Midterm III answer

2021.06.08

1. What is the systematic name of the following compound? (4 point)

(A) 3-methyl-4-oxopentanal

(B) 3-methyl-2-oxopentanal

(C) 3-methyl-2-oxo-5-pentanal

(D) 3-methyl-5-oxo-2-pentanone

(E) 3-methylpentan-5-one-1-al

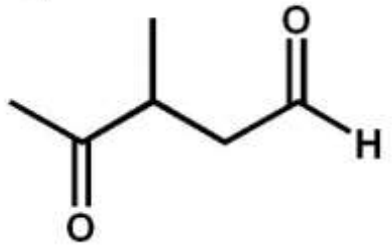
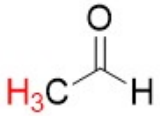
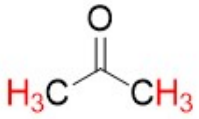


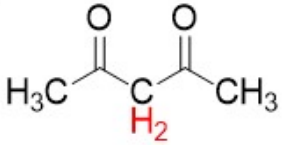
Table 16.1 Functional Group Nomenclature

	Class	Suffix name	Prefix name
increasing priority	Carboxylic acid	-oic acid	Carboxy
	Ester	-oate	Alkoxycarbonyl
	Amide	-amide	Amido
	Nitrile	-nitrile	Cyano
	Aldehyde	-al	Oxo (=O)
	Aldehyde	-al	Formyl (CH=O)
	Ketone	-one	Oxo (=O)
	Alcohol	-ol	Hydroxy
	Amine	-amine	Amino
	Alkene	-ene	Alkenyl
	Alkyne	-yne	Alkynyl
	Alkane	-ane	Alkyl
	Ether	—	Alkoxy
	Alkyl halide	—	Halo

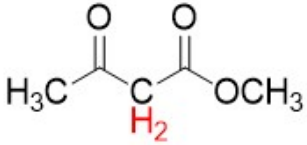
2. Which is the correct order of decreasing acidity (increasing pKa)? (4 point)

(a) 

(b) 

(c) 

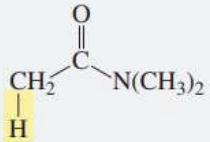
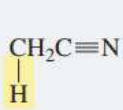
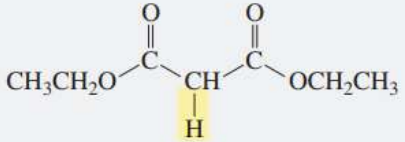
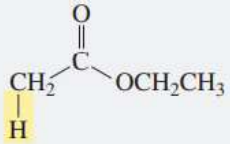
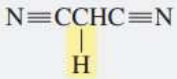
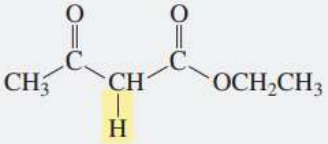
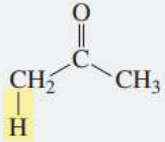
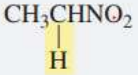
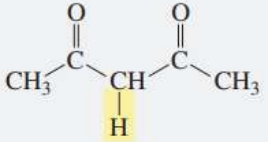
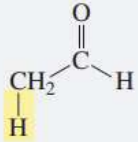
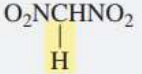
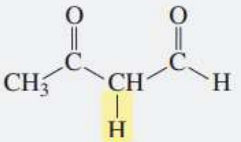
(d) CH_3CH_2CN

(e) 

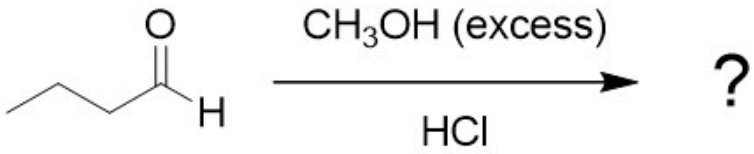
(A) e > c > d > b > a (B) c > e > b > a > d (C) e > c > b > a > d

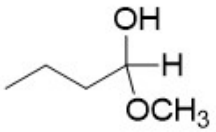
(D) c > e > a > b > d (E) e > d > c > b > a

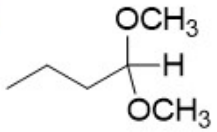
Table 17.1 The pK_a Values of Some Carbon Acids

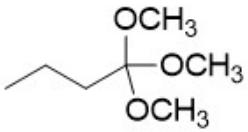
	pK_a		pK_a		pK_a
	30		25		13.3
	25		11.8		10.7
	20		8.6		8.9
	17		3.6		5.9

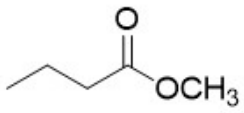
3. What is the product of the following reaction? (4 point)



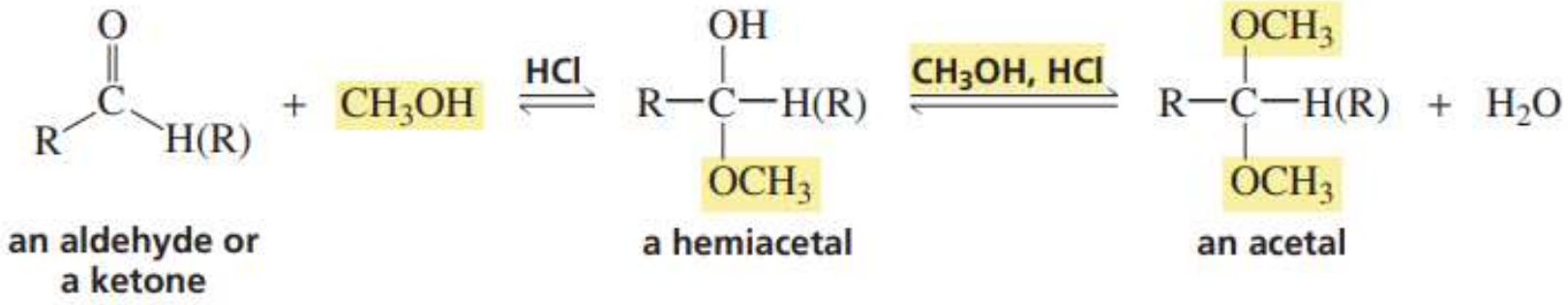
(A) 

(B) 

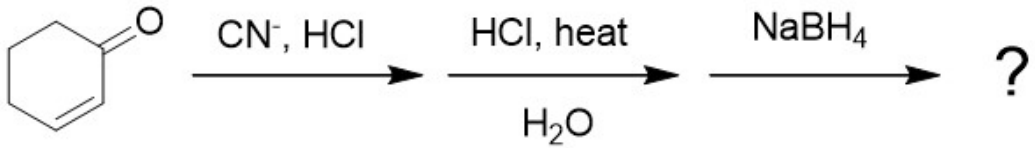
(C) 

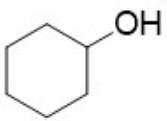
(D) 

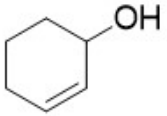
(E) No reaction

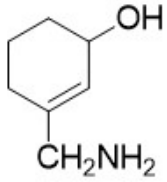


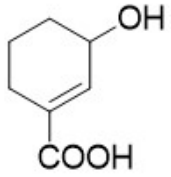
4. What is the product of the following sequence of reactions? (4 point)

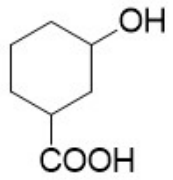


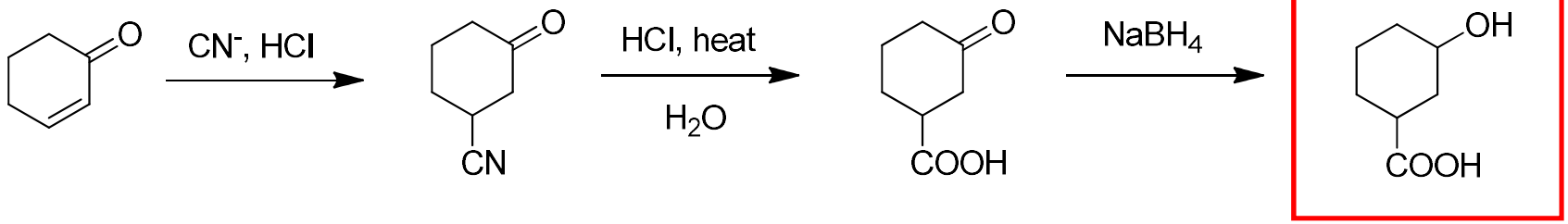
(A) 

(B) 

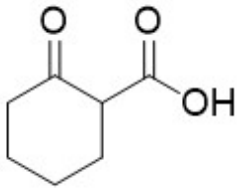
(C) 

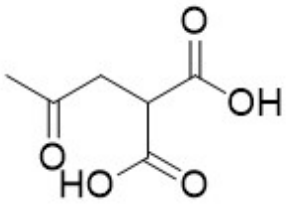
(D) 

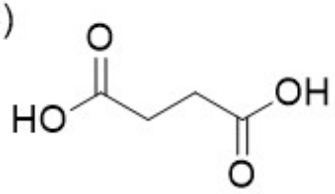
(E) 

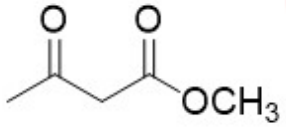


5. After heated (~160°C), which of the following compounds will generate CO_2?
(more than one correct answers) (10 point)

(A) 

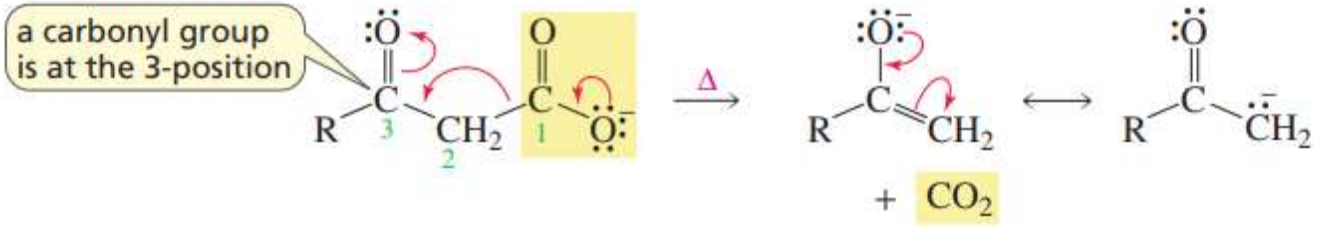
(B) 

(C) 

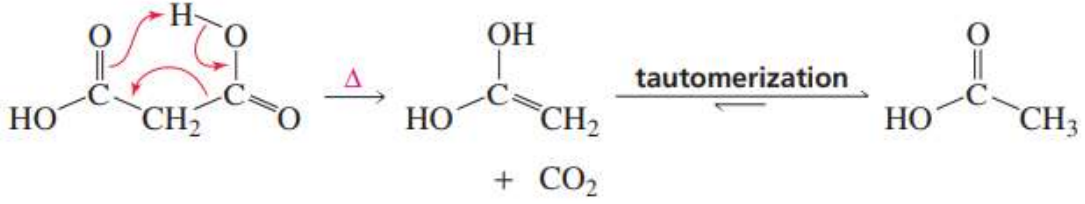
(D) 

(E) $NaHCO_3$

removing CO_2 from an α-carbon

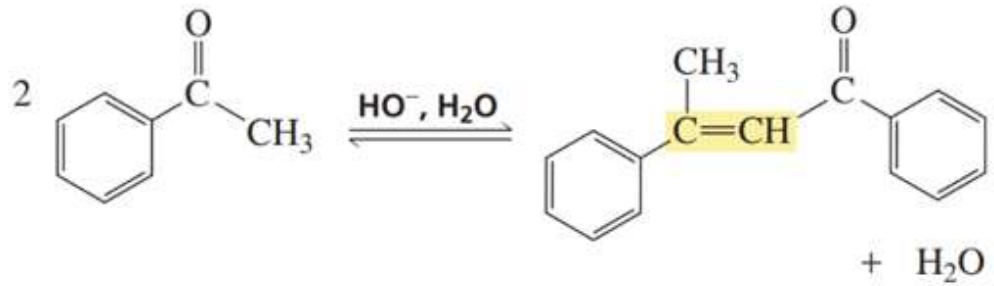


We saw in Section 17.1 that it is harder to remove a proton from an α-carbon if the electrons are delocalized onto the carbonyl group of an ester rather than onto the carbonyl group of a ketone. For the same reason, a higher temperature (~135 °C) is required to decarboxylate a β-dicarboxylic acid such as malonic acid than to decarboxylate a β-keto acid.



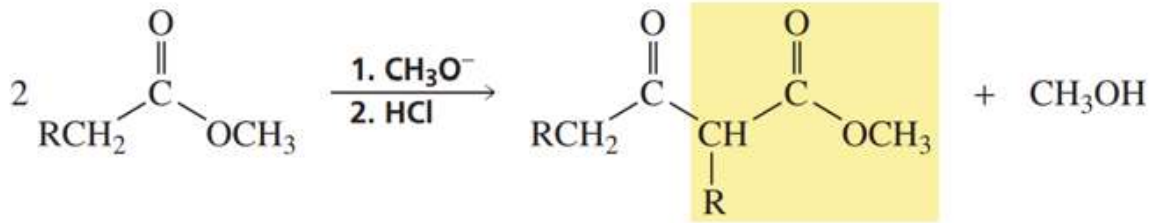
6. Indicate the name to the following reaction. (4 point each)

(a)



(2) Aldol condensation

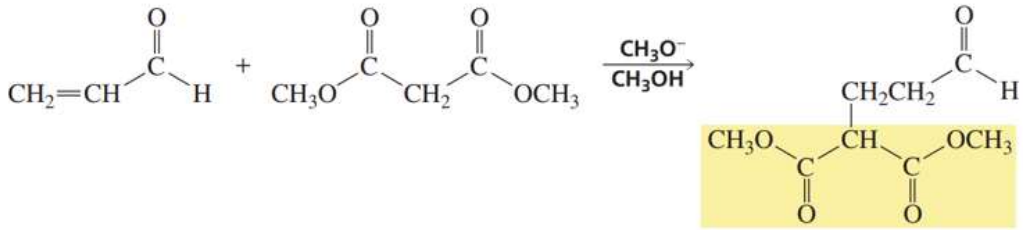
(d)



(4) Claisen condensation

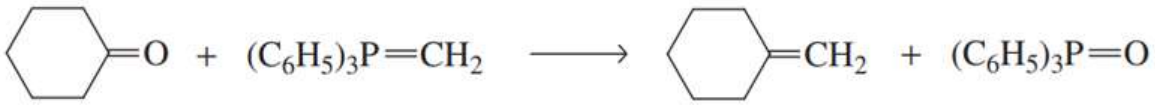
6. Indicate the name to the following reaction. (4 point each)

(b)



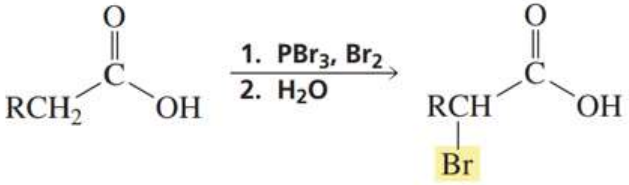
(5) Micheal addition

(c)



(1) Wittig reaction

(e)

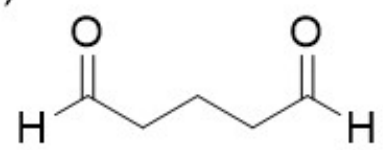


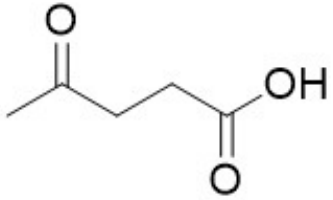
(3) Hell-Volhard-Zelinski reaction

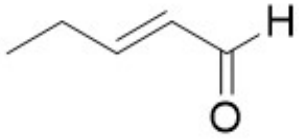
6. Indicate the name to the following reaction. (4 point each)

- (a) -> (2)
- (b) -> (5)
- (c) -> (1)
- (d) -> (4)
- (e) -> (3)

7. Give **systematic names** to the following compounds. (4 point each)

(a) 

(b) 

(c) 

- (a) 1,5-pentanedial
- (b) 4-oxopentanoic acid
- (c) 2-pentenal

Table 16.1 Functional Group Nomenclature

	Class	Suffix name	Prefix name
increasing priority	Carboxylic acid	-oic acid	Carboxy
	Ester	-oate	Alkoxycarbonyl
	Amide	-amide	Amido
	Nitrile	-nitrile	Cyano
	Aldehyde	-al	Oxo (=O)
	Aldehyde	-al	Formyl (CH=O)
	Ketone	-one	Oxo (=O)
	Alcohol	-ol	Hydroxy
	Amine	-amine	Amino
	Alkene	-ene	Alkenyl
	Alkyne	-yne	Alkynyl
	Alkane	-ane	Alkyl
	Ether	—	Alkoxy
	Alkyl halide	—	Halo

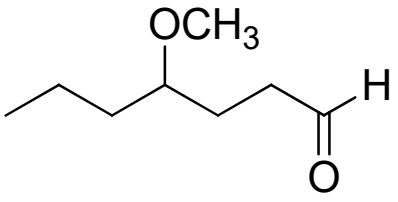
8. Give structures to the following compounds. (4 point each)

(a) 4-methoxyheptanal

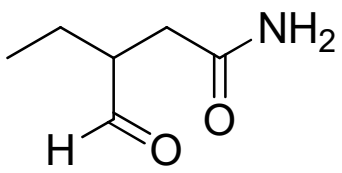
(b) 3-formylpentanamide

(c) 3-methylcyclohexane carbaldehyde

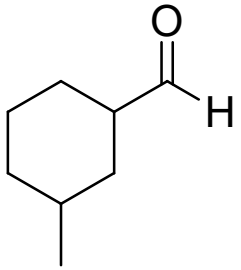
(a)



(b)

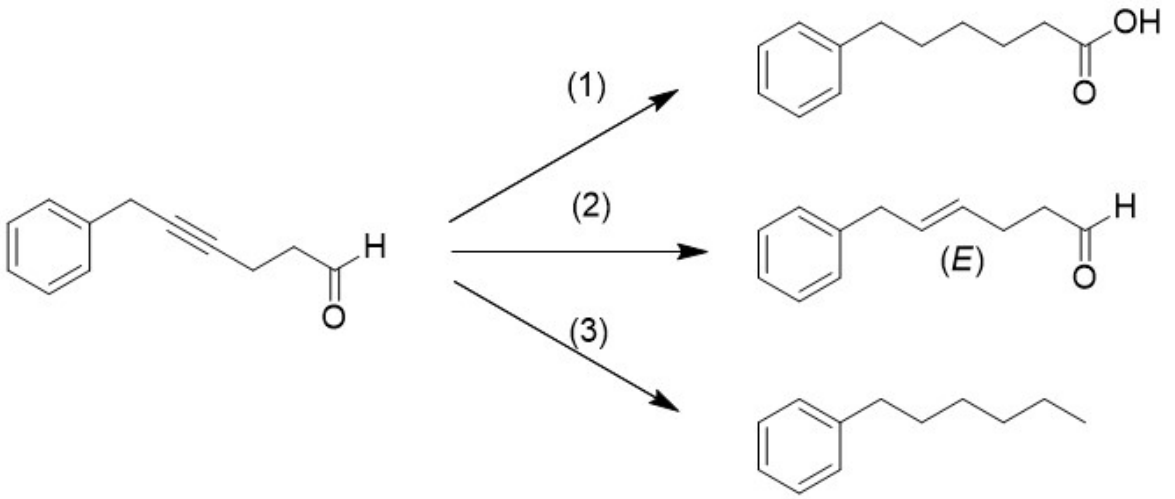


(c)



9. Design a multi-step synthesis to show how each compounds could be prepared from the given starting material. Show all necessary reagent(s) and also **intermediate(s)**.

(a) (15 point)



(1) 1. $2H_2$, Pd/C 2. $KMnO_4$ (or $CF3COOO^-$)

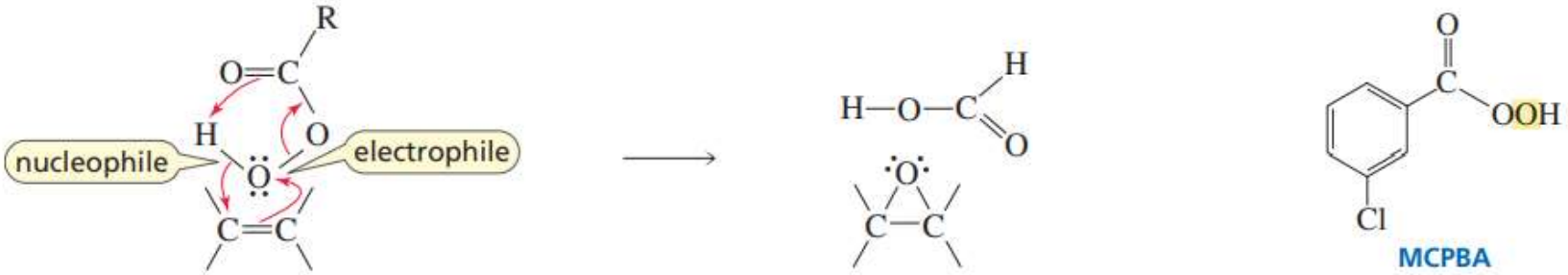
(2) Na, NH_3(l)

(3) 1. $2H_2$, Pd/C 2. $NaBH_4$, H_2O 3. H_2SO_4, heat 4. H_2, Pd/C

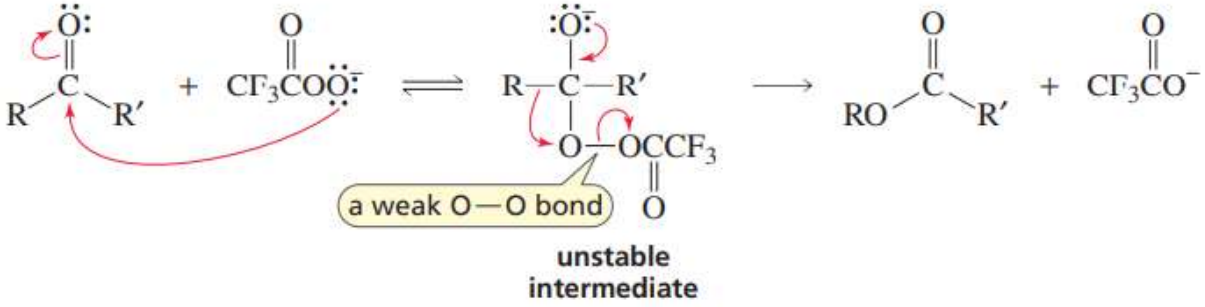
or 1. $3H_2$, Raney Ni 2. H_2SO_4, heat 3. H_2, Pd/C

MCPBA vs RCOOOR vs CF_3COOO^-

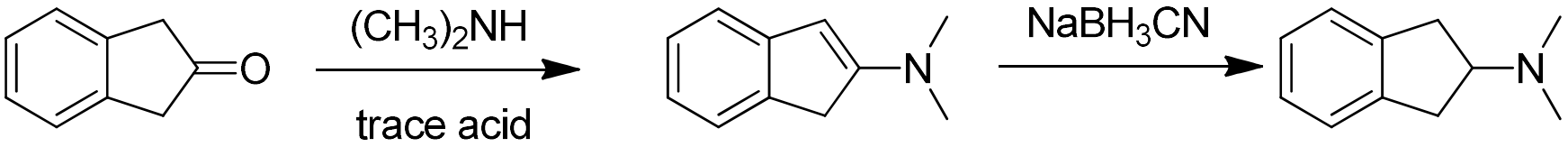
*MCPBA and RCOOOR



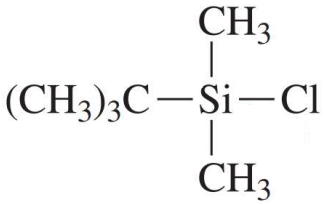
*CF_3COOO^-



(b) (10 point)

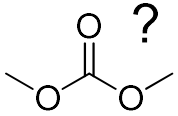


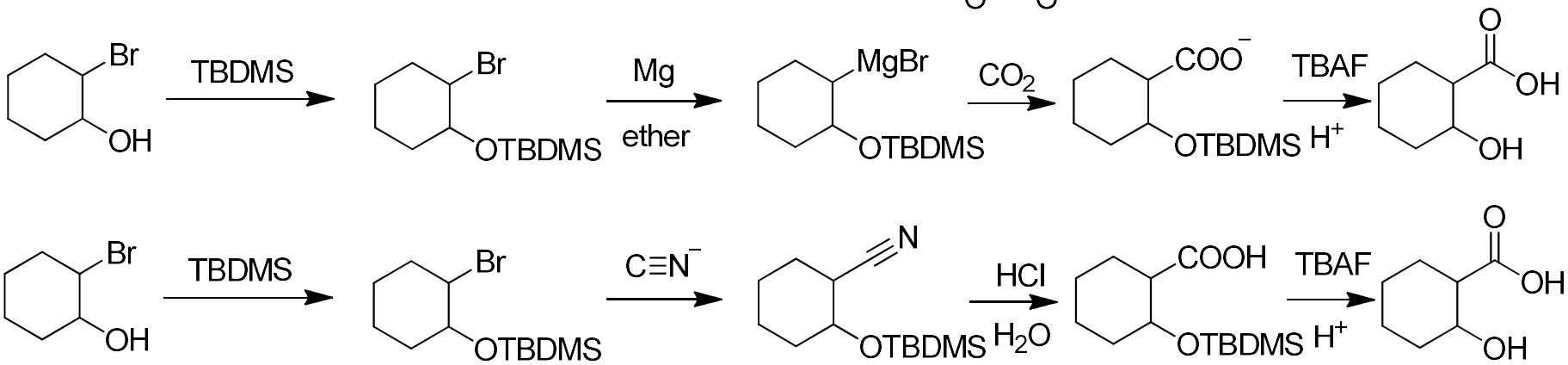
(c) provide the structure and usage of TBDMS, then finish the following synthesis (20 point)



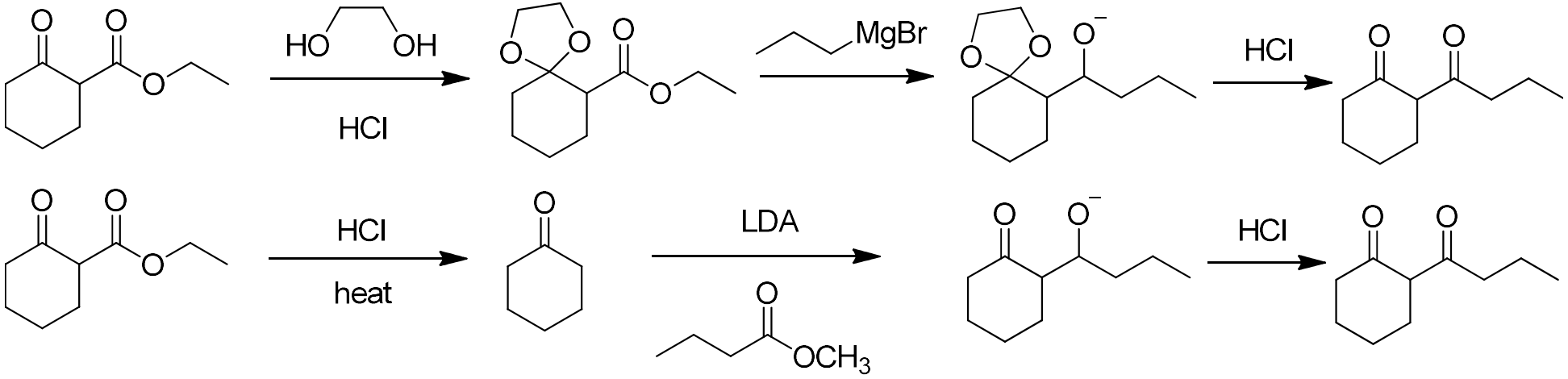
Usage: to protect OH group from deprotonate

***tert*-butyldimethylsilyl chloride**

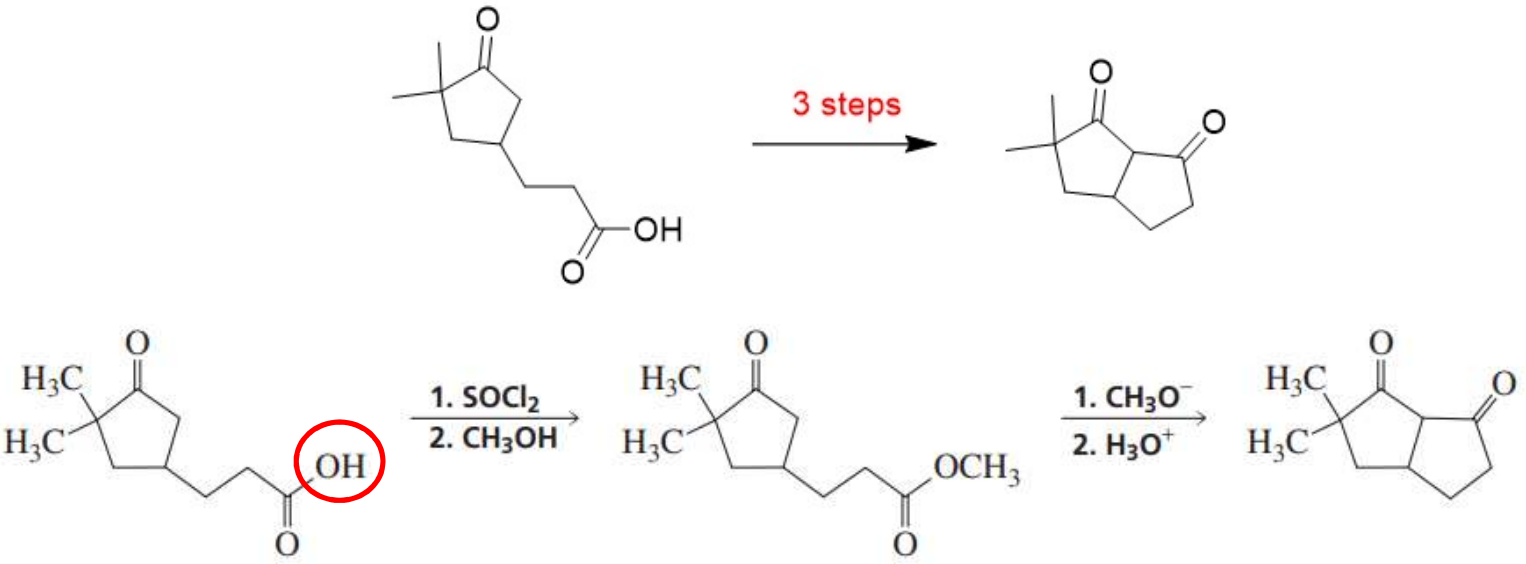




(d) (15 point)



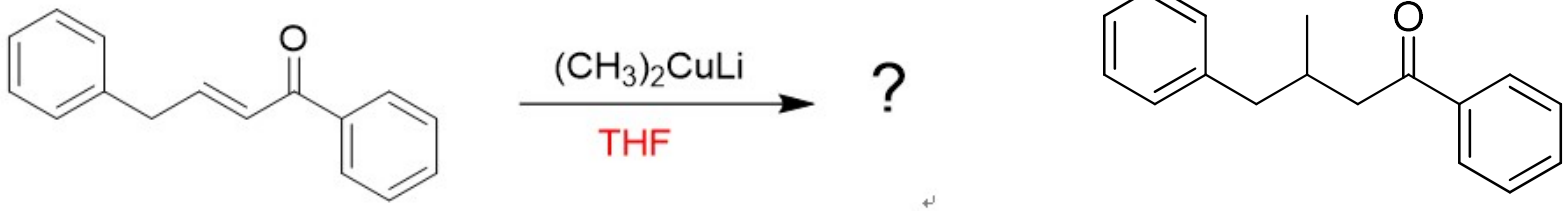
(e) hint: activate carboxylic acid first (15 point)



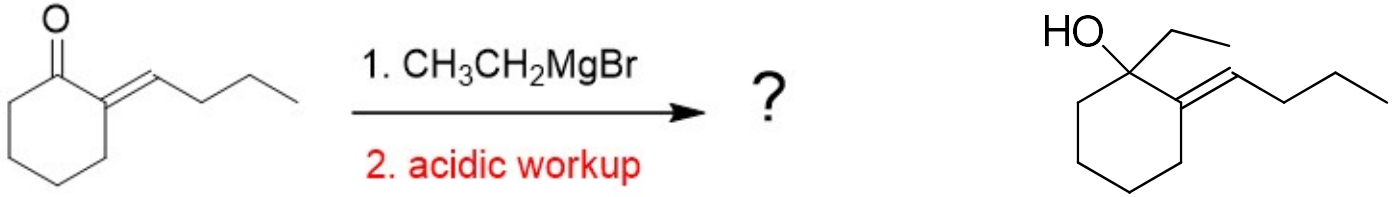
*不能直接加任何鹼 (LDA、CH_3ONa…)，會跟酸中和

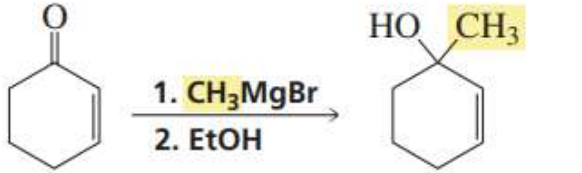
10. Complete each of following reactions by providing **major product**.

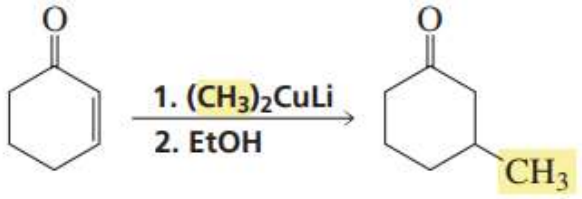
(a) (10 point)



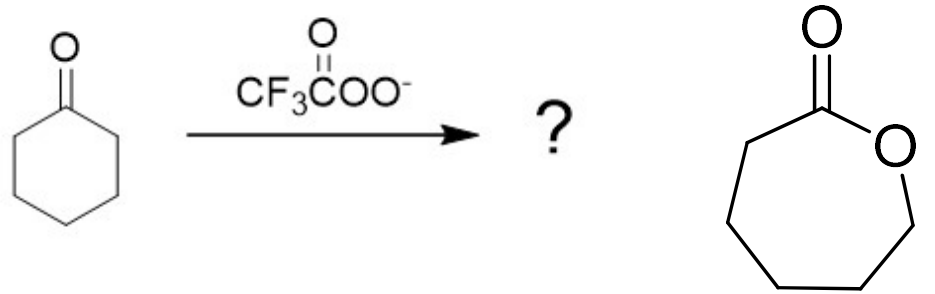
(g) (10 point)

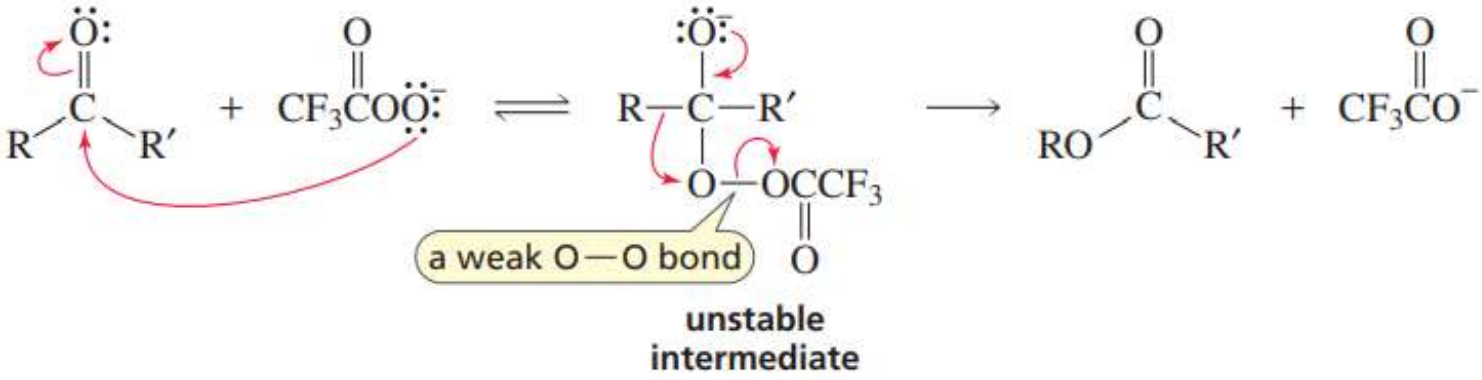




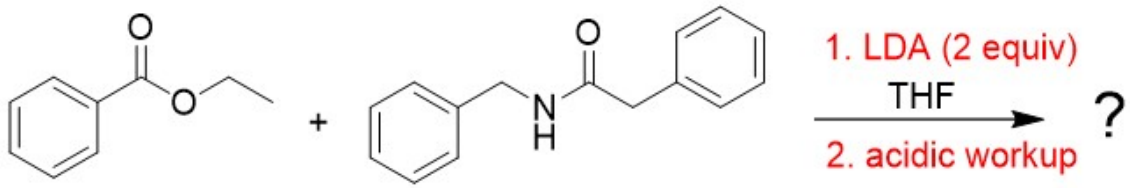


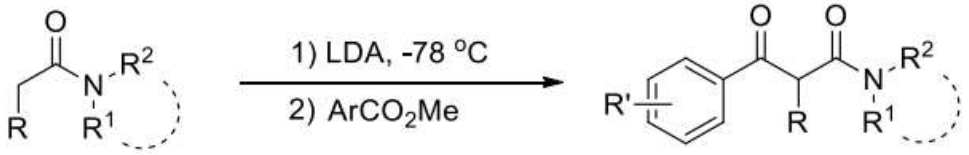
(b) (10 point)


O
O
CF3COO-
?
O
O


R
R′
CF3COO
R
R′
O
OCCF3
O
a weak O—O bond
unstable intermediate
RO
R′
CF3CO−

(c) (10 point)





Under argon atmosphere, lithium diisopropylamide (2.0 M in THF, 10 mL, 20 mmol) was added to a solution of amide (10 mmol) in THF (10 mL) at -78 °C. The resulting solution was stirred at the same temperature for 2 h and then ester (12 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for further 12 h. The reaction was quenched by addition of saturated aqueous ammonium chloride. After phase separation, the aqueous phase was extracted with ethyl acetate for 3 times. The combined organic phase was washed with brine, dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using a mixture of ethyl acetate/petroleum ether as eluent to yield α-substituted-β-ketoamide.

*Yield: 69 – 94%

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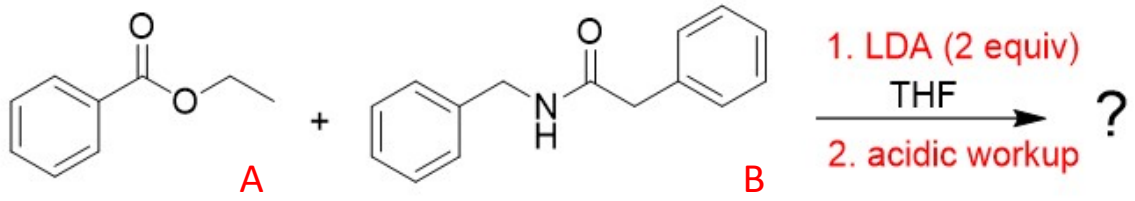
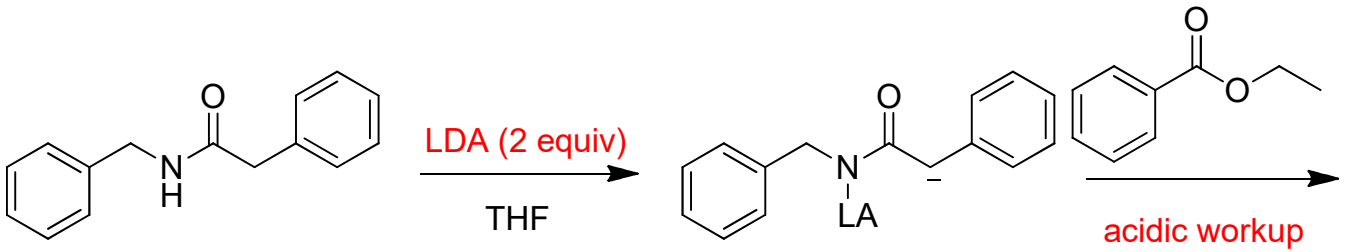
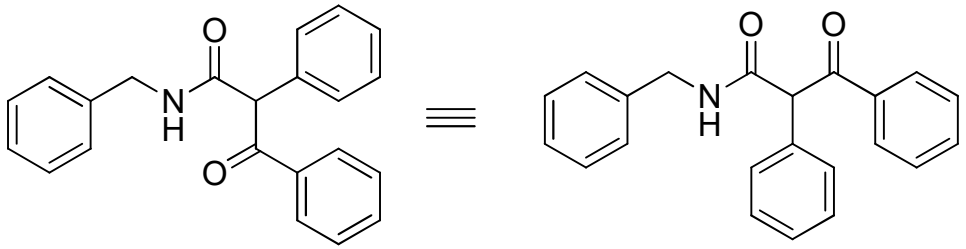
(c) (10 point)



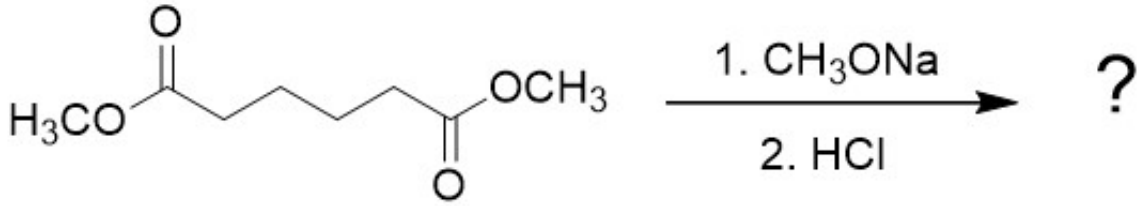


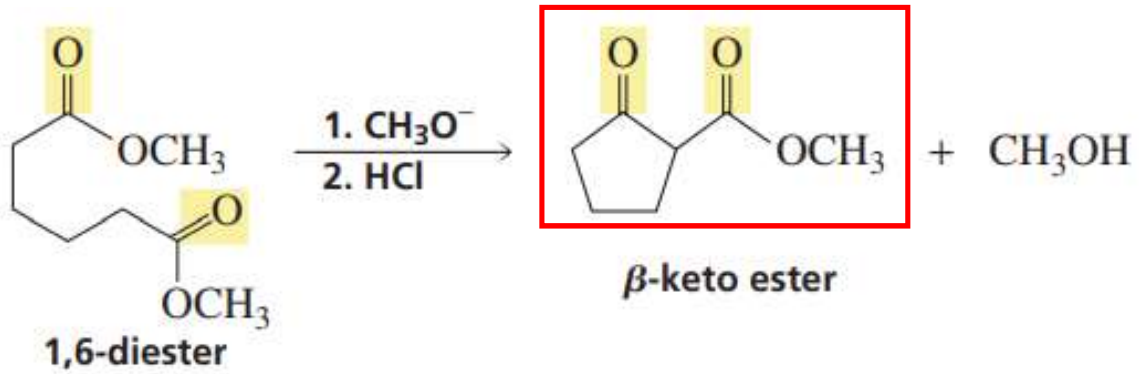
You will get: A + B -> A'B'

Not: 2A + B -> A_2'B'



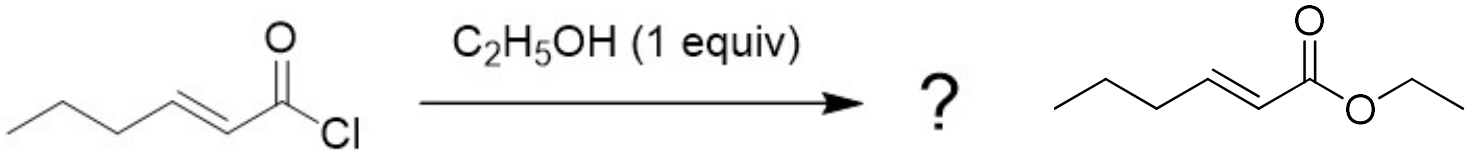
(d) (10 point)

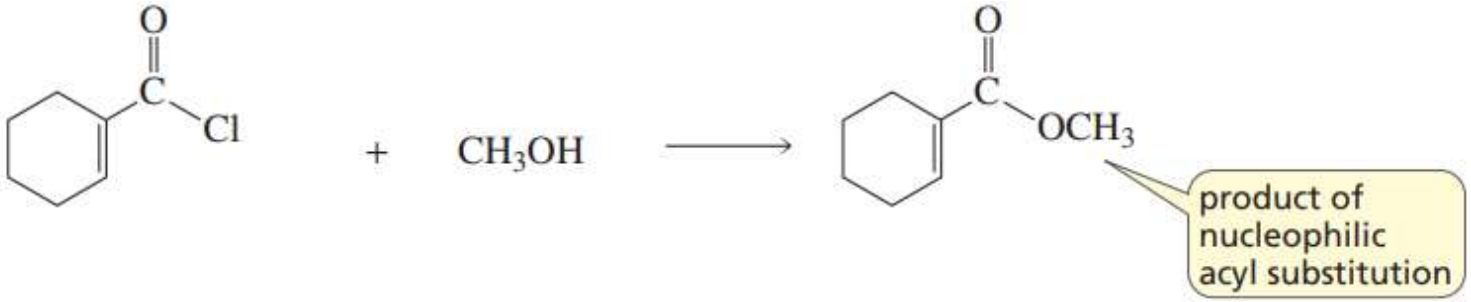




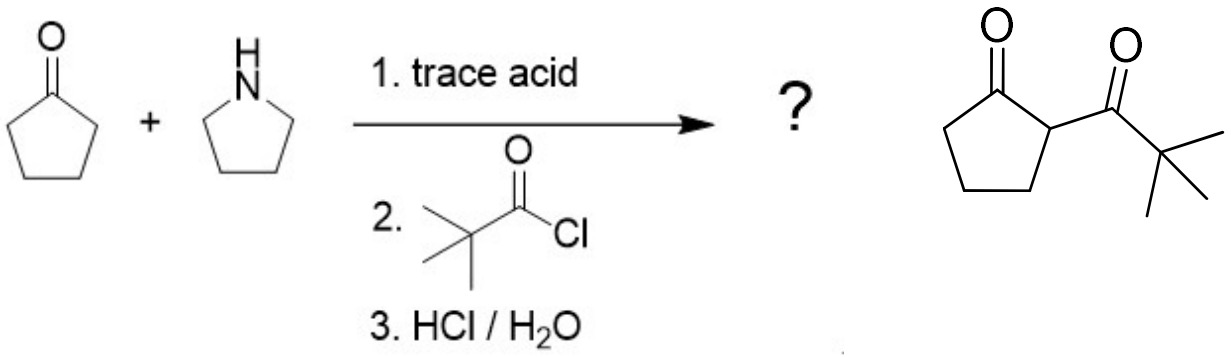
Dieckmann Condensation

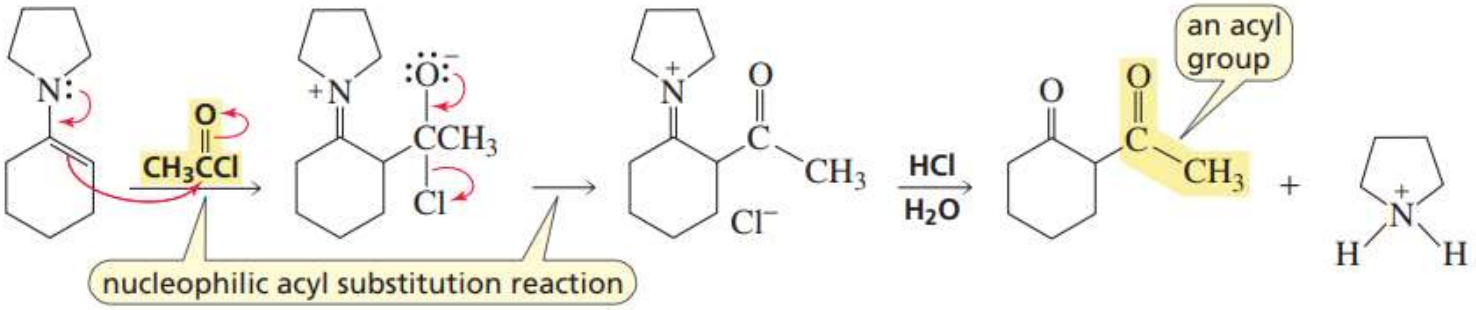
(e) (10 point)


O
Cl
C2H5OH (1 equiv)
?
O
O

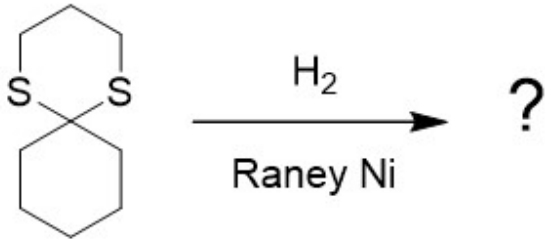

O
C
Cl
+
CH3OH
O
C
OCH3
product of
nucleophilic
acyl substitution

(f) (10 point)

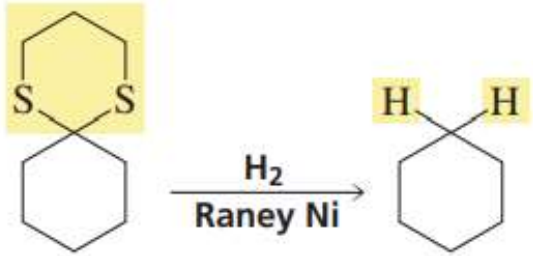

1. trace acid
2.
Cl
3. HCl / H2O
?


CH3CCl
CCH3
Cl
CH3
Cl−
HCl
H2O
an acyl group
nucleophilic acyl substitution reaction

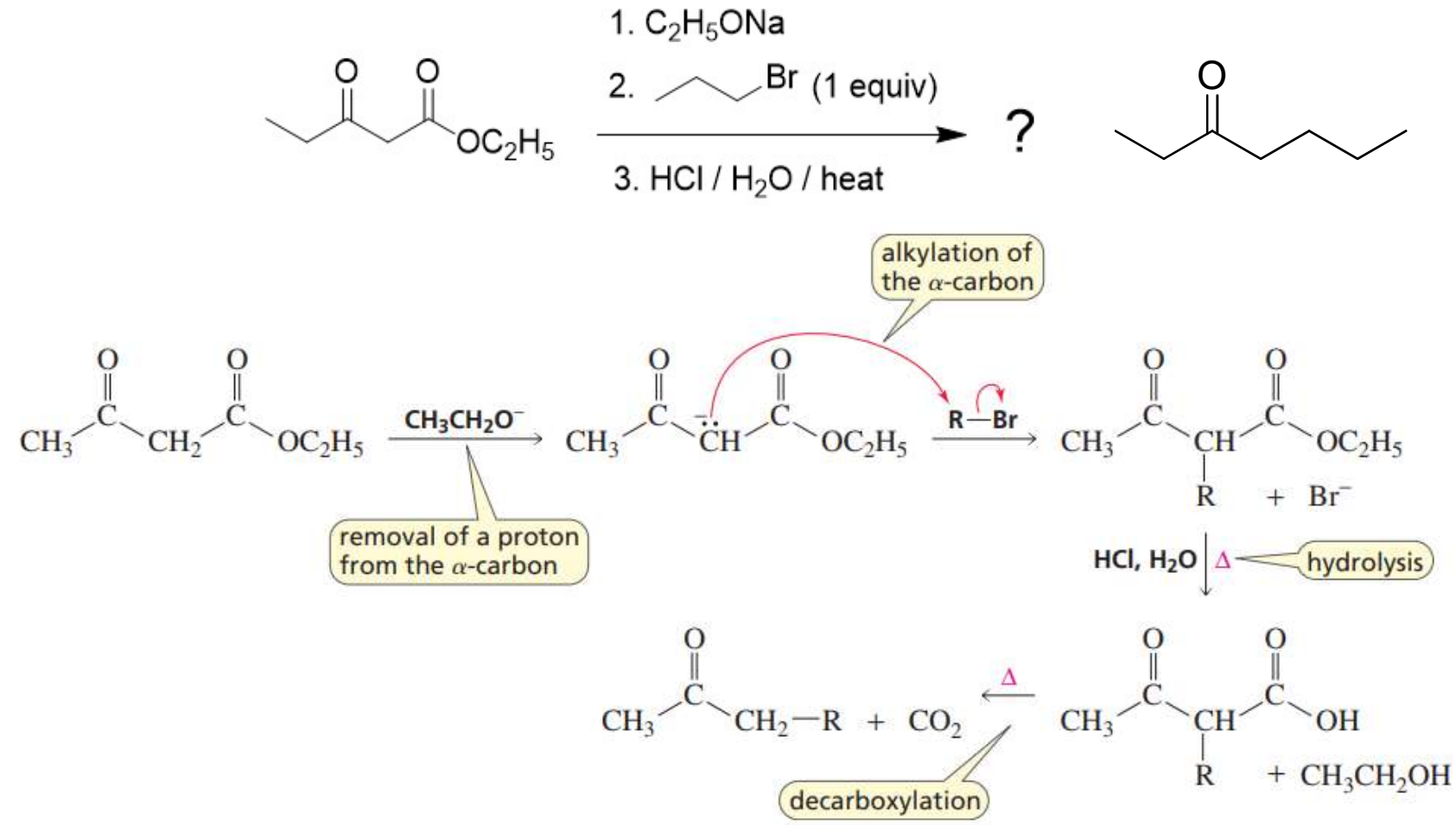
(h) (10 point)



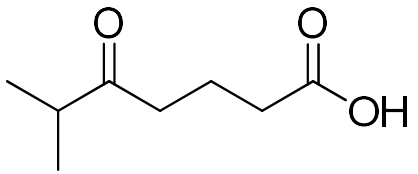
Thioacetal formation is useful in organic synthesis because a thioacetal is desulfurized when it reacts with H_2 and Raney nickel. **Desulfurization** replaces the C—S bonds with C—H bonds.



(i) (10 point)

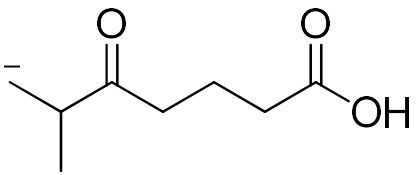

1. C_2H_5ONa
2. Br (1 equiv)
3. HCl / H_2O / heat
?
alkylation of the α-carbon
$CH_3CH_2O^-$
removal of a proton from the α-carbon
R—Br
+ Br^-
HCl, H_2O
Δ
hydrolysis
decarboxylation
+ CO_2
+ CH_3CH_2OH

Question: Choose the correct product.

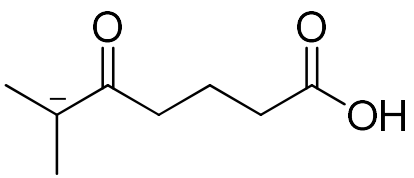


LDA (1 equiv.) → ?

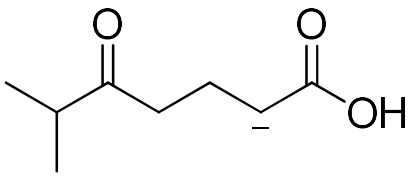
(A)



(B)



(C)



(D) non of above

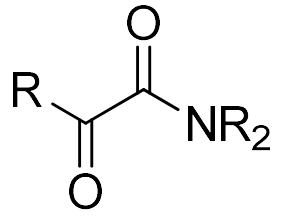
Please Email the answer to TA before 9:30

TA's email: chacharlie001@gmail.com

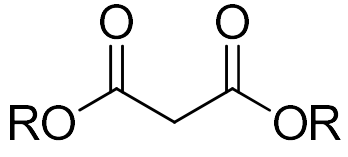
11. Give an example for each of the following type of compounds. (5 point each)

(a) α-keto amide (b) β-diester

(a)



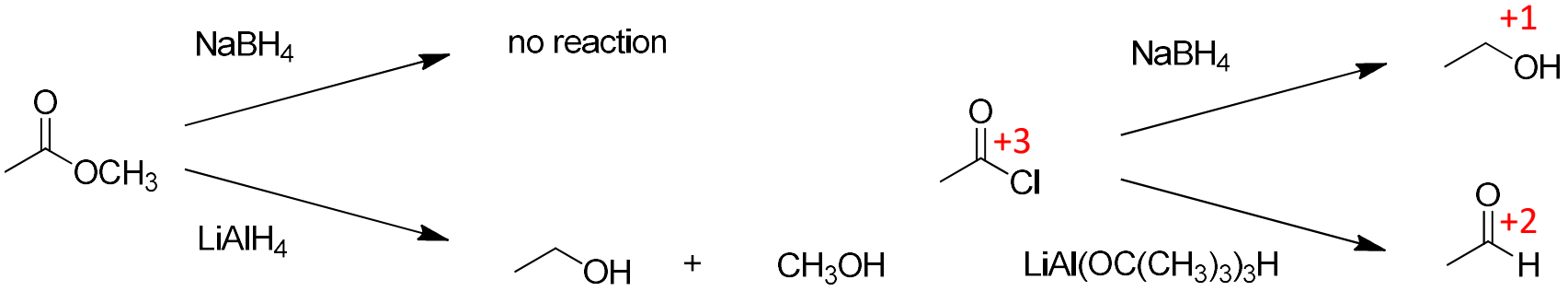
(b)



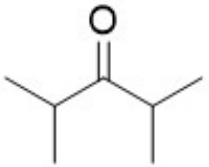
12. Rank the reactivity for following reductant, and give some examples to explain the chemoselectivity order. (15 point)

(a) $NaBH_4$ (b) $LiAlH_4$ (c) $LiAl(OC(CH_3)_3)_3H$

$$LiAlH_4 > NaBH_4 > LiAl(OC(CH_3)_3)_3H$$

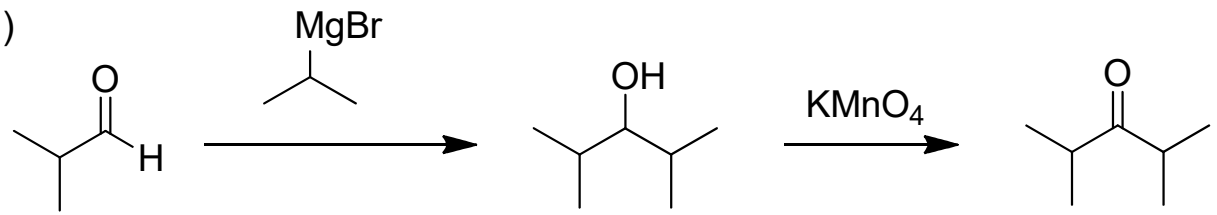


13. Design two different pathways to synthesize compound **A**, noted that all starting material should less than four carbon. (20 point)

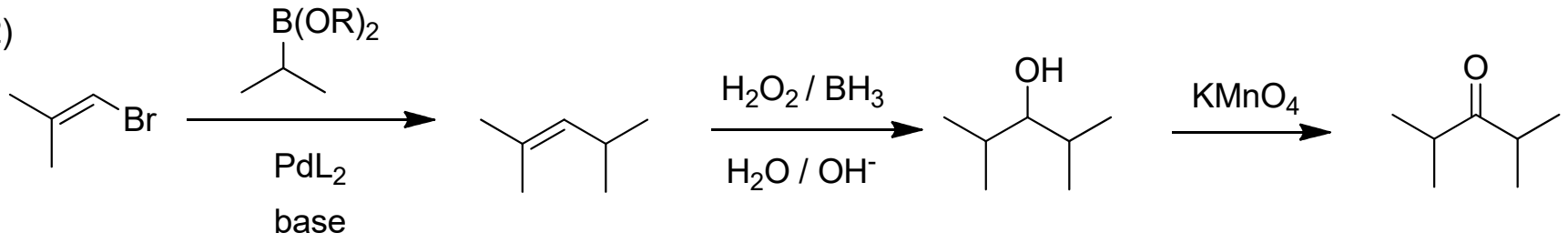


A

(1)

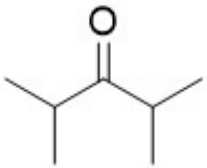


(2)



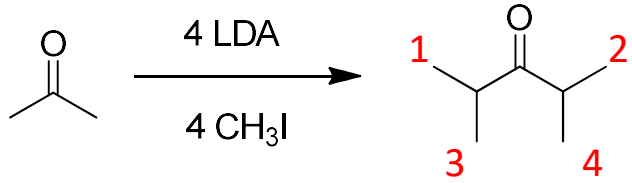
Provide by classmates

13. Design two different pathways to synthesize compound **A**, noted that all starting material should less than four carbon. (20 point)

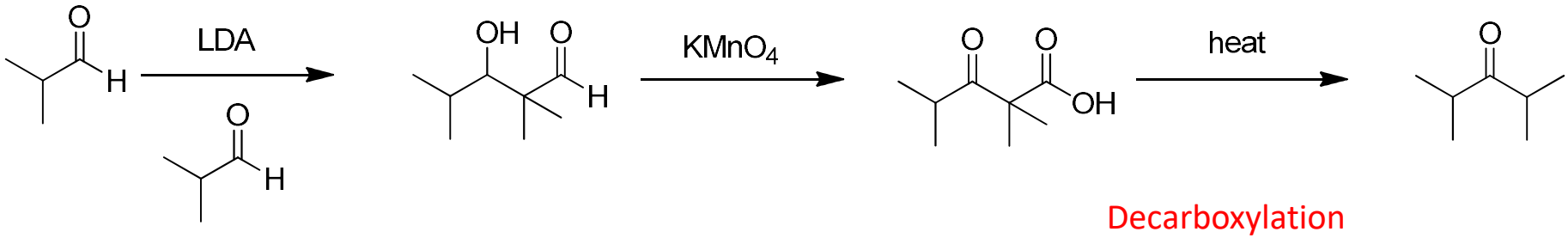


A

(3)



(4)

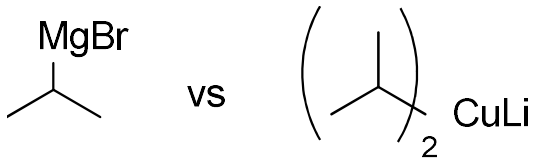


Aldol condensation

Decarboxylation

3 cases of duplicate

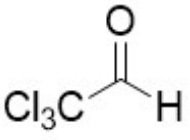
- Similar reactant



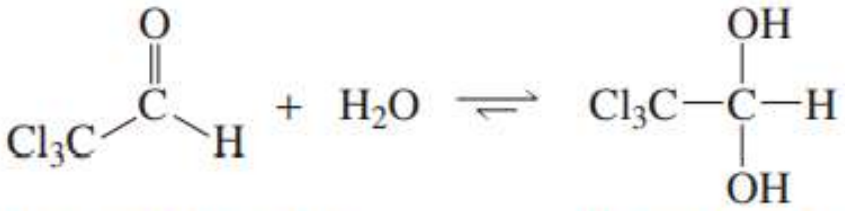
- Change the protecting group

- One more step different for starting material

14. A student preserved compound **B** in open air at room temperature. A few days later, due to high humidity (濕度), he noticed that almost all compound **B** were decomposed, but another general aldehyde preserved near by didn't show the same result. Please explain this strange phenomena, and predict the structure after decomposition. (10 point)



B



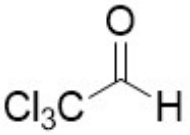
trichloroacetaldehyde chloral hydrate

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[\text{hydrate}]}{[\text{carbonyl compound}][H_2O]}$$

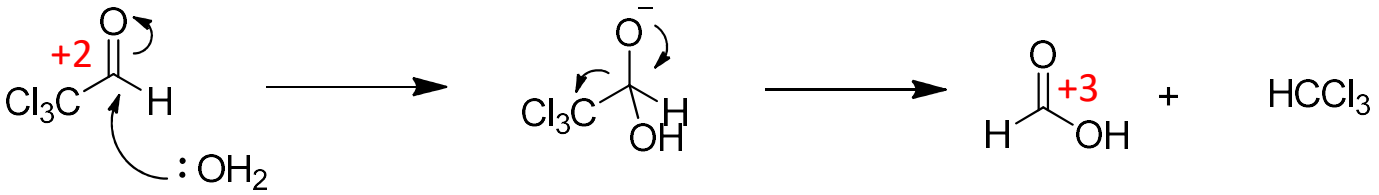
In summary, the percentage of hydrate present in solution at equilibrium depends on both electronic and steric effects:

- electron-donating substituents and bulky substituents (such as the methyl groups of acetone) decrease the percentage of hydrate present at equilibrium.
- electron-withdrawing substituents and small substituents (the hydrogens of formaldehyde) increase the percent of hydration present at equilibrium.

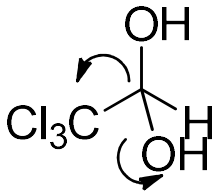
14. A student preserved compound **B** in open air at room temperature. A few days later, due to high humidity (濕度), he noticed that almost all compound **B** were decomposed, but another general aldehyde preserved near by didn't show the same result. Please explain this strange phenomena, and predict the structure after decomposition. (10 point)



B

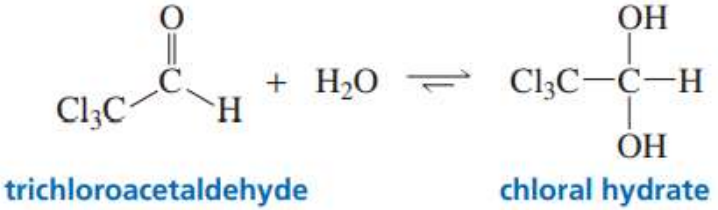


- 2 challenge
  1. Which group will leave? C anion or O anion
  2. How oxidant (氧化劑) join the side reacion

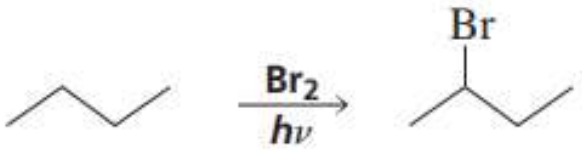


4 type of sensitive substance in lab

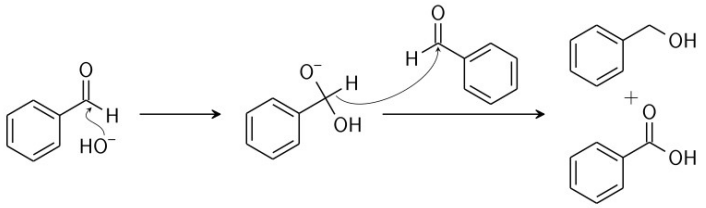
- Water (as Louis acid or base)



- Oxygen (as oxidant) ex: Pd(0) catalyst
- Light (as radical initiator)



- Heat

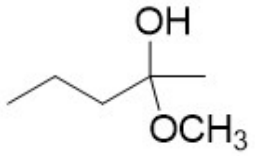


Cannizzaro Rxn (with water, heat)

15. (a) Which of the following compound(s) are acetal? (5 point) 4,6

(b) Which of the following compound(s) are hydrate? (5 point) 3

(1)

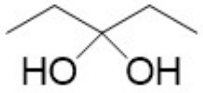


hemiacetal

(2)

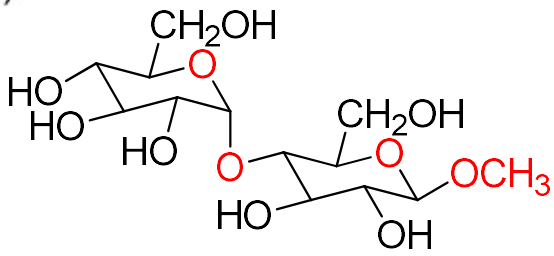
diol

(3)



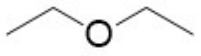
hydrate

(4)



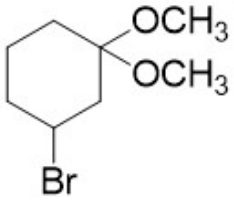
acetal

(5)



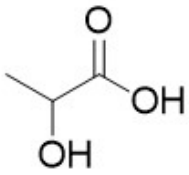
ether

(6)

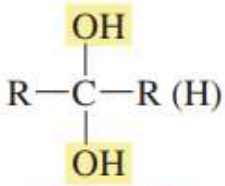


acetal

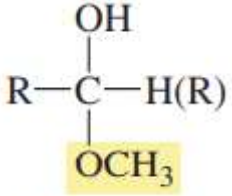
(7)



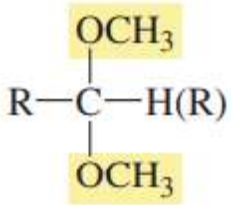
α-hydroxyacid



a *gem*-diol
a hydrate



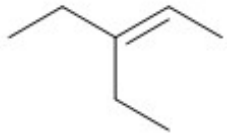
a hemiacetal



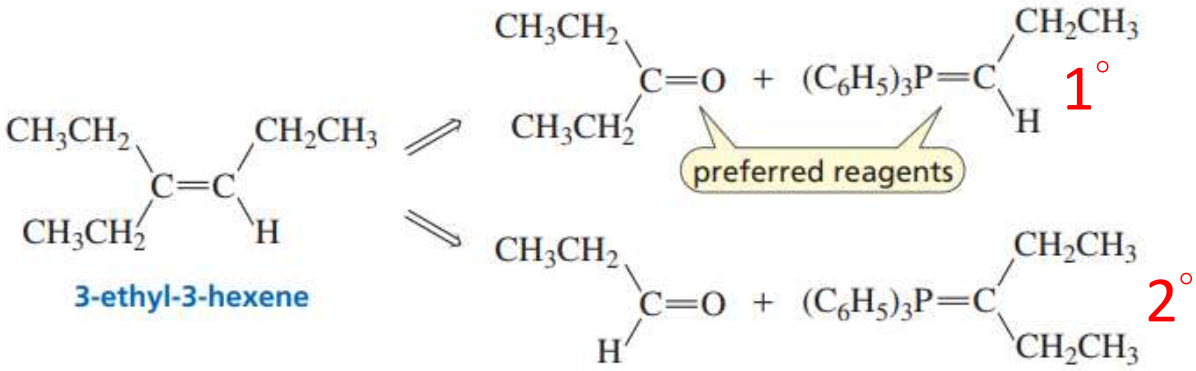
an acetal

16. (a) Provide two sets of starting material to synthesize compound **C**, both of them will undergo Wittig reaction. (5 point each)

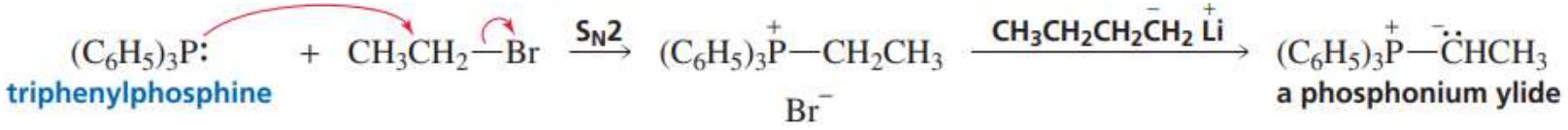
(b) Give an explain that which set of compound is better way in practice. (10 point)



C

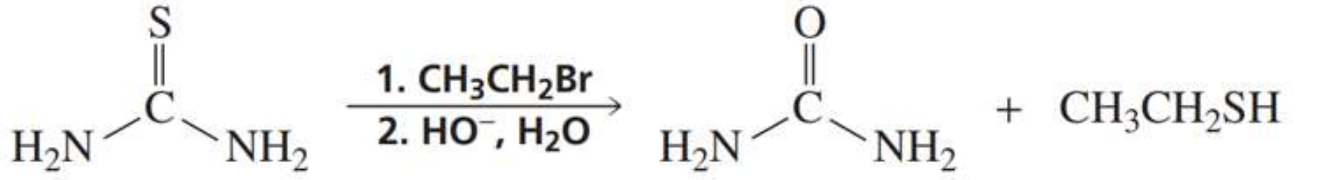


For the synthesis of 3-ethyl-3-hexene, for example, it is better to use a three-carbon alkyl halide for the ylide and a five-carbon carbonyl compound than a five-carbon alkyl halide for the ylide and a three-carbon carbonyl compound, because it is easier to form an ylide from a primary alkyl halide (1-bromopropane) than from a secondary alkyl halide (3-bromopentane).

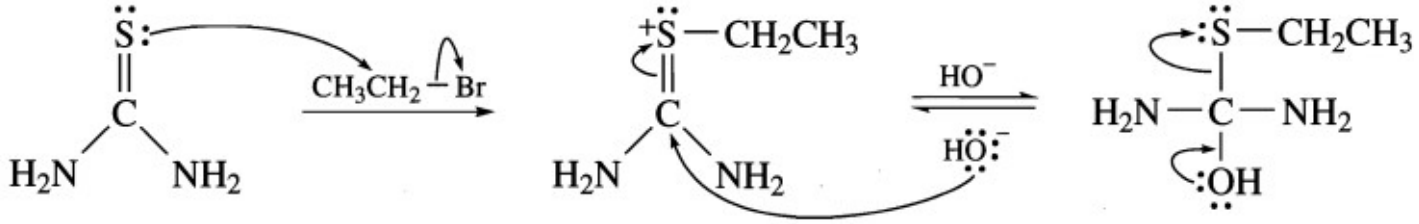


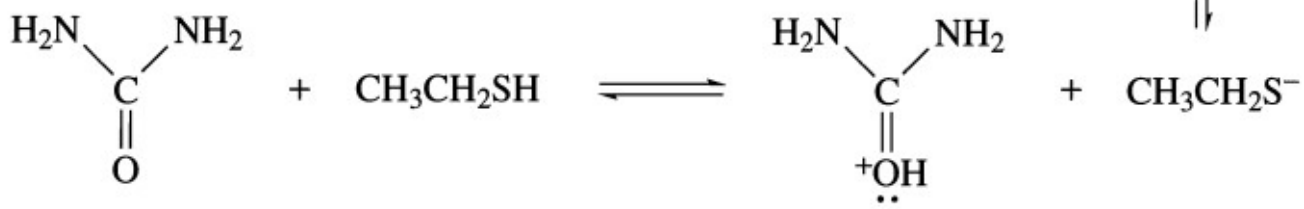
17. Propose a reasonable mechanism for the following reaction. (15 point each)

(a)

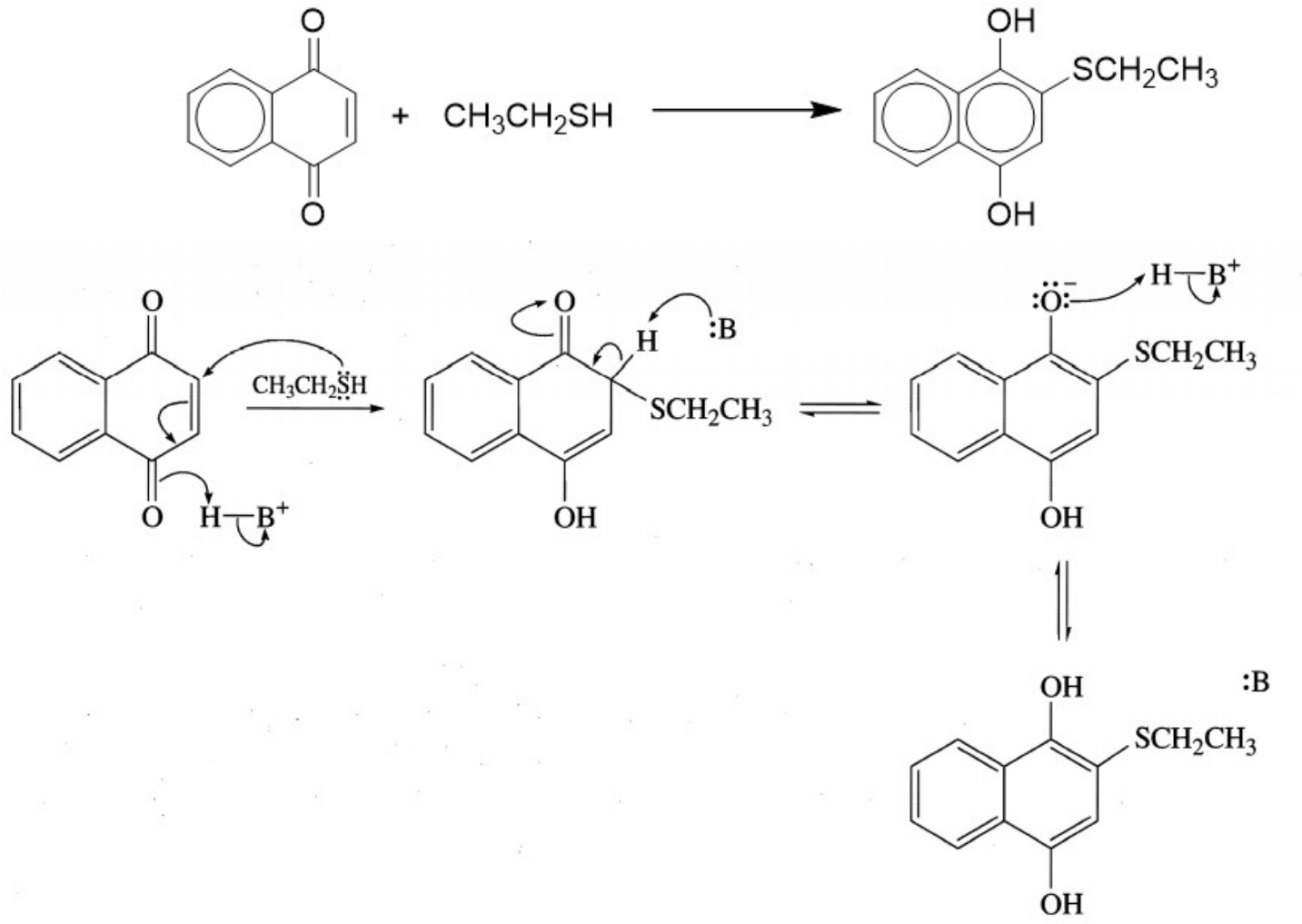


a.





(b)



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繳費單相關作業(出納組
退費查詢
所得相關查詢
出納傳票付款查詢
就學貸款
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Finished!

Please ask me for mistake about midterm before today (6/8) end.