

I. Determine the structures of A, B, C, D, and E based on their spectroscopic data. (20%)

(A) $C_7H_{12}O_3$

UV: $\lambda_{max} = 275 \text{ nm}$ ($\epsilon = 25$, ethanol)

IR: 1130 cm^{-1} , 1700 cm^{-1}

HNMR: 1.2 ppm, triplet, 3 H; 2.1 ppm, singlet, 3 H

2.5 ppm, triplet, 4 H; 4.0 ppm, quartet, 2 H

(B) $C_8H_{11}N$

IR: 690 cm^{-1} , 730 cm^{-1} , 3500 cm^{-1}

HNMR: 1.4 ppm, singlet, 1 H; 2.5 ppm, singlet, 3 H

3.8 ppm, singlet, 2 H; 7.3 ppm, singlet, 5 H

(C) $C_9H_{11}BrO$

IR: 690 cm^{-1} , 760 cm^{-1} , 1250 cm^{-1}

HNMR: 2.3 ppm, quintet, 2 H; 3.6 ppm, triplet, 2 H

4.1 ppm, triplet, 2 H; 7.0 ppm, multiplet, 5 H

(D) Ozonolysis of D, $C_{11}H_{12}O$, gives H_2CO and E, $C_{10}H_{10}O$. Both D and E give a precipitate from reaction with I_2/OH^- . The HNMR spectrum of E shows two singlets integrating 3:2. Its ^{13}C spectrum has four signals.

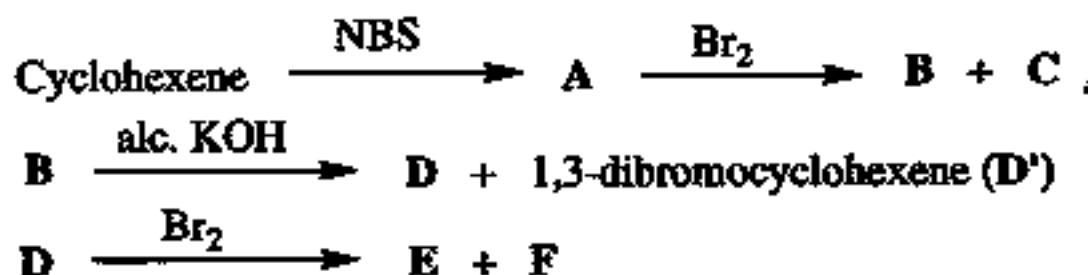
II. When trans-2-methylcyclohexanol is treated with tosyl chloride followed by KOEt, 3-methylcyclohexene is the only product. However, this sequence with cis-2-methylcyclohexanol gives 1-methylcyclohexene as the main product. Account for the difference in products. (8%)

III. Optically active (2S,3R)-3-bromo-2-butanol (X) reacts with KOH in MeOH to give Y, an optically active epoxide. Y is then treated with KOH in H_2O , giving 2,3-butanediol (Z).

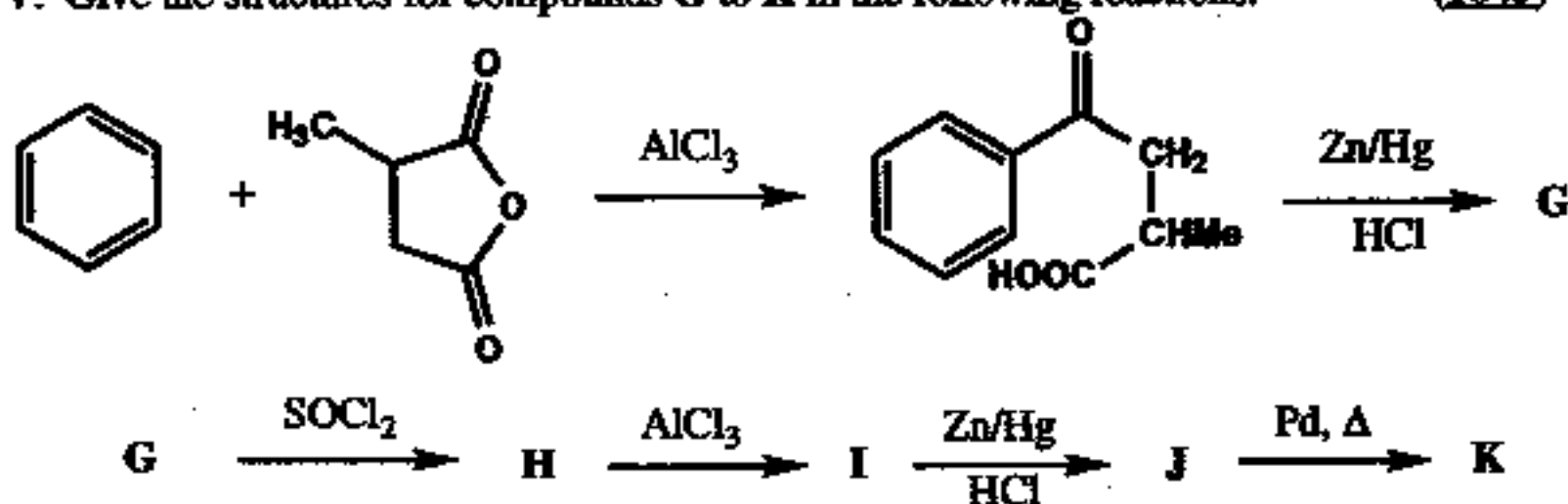
(A) Write three dimensional structures of X, Y, and Z.

(B) Do you expect C to show optical rotation? Explain. (8%)

- IV. (a) Draw the structure of A to F in the following reaction. (12%)
 (b) Explain why C won't give D or D' on treatment with alc. KOH. (2%)



- V. Give the structures for compounds G to K in the following reactions. (10%)



- VI. Choose a correct answer for each of the following questions. (40%)

- Calculate the formal charges on the carbons in a carbene, a carbocation, and a radical.
 - (1) -2, +1, 1
 - (2) -1, +2, 0
 - (3) 0, +1, 0
 - (4) -2, +1, 0
- How many grams of cyclohexanol must be reacted to produce 20 g of cyclohexene, if the % yield is 54%? The equation is $\text{C}_6\text{H}_{11}\text{OH} \rightarrow \text{C}_6\text{H}_{10} + \text{H}_2\text{O}$.
 - (1) 40 g
 - (2) 45 g
 - (3) 50 g
 - (4) 55 g

3. Determine the oxidation number of the underlined atom in each of the following species.



- (1) 0, +3, +5, +4
- (2) +4, -3, -5, +4
- (3) +4, +3, +5, +6
- (4) +4, +3, +5, +4

4. Compare the acid strength of the following compound (from smallest to the largest).



- (1) I, II, III, IV
- (2) IV, II, I, III
- (3) I, III, II, IV
- (4) I, IV, III, II

5. Place the three isomeric pentanes in order of increasing stability at room temperature.



- (1) III, II, I
- (2) III, I, II
- (3) II, I, III
- (4) I, II, III

6. The specific rotation of a pure enantiomer is $+12^\circ$. What is its observed rotation if it is isolated from reaction with 20% racemization and 80% retention?

- (1) -2.4°
- (2) $+2.4^\circ$
- (3) -9.6°
- (4) $+9.6^\circ$

7. How many stereoisomers of 2,3-butanediol are possible?

- (1) 2
- (2) 3
- (3) 4
- (4) 5

8. Assuming the absence of any steric hindrance, list the following alkenes in decreasing order of reactivity towards electrophilic addition:

I. $\text{ClCH}_2\text{CH}=\text{CH}_2$ II. $(\text{CH}_3)_2\text{C}=\text{CH}_2$ III. $\text{CH}_3\text{CH}=\text{CH}_2$ IV. $\text{H}_2\text{C}=\text{CHCl}$

- (1) II, III, I, IV
(2) IV, I, III, II
(3) III, II, IV, I
(4) I, IV, II, III

9. Analyze the following generalized rate data to derive the rate expression for the reaction:



	[RX]	[Nu ⁻]	rate
(i)	0.10	0.10	1.2×10^{-4}
(ii)	0.20	0.10	2.4×10^{-4}
(iii)	0.10	0.20	2.4×10^{-4}
(iv)	0.20	0.20	2.4×10^{-4}

- (1) $\text{rate} = k[\text{RX}]^2$
(2) $\text{rate} = k[\text{Nu}^-]^2$
(3) $\text{rate} = k[\text{RX}][\text{Nu}^-]$
(4) $\text{rate} = k[\text{RX}][\text{Nu}^-]^2$

10. Based on the pK_a values given in parentheses: H_2 (>35), CH_4 (>40), CH_3OH (17), C_2H_2 (25), HCN (9), which of the following reaction will not occur?

- (1) $\text{HCCNa} + \text{CH}_3\text{OH}$
(2) $\text{C}_2\text{H}_2 + \text{CH}_3\text{Li}$
(3) $\text{C}_2\text{H}_2 + \text{NaH}$
(4) $\text{C}_2\text{H}_2 + \text{NaCN}$

11. Place the following compounds in the order of their relative reactivity with E^+ .

I. $p\text{-CH}_3\text{C}_6\text{H}_4\text{COOH}$ II. $p\text{-HOOC}\text{C}_6\text{H}_4\text{COOH}$ III. $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3$ IV. $\text{C}_6\text{H}_5\text{CH}_3$

- (1) III > IV > I > II
(2) II > I > III > IV
(3) I > II > III > IV
(4) II > I > IV > III

12. A 9.6×10^{-5} M solution in a 1.0-cm cuvette cell at $\lambda_{\text{max}} = 235$ nm has an absorbance of 1.2. Calculate ϵ_{max} for this transition.
- (1) $2.45 \times 10^6 \text{ M}^{-1}\text{-cm}^{-1}$
 - (2) $1.25 \times 10^4 \text{ L/mol-cm}$
 - (3) $1.25 \times 10^5 \text{ L/mol-cm}$
 - (4) $8 \times 10^{-5} \text{ M/cm}$
13. Which of the following atoms are not NMR active: ^{32}S , ^{31}P , ^{19}F , ^{16}O , ^{15}N , ^{14}N , ^{12}C , ^2D ?
- (1) ^{32}S , ^{19}F , ^{16}O , ^{15}N , ^{14}N , ^2D
 - (2) ^{32}S , ^{16}O , ^{14}N , ^2D
 - (3) ^{32}S , ^{16}O , ^{12}C , ^2D
 - (4) ^{32}S , ^{16}O , ^{12}C
14. Place the following benzyl alcohols in decreasing order of reaction rate with HBr.
- I. $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ II. $p\text{-CH}_3\text{OCH}_2\text{OH}$ III. $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{OH}$ IV. $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{OH}$
- (1) I, II, III, IV
 - (2) II, IV, I, III
 - (3) III, IV, II, I
 - (4) II, I, IV, III
15. Compare the basicity of following amines.
- I. $\text{CH}_2=\text{CHCH}_2\text{NH}_2$ II. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ III. $\text{HC}\equiv\text{CCH}_2\text{NH}_2$
- (1) I>II>III
 - (2) II>I>III
 - (3) I>III>II
 - (4) III>I>II
16. Which of the following statements about α -amino acid is true?
- (1) Most natural α -amino acids have S configurations.
 - (2) Most natural α -amino acids have D configurations.
 - (3) All α -amino acid have one chiral center.
 - (4) L-cysteine has the same stereo configuration as L-serine.

17. The side chain residue of an amino acid can be modified chemically, which of the following statements is correct?
- (1) OH group can be protected by ester and removed by weak alkali.
 - (2) COOH group can be blocked by benzyl and removed by Na in liq. NH_3 .
 - (3) NH_2 group can be blocked by Boc and removed by CF_3COOH , HBr in HOAc.
 - (4) Imidazole group can be blocked by benzyl ester and removed by weak alkali.
18. Which two functional groups are present in typical carbohydrates?
- (1) OH and COOH
 - (2) CH_3 and OH
 - (3) OH and $\text{C}=\text{O}$
 - (4) $\text{C}=\text{O}$ and COOH
19. Which of the following reactions does not involve carbon-carbon bond formation?
- (1) Grignard
 - (2) Friedel-Crafts
 - (3) Aldol condensation
 - (4) Pinacol rearrangement
20. Which of the following reactions does not involve cleavage of carbon-carbon bond?
- (1) Hofmann degradation
 - (2) Diels-Alder
 - (3) ozonolysis
 - (4) Cope rearrangement