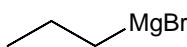
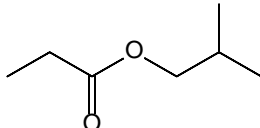
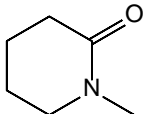
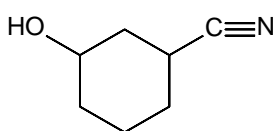
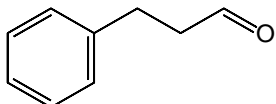
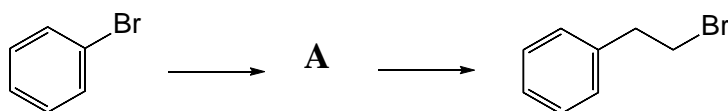


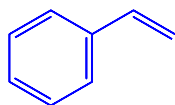
1. [5 x 2 pts] Give the systematic name for each of the following compounds.

- (a)  propylmagnesium bromide
- (b)  isobutyl propanoate or 2-methylpropyl propionate
- (c)  N-methyl-2-azacyclohexanone
- (d)  3-hydroxycyclohexane(-1-)carbonitrile
- (e)  3-phenylpropanal

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.



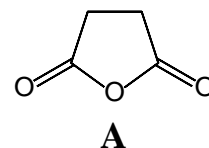
(b) [3 x 2 pts] There can be three [3] methods for the first step. Show the reagents needed for each method.

- (1) $(\text{CH}_2=\text{CH})_2\text{CuLi}$
- (2) $\text{CH}_2=\text{CH}-\text{B}(\text{OR})_2 / \text{L}_2\text{Pd}$
- (3) $\text{CH}_2=\text{CH}_2 / \text{L}_2\text{Pd}$

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

HBr / ROOR

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.

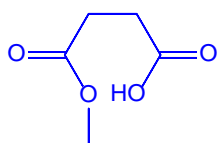


- (a) [3 pts] Give the name of the compound **A**, **B**, and **C**.

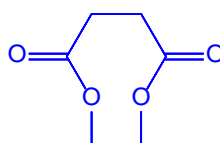
A succinic anhydride
B 4-methoxy-4-oxobutanoic acid
C dimethyl succinate

- (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 alcoholysis, transesterification, ester exchange, or acyl substitution
- 2 Fischer esterification (alcoholysis, transesterification, ester exchange, or acyl substitution)

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

Reaction 1 is from more reactive anhydride to less reactive ester and carboxylic acid, which proceeds without any catalyst. [2 pts]

As an acid catalyst is present in reaction 2, (poor-leaving) carboxylic acid group of compound **B** can be converted to ester through the reaction with poor nucleophile CH_3OH . [2 pts]

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

Either of the following two answers gets the full 3 points.

Yes. Since compound **B** is smaller than **C**, molecular ion $[\text{M}]$ should be different, and peaks for $\text{M}-\text{OH}$ and $\text{M}-\text{COOH}$ should be found for **B**. [3 pt]

No, not marked. Since the fragmentation of $-\text{OH}$ or $-\text{COOH}$ (McLafferty) needs gamma-hydrogen, which is not present in the compound **B**, the peak for $\text{M}-\text{OH}$ and $\text{M}-\text{COOH}$ should not be marked. [3 pts]

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

IR spectra for **B** should show intense and broad band for $-\text{OH}$ between $3200 - 2500 \text{ cm}^{-1}$ [2 pts] and two carbonyl peaks between $1740 - 1700 \text{ cm}^{-1}$ [1 pt].

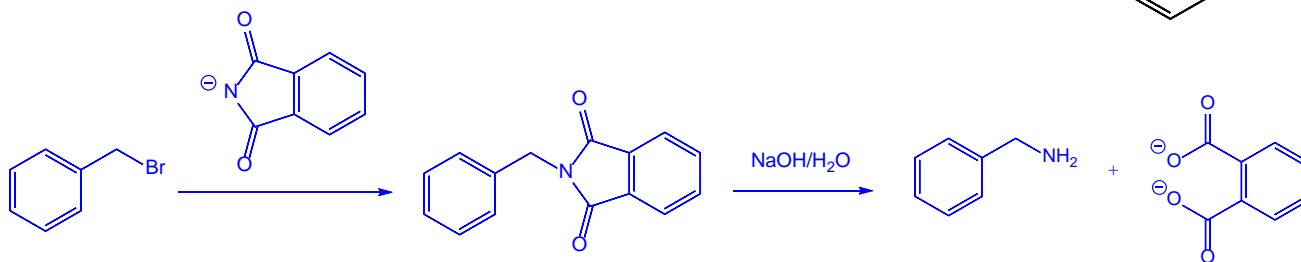
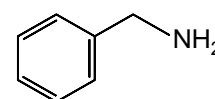
- (g) [4 pts] How would the NMR spectrum of the compound **B** is different from that of **C**? Discuss in terms of number, position, and splitting of the signals.

for **B**, 4 signals, OH (singlet) at as high as 10 ppm, methoxy (singlet) at 3-4 ppm, 2 methylenes (triplets) at 2-3 ppm

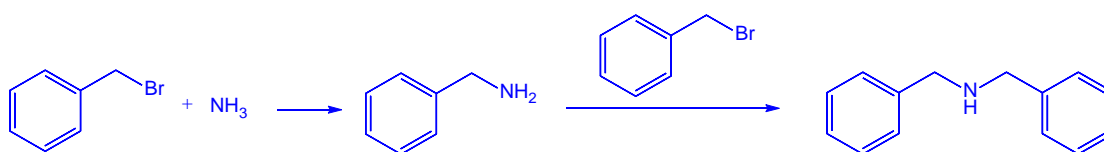
for **C**, 2 signals, methoxy (singlet) at 3-4 ppm, methylene (singlet) at 2-3 ppm

4. [16 pts] Answer the following questions.

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

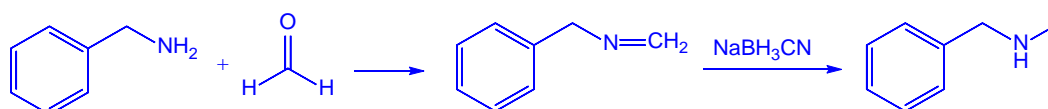
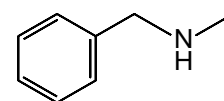


- (b) [3 pts] Show why this method is advantageous over the direct substitution of benzyl halide with ammonia.

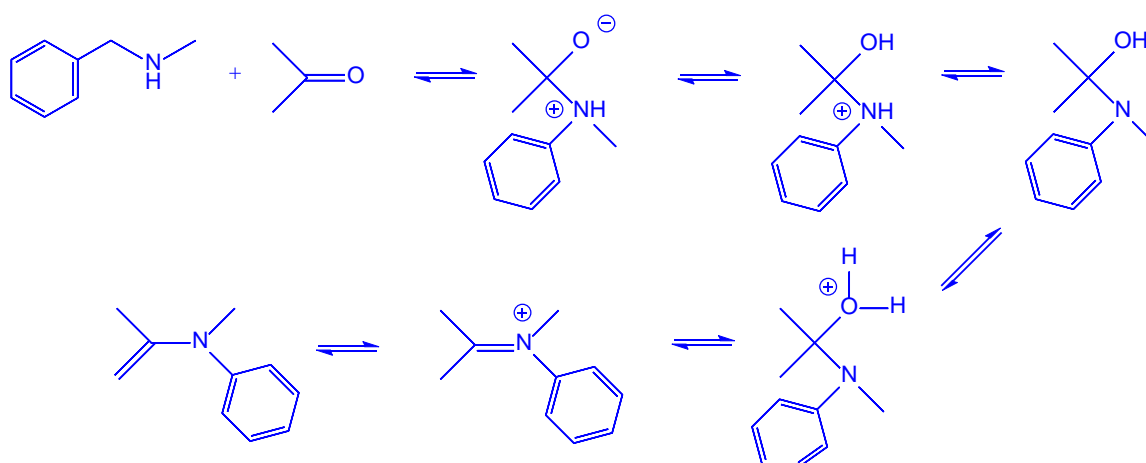
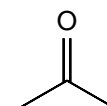


Since benzyl amine is a better nucleophile than ammonia, the substitution to secondary amine is unavoidable. Phthalimide is a weaker nucleophile and substitute halide only once.

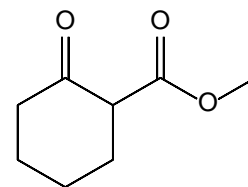
- (c) [3 pts] Show the synthetic steps for the preparation of the compound on the right from benzylamine and a carbonyl compound.



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



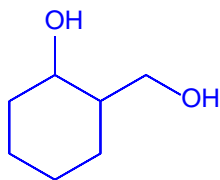
5. [15 points] For the reduction of the β -keto ester on the right, answer the following questions.



- (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?

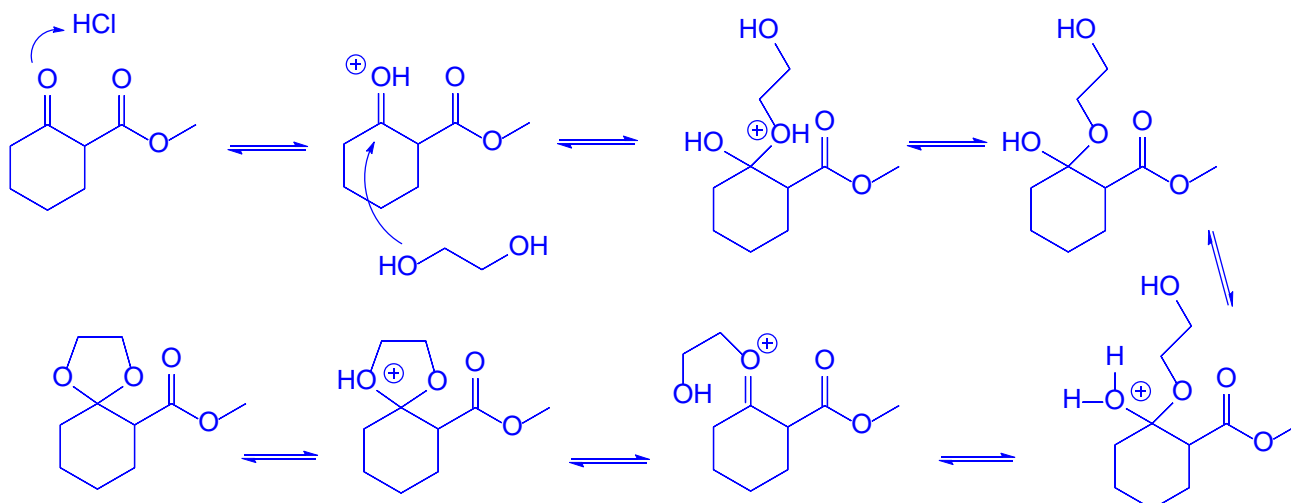
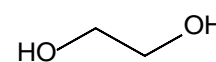
reducing agent LiAlH_4

structure of product

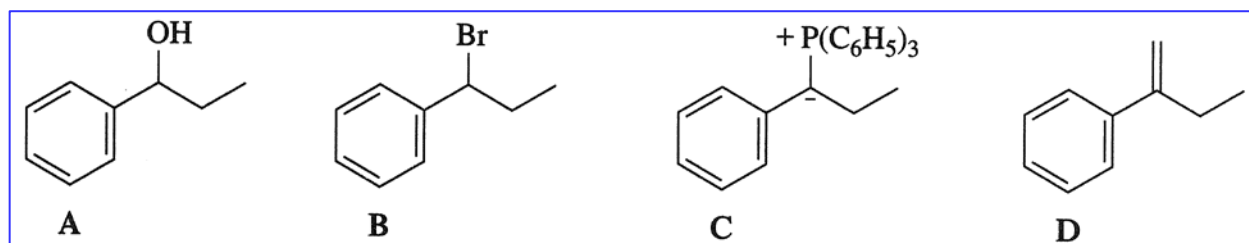
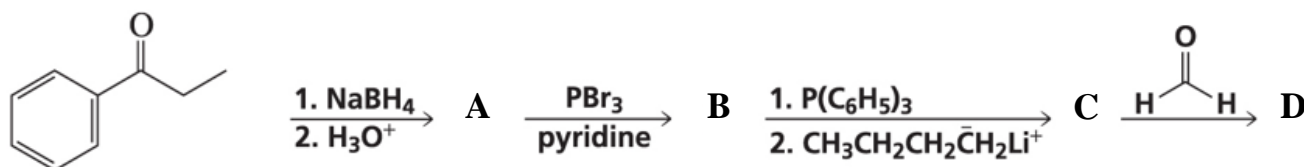


- (b) [2 pts] If you want to reduce only the keto group, what reagent would you use? NaBH_4

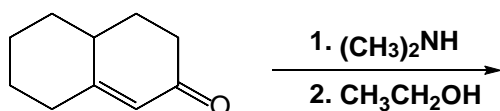
- (c) [8 pts] If you want to reduce only the ester group, you have to convert the keto group to a protecting group like cyclic acetal group. Using 1,2-ethanediol $[\text{HOCH}_2\text{CH}_2\text{OH}]$ as the reagent and HCl as the catalyst, show the detailed mechanism for the protection reaction. (Hint: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



6. [4 x 3 pts] Draw the structure of A – D. No need to explain. **Problem 16.79 of the textbook.**

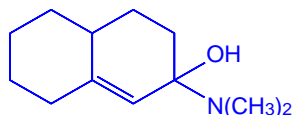


7. [12 pts] For the reaction of an α,β -unsaturated ketone below, answer the following questions. **Homework Q7 and Problem 16.51.**

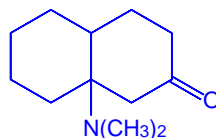


- (a) [4 pts] Draw the structure of the kinetic and thermodynamic products.

kinetic product



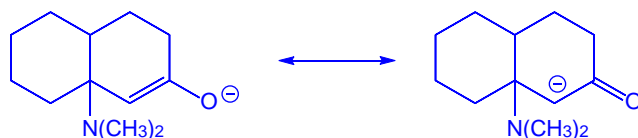
thermodynamic product



- (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.

Of the two electrophilic carbons of α,β -unsaturated carbonyls, carbonyl carbon is more electrophilic than β carbon, resulting in the lower-energy transition state and lower activation energy of the first step to the kinetic product. [2 pts]

The intermediate of the thermodynamic product is more stable than that of the kinetic product due to the resonance shown below (You don't need to show), which is not available in the latter. The thermodynamic product having C=O is also more stable than the kinetic product with C=C. [2 pts]



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

Since amine is a weak (nitrogen) nucleophile, conjugate [thermodynamic] product should be the major product. [2pts] The result (50/50) may be due to the steric hindrance on the β -carbon site. [2 pts]