

Organic Chemistry (2nd semester)

First term examination (Tuesday, Mar. 30st, 2021, 8:00 ~ 9:50)

Name: 申基泰 ; Student ID number: 168123456 ; Score: _____ /320

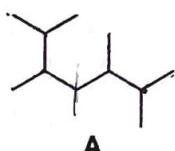
1. Which proton will show the signal < 0 ppm in ^1H NMR? (5 point)

- C (A) R-C-H (B) R-S-H (C) R-Al-H (D) R-COOH (E) R-O-OH

2. For compound A, after underwent a radical reaction, how many kinds of monochlorination

C product would form? (5 point)

- (A) 3 (B) 4 (C) 5 (D) 8 (E) 10



3. Which statement is true for "a proton is upfield"? (5 point)

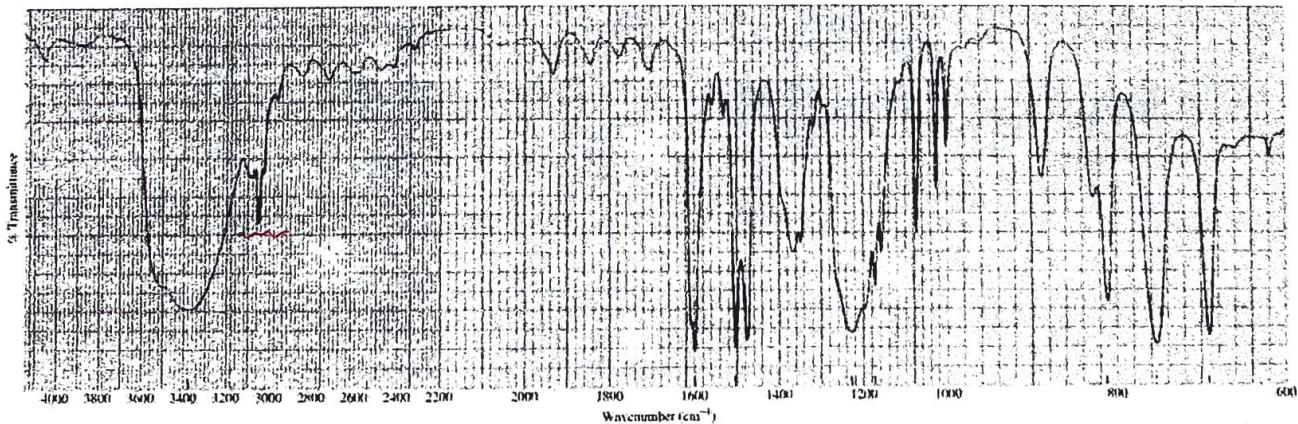
- E (A) it has more splitting
(B) it has less splitting
(C) it connects to high electronegative atom
(D) its peak shown at high frequency
(E) its peak shown at low frequency

4. Which of following compound is least apt to form a peroxide? (5 point)

- D (A) (B) (C) (D) (E) tert-butyl methyl ether

5. Which compound produced the IR spectrum shown below? (5 point)

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



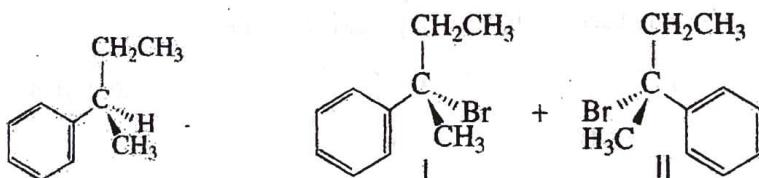
6. Which of the following is the most stable radical? (5 point)

- E I. $\text{CH}_2=\dot{\text{C}}\text{H}$ IV. $\text{CH}_3\dot{\text{C}}\text{H}_2$
II. $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{H}_3$ V. $\text{CH}_3\dot{\text{C}}\text{H}-\text{C}_6\text{H}_5$ (A) I (B) II (C) III (D) IV (E) V
III. $\text{CH}_3\dot{\text{C}}\text{HCH}_3$

7. Regarding the use of Hammond Postulate to explain why free radical brominations are more selective than free radical chlorinations, which of the following statement is not correct? (5 point)

- (A) The first propagation step in free radical bromination is endothermic.
(B) The first propagation step in free radical chlorination is exothermic.
(C) The transition state for the bromination is product-like (ie, radical-like).
(D) The transition state for the chlorination is product-like (ie, radical-like).
(E) The stability of the intermediate radical in the bromination determines the bromination selectivity.

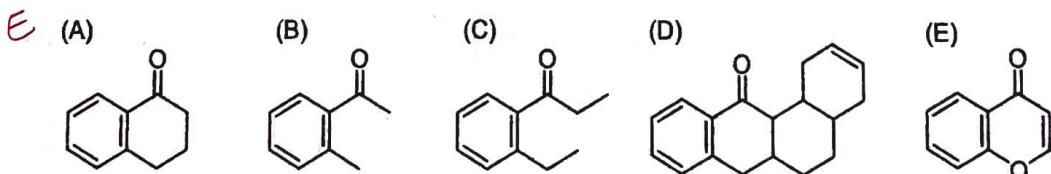
B 8. A sample of (*R*)-2-phenylbutane, reacts with Br_2 in the presence of light, and all the products having the formula $\text{C}_9\text{H}_{13}\text{Br}$ were isolated. Two possible isomers are shown below:



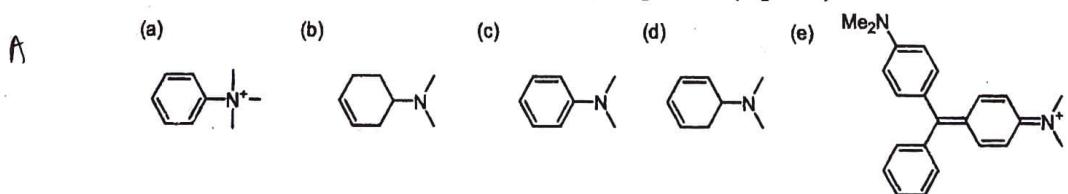
Of these: (5 point)

- (A) only I was formed. (B) both I and II were formed in equal amounts.
(C) neither I nor II was formed. (D) only II was formed.
(E) both I and II were formed in unequal amounts.

9. Which of the following compounds does not possess the same chromophore? (5 point)



10. Rank a set of compounds in order of decreasing λ_{max} : (5 point)

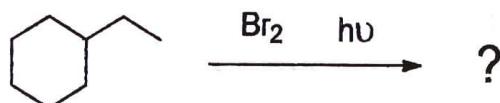


- (A) e > c > a > d > b (B) c > e > a > d > b (C) e > d > a > c > b (D) a > e > c > d > b
(E) b > e > a > d > b

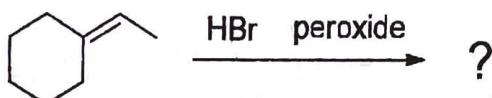
D

11. Complete each of following reactions by providing major product.

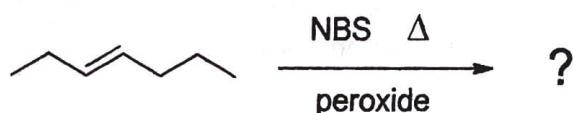
(a) (5 point)



(b) (5 point)

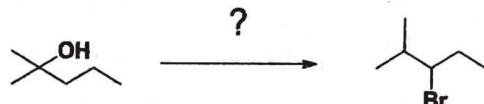


(c) provide all product include stereoisomer (12 point)

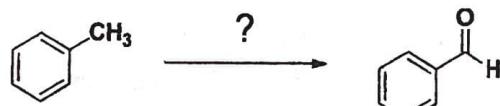


12. Design a multi-step synthesis to show how each compounds could be prepared from the given starting material. Show all necessary reagent(s) and also intermediate.

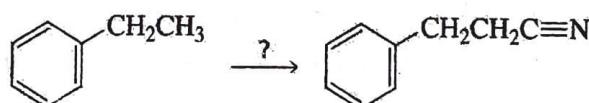
(a) (10 point)



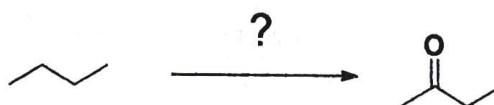
(b) (10 point)



(c) (10 point)



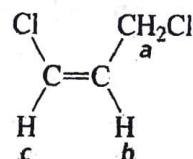
(d) (10 point)

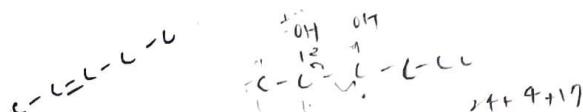


13. Which compound would be the reference in ^1H NMR (that is, show a peak at 0 ppm)?

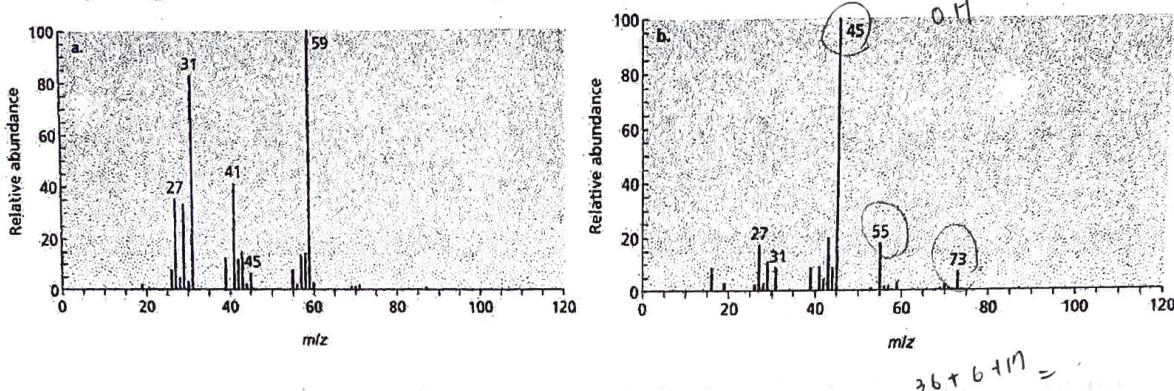
Please provide its name and structure. (5 point)

14. Draw a splitting diagram for the H_b proton if $J_{bc} = 10$ and $J_{ba} = 5$, then show the integral ratio of each peak. (10 point)

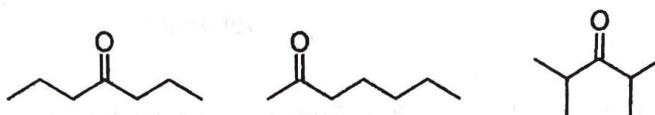




15. The reaction of (*Z*)-2-pentene with water and a trace of H_2SO_4 forms two products. Identify the products from their mass spectra. (9 point)



16. Draw the mechanism for formation of the fragments you would expect to see in the mass spectrum of each of the following compounds: (18 point)



17. If a compound shows a signal at 4.0 ppm in 300 MHz ^1H NMR spectrum, where does this signal appear in 500 MHz ^1H NMR spectrum? In 500 MHz ^1H NMR spectrum, what is frequency difference compare to the signal at 0.0 ppm? (5 point each)

18. Predict the relative intensities of the molecular ion peak (M^+), $\text{M}+2$ peak, $\text{M}+4$ peak, and $\text{M}+6$ peak in mass spectrum for a compound which contain 3 chlorine atoms. (8 point)

19. The following compound will undergo a chlorine radical reaction. Please predict all the monochlorination product(s) and the ratio of each product. (9 point each)

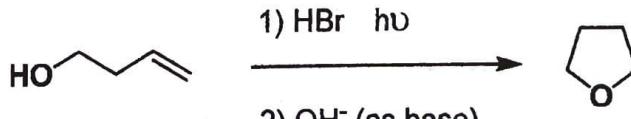
(a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (b) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$ 4b:4

Primary	Secondary	Tertiary
1.0	3.8	5.0

▲relative rates of alkyl radical formation by a chlorine radical

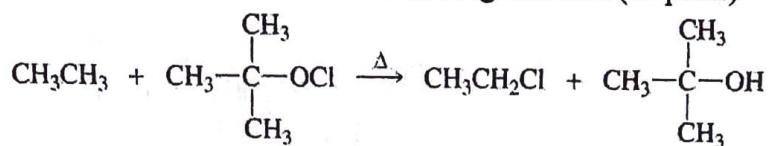
20. Provide all structures of isomers for the compound "dichlorocyclopropane", then predict the sets of signal(s) would be shown in ^1H NMR spectrum. (15 point)

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



22.

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

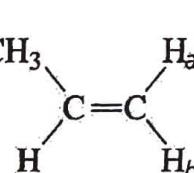
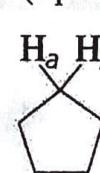
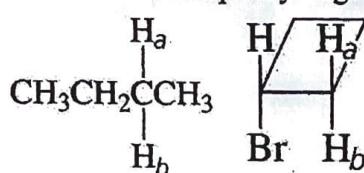
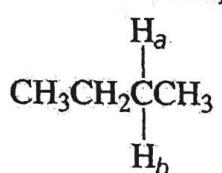


(b) Predict the byproducts (副產物) and describe how they are formed. (as much as possible, assume that once product form, it will not react with a radical second time) (10 point)

23. For the following compounds,

(a) which pair of hydrogens (H_a and H_b) are enantiotopic hydrogens? (5 point)

(b) Which pairs are diastereotopic hydrogens? (5 point)



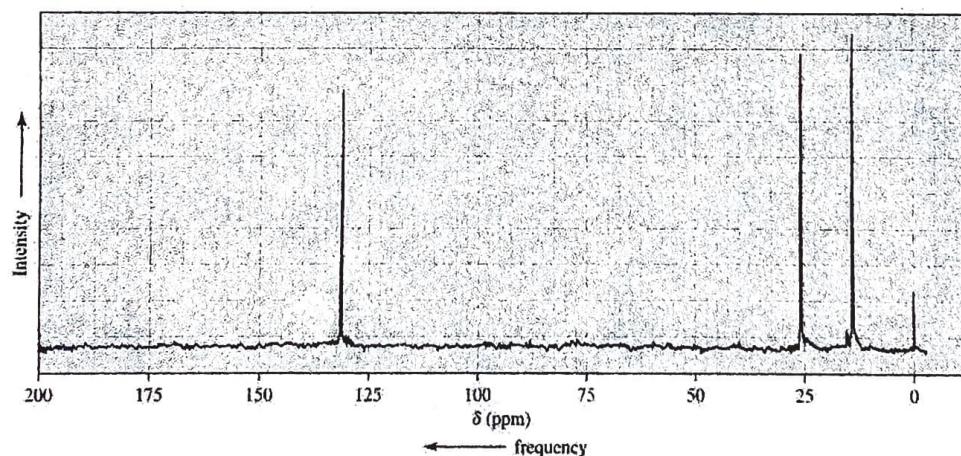
A

B

C

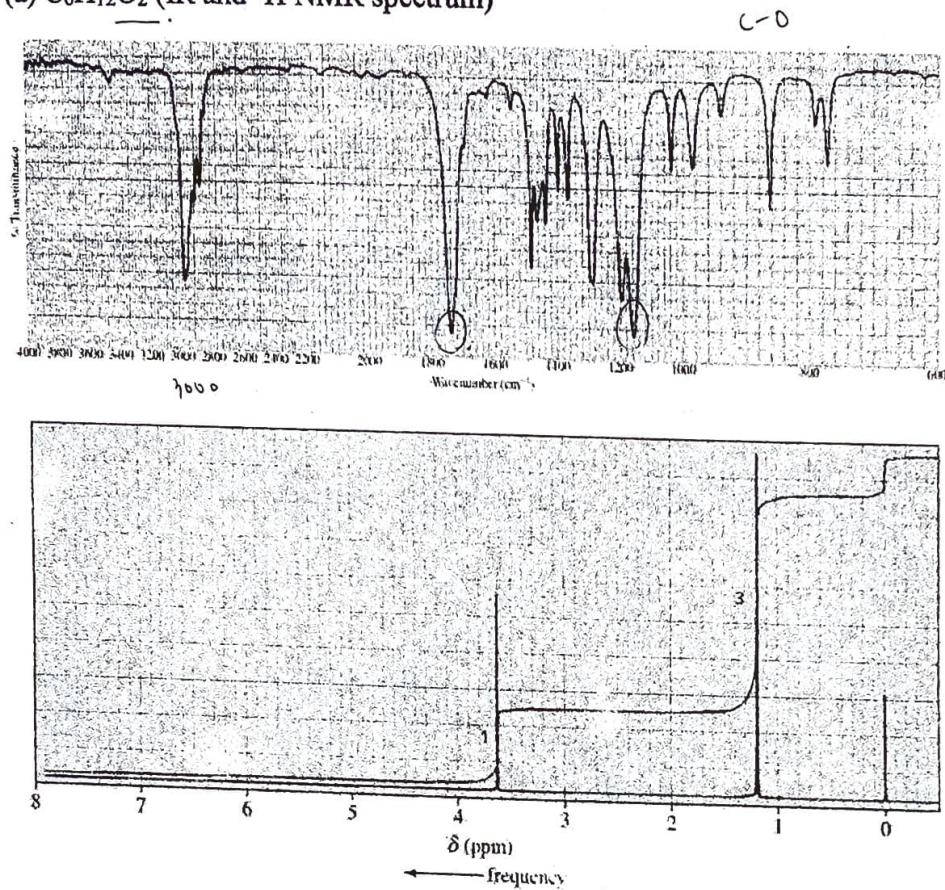
D

24. Identify the following compound from its molecular formula (C_6H_{12}) and its ^{13}C NMR spectrum. (10 point)

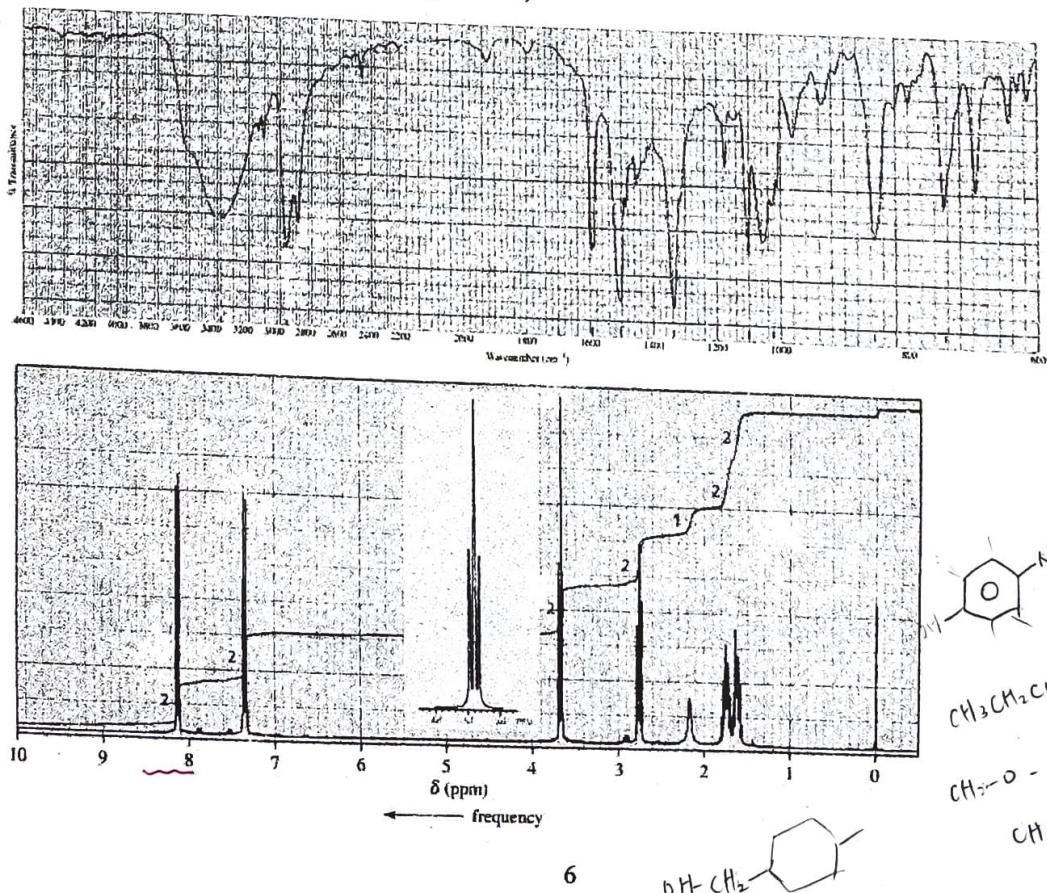


25. Please identify each compound by the following spectrum. (10 point each)

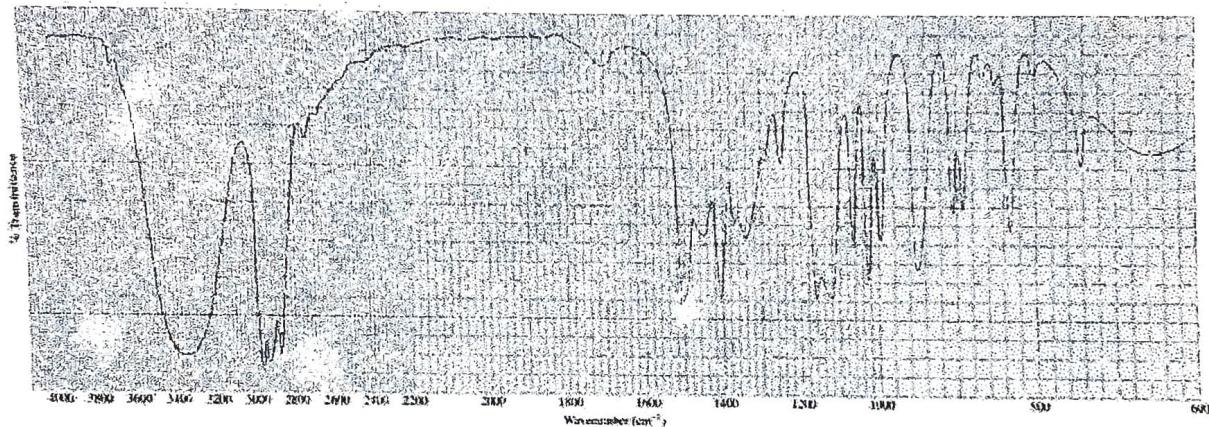
(a) C₆H₁₂O₂ (IR and ¹H NMR spectrum)



(b) C₁₀H₁₃NO₃ (IR and ¹H NMR spectrum)



26. The IR spectrum of compound A with a molecular formula of $C_5H_{12}O$ is shown below. Compound A is oxidized to give compound B, a ketone with a molecular formula of $C_5H_{10}O$. When compound A is heated with H_2SO_4 , compounds C and D are obtained. Much more D is obtained than C. Reaction of compound C with O_3 , followed by treatment with dimethyl sulfide, gives two products: formaldehyde and compound E, with a molecular formula of C_4H_8O . Reaction of compound D with O_3 , followed by treatment with dimethyl sulfide, gives two products: compound F, with a molecular formula of C_3H_6O , and compound G, with a molecular formula of C_2H_4O . What are the structures of compounds A through G? (hint: if alkene is treated with ozone followed by DMS, two carbonyl products will obtain) (35 point)



c - c - c - c - c