Name_____

Department of Chemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #4 - May 5, 1997

INSTRUCTIONS ---

This examination has two parts. Part I is in multiple choice format and the answers should be placed on the "Test Scoring Answer Sheet" which must be turned in and will be machine graded.

Part II requires your responding to questions by writing answers into the spaces provided in this booklet. This entire Exam Booklet must be handed in and will be returned to you with a grade. Write your name in the space above NOW.

On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your student (Social Security) number, course number (30032201) and the test number (04); darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

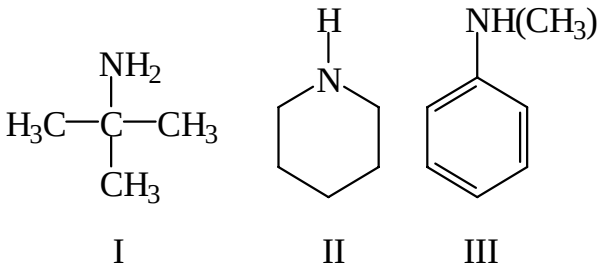
You may use a set of molecular models but no other aids during the exam.

Answer all questions. The questions on Part I are worth 3 points each.

You have 90 minutes. Good luck!

1. Classify the following amines in order I, II, III, as to whether they are primary, secondary, or tertiary:

(a) primary, secondary, tertiary,
(b) tertiary, secondary, secondary,
(c) primary, secondary, secondary,
(d) secondary, primary, tertiary,
(e) None of the above is correct.



I II III

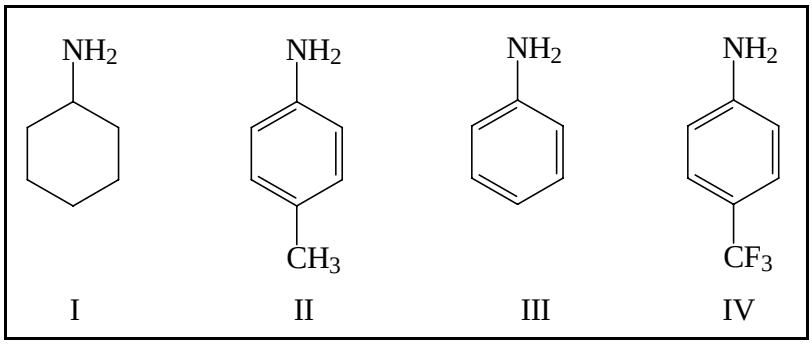
2. Using the information in the table below, rank the amines, X, Y, and Z, in order of decreasing base strength (most basic first):

Amine	X	Y	Z
pK_a of conjugate acid	-5	5	10

(a) X > Y > Z, (b) Z > Y > X, (c) Y > X > Z, (d) Z > X > Y.

3. Rank the following amines in order of decreasing base strength (most basic first).

(a) I > II > III > IV,
(b) IV > III > II > I,
(c) II > I > III > IV,
(d) II > III > IV > I
(e) none of the above answers

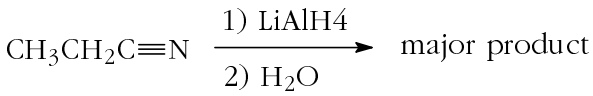


4. Which of the following general methods could you use to synthesize Ph-$CH(CH_3)NH_2$?

(I) ammonolysis of an alkyl halide, (II) reductive amination of a ketone, (III) reduction of a nitrile, (IV) Hofmann rearrangement of an amide.

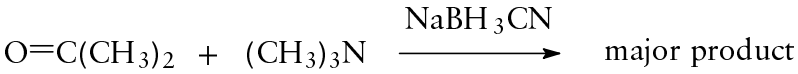
(a) I-IV, (b) I-III, (c) II-IV, (d) I, II, IV, (e) I, III, IV

5. Select the major product of the following reaction.



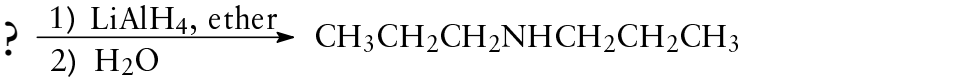
(a) $CH_3CH_2NH_2$, (b) CH_3CH_2CN, (c) $CH_3CH_2CH_2NH_2$,
(d) $CH_3CH_2CH{=}NH$, (e) none of the previous answers

6. Select the major product of the following reaction.



(a) $CH_2{=}C(CH_3)\text{-}N(CH_3)_2$, (b) $(CH_3)_2C(CN)\text{-}N(CH_3)_2$,
(c) $(CH_3)_2C{=}N^+(CH_3)_2\ CN^-$, (d) $(CH_3)_2CH\text{-}N(CH_3)_2$,
(e) None of the above answers is correct.

7. Which of the following compounds could be the starting material in this synthesis:



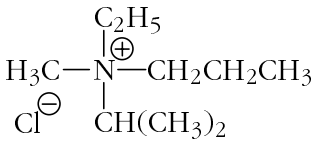
(a) $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}NHCH_2CH_2CH_3$ (b) $CH_3CH_2\overset{O}{\overset{\|}{C}}NHCH_2CH_2CH_3$

(c) $(CH_3CH_2CH_2)_3N$ (d) $CH_3CH_2CH_2NH_2$

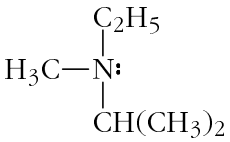
8. Which of the following is true of phase transfer catalysis?

(a) An inorganic ion is transferred into an organic phase.
(b) An inorganic ion is transferred into an aqueous phase.
(c) An organic molecule is transferred into an aqueous phase.
(d) An organic molecule is transferred into an organic phase.

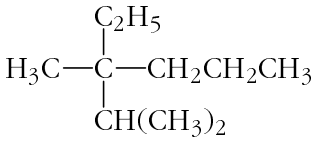
9. For which of the following compounds would it ordinarily be impossible to resolve enantiomers?



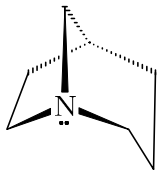
I



II



III



IV

(a) I, (b) II, (c) III, (d) IV, (e) I & II, (f) II & IV, (g) I, II & IV

10. Which sequence is suitable for preparing propylamine from 1-butanol?

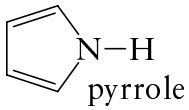
(a) $K_2Cr_2O_7/H_2SO_4$, then $SOCl_2$, then NH_3, then Br_2 and KOH.
(b) PBr_3, then NaN_3, then H_2/Pt.
(c) PBr_3, then NaCN, then $LiAlH_4$, then H_2O.
(d) PBr_3, then Mg, then CH_3NH_2.
(e) $K_2Cr_2O_7$, then $CH_3NH_2/NaBH_3CN$.

11. Which of the following compounds may be *hydrolyzed* to give propylamine, $CH_3CH_2CH_2NH_2$?

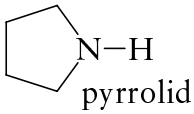
(a) CH_3CH_2CN, (b) $CH_3CH_2CO\text{-}NHCH_2CH_2CH_3$,
(c) $(CH_3CH_2CH_2)_2NH$, (d) $CH_3CH_2CH_2CN$,
(e) none of the above

12. In which of the following phenomena does resonance *not* play a role?

(a) Aniline, $Ph\text{-}NH_2$, is less basic than benzylamine, $Ph\text{-}CH_2NH_2$.
(b) Acetamide, CH_3CONH_2, is less basic than ethylamine.
(c) 2,2,2-Trifluoroethylamine is less basic than ethylamine.
(d) Pyrrole is less basic than pyrrolidine.

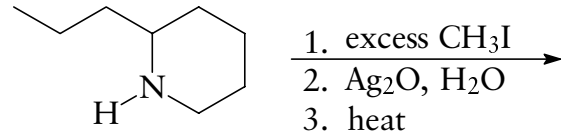


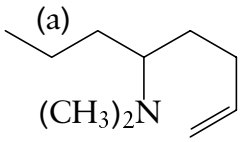
pyrrole

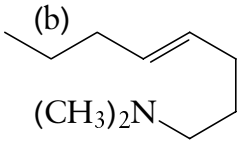


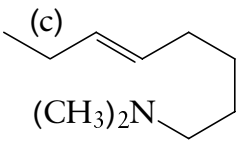
pyrrolidine

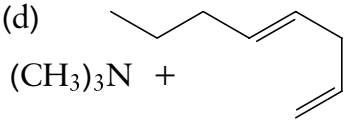
13. Coniine, $C_8H_{17}N$, is the toxic principle of poison hemlock, the Socrates martini. When subjected to Hofmann elimination, what will be the major product(s)?

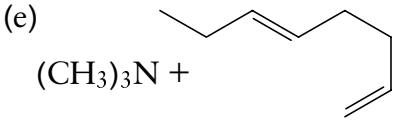


(a) 

(b) 

(c) 

(d) 

(e) 

14. Select *sec*-butylamine.

(a) $CH_3CH_2CH_2CH_2NH_2$ (b) $CH_3\overset{\displaystyle NH_2}{\overset{|}{C}}HCH_2CH_3$

(c) $(H_3C)_2CHCH_2NH_2$ (d) $H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-NH_2$

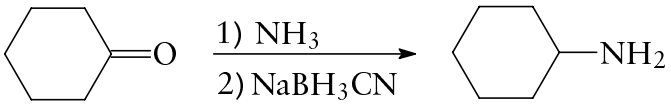
15. Which of the following compounds has the lowest boiling point?

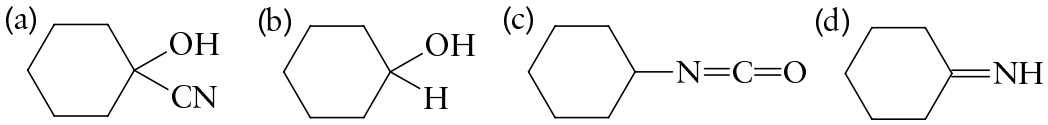
(a) $CH_3CH_2CH_2NH_2$, (b) $(CH_3)_3N$, (c) $CH_3CH_2CH_2NH_3^+\ Cl^-$,
(d) $(CH_3)_3NH^+\ Cl^-$

16. Amines can best be separated from nitro compounds by an extraction procedure employing diethyl ether and

(a) water. (b) aqueous hydrochloric acid. (c) aqueous sodium hydroxide.
(d) concentrated sulfuric acid.

17. Which of the following is an intermediate in the reaction shown?

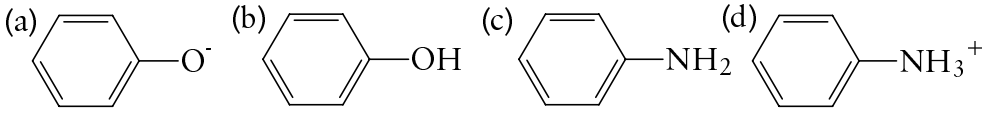




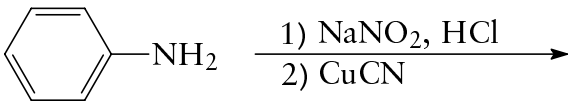
18. Which of the following compounds gives a 0.1*M* aqueous solution having the lowest pH?

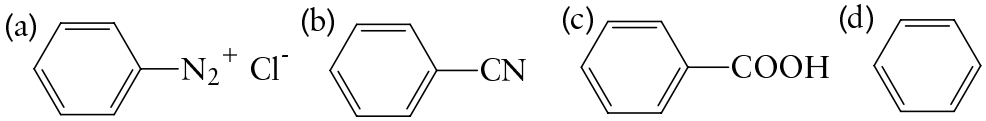
(a) $(CH_3)_4N^+ OH^-$, (b) $(CH_3)_4N^+ Cl^-$, (c) $(CH_3)_3N$, (d) $(CH_3)_3NH^+ Cl^-$

19. Which of the following undergoes coupling reactions with diazonium salts least readily?



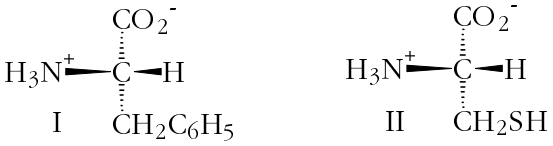
20. Select the major product of the following reaction.





21. Which of the amino acids shown to the right have the L configuration?

(a) I only, (b) II only, (c) I&II
(d) Neither I nor II



22. In the following table three amino acids are listed in the first column and their isoelectric points (pI) are listed in the second column. An electrophoresis experiment is performed in which the buffer is adjusted to a pH of 6.0. Select the answer which correctly indicates how each amino acid migrates in the experiment: to the anode (+), to the cathode (-), or dnm (does not migrate).

Compound	pI	(a)	(b)	(c)	(d)
alanine [$-CH_3$]	6.0	dnm	dnm	+	-
aspartic acid [$-CH_2COOH$]	3.0	+	-	dnm	dnm
lysine [$-(CH_2)_4NH_2$]	10.5	-	+	-	+

(e) None of the above answers is correct.

23. Which of the following statements about naturally-occurring α-amino acids is untrue?

(a) They belong to the L-family of chiral compounds related to L-glyceraldehyde.
(b) In neutral aqueous solution all of them exist predominantly in ionic form, either as cations or anions.
(c) Each has a characteristic isoelectric point, at which point it will not migrate in an electrophoresis experiment.
(d) They form salts with both strong acids and strong bases.

24. Which of the following synthetic sequences would be successful for the preparation of alanine in good yield?

(a) $CH_2{=}CHCOOH \xrightarrow{NH_3} CH_3CH(N^+H_3)COO^-$

(b) $CH_3CH_2COOH \xrightarrow[2.\ NH_3]{1.\ Br_2,\ h\nu} CH_3CH(N^+H_3)COO^-$

(c) $CH_3CHO \xrightarrow[2.\ H_3O^+]{1.\ NH_4Cl/KCN} CH_3CH(N^+H_3)COO^-$

(d) $CH_3CH_2COOH \xrightarrow[3.\ NH_3]{1.\ Br_2,\ P;\ 2.\ H_2O} CH_3CH(N^+H_3)COO^-$

(e) $CH_3CH_2COOH \xrightarrow[2.\ NH_3]{1.\ SOCl_2} CH_3CH(N^+H_3)COO^-$

(f) a & b, (g) c & d

25. An Edman degradation performed on the pentapeptide Ala-Gly-Pro-Glu-Ile would result in the formation of a phenylthiohydantoin and

(a) a soup of the amino acids Gly, Pro, Glu and Ile.
(b) a soup of the amino acids Ala, Gly, Pro and Glu.
(c) Gly-Pro-Glu-Ile.
(d) Ala-Gly-Pro-Glu.
(e) None of the above answers is correct.

26. One of the major problems in peptide synthesis concerns racemization of the amino acids. Thus, although one may start with enantiomerically pure amino acids, because of deprotonation at the α-carbons (reltively easy owing to the nearby electronegative groups), and subsequent reprotonation, racemic mixtures can result. If all the chiral centers at the α-carbons of a polypeptide containing 10 different amino acids (excluding glycine) were racemized during the synthesis, how many stereoisomers would be present?

(a) 10, (b) 20, (c) 100, (d) 1024, (e) 2048

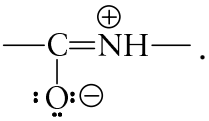
27. If you wished to make the dipeptide Phe-Gly would you protect

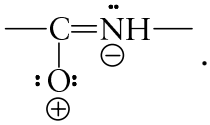
(a) the amino and carboxyl group of Phe?
(b) the amino and carboxyl group of Gly?
(c) the amino group of Phe and the carboxyl of Gly?
(d) the amino group of Gly and the carboxyl of Phe?

28. The two polypeptide chains that make up insulin are held together by

(a) hydrogen bonds. (b) peptide bonds. (c) disulfide bridges.
(d) hydrophobic interactions. (e) Velcro.®

29. The peptide (amide) linkage in proteins and polypeptides is planar and has restricted rotation because

(a) the linkage is stabilized by resonance which involves  .

(b) the linkage is stabilized by resonance which involves  .

(c) the linkage is hydrogen bonded to other amide groups.
(d) the carbonyl group is a planar group.

30. Linus Pauling is credited with being the first to describe how polypeptide chains in protein molecules arrange themselves in helix patterns (α-helix) or pleated sheets held together by hydrogen bonds. These structural features are referred to as the protein's

(a) primary structure. (b) secondary structure. (c) tertiary structure.
(d) quaternary structure.

31. In addition to the polypeptide part, most enzymes also have small nonprotein parts called ___I___s. ___I___s can be either inorganic ions or small organic molecules, called ___II___s. If the ___I___ is tightly bound to the protein it is called a ___III___.

(a) I: cofactor, II: coenzyme, III: prosthetic group.
(b) I: coenzyme, II: cofactor, III: prosthetic group.
(c) I: prosthetic group, II: coenzyme, III: cofactor.
(d) I: coenzyme, II: prosthetic group, III: cofactor.
(e) None of the above answers is correct.

32. Some vitamins are

(a) globular proteins. (b) enzymes. (c) coenzymes. (d) fibrous proteins.

33. Hemoglobin consists of of an association of four globins and their associated hemes. This aspect of hemoglobin is referred to as its

(a) primary structure. (b) secondary structure. (c) tertiary structure.
(d) quaternary structure.

Do Not Detach The Following Sheets From The Rest Of The Exam

Part II. Enter your answers in the space provided. If there is inadequate room, continue on the back of the page and clearly indicate on the front of the page that you have done this.
Hand in this entire exam booklet when you are finished; it will be returned to you with your grade. Make sure your name is on the front sheet.

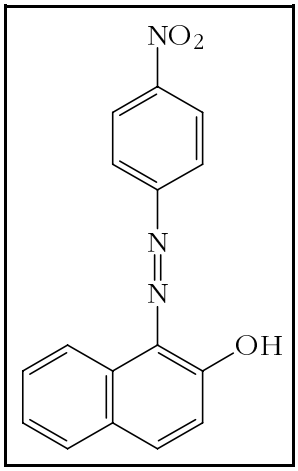
1. **Synthesis.**

Outline the following syntheses. Show all reagents and any important conditions. Do not show mechanisms or balance equations.

(a) Make pentylamine, $CH_3(CH_2)_4NH_2$, from pentanoic acid, $CH_3(CH_2)_4COOH$, in good yield. You may use any other materials you need.

(b) Make alanine, $CH_3CH(NH_2)COOH$, starting with iodomethane, CH_3I. You may use any other materials you need.

(c) Make para red from acetanilide, CH_3-CO-NHPh. You may use any other materials you need.



Para Red

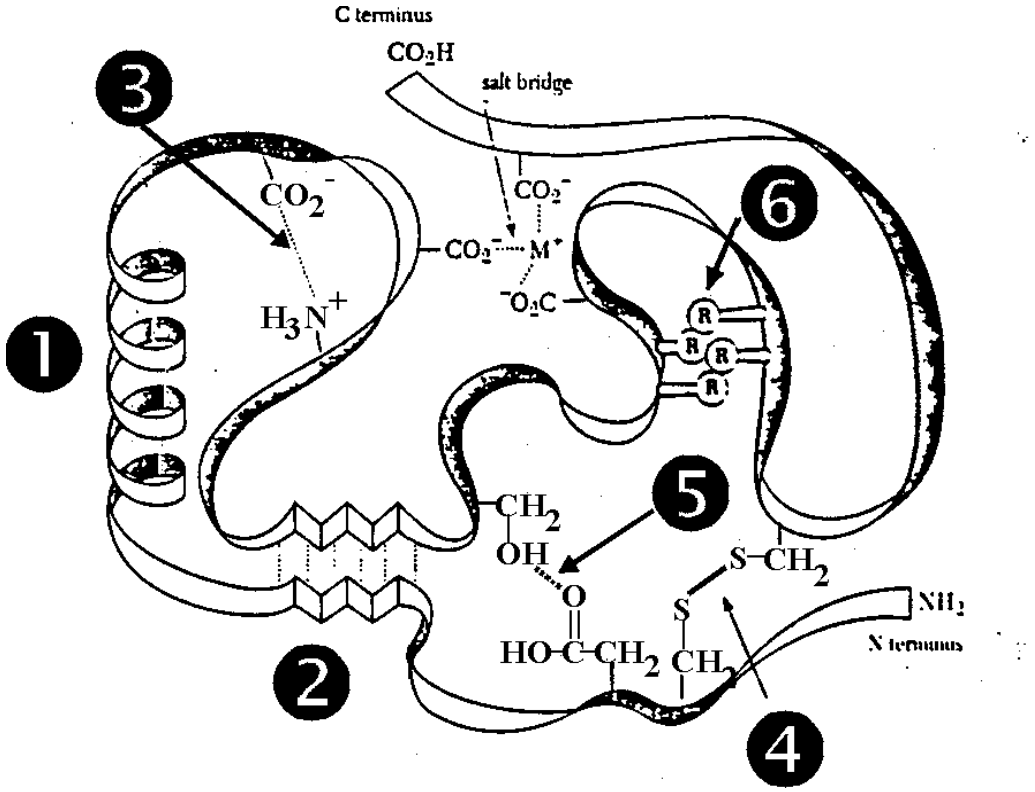
2. (a) Partial hydrolysis of a hexapeptide produces the following dipeptides: Gly-Ala, His-Phe, Ala-Phe, Leu-His, and Phe-Leu. Write down the primary structure of this hexapeptide.

(b) Identify the protein structural features indicated on the figure below.

1. 2.

3. 4.

5. 6.



Part I (100)_____	
Part II	
1. (15)_____	
2. (11)_____	
Total (127)_____	

Please return the pen