

**State University of New York at Stony Brook  
Department of Chemistry**

**CHE 322, Organic Chemistry II**

**Final Exam  
Form I**

**May 14, 2004**

Please answer all questions specifically, concisely, and readably in the designated spaces on the answer sheet, which we will collect at the end of the exam. Your Student Identification Number must be written and coded on the answer sheet, and your printed name and signature must be entered at the upper right.

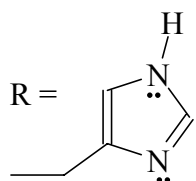
Think before writing. Include stereochemistry wherever relevant. Use the fronts and backs of the question pages for scratch work. Since the answer sheets will not be returned, we suggest that you record your answers on the question pages for comparison with the answers, which will be posted on Blackboard. Numerical grades will also be posted there.

The first sixteen questions are multiple choice, worth seven points apiece. Enter your choices (only one per question) into spaces 1-16 of the answer sheet.

Some useful information:

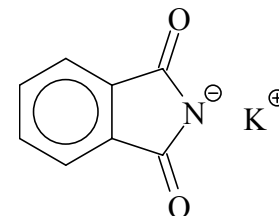
Amino acids,  $RCH(NH_3^+)CO_2^-$  and  $pK_a$ 's:

Asparagine, R = $-CH_2C(=O)NH_2$	2.02, 8.80
Aspartic Acid, R = $-CH_2COOH$	2.10, 3.86, 9.82
Cysteine, R = $-CH_2SH$	2.05, 8.00, 10.25
Leucine, R = $-CH_2CH(CH_3)_2$	2.33, 9.74
Lysine, R = $-(CH_2)_4NH_3^+$	2.18, 8.95, 10.53
Phenylalanine, R = $-CH_2Ph$	2.58, 9.24
Serine, R = $-CH_2OH$	2.21, 9.15
Histidine,	1.77, 6.10, 9.18



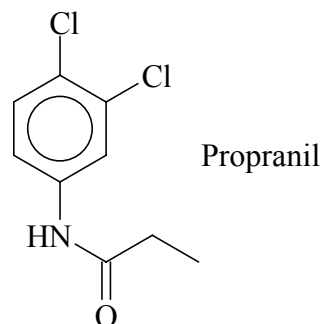
NAD<sup>+</sup> = nicotinamide adenine dinucleotide  
FAD = flavin adenine dinucleotide  
PCC = pyridinium chlorochromate

Potassium phthalimide =

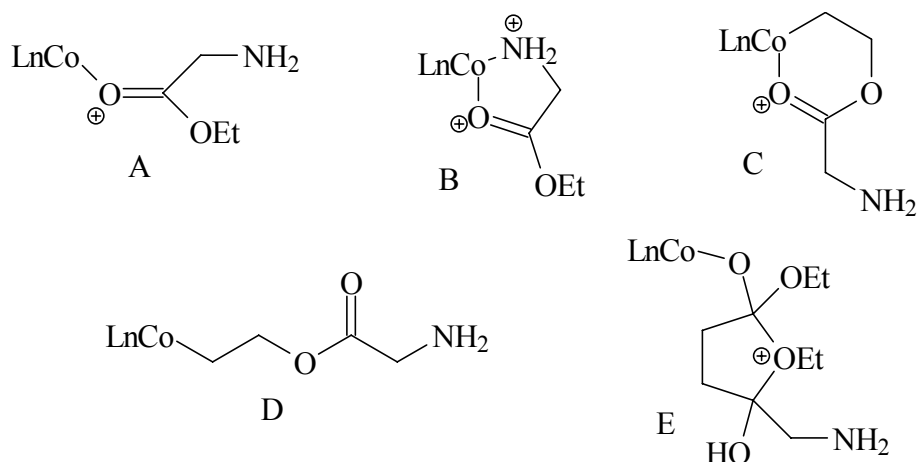


1. The herbicide Propranolol, shown below, is synthesized commercially from chlorobenzene. Which sequence of reactions would be most effective for carrying out this synthesis?

- A. Chlorination, nitration, reduction, acylation.  
 B. Chlorination, reduction, nitration, acylation.  
 C. Nitration, chlorination, reduction, acylation.  
 D. Nitration, reduction, chlorination, acylation.  
 E. It doesn't matter; they would all work equally well.



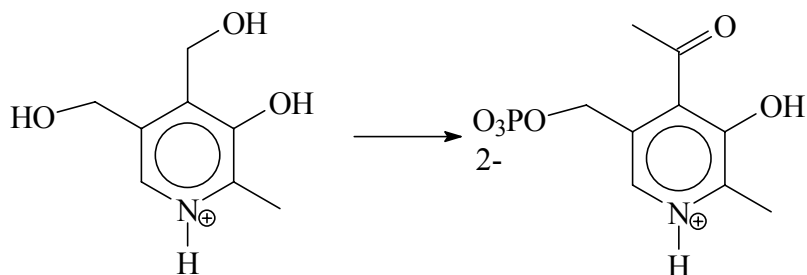
2. Which statement is **not** true about catalysts (including enzymes)?
- A. A catalyst can increase the rate of a chemical reaction.  
 B. A catalyst can change the mechanism of a chemical reaction.  
 C. A catalyst can change the equilibrium position of a chemical reaction.  
 D. A catalyst can directly participate in a chemical reaction.  
 E. A catalyst can decrease the activation energy of a chemical reaction.
3. Which amino acid side chain can function as either an acid or a base in an enzyme-catalyzed process? (See the cover page for structures).
- A. The thiol group of cysteine.  
 B. The isobutyl group of leucine.  
 C. The benzene ring of phenylalanine.  
 D. The imidazole group of histidine.  
 E. The carboxylate group of aspartate.
4. Cobalt (III) catalyzes the reaction shown below. Which of the following is the most likely intermediate responsible for the catalysis? ( $L_nCo$  represents the cobalt with attached ligands such as water.)



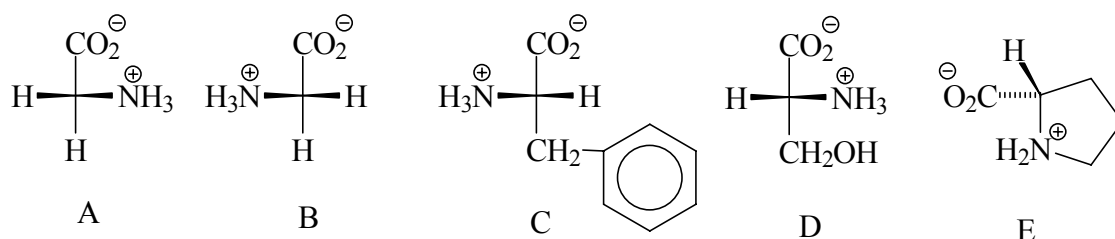
5. Which is the principal interaction that stabilizes  $\alpha$ -helices and  $\beta$ -pleated sheets in proteins?
- Hydrogen bonding
  - Salt bridges
  - Hydrophobic interactions
  - Van der Waals forces
  - Disulfide linkages
6. In a globular protein in water solution, which amino acid side chain would most likely be in the interior of the protein? (See the cover page for structures).
- The isobutyl side chain of leucine.
  - The hydroxymethyl side chain of serine.
  - The acetate side chain of aspartate.
  - The acetamide side chain of asparagine.
  - The 4-aminopropyl side chain of lysine.

7. Pyridoxine in the diet (vitamin B6) must be oxidized to pyridoxal for use as a coenzyme. What species is likely to catalyze this conversion in the body?

- FAD
- FAD<sup>+</sup>
- NAD<sup>+</sup>
- NADPH<sup>+</sup>
- PCC

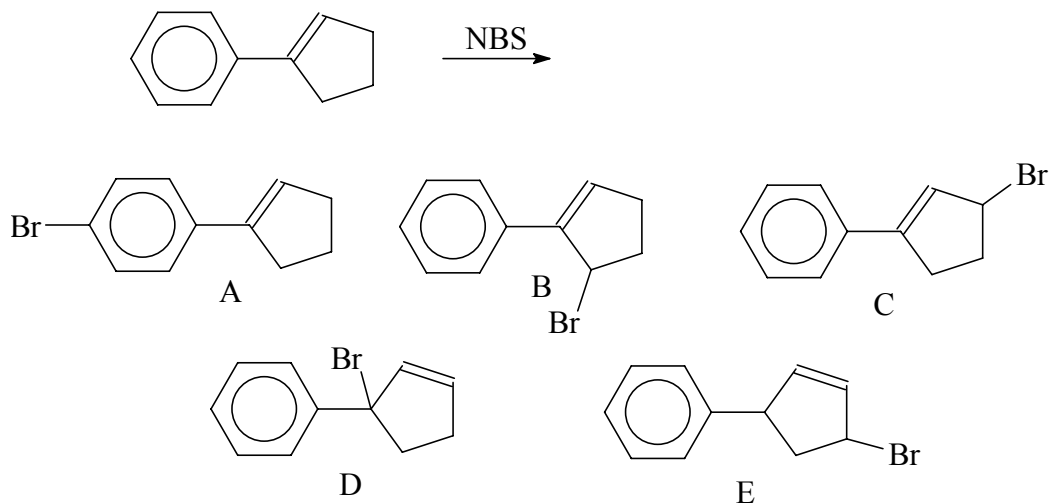


8. Which of the following amino acids is **not** likely to be found in a natural protein?

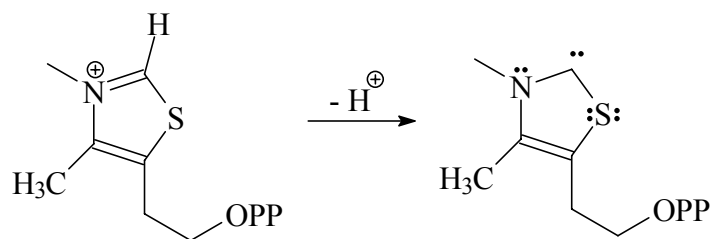


9. A reagent useful for forming a tertiary alcohol  $R_3COH$  from a Grignard reagent  $RMgBr$  in one step is:
- Ethyl formate,  $HCO_2Et$ .
  - Ethyl acetate,  $CH_3CO_2Et$
  - Formaldehyde,  $CH_2O$
  - Diethyl carbonate,  $EtOCO_2Et$
  - Diethyl oxalate,  $EtOCOCO_2Et$

10. Which of the products shown below would be the principal product formed in the bromination of 1-phenylcyclopentene by NBS in the presence of a peroxide initiator?



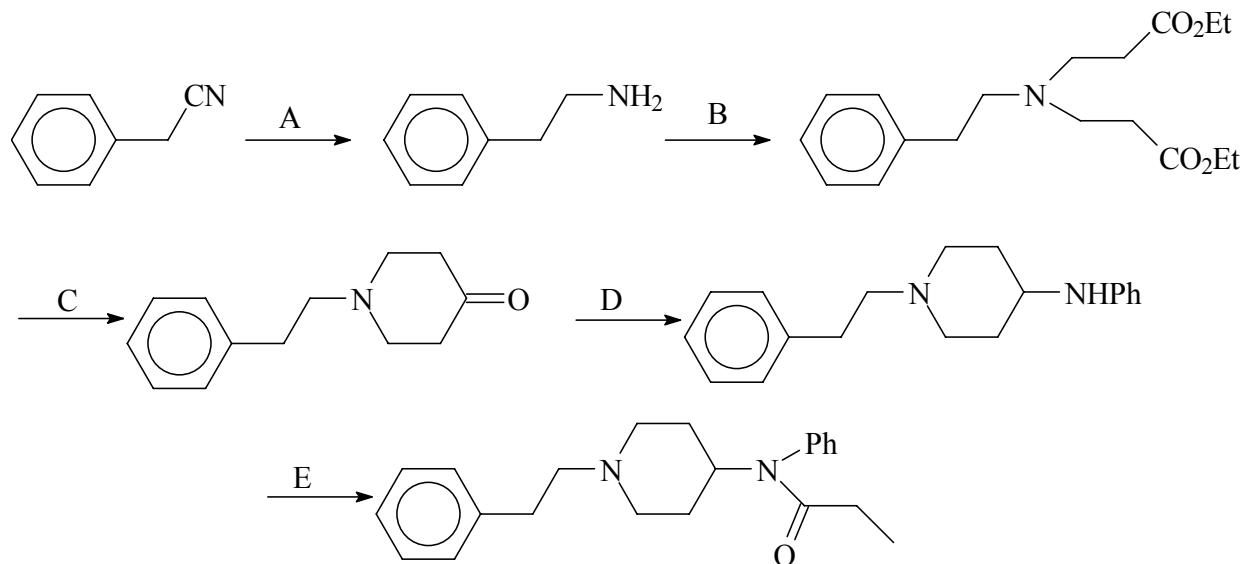
11. Thiamine pyrophosphate in the body carries out its catalytic functions in a deprotonated form which can be represented as shown below:



Which statement about this deprotonated species is **not** true?

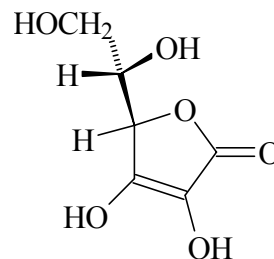
- A. The structure shown is unusual because it incorporates a divalent carbon.
  - B. There are additional contributing structures of a zwitterionic nature.
  - C. The ring is antiaromatic because it has eight circulating pi-electrons.
  - D. The ring is aromatic because it has six circulating pi-electrons.
  - E. Deprotonation does not alter the aromaticity to a significant degree.
12. A  $\beta$ -ketoester is most likely to have been synthesized by use of which reaction?
- A. Aldol reaction
  - B. Michael addition
  - C. Claisen condensation
  - D. Grignard reaction
  - E. Friedel-Crafts reaction.

Questions 13-16 relate to the commercial synthesis of Fentanyl, a powerful analgesic, which is the final product shown below: (Ph = phenyl, C<sub>6</sub>H<sub>5</sub>)



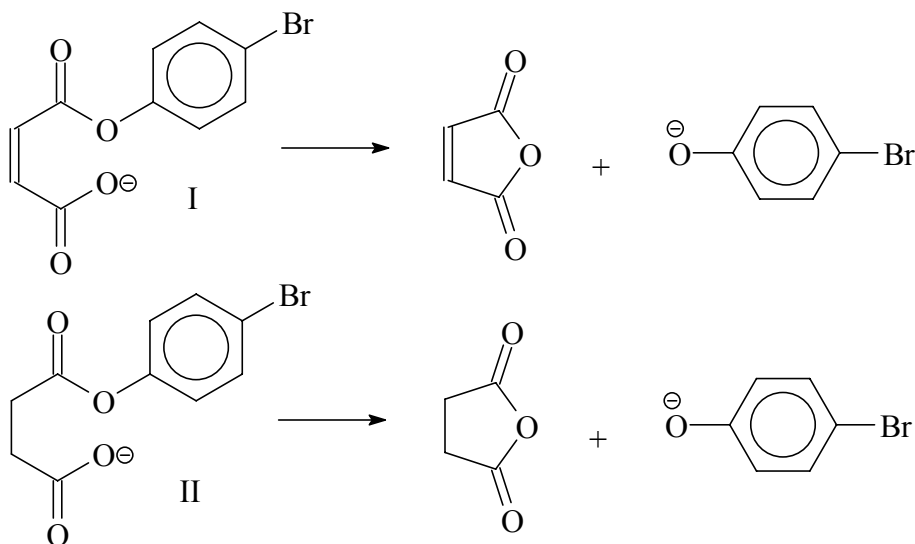
13. Which step involves a sequence of reactions including Claisen condensation, hydrolysis, and decarboxylation? (Enter the letter in the question 13 space on the answer sheet).
14. Which step involves a conjugate addition of a nucleophile to an electron-deficient double bond? (Enter the letter in the question 14 space on the answer sheet).
15. Which reagent would you recommend for the last step, Step E?
- Propanoic acid
  - Sodium propanoate
  - Propanamide
  - Propanoyl chloride
  - Propanal.
16. Which of the following reagents would be useful for carrying out Step A?
- Lithium aluminum hydride, LiAlH<sub>4</sub>.
  - Sodium borohydride, NaBH<sub>4</sub>
  - Sodium cyanoborohydride, NaBH<sub>3</sub>CN
  - Sodium azide, NaN<sub>3</sub>
  - Potassium phthalimide.

17. (16 points) Ascorbic acid (vitamin C) has a  $pK_{A1}$  of 4.17 and a  $pK_{A2}$  of 11.57. What is the predominant form of ascorbic acid at physiological pH (7.4)?

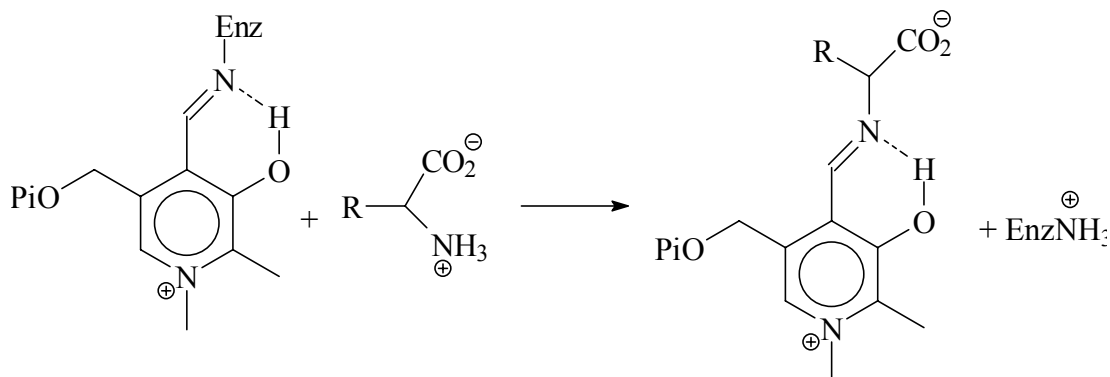


18. (16 points) Dehydration of serine,  $\text{HOCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$ , leads to formation of pyruvate,  $\text{CH}_3\text{C}(=\text{O})\text{CO}_2^-$ . Show how the initial dehydration product is converted to pyruvate under physiological conditions.

19. (12 points) *p*-Bromophenyl maleate, **I**, forms a cyclic anhydride by intramolecular displacement 45 times faster than its saturated analog, *p*-bromophenyl succinate, **II**. Explain why **I** reacts faster than **II**.

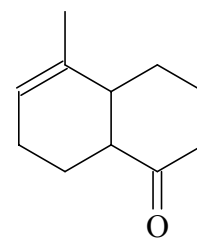


20. (16 points) The first step in PLP-catalyzed reactions is transimination, in which the enzyme-bound coenzyme is transferred to the amino acid substrate:

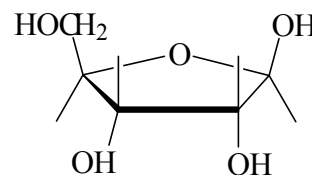


Show the steps in the transimination process. (Use  $\text{ArCH}=\text{NEnz}$  for the starting material to save space.)

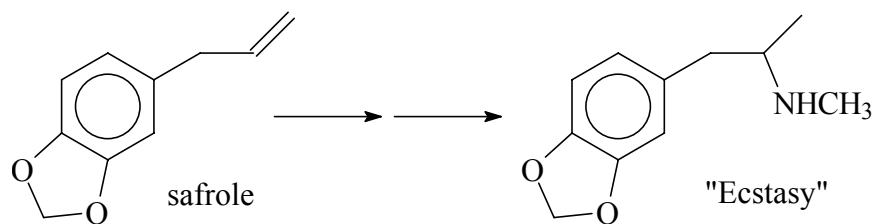
21. (12 points) The compound shown on the right was formed in an intramolecular Diels-Alder reaction. Show the structure of the starting material.



22. (16 points) Ribose, because of its role in nucleic acids, is the most important pentose. Given the  $\beta$ -furanose structure of ribose at the right, draw its Fischer projection.



23. BONUS (20 points) Recent news reports have indicated that persons unknown have attempted to secure large quantities of safrole, the principal component of oil of sassafras, responsible for the flavor of traditional root beer. Safrole is a restricted compound because of its structural relationship to the drug of abuse called "Ecstasy," 3,4-methylenedioxy-methamphetamine.



Show how an unscrupulous person might chemically convert safrole to "Ecstasy." (But do not attempt to do this at home.)