R—OH	Variable, 2–5
—CH ₂ —	1.20	—C≡C—H	2.4	Br—C—H	2.5–4		Variable, 4–7
—CH—	1.55	R—O—CH ₃	3.3	Cl—C—H	3–4		6.5–8
—C=C—CH ₃	1.7	R—C=CH ₂	4.7	F—C—H	4–4.5		9.0–10
	2.1	R—C=C—H	5.3	R—NH ₂	Variable, 1.5–4		Variable, 10–12
							Variable, 5–8

*The values are approximate because they are affected by neighboring substituents.