

Organic Chemistry (2nd semester)

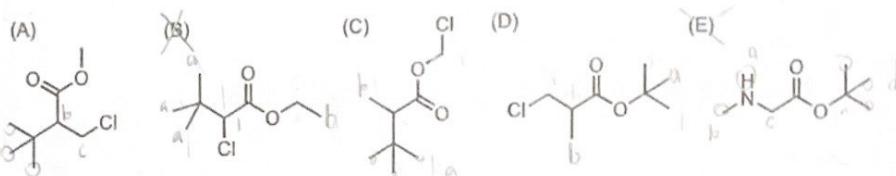
Second term examination (Friday, Mar. 14th, 2025, 8:00 ~ 10:00)

Name: 賴政奇; Student ID number: 112023019; Score: 145 / 336

A. Select suitable option of the following question (每題 5 分共 150 分) 143 / 150

A

1. The ratios of the chemically nonequivalent protons in an ester compound (m/z : 178 and 180 in 3:1 intensity ratio) with the integration curves measure 40.5, 27, 13, and 118 mm, from left to right across the spectrum. Which compound of the following structures whose ^1H NMR spectrum would show these correct integrals in the observed order with chemical shifts of 3.70, 3.59, 2.34, 0.99 ppm?



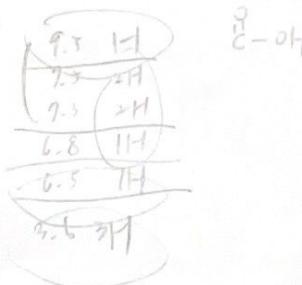
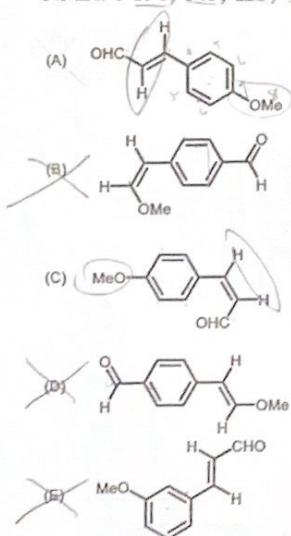
B

2. In an MO depiction of the carbonyl's reactivity with an amine nucleophile, the most important MO overlap occurs between the amine's lone pair and the carbonyl's _____.

- (A) $\pi_{\text{C}-\text{O}}$ (B) $\pi^*_{\text{C}=\text{O}}$ (C) $\sigma_{\text{C}-\text{O}}$ (D) $\sigma^*_{\text{C}-\text{O}}$ (E) l_{pO}

A

3. Select the chemical structure that best fits for compound $\text{C}_{10}\text{H}_{10}\text{O}_2$ with the following NMR data. ^1H NMR data: δ 9.5 (1H, d, $J = 7$ Hz), 7.5 (2H, d, $J = 6$ Hz), 7.3 (2H, d, $J = 6$ Hz), 6.8 (1H, dd, $J = 14, 7$ Hz), 6.5 (1H, d, $J = 14$ Hz), 3.6 (3H, s). ^{13}C NMR: δ 190, 145, 135, 130, 125, 120, 115, 60.

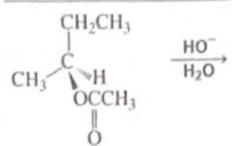


C1H1O1L

654418

E

4. What is a correct structure of the alcohol product for the following reaction?

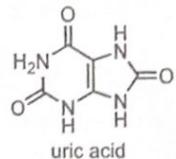


- (A) 1-butanol (B) (*R*)-2-butanol (C) (\pm)-2-butanol
(D) *tert*-butanol (E) (*S*)-2-butanol

X

5. Which structure of the following compounds is not a metabolized product of uric acid?

C

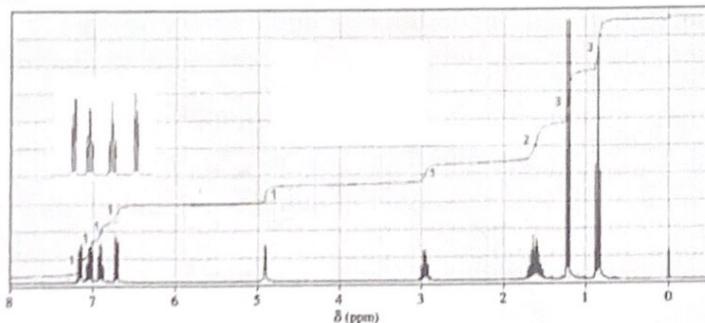


- (A)
(B)
(C)
(D)
(E)

E

6. Which structure of the following compounds shows the correct ^1H NMR spectrum below?

b.

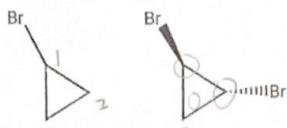


- (A)
(B)
(C)
(D)
(E)

A X

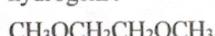
7. How many signals would you expect to see in the ^1H NMR spectrum of the

following compounds ? (The order of answers is bromocyclopropane first)



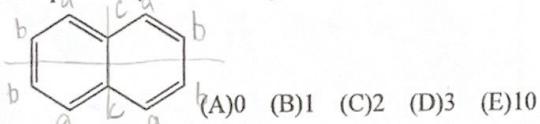
- (A) 3 and 2 (B) 2 and 3 (C) 3 and 4 (D) 3 and 3 (E) 4 and 2

A ~~D~~ 8. What splitting pattern is observed in the proton NMR spectrum for the indicated hydrogens?



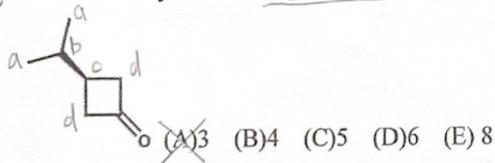
- (A) Singlet (B) Doublet (C) Triplet (D) Quartet (E) Septet

C ~~D~~ 9. How many signals will be observable in the DEPT ^{13}C NMR spectrum of the naphthalene (shown below)?



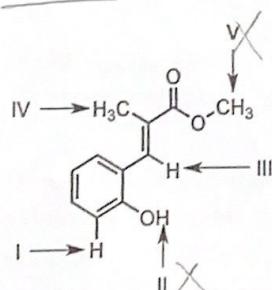
- (A) 0 (B) 1 (C) 2 (D) 3 (E) 10

C 10. How many ^1H NMR signals are expected for the following compound?



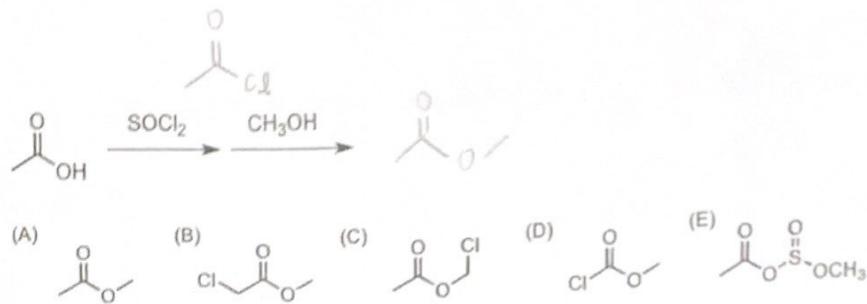
- (A) 3 (B) 4 (C) 5 (D) 6 (E) 8

D 11. Which of the following protons gives an NMR signal with the lowest chemical shift value?



- (A) I (B) II (C) III (D) IV (E) V

A 12. What is the major product obtained from the following sequence of reactions?



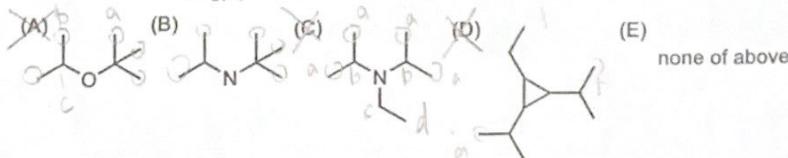
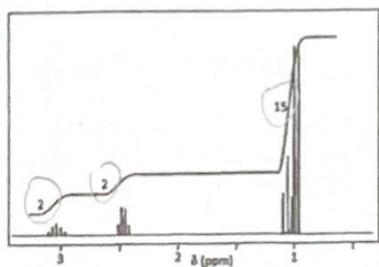
A

13. What type of NMR spectroscopy provides information about $^1\text{H}-^1\text{H}$ coupling?

(A) COSY (B) DEPT (C) HETCOR (D) INADEQUATE (E) NOSEY

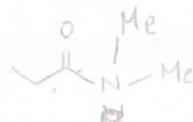
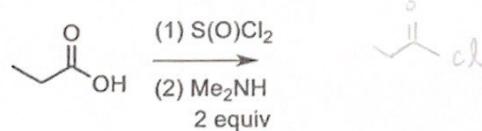
~~C~~

14. Which of the following compounds has the ^1H NMR spectrum shown below?



A

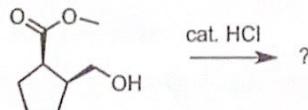
15. Give the product of the reaction.

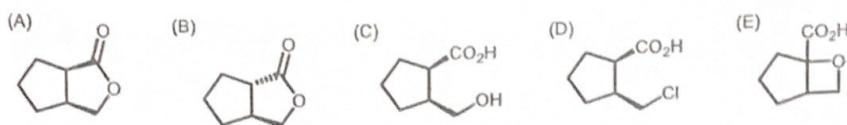


- (A) $\text{CH}_3\text{CH}_2\text{C(O)N(CH}_3)_2 + (\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$
 (B) $\text{CH}_3\text{CH}_2\text{C(O)O-S(O)NMe}_2 + \text{CH}_3\text{NH}_3^+\text{Cl}^-$
 (C) $\text{CH}_3\text{CH}_2\text{C(O)NH(CH}_2\text{Cl}) + \text{Me}_2\text{NH}_2^+\text{Cl}^-$
 (D) $\text{CH}_3\text{C(O)NH(CH}_3) + (\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$
 (E) $\text{CH}_3\text{CH}_2\text{C(O)N(CH}_3)_2 + [(\text{CH}_3)_2\text{N}]_2\text{S(O)}$

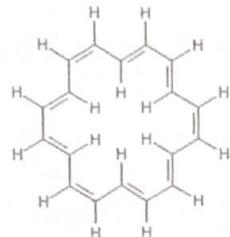
A

16. What product would you expect to obtain from the following reactions?





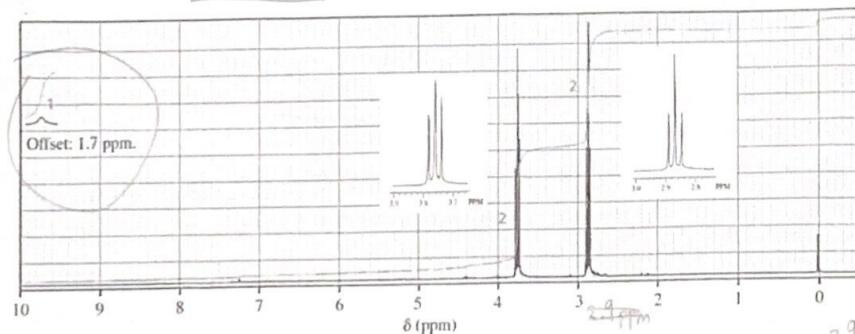
~~E~~ 17. Only two sets of ^1H NMR signals were observed for [18]-annulene. What are the expected chemical shifts?



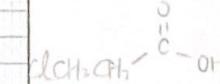
- (A) 7.88 and 6.54 (B) 5.25 and 4.25 (C) 7.60 and -7.60
~~(D)~~ 9.25 and 2.88 (E) 9.25 and -2.88

~~5.10 H~~

~~A~~ 18. The ^1H NMR spectra of an unknown carbonyl-containing compound with molecular formula $\text{C}_3\text{H}_5\text{O}_2\text{Cl}$ is shown below. Identify the structure of the compound.



- (A) $\text{ClCH}_2\text{CH}_2\text{C}(\text{O})\text{OH}$ (B) $\text{CH}_3\text{CH}(\text{Cl})\text{C}(\text{O})\text{OH}$ (C) $\text{HOCH}_2\text{CH}_2\text{C}(\text{O})\text{Cl}$
(D) $\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{O})\text{Cl}$ (E) $\text{HOCH}_2\text{C}(\text{O})\text{CH}_2\text{Cl}$

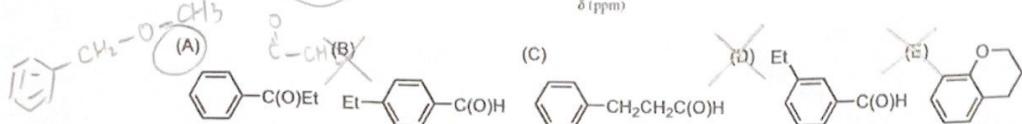
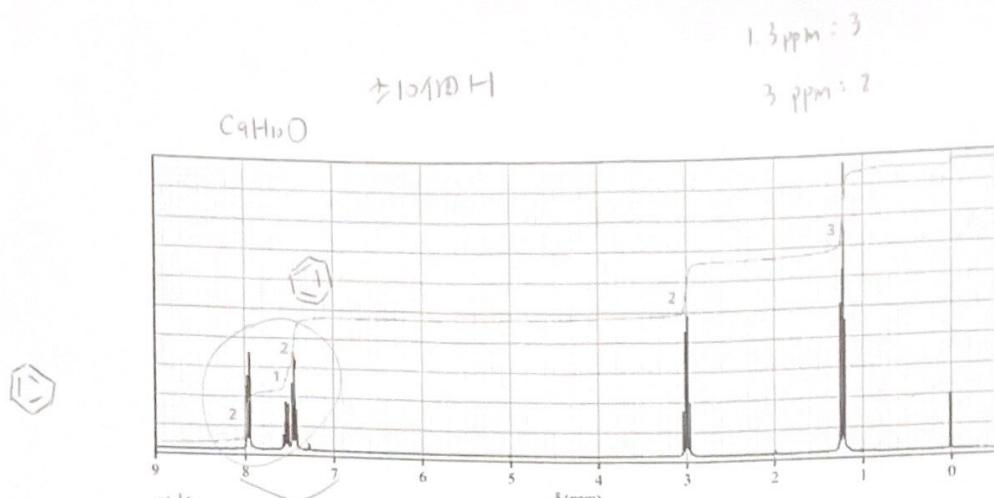


2.9 ppm: 2 triple
3.8 ppm: 2 triple

~~B~~ 19. If a chemical shift of an NMR signal is 7.2 ppm measured in a 300 MHz NMR spectrometer, how many Hz would this signal be from the TMS signal?
(A) 41.5 Hz (B) 2160 Hz (C) 2.4 Hz (D) 360 Hz (E) 300 Hz

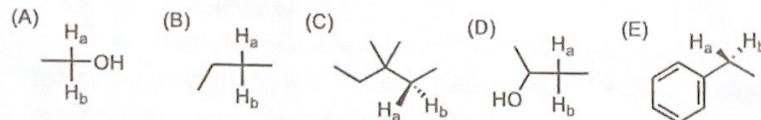
7.2×300

~~A~~ 20. Identify the compound with molecular formula $\text{C}_9\text{H}_{10}\text{O}$ that gives the ^1H NMR spectrum shown below.



ACE B D

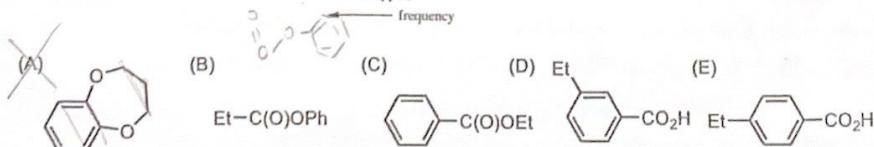
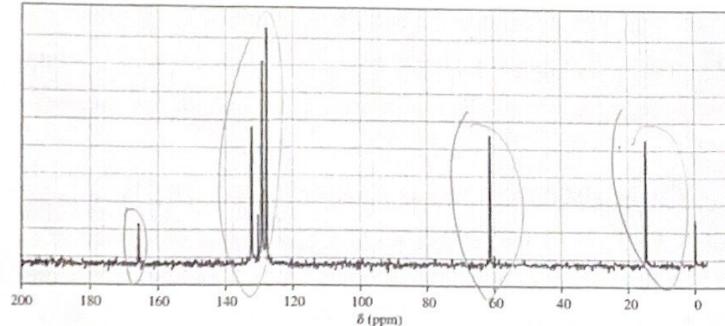
21. Which pairs of hydrogens (H_a and H_b) are enantiotopic hydrogens?



C D

22. Identify the compound with molecular formula $\boxed{\text{C}_9\text{H}_{10}\text{O}_2}$ that gives the following ^{13}C NMR spectrum.

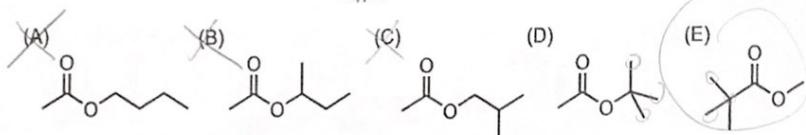
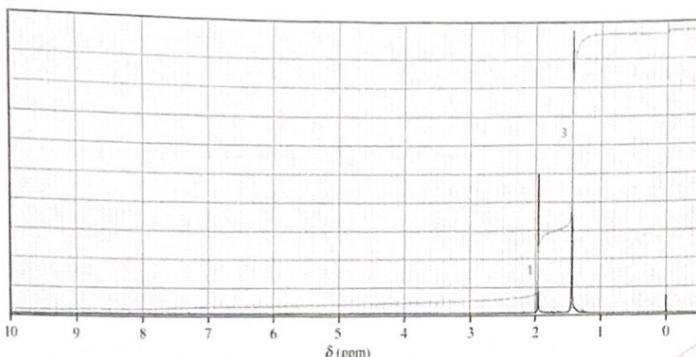
δ ppm: 200, 160, 140, 120, 100, 80, 60, 40, 20, 0



D X

23. The following ^1H NMR spectrum is for a compound sensitive to trifluoroacetic acid with molecular formula of $\text{C}_6\text{H}_{12}\text{O}_2$. Identify the compound structure.

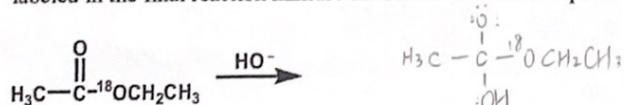
$C_6H_{12}O_2$
 $\text{CH}_3CH_2CO_2H$
 1.5 ppm 9H
 2 ppm 3H



C 24. Which of the following statements is not true about the reactions of carboxylic acid derivatives?

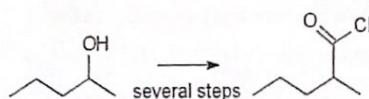
- (A) Carboxylic acid derivatives form a tetrahedral intermediate.
- (B) The weaker base will be the leaving group.
- (C) Less reactive derivatives can be converted directly into more reactive derivatives.
- (D) For a reaction to occur, the added group must be a stronger base than the group attached to the acyl group.
- (E) The weakest bond in the reaction is the pi bond, so it breaks first.

B 25. Upon aqueous hydrolysis of ^{18}O -labeled ethyl acetate, which oxygen(s) will be labeled in the final reaction mixture after mild acidic workup?

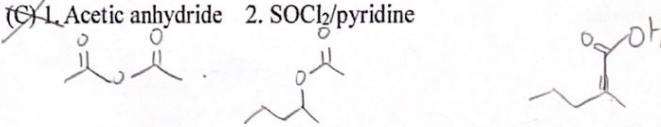


- (A)
- (B)
- (C)
- (D)
- (E) C and D

B 26. Which set of reagents will produce the indicated product?



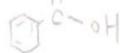
- (A) 1. H_2CrO_4 2. $\text{SOCl}_2/\text{pyridine}$ 3. H_2O
- (B) 1. $\text{TsCl}/\text{pyridine}$ 2. NaCN 3. $\text{H}_3\text{O}^+/\Delta$ 4. $\text{SOCl}_2/\text{pyridine}$
- (C) 1. Acetic anhydride 2. $\text{SOCl}_2/\text{pyridine}$



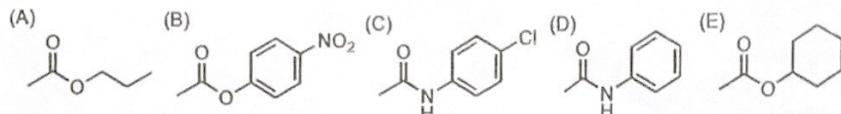
- (D) 1. Acetic acid/ H_3O^+ 2. PCl_3 /pyridine
 (E) 1. Ethyl acetate/ H_3O^+ 2. NaCl

$\text{pK}_{\text{a}} \uparrow$ means

- A 27. Which of the following dicarboxylic acids has the smallest pK_{a1} value?
 (A) HOOC(O)C(O)OH (B) $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$ (C) $\text{HO}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{H}$
 (D) $\text{HO}_2\text{C}(\text{CH}_2)_3\text{CO}_2\text{H}$ (E) phthalic acid

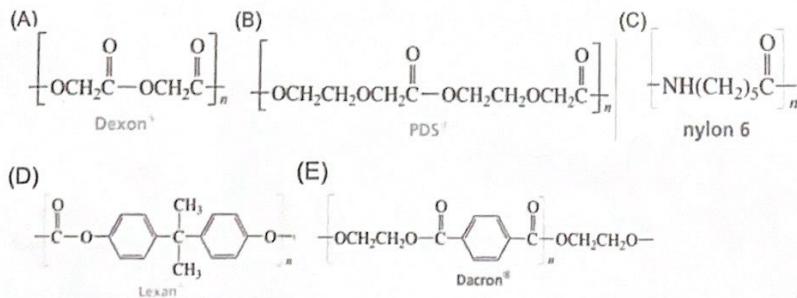


- B 28. Which of the following compounds show the fastest hydroxide-promoted hydrolysis?



- D 29. Which of the following sequence of reactions would not produce the desired primary 1-propanamine in satisfactory yield?
 (A) 1-bromopropane + NaN_3 then H_2 , Pd/C
 (B) bromoethane + NaCN then H_2 , Raney-Ni
 (C) (i) phthalimide/ NaH (ii) 1-bromopropane, (iii) $\text{H}_2\text{N-NH}_2$
 (D) 1-bromopropane + NH_3
 (E) (i) phthalimide/ OH^- (ii) 1-bromopropane, (iii) $\text{H}_3\text{O}^+/\text{heat}$, (iv) OH^- .

- A 30. Which of the following polymers will undergo the fastest enzymatic hydrolysis?



B. Provide suitable products or reagent for each of the following transformation

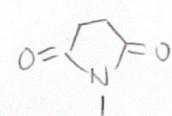
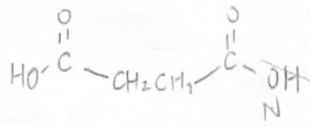
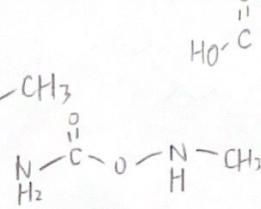
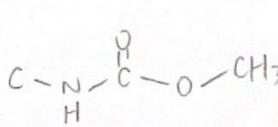
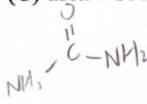
1. What products would you expect to obtain from the following reactions?

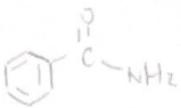
Just write the product (6 points for each question)

- (A) methyl carbamate + methylamine

- (B) succinic acid + acetic anhydride (provide the anhydride product)

- (C) urea + sodium cyanide





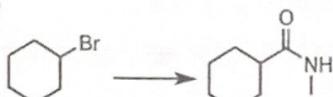
(E) Some credit card sales slips have a top sheet of "carbonless paper" that transfers an imprint of a signature to a sheet lying underneath (the customer receipt).

The paper contains tiny capsules filled with the following colorless compound. When you press on the paper, the capsules burst, and the colorless compound comes into contact with the acid-treated bottom sheet, forming a highly colored compound. What is the structure of the colored compound?

2. Propose an efficient synthesis for each of the following transformations

(10 points for each question)

(A)



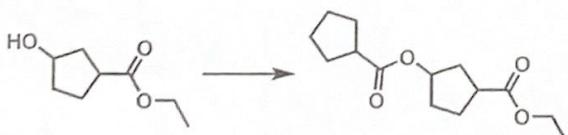
(B)



(C)

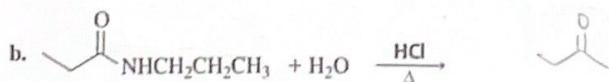
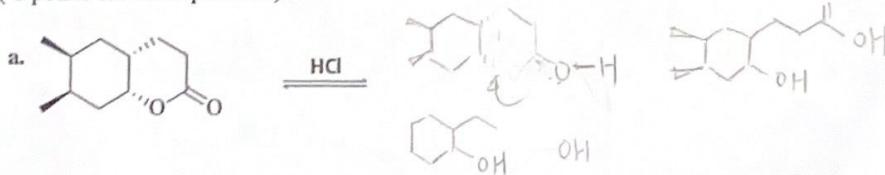


(D)



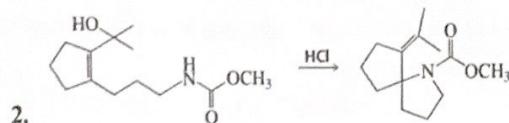
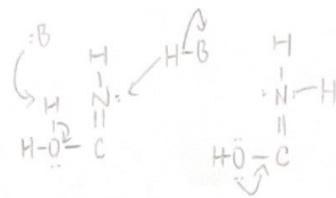
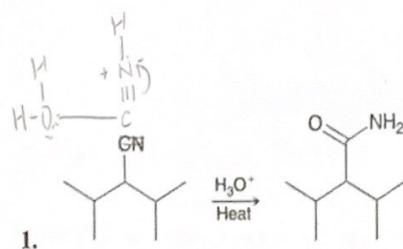
3. What compounds are obtained from the following hydrolysis reactions?

(8 points for each question)



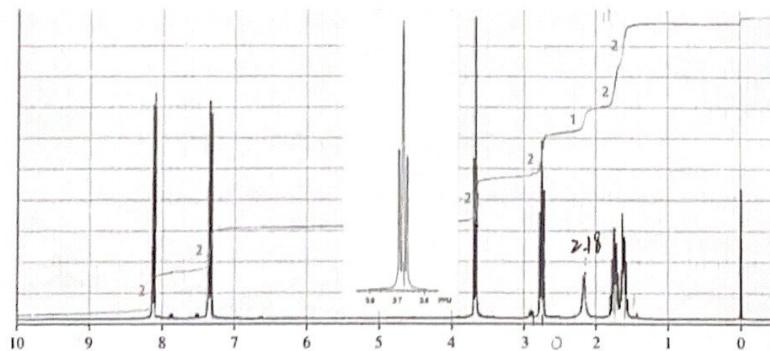
C. Propose a mechanism for each of the following transformation

(10 points for each question)

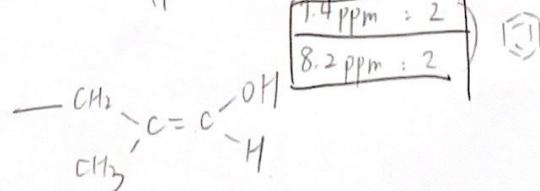
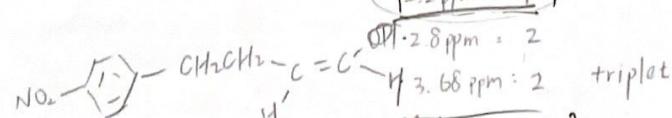
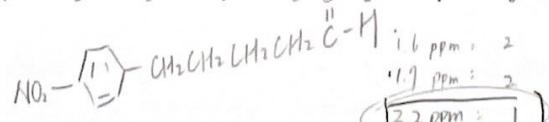


D. Please predict the structure from the spectra provided below and explain your reasons in detail. (10 points for structure and 10 points for reason)

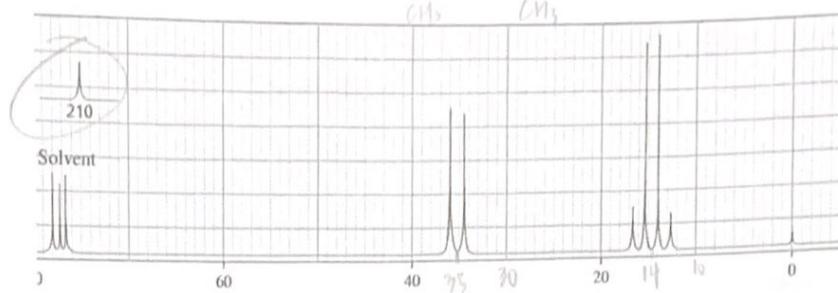
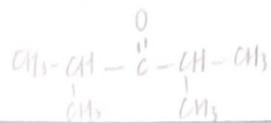
1. $C_{10}H_{13}NO_3$ (hint: addition of D_2O led to the disappearance of the proton signal at 2.18 ppm)



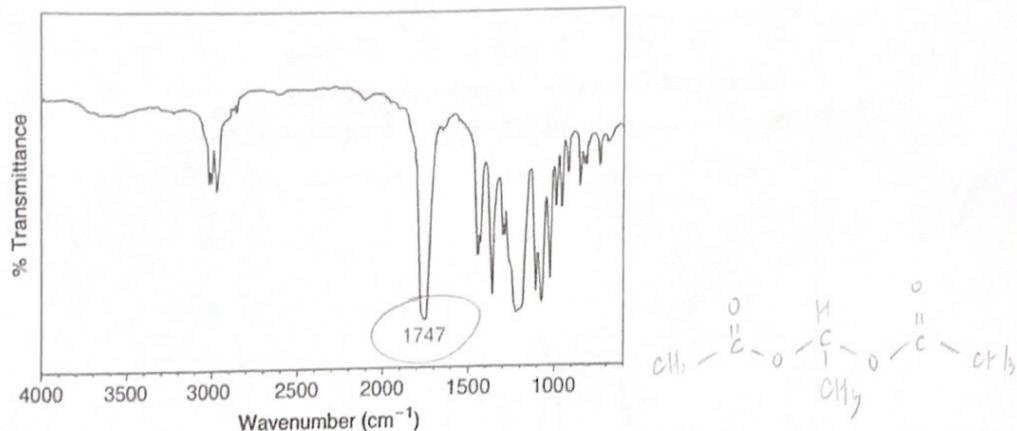
2. $C_7H_{14}O$



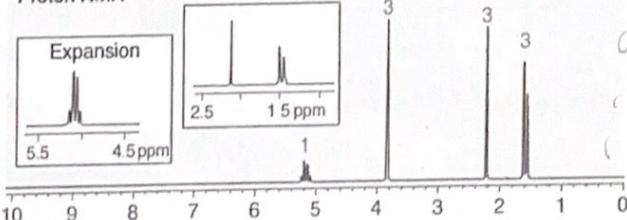
$C_7H_{14}O$



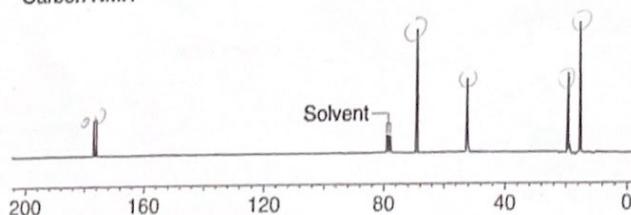
3. $C_6H_{10}O_4$



Proton NMR



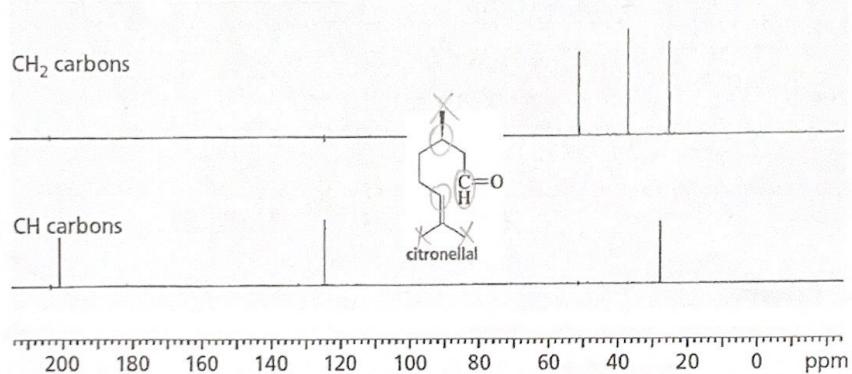
Carbon NMR



E. Answer according to the question(10 points for each question)

- Assign the three CH_2 carbons and three CH carbons in the following DEPT

spectra for citronellal



2. The ^1H NMR spectrum of 2-propen-1-ol is shown here. Indicate the protons in the molecule that are responsible for each of the signals in the spectrum.

