

注意：本試題包含單選題及問答題兩部份

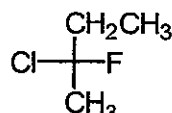
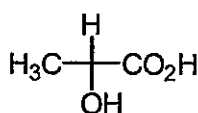
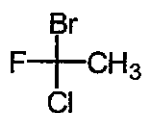
Part I. 單選題 (30 題, 2 分/題, 共 60 分)

※ 本大題請於試卷內之「選擇題作答區」依序作答。

1. Chain-growth polymerization proceeds by which of the following mechanisms?

- (A) radical polymerization      (B) cationic polymerization      (C) anionic polymerization  
(D) A and B      (E) A, B, and C

2. Identify the following compounds as *R* or *S*.



- (A) *S, S, R*      (B) *S, R, S*      (C) *R, S, S*      (D) *S, S, S*      (E) *R, R, R*

3. What is the carbon nucleophile which attacks molecular bromine in the acid-catalyzed  $\alpha$ -bromination of a ketone?

- (A) an enolate      (B) a Grignard reagent      (C) an acetylide  
(D) a carbocation      (E) an enol

4. In nucleophilic acyl substitution

- (A) protonation of the carbonyl is followed immediately by loss of the leaving group.  
(B) loss of the leaving group is followed by rearrangement of the carbocation.  
(C) addition to the carbonyl by a nucleophile is followed by loss of the leaving group.  
(D) ester hydrolysis is followed by deprotonation.  
(E) an  $S_N2$  reaction occurs.

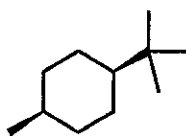
5. Dicyclohexylcarbodiimide (DCC) is used

- (A) to determine the *N*-terminal amino acid of a peptide.  
(B) to sequence amino acids in a peptide.  
(C) to detect amino acids derived from hydrolysis of a peptide.  
(D) to couple amino acids during solid-phase peptide synthesis.  
(E) to hydrolyze peptides on the carboxyl side of aromatic amino acid residues.

6. What type of intermediate is present in the  $S_N2$  reaction of cyanide with bromoethane?

- (A) carbocation      (B) free radical      (C) carbene  
(D) carbanion      (E) This reaction has no intermediate.

7. Predict the specific rotation of the compound shown.



- (A) It is impossible to predict; it must be determined experimentally.  
(B) Because both asymmetric centers are *R*, the compound is dextrorotatory.  
(C) Because both asymmetric centers are *S*, the compound is dextrorotatory.  
(D) Zero; the compound is achiral.  
(E) Because this compound represents a racemic mixture, the compound is dextrorotatory.

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8. Which molecule below has a significant band in the  $1720-1780\text{ cm}^{-1}$  range of its IR spectrum?  
(A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (B)  $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$  (C)  $\text{CH}_3\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_3$   
(D)  $(\text{CH}_3)_3\text{N}$  (E)  $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$
9. Which of the compounds below undergoes solvolysis in aqueous ethanol most rapidly?  
(A) 3-iodo-3-methylpentane (B) methyl iodide (C) isopropyl chloride  
(D) 3-chloropentane (E) cyclohexyl bromide
10. Which of the following statements best describes what **vulcanization** means?  
(A) a process by which rigid and non-sticky rubber can be made soft and sticky.  
(B) the heating of rubber with sulfur.  
(C) a chemical process discovered by Charles Schultz in 1944.  
(D) a chemical process that destroys cross-linking in rubber.  
(E) a chain transfer reaction.
11. How many distinct monochlorinated products, **including all stereoisomers**, can result when methylcyclobutane is heated in the presence of  $\text{Cl}_2$ ?  
(A) 2 (B) 6 (C) 5 (D) 4 (E) 3
12. What is the major organic product obtained from the following reaction?
- The reaction shows 2-methyloxirane (propylene oxide) reacting with ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) in the presence of an acid catalyst ( $\text{H}^+$ ). The products are shown in a box:

  - I:  $\text{H}_3\text{C}-\text{C}(\text{CH}_3)(\text{OH})-\text{CH}_2\text{OCH}_2\text{CH}_3$
  - II:  $\text{H}_3\text{C}-\text{C}(\text{CH}_3)(\text{OH})-\text{CH}_2\text{OH}$
  - III:  $\text{H}_3\text{C}-\text{C}(\text{CH}_3)(\text{OH})-\text{COCH}_2\text{CH}_3$
  - IV:  $\text{H}_3\text{C}-\text{C}(\text{CH}_3)(\text{OCH}_2\text{CH}_3)-\text{CH}_2\text{COCH}_3$
  - V:  $\text{H}_3\text{C}-\text{C}(\text{OH})(\text{CH}_3)-\text{CH}_2\text{OCH}_2\text{CH}_3$
- (A) I (B) II (C) III (D) IV (E) V
13. When  $\text{CH}_3\text{CH}_2\text{CHO}$  reacts with  $\text{PhNHNH}_2$  under conditions of acid catalysis, the major organic product is \_\_\_\_\_.  
(A) a nitrile (B) an imine (C) a hydrazone  
(D) an oxime (E) a ketone
14. What compound results from the 1,4-addition of one equivalent of  $\text{HBr}$  to 1,3-butadiene?  
(A) 1-bromo-1-butene (B) 1-bromo-2-butene (C) 4-bromo-1-butene  
(D) 3-bromo-1-butene (E) 2-bromo-2-butene
15. Which of the following is aromatic?  
(A) cycloheptatrienyl cation (B) 1,3,5-hexatriene (C) cyclobutenyl anion  
(D) 1,3-cyclohexadiene (E) cyclopentadienyl cation
16. How many hydrogens in the structure of 2,3-dimethylcyclopentanone are replaced by deuteriums when it is shaken in  $\text{D}_2\text{O}$  containing trace hydroxide?  
(A) 1 (B) 2 (C) 3 (D) 6 (E) 7

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17. Consider molecules with the formula  $C_{10}H_{14}Br_2O_2$ . Which of the following structural features is possible within this set of molecules?

- (A) 3 triple bonds (B) 2 rings and 1 double bond (C) 2 rings and 1 triple bond  
(D) 4 double bonds (E) 3 rings and 2 double bonds

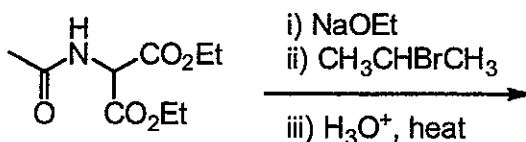
18. Predict the two most likely mechanisms for the reaction of 2-iodohexane with sodium ethoxide.

- (A)  $S_N2$  and  $S_N1$  (B) E1 and E2 (C)  $S_N2$  and E2  
(D) E1 and  $S_N1$  (E) E2 and  $S_N1$

19. When 1,3-butadiene reacts with  $CH_2=CHCN$ , which of the terms below best describes the product mixture?

- (A) a mixture of two diastereomers (B) a single compound  
(C) a racemic mixture (D) optically active  
(E) a mixture of bicyclic compounds

20. Give the product for the following reaction.



- (A) alanine (B) leucine (C) valine  
(D) isoleucine (E) glycine

21. Which of the following statements correctly describes the contribution of  $\Delta S^\circ$  to  $\Delta G^\circ$ ?

- (A) The entropy term makes a greater contribution to  $\Delta G^\circ$  at high temperatures.  
(B) The entropy term makes a greater contribution to  $\Delta G^\circ$  at low temperatures.  
(C) The entropy term makes a greater contribution to  $\Delta G^\circ$  in exothermic reactions.  
(D) The entropy term makes a greater contribution to  $\Delta G^\circ$  in endothermic reactions.  
(E) The entropy term always makes a more significant contribution to  $\Delta G^\circ$  than does the enthalpy term.

22. What compound is produced when *N,N*-dimethylpropanamide is treated with  $LiAlH_4$ ?

- (A)  $CH_3CH_2CONH_2$  (B)  $CH_3CH_2CH_2NH_2$  (C)  $CH_3CH_2CH_2OH$   
(D)  $CH_3CH_2CH_2N(CH_3)_2$  (E)  $CH_3CH_2N(CH_3)_2$

23. Which of the following is a vicinal dihalide?

- (A) *cis*-1,2-dibromocyclopentane (B) 3,3-dichloropentane  
(C) *trans*-1,4-diiodocyclohexane (D) isobutyl chloride  
(E) 1,3-dibromoheptane

24. Reduction of a 2-ketohexose with  $NaBH_4$  yields:

- (A) a single aldohexose (B) a mixture of acetals (C) a mixture of alditols  
(D) a mixture of pyranoses (E) a mixture of cyclic hemiacetals

25. When the 1,7-diester  $CH_3O_2CCH_2CH_2CH(CH_3)CH_2CH_2CO_2CH_3$  is treated with sodium methoxide and the reaction mixture is subsequently neutralized with acid, what kind of compound is the major organic product?

- (A) a cyclic  $\beta$ -diketone (B) a cyclic  $\beta$ -ketoester (C) an acyclic  $\beta$ -diester  
(D) an acyclic  $\beta$ -ketoacid (E) a cyclic  $\beta$ -diketone

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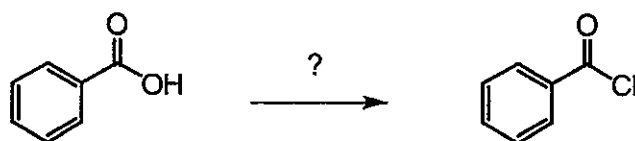
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26. When thiols form disulfide bonds, the reaction can be described as \_\_\_\_\_.
- (A) elimination (B) sulfation (C) sulfonation  
(D) oxidation (E) reduction
27. Which of the following compounds will not undergo Friedel-Crafts acylation when treated with  $\text{CH}_3\text{CH}_2\text{COCl}$ ,  $\text{AlCl}_3$ ?
- (A) toluene (B) *p*-xylene (C) anisole (D) benzophenone (E) ethoxybenzene
28. What is the major product when  $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$  is subjected to the following reaction sequence: (i) Mg, (ii)  $\text{CO}_2$ , (iii)  $\text{H}_3\text{O}^+$ ?
- (A) 3-methyl-1-butanol (B) 2-methyl-2-butanol (C) 4-methyl-1-pentanol  
(D) 4-methylpentanoic acid (E) 3-methylbutanoic acid
29. If a signal is observed in the 170 to 200 ppm range in a C-13 NMR spectrum, what is the most likely type of functional group associated with that carbon atom?
- (A) carbonyl carbon (B) allylic carbon (C) aromatic carbon  
(D) carbon/carbon triple bond (E) carbon/carbon double bond

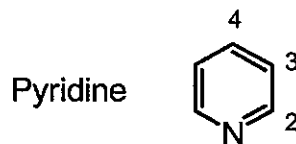
30. Which of the following reagents is used in the following reaction?



- (A)  $\text{Cl}_2/\text{CCl}_4$  (B) HCl (C)  $\text{Cl}_2/h\nu$  (D)  $\text{HClO}_4$  (E)  $\text{PCl}_5$

Part II. 問答題 (3 題, 共 40 分)

1. Which would you expect to undergo E2 elimination faster, *trans*-1-bromo-4-*tert*-butylcyclohexane or *cis*-1-bromo-4-*tert*-butylcyclohexane? Draw each molecule in its more stable chair conformation, and **explain your answers**. (10 points)
2. Electrophilic aromatic substitution reactions of pyridine normally occur at C3. Draw the carbocation intermediates resulting from reaction of an electrophile at C2, C3, and C4, and **explain the observed result**. (14 points)



3. Reacting carboxylic acids with diazomethane,  $\text{CH}_2\text{N}_2$ , is a common method for the synthesis of methyl esters. The reaction occurs in two steps; (i) protonation of diazomethane by the carboxylic acid to yield  $\text{CH}_3\text{N}_2^+$  and a carboxylate ion, and (ii) reaction of the carboxylate ion with  $\text{CH}_3\text{N}_2^+$ .



- (a) Please draw two key resonance structures of diazomethane. (8 points)
- (b) Use **curved arrows** to describe the detailed mechanism of these two steps. (8 points)

試題隨卷繳回