

※ 考生請注意：本試題不可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

### Organic Chemistry (100 pts)

#### I. Multiple-choice questions (20 pts)

[1] Including all possible stereoisomeric forms, how many distinct allylic bromides could be produced when 2-methylpent-1-ene is treated with NBS under irradiation by a sunlamp?

- (A) 2 (B) 3 (C) 4 (D) 5 (E) 6

[2] Why do acetal-forming reactions that use ethylene glycol have more favorable equilibrium constants than those using methanol?

- (A) Ethylene glycol reacts more rapidly. (B) They are more favorable on entropy grounds.  
(C) They are more favorable on enthalpy grounds. (D) Ethylene glycol is acidic and catalyzes the reaction. (E) The ethylene acetal can serve as a protecting group.

[3] Which of the following could result from the dehydration of a self-aldol condensation product?

- (A) 4-methyl-3-penten-2-one (B) 4-methyl-4-penten-2-one (C) 4-methyl-5-hexen-2-one  
(D) 4-methyl-4-hexen-2-one (E) 3-methyl-4-penten-2-one

[4] Both (*E*)- and (*Z*)-hex-3-ene can be subjected to a hydroboration-oxidation sequence. How are the products from these two reactions related to each other?

- (A) The (*E*)- and (*Z*)-isomers generate the same products but in differing amounts.  
(B) The (*E*)- and (*Z*)-isomers generate the same products in exactly the same amounts.  
(C) The products of the two isomers are related as constitutional isomers.  
(D) The products of the two isomers are related as diastereomers.  
(E) The products of the two isomers are not structurally related.

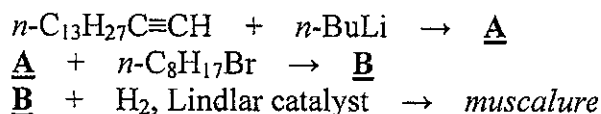
[5] What type of carbon environment does not generate a signal in the DEPT-90 spectrum and gives a positive peak in the DEPT-135 spectrum?

- (A) quaternary (B) methane (C) methylene (D) methyl (E) carbonyl

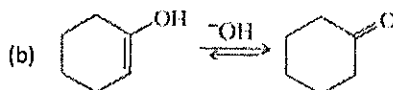
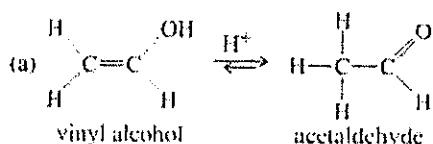
II. *Choline*, a constituent of phospholipid, has the formula  $C_5H_{15}O_2N$ . It dissolves in water to form a strongly basic solution. It can be prepared by the reaction of ethylene oxide with trimethylamine in the presence of water. (a) What is a likely structure for *Choline*? (b) What is a likely structure for its acetyl derivative, *acetylcholine*,  $C_7H_{17}O_3N$ , important in nerve action. (10 pts)

III. *cis*-4-*tert*-Butylcyclohexyl tosylate reacts rapidly with NaOEt in EtOH to yield 4-*tert*-butylcyclohexene; the reaction rate is proportional to the concentration of both tosylate and ethoxide ion. Under the same condition, *trans*-4-*tert*-butylcyclohexyl tosylate reacts slowly to yield the alkene (plus 4-*tert*-butylcyclohexyl ethyl ether); the reaction rate depends only on the concentration of the tosylate. How do you account for these observations? (10 pts)

IV. On the basis of the following synthesis, give the structure of *muscalure* and the intermediates **A** and **B**. (10 pts)



- V. Aniline reacts with nitrous acid,  $\text{HNO}_2$ , to yield a stable diazonium salt. This diazonium salt undergoes electrophilic aromatic substitution with *N,N*-dimethylaniline to yield brightly colored azo compounds that are widely used as dyes. Give detail mechanisms of the above reactions. Show all electron flow with arrows on the structures you drew. (10 pts)
- VI. (a) Draw a Newman projection of the most stable conformation of (2*R*,3*S*)-dibromobutane sighting down the C2–C3 bond. (b) Draw a Fischer projection of (2*R*,3*S*)-dibromobutane. Is (2*R*,3*S*)-dibromobutane a *meso* compound? Give your explanation. (10 pts)
- VII. Compound **A**,  $\text{C}_9\text{H}_{16}$ , was found to be optically active. On catalytic reduction over a palladium catalyst, 2 equivalents of hydrogen were absorbed to yield compound **B**. Ozonolysis of **A** gave two compounds. One was identified as acetaldehyde,  $\text{CH}_3\text{CHO}$ . The other compound, **C**, was an optically active dialdehyde,  $\text{C}_5\text{H}_8\text{O}_2$ . Formulate the reactions and draw structures for compounds **A**, **B** and **C**. (10 pts)
- VIII. Vinyl alcohols are generally unstable, quickly isomerize to carbonyl compounds. Propose mechanisms for the following isomerization. (10 pts)



- IX. Provide a structure that is consistent with the data below, and give detailed explanations for your answer. (10 pts)

$\text{C}_7\text{H}_{16}\text{O}$

IR ( $\text{cm}^{-1}$ ): 3200 ~ 3600 (broad), 2950

$^1\text{H}$  NMR (ppm): 2.8 (1H, broad s), 1.0 (6H, s), 0.9 (9H, s)

$^{13}\text{C}$  NMR (ppm): 68 (s), 39 (s), 16 (q), 13 (q)