Organic Chemistry (2nd semester)

Second term examination (Tuesday, Apr. 27th, 2021, 8:00 ~ 9:50)

Name: 許秉宜 ; Student ID number: 108023002 ; Score: _____/320

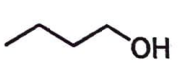
A 1. Rank the reactivity order of nucleophilic acyl substitution reaction for the following acid derivatives. (5 point)

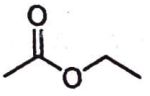
(a) Ester (b) Acid anhydride (c) Amide (d) Acid chloride

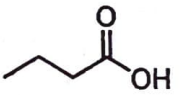
(A) b > d > a > c (B) d > b > a > c (C) d > a > b > c (D) c > a > b > d

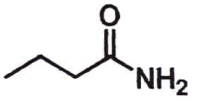
(E) b > c > a > d

A 2. Rank the following compounds in order of increasing boiling point. (5 point)

(a) 

(b) 

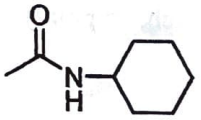
(c) 

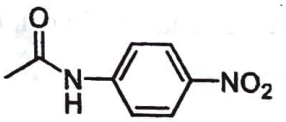
(d) 

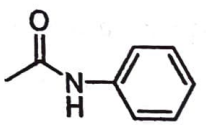
(A) d > c > a > b (B) d > c > b > a (C) c > d > a > b (D) c > d > b > a

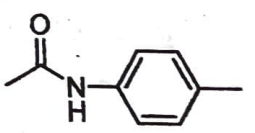
(E) b > a > d > c

D 3. Rank the following amides from greatest reactivity to least reactivity toward acid-catalyzed hydrolysis. (5 point)

(a) 

(b) 

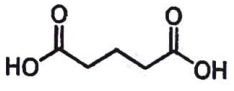
(c) 

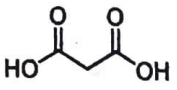
(d) 

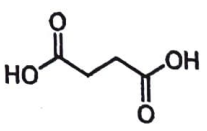
(A) b > c > a > d (B) a > d > c > b (C) a > c > d > b (D) d > c > b > a

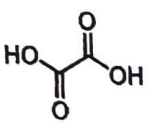
(E) b > c > d > a

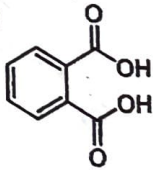
D 4. Which of the following dicarboxylic acids is the most acidic? (5 point)

(A) 

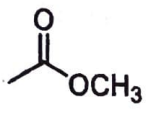
(B) 

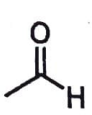
(C) 

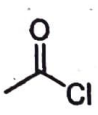
(D) 

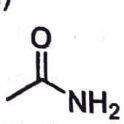
(E) 

A 5. Rank the following compounds in order of decreasing frequency of the carbon-oxygen double-bond stretch. (5 point)

(a) 

(b) 

(c) 

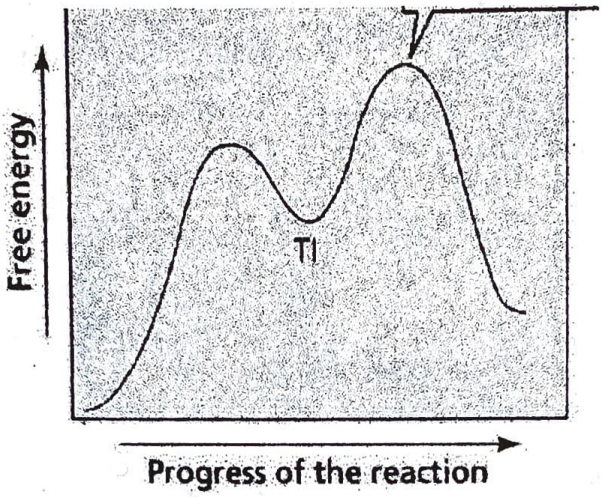
(d) 

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

(E) b > c > a > d

6. For this nucleophilic addition–elimination reaction coordinated diagram, which of the following statement is not correct?

B



(A) In this diagram, the carbonyl compound is less reactive.

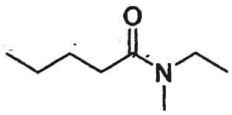
(B) A substitution product will form.

(C) The nucleophile is a weaker base than the group attached to the acyl group in the reactant.

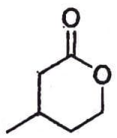
(D) In this diagram, the leaving group is poor.

7. Name the following compounds in **systematic name**. (5 point for each, 15 point)

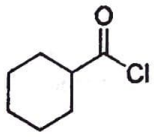
(a)



(b)



(c)



8. Draw a structure for each of the following: (5 point for each, 15 point)

(a) methyl 3-bromobutanoate

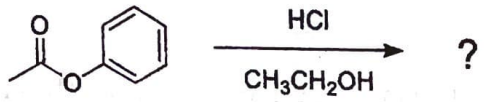
(b) benzenecarbonitrile

(c) 2-methoxybutanoic acid

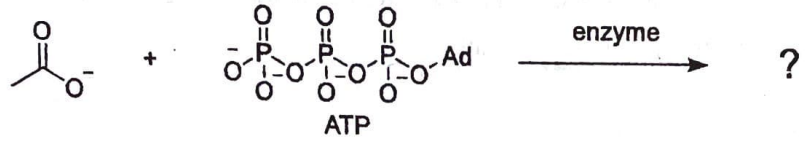
9. Complete each of following reactions by providing **major product** or reactant (5 point for each mark, 75 point)

(a)

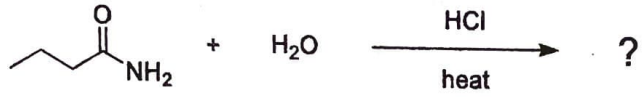
(b)



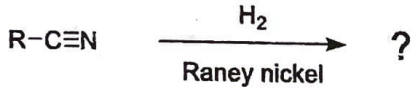
(c)



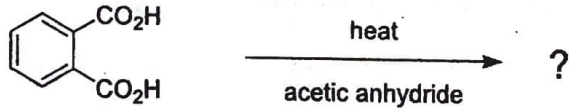
(d)



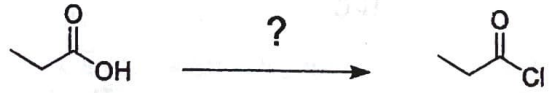
(e)



(f)

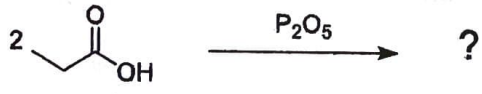


(g)

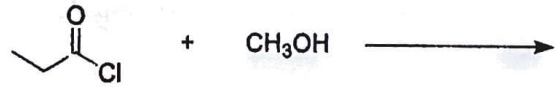


(h)

(i)

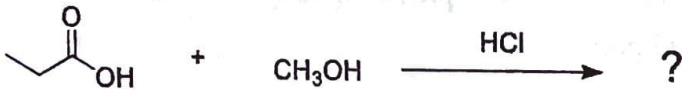


(j)

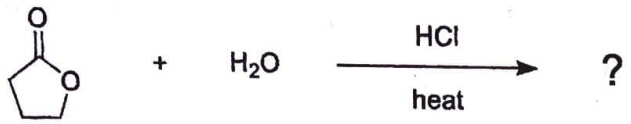


(k)

(l)

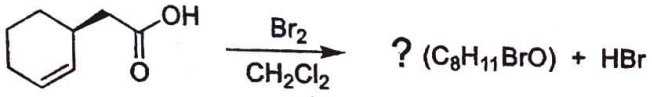


(m)

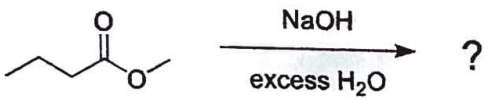


10. Propose and draw the intermediate and major product in the following reactions. Using curved arrow to **show the details of the mechanism** and indicate the flow of electrons. (15 point for each part, 90 point)

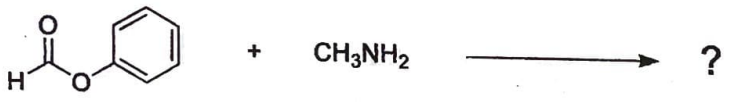
(a)



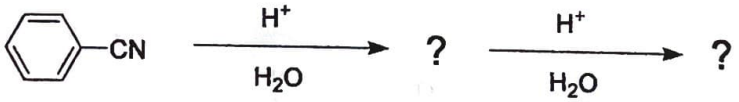
(b)



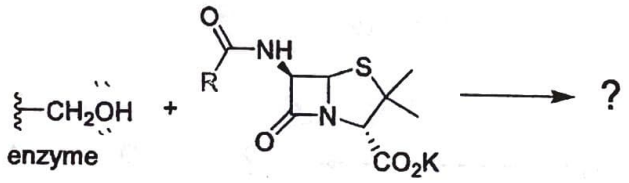
(c)



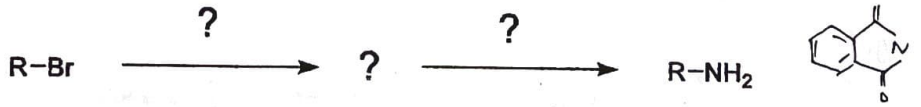
(d)



(e)

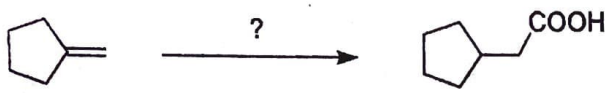


11. Show reagent(s) and intermediate for the Gabriel synthesis from alkyl halide to primary amine. (10 point)

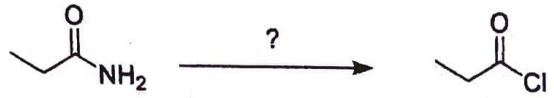


12. Design a multi-step synthesis to show how each compounds could be prepared from the given starting material. Show all **necessary reagent(s)** and also **intermediate.** (10 point for each, 30 point)

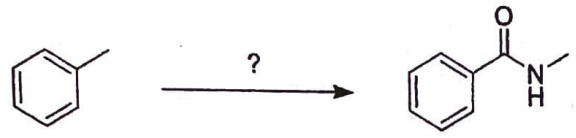
(a)



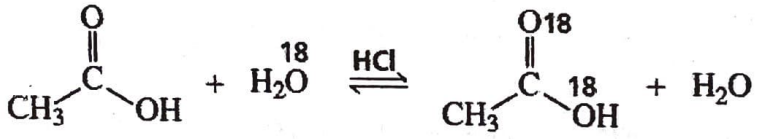
(b)



(c)

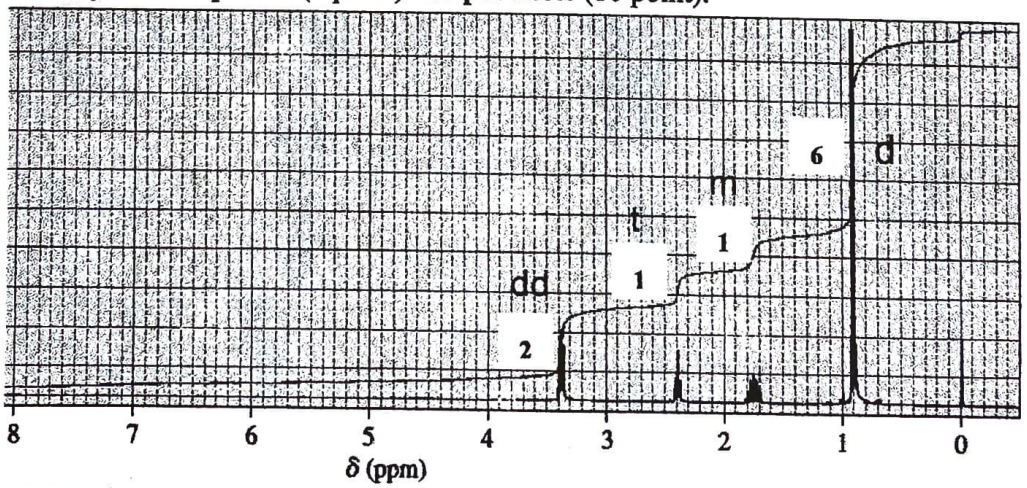


13. (a) When acetic acid is dissolved in isotopically labeled water ($H_2{}^{18}O$) and an acid catalyst is added, the label is incorporated into both oxygens of the acid. Propose a mechanism to account for this. (10 point)

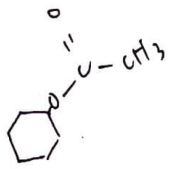


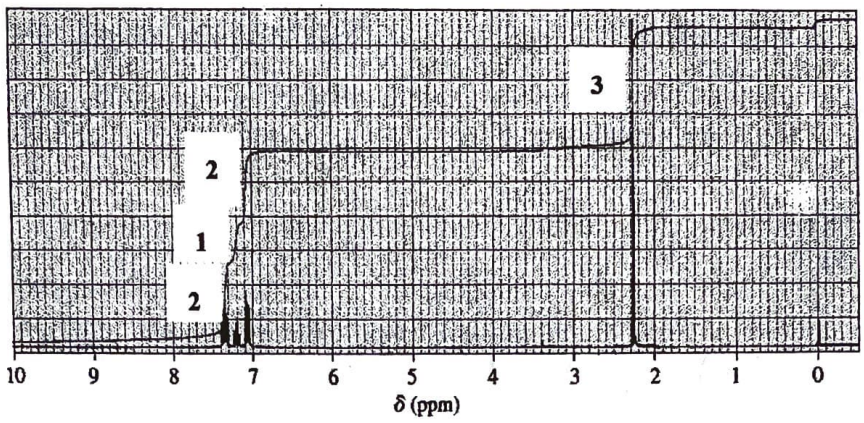
(b) If acetic acid is dissolved in isotopically labeled methanol ($CH_3{}^{18}OH$) and an acid catalyst is added, where will the label reside in the product? (5 point)

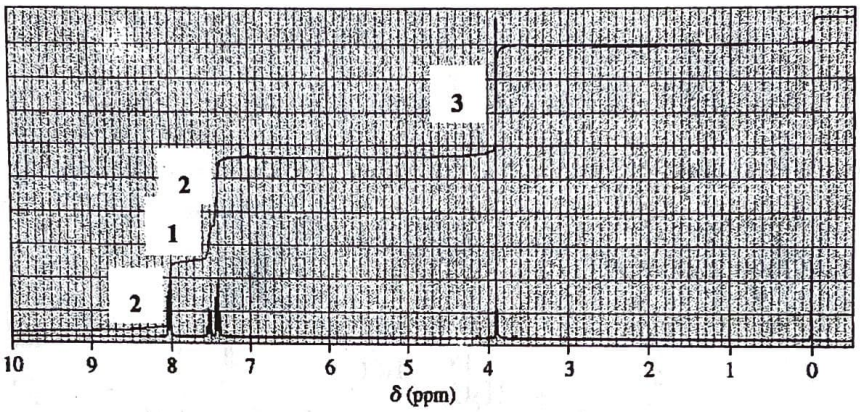
14. When a compound with molecular formula $C_{11}H_{14}O_2$ undergoes acid-catalyzed hydrolysis, one of the products that is isolated gives the following ^1H NMR spectrum. Identify the **compound** (5 point) and **products** (10 point).



15. The ^1H NMR spectra for two esters with molecular formula $C_8H_8O_2$ are shown below. (a) Determine their structures (5 point for each) (b) Which of the esters is hydrolyzed more rapidly in an aqueous solution with a pH of 10? (5 point)







16. A compound with molecular formula $C_5H_{10}O_2$ gives the following IR spectrum. When it undergoes acid-catalyzed hydrolysis, the compound with the ^1H NMR spectrum shown below is formed. **Identify the two compounds.** (5 point for each)