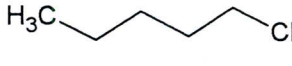
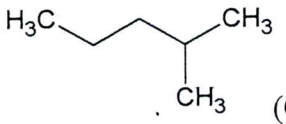
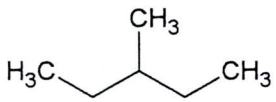
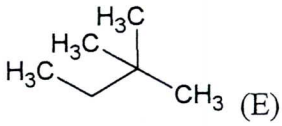
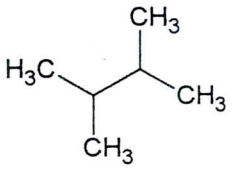
國　立　清　華　大　學　命　題　紙

99 學年度生命科學院乙組及醫學生物科技學程碩士班入學考試

科目 有機化學 科目代碼 0302、0506 共 5 頁第 1 頁 *請在【答案卷】內作答

PART I. 選擇題 (共十題 1-10，每題 2%)

1. Which of the following compounds has the lowest boiling point? (A)  (B)  (C)  (D)  (E) 

2. Which of the following properties is different for the dextrorotatory and levorotatory forms of sec-butyl alcohol? (A) boiling point (B) NMR spectrum (C) adsorption on alumina (D) refractive index (E) none of above.

3. Which of the following alcohols has the highest reactivity toward gaseous HBr? (A) 3-pentanol (B) 2-fluoro-3-pentanol (C) 2,2-difluoro-3-pentanol (D) 1-fluoro-3-pentanol (E) all alcohols have the same activity.

4. Which of the following compounds does not show geometric (*cis-trans*) isomerism? (A) 2-butene (B) 1,2-dichloroethene (C) 4-ethyl-3-methyl-3-hexene (D) 2-pentene (E) 2,4-hexadiene

5. Which of the following is wrong about the reactivity of alkenes toward addition of H_2SO_4? (A) propylene > ethylene (B) propylene > 2-butene (C) ethylene > vinyl bromide (D) isobutylene > 2-butene (E) vinyl chloride > 1,2-dichloroethene

6. What compound in the following has the highest reactivity toward S_N1 substitution? (A) sec-butyl tosylate (B) sec-butyl triflate (C) sec-butyl chloride (D) sec-butyl bromide (E) all are the same

7. Which statement is wrong? (A) IR absorption is due to molecular vibration (B) NMR signal is due to the radioactivity of nucleus under the influence of external magnetic field (C) The UV/Visible absorption for organic compounds involves the electronic transition in the π orbitals (D) Mass spectrometry resolves particles according to the charge/mass ratio (E) The bending frequency is often smaller than the stretching frequency of a molecular bond.

8. Which of the following compounds is aromatic? (A) C_9H_{10} (B) $C_9H_9^+$ (C) $C_9H_9^-$ (D) $C_5H_5^+$ (E) C_5H_5

9. Which of the following compounds is most reactive toward ring nitration? (A) benzene (B) bromobenzene (C) nitrobenzene (D) toluene (E) all are the same

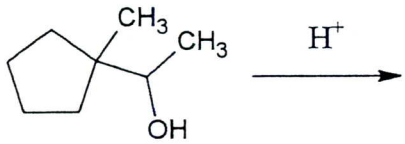
10. Upon addition of Br_2 to 1-phenyl-1,3-butadiene, what is the number of all possible products? (A) 2 (B) 3 (C) 4 (D) 5 (E) 6

PART II. 簡答填充題 (共十題 11-20，每題 3%)

11. Give the structure of the most stable isomer of 1,2,3,4,5,6-hexachlorocyclohexanes, and show its preferred conformation.

What are the final products of the following reactions?

12.

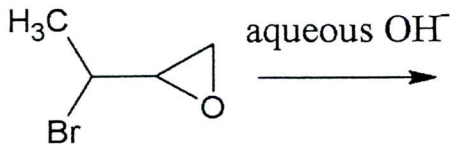


13. cis-1,2-diphenylethene + O_3, then H_2O/Zn ⟶

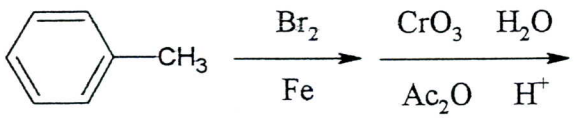
14. *p*-chlorotoluene + hot $KMnO_4$ ⟶

15. $C_6H_5OC_2H_5 + HNO_3, H_2SO_4$ ⟶

16.

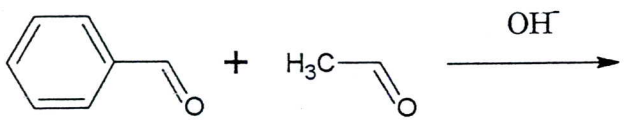


17.



18. n-butyryl chloride + C_6H_5MgBr ⟶

19.



20. methyl formate + aniline ⟶

PART III. 問答題 (21-25)

21. (**5%**) The structure of the terpene α-terpineol found in oils of cardamom and marjoram was proved in part by the following synthesis:

p-toluic acid + fuming sulfuric acid ⟶ MM ($C_8H_8O_5S$)

MM + KOH ⟶ NN ($C_8H_8O_3$)

NN + Na, alcohol ⟶ OO ($C_8H_{14}O_3$)

OO + HBr ⟶ PP ($C_8H_{13}O_2Br$)

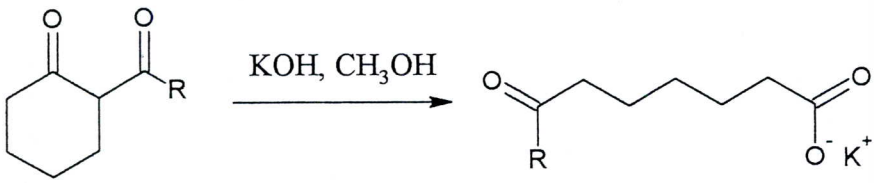
PP + base, heat ⟶ QQ ($C_8H_{12}O_2$)

QQ + C_2H_5OH, HCl ⟶ RR ($C_{10}H_{16}O_2$)

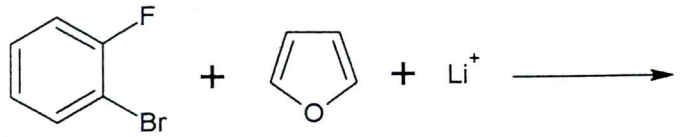
RR + CH_3MgI, then H_2O ⟶ α-terpineol ($C_{10}H_{18}O$)

What is the most likely structure for α-terpineol? (partial credits will be given for answering the structures of the intermediates)

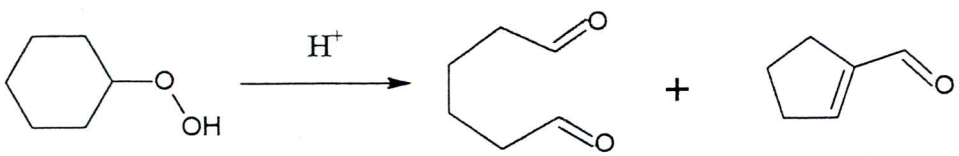
22. (**5%**) Suggest a mechanism for the alkaline cleavage of β-diketones, as, for example:



23. (**5%**) Account for the following reaction and write down the product.



24. (**10%**) Show all steps in the mechanisms probably involved in the following transformation.

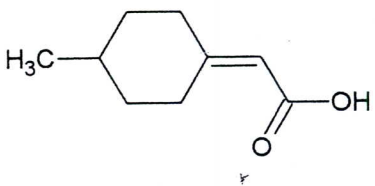


25. (**5%**) The following compounds can be resolved into optically active enantiomers.

(a)

3,3'-diaminospiro[3.3]heptane

(b)

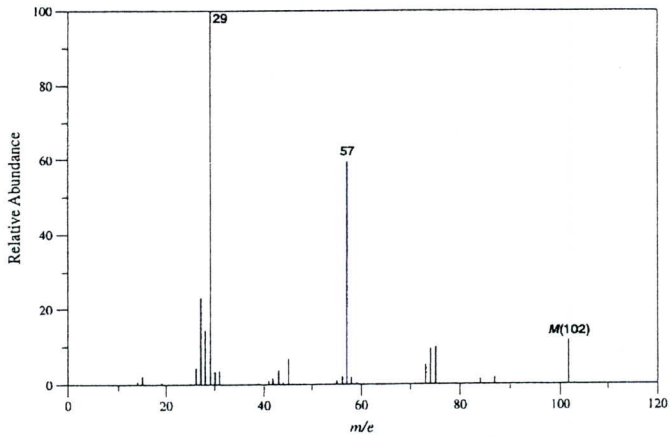


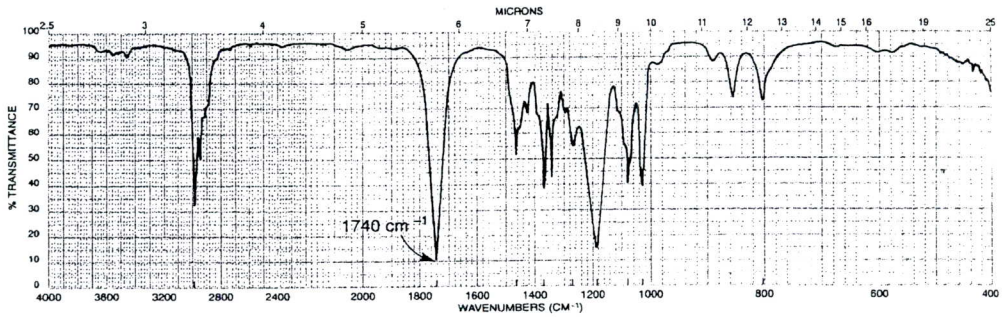
4-methylcyclohexylideneacetic acid

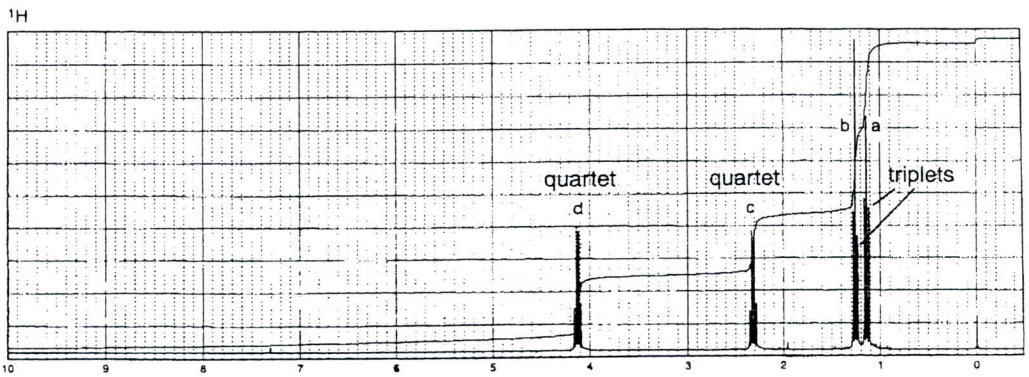
Using models and the drawing three-dimensional formulas, account for this. Label the chiral center in each compound.

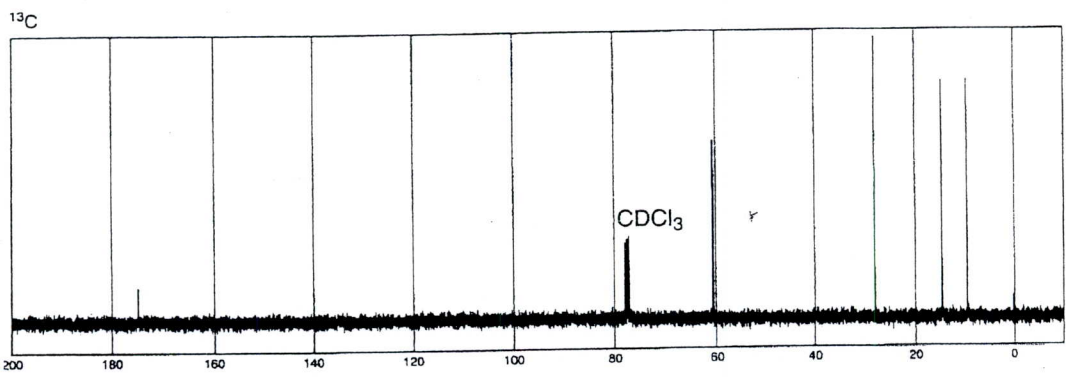
PART IV. 有機光譜分析 (26-27)

26. (**10%**) The UV, MASS, IR, and NMR spectra for a totally unknown compound were obtained. Figure out the chemical structure of the compound.









27. (**10%**) The unknown compound has the molecular formula $C_{10}H_9NO_2$ with following spectra. Determine its chemical structure.