

Name _____

**Department of Chemistry
SUNY/Oneonta**

**Chem 322 - Organic Chemistry II
Examination #4 - May 8, 1995**

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.

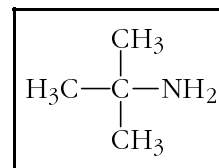
On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your student (Social Security) number, course number (30032201) and the test number (04); darken the appropriate bubbles under the entries, making dark black marks 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 2.857142857 points each.

You have 90 minutes. Good luck!

1. The compound shown to the right is



- (a) *sec*-butylamine, (b) *tert*-butylamine, (c) trimethylamine,
(d) amino-*t*-butane

2. The amine shown in the above question is a _____ amine.

- (a) primary, (b) secondary, (c) tertiary, (d) quaternary

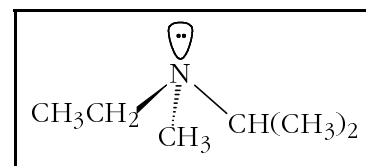
3. Low molecular weight amines can be described as having a _____ odor.

- (a) citrus, (b) spicy, (c) floral, (d) fishy

4. 3-Methylaniline and _____ are the same compound.

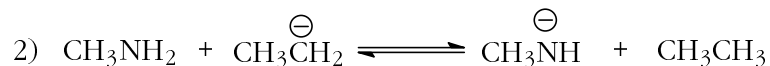
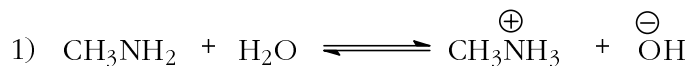
- (a) *o*-toluidine, (b) *m*-toluidine, (c) *p*-toluidine, (d) 3-methylpyridine,
(e) 3-methylpiperidine

5. Which of the following statements is most accurate with regard to the structure shown to the right?



- (a) This amine is chiral and can be separated from its enantiomer by the process of resolution.
(b) This amine is chiral but cannot be separated from its enantiomer because they both undergo rapid pyramidal inversion which converts one into the other.
(c) This amine is chiral but cannot be separated from its enantiomer because the nitrogen-carbon bonds are weak and break heterolytically forming a carbocation and an $\text{RR}'\text{N}^-$ anion. When these ions rejoin, the configuration around the nitrogen may be the same as, or opposite to, the initial situation.
(d) This amine is chiral but cannot be separated from its enantiomer because the nitrogen-carbon bonds are weak and break homolytically forming two free radicals. When these radicals rejoin, the configuration around the nitrogen may be the same as, or opposite to, the initial situation.
(e) Whoa, dude! Tryin' to put one over on us snowboarders? This amine is, like, achiral because it does not have a diastereomer.

6.



In reaction #1 above the amine is functioning as a(n) _____; in reaction #2 above the amine is functioning as a(n) _____.

(a) acid; acid, (b) base; base, (c) acid; base, (d) base; acid

7. Some of the chemistry of amines can be best understood by remembering that they often function as _____ or _____.

(a) acids, electrophiles, (b) bases, nucleophiles,
(c) acids, nucleophiles, (d) bases, electrophiles

8. In each of the following two cases, which of the compounds is the stronger base?

- (I) $\text{CH}_3\text{CH}_2\text{NH}_2$ or (II) $\text{FCH}_2\text{CH}_2\text{NH}_2$
- (III) $(\text{CH}_3\text{CH}_2)_2\text{NH}$ or (IV) $\text{CH}_3\text{CH}_2\text{NH}_2$

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

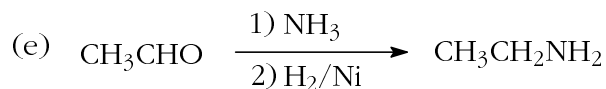
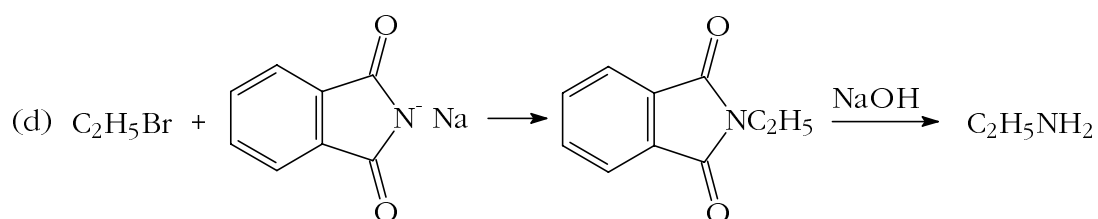
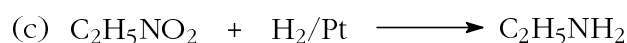
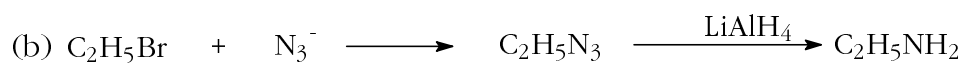
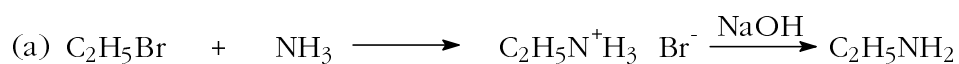
9. Which sequence is suitable for preparing butylamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, from 1-propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$?

- (a) KMnO_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 H_2/Pt .
(d) PBr_3 , then Mg , then NaCN , then H_2/Pt .

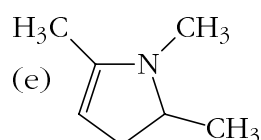
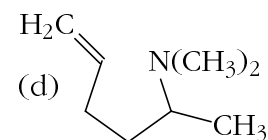
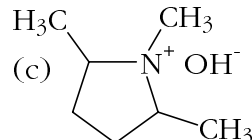
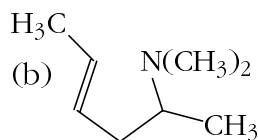
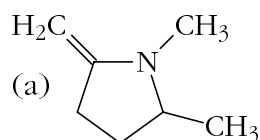
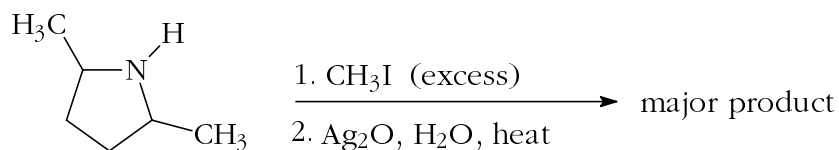
10. Which of the following compounds may be hydrolyzed to give propylamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$?

- (a) $\text{CH}_3\text{CH}_2\text{CN}$, (b) $\text{CH}_3\text{CH}_2\text{-CO-NHCH}_2\text{CH}_2\text{CH}_3$, (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_3$,
(d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$

11. One of the methods of preparing amines shown below gives poor yields and mixtures of products. Which one is it?

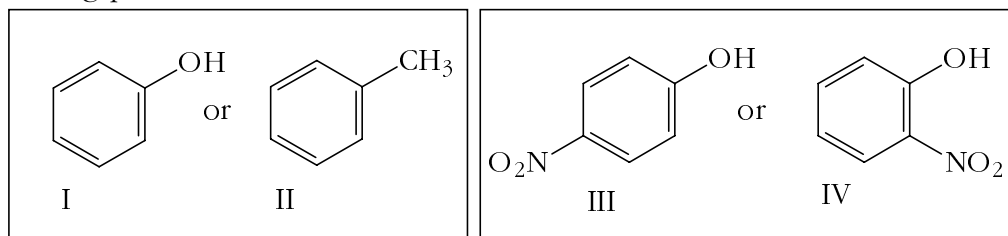


12. Select the principal product of the following reaction.



13. Which of the following compounds is the weakest base?
- (a) $\text{CH}_3\text{CH}_2\text{NH}_2$, (b) $(\text{CH}_3)_2\text{NH}$, (c) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, (d) $\text{C}_6\text{H}_5\text{NH}_2$
(e) All of the above amines are equally basic.
14. Aniline is less basic than methylamine because
- (a) resonance in aniline increases the electron density on nitrogen; this effect is not possible for methylamine.
(b) resonance in aniline stabilizes the non-protonated base but does not stabilize the protonated base to the same extent; in methylamine resonance is of no importance for the protonated or unprotonated forms.
(c) the acid-base reaction of aniline with a proton is kinetically rather than thermodynamically controlled.
(d) the ortho hydrogens of aniline interfere with protonation of its amino group.
(e) The question is incorrect; aniline is actually more basic than methylamine.
15. To convert nitrobenzene to acetanilide, the correct synthetic sequence employs
- (a) acetic anhydride, then tin with hydrochloric acid.
(b) tin with hydrochloric acid, then acetic acid.
(c) tin with hydrochloric acid, then acetic anhydride.
(d) acetic acid at 180°C , then tin with hydrochloric acid.
(e) tin with hydrochloric acid, then sodium nitrite with hydrochloric acid, then acetic anhydride.
16. Reaction of aniline with nitrous acid produces
- (a) a diazonium salt. (b) *p*-nitrosoaniline. (c) a mixture of alcohols and alkenes.
(d) an amide. (e) N-nitrosoaniline.
17. Reaction of N,N-dimethylaniline with nitrous acid produces
- (a) a diazonium salt. (b) *p*-nitroso-N,N-dimethylaniline. (c) a mixture of alcohols and alkenes. (d) an amide. (e) N,N-dimethyl-N-nitrosoaniline.

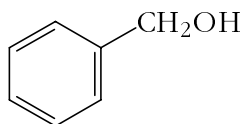
18. An aromatic diazonium salt is not a useful intermediate in a two-step synthesis of
- (a) ArCl from ArNH₂. (b) ArF from ArNH₂. (c) ArCH₃ from ArNH₂.
(d) ArOH from ArNH₂. (e) ArCN from ArNH₂.
19. Which of the following reaction sequences will bring about the conversion of benzene to 1,3,5-tribromobenzene?
- (a) benzene + HNO₃/H₂SO₄; then NaNO₂/HCl; then Br₂ (3 equivalents); then H₃PO₂,
(b) benzene + Br₂ (3 equivalents)/Fe,
(c) benzene + HNO₃/H₂SO₄; then Br₂ (3 equivalents)/Fe; then Sn/HCl; then NaNO₂/HCl; then H₃PO₂,
(d) benzene + HNO₃/H₂SO₄; then Sn/HCl; then NaNO₂/HCl; then Br₂ (3 equivalents); then H₃PO₂,
(e) benzene + HNO₃/H₂SO₄; then Sn/HCl; then Br₂ (3 equivalents); then NaNO₂/HCl; then H₃PO₂
20. Which of the following aromatic compounds will not react with phenyl diazonium chloride, Ph-N₂⁺ Cl⁻, to form an azo compound?
- (a) benzene, (b) phenol, (c) N,N-dimethylaniline, (d) 2-naphthol,
(e) resorcinol (1,3-dihydroxybenzene)
21. Which compound in each of the following pairs of compounds will have the higher boiling point?



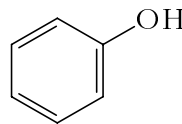
- (a) I&III, (b) I&IV, (c) II&III, (d) II&IV

22. Which of the following compounds will react essentially completely with aqueous sodium hydroxide solution to form a salt?

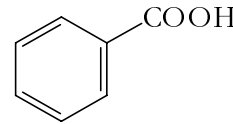
(a) I, (b) II, (c) III,
(d) I&II, (e) II&III



I



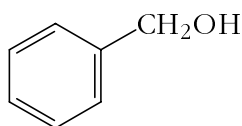
II



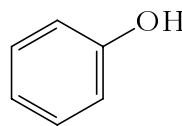
III

23. Which of the following compounds will react essentially completely with aqueous sodium bicarbonate solution to form a salt?

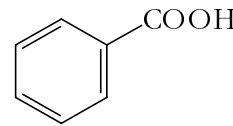
(a) I, (b) II, (c) III,
(d) I&II, (e) II&III



I

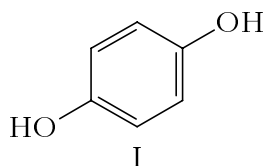


II

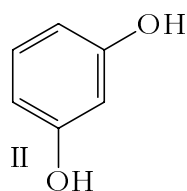


III

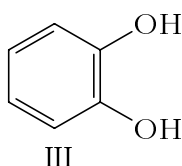
24. Which of the following compounds will not give a quinone upon mild oxidation?



I



II

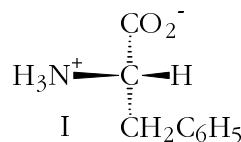


III

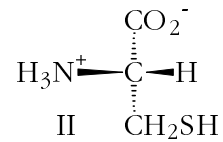
(a) I, (b) II, (c) III,
(d) I&II, (e) II&III

25. 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



I



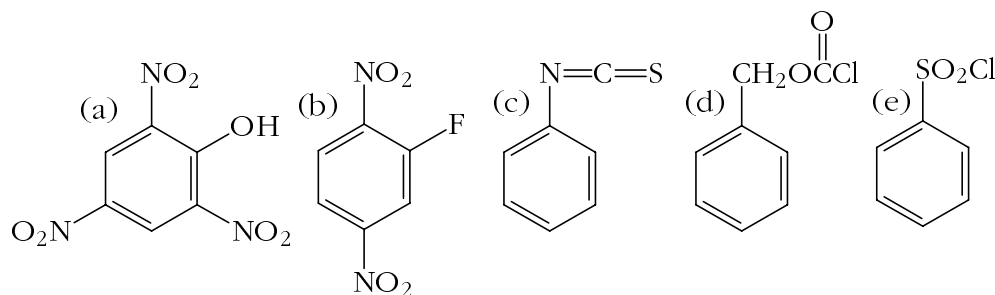
II

26. In the following table, which column has the isoelectric points (pI) correctly matched with the amino acids (R-groups shown) on the left?

	(a)	(b)	(c)	(d)	(e)
alanine [-CH ₃]	10.5	3.0	6.0	6.0	3.0
aspartic acid [-CH ₂ COOH]	6.0	10.5	10.5	3.0	6.0
lysine [-(CH ₂) ₄ NH ₂]	3.0	6.0	3.0	10.5	10.5

27. Which of the following statements about naturally occurring α -amino acids is untrue?
- (a) They belong to the D-family of chiral compounds, related to D-glyceraldehyde.
 (b) In neutral aqueous solution they exist predominantly in the dipolar "zwitterion" form.
 (c) Each has a characteristic isoelectric point, the pH at which no net migration of the amino acid toward either electrode in an electrophoresis experiment is observed.
 (d) They form salts with both strong acids and strong bases.
28. Which of the following synthetic sequences would be best for the preparation of alanine?
- (a) $\text{CH}_2=\text{CHCOOH} \xrightarrow{\text{NH}_3} \text{CH}_3\text{CH}(\text{N}^+\text{H}_3)\text{COO}^-$
- (b) $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[2. \text{NH}_3]{1. \text{Br}_2, h\nu} \text{CH}_3\text{CH}(\text{N}^+\text{H}_3)\text{COO}^-$
- (c) $\text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow[3. \text{CO}_2]{1. \text{Br}_2, h\nu, 2. \text{Mg}} \text{CH}_3\text{CH}(\text{N}^+\text{H}_3)\text{COO}^-$
- (d) $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[3. \text{NH}_3]{1. \text{Br}_2, \text{P}, 2. \text{H}_2\text{O}} \text{CH}_3\text{CH}(\text{N}^+\text{H}_3)\text{COO}^-$
- (e) $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[2. \text{NH}_3]{1. \text{SOCl}_2} \text{CH}_3\text{CH}(\text{N}^+\text{H}_3)\text{COO}^-$
29. Which of the following compounds contains a peptide bond?
- (a) $\text{CH}_3\text{-CO-NH-CO-CH}_3$, (b) $\text{CH}_3\text{-CH=N-CO-CH}_3$, (c) $\text{CH}_3\text{-NH-CO-NH-CH}_3$,
 (d) $\text{CH}_3\text{-CO-NH-CH}_3$, (e) $\text{CH}_3\text{-COOCH}_3$

30. An Edman degradation of a polypeptide requires the reagent:



31. A pentapeptide was found to contain the amino acids Phe, Gly, Met, Ala, and Ser. N-Terminal analysis with Sanger's reagent yielded N-(2,4-dinitrophenyl)alanine. Partial hydrolysis of the pentapeptide yielded the dipeptides Gly-Ser, Ala-Gly, and Ser-Met. The primary structure of the pentapeptide is:

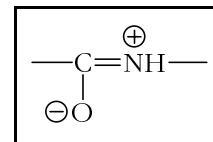
- (a) Ala-Gly-Ser-Phe-Met, (b) Ala-Gly-Ser-Met-Phe, (c) Phe-Ser-Gly-Met-Ala,
(d) Phe-Met-Ser-Gly-Ala, (e) Phe-Ala-Gly-Ser-Met

32. Why is the acetyl group, $\text{H}_3\text{C-CO-}$, not used as an N-protecting group in peptide synthesis?

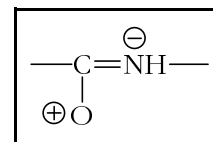
- (a) It is too small to give adequate steric hindrance to side reactions.
(b) It is too easily hydrolyzed under the conditions of peptide bond formation.
(c) It cannot be prepared in good yield from amino acids.
(d) It cannot be removed without hydrolyzing peptide bonds as well.
(e) Bogus question! The acetyl group is widely used as an N-protecting group in peptide synthesis.

33. The amide linkage in proteins and peptides is planar and has restricted rotation because

(a) the linkage is stabilized by resonance which involves the structure shown to the right.



(b) the linkage is stabilized by resonance which involves the structure shown to the right.



(c) the linkage is hydrogen bonded to other amide groups.

(d) the carbonyl group is a planar group.

34. Linus Pauling is credited with being the first to describe how polypeptide chains in protein molecules arrange themselves in helix patterns held together by hydrogen bonds. This so-called α -helix (and also the "pleated sheet") is what today we refer to as a protein's

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

35. The joining of two α -globins and two β -globins together (along with their associated hemes) to form hemoglobin is known as the _____ of hemoglobin.

(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.

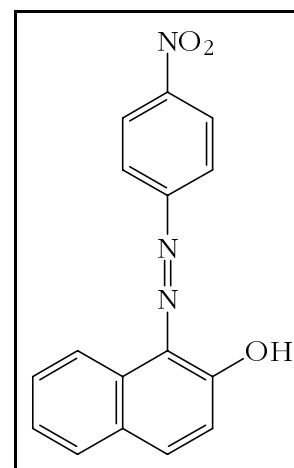
1. **SYNTHESIS.**

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

(a) Make pentylamine, $\text{CH}_3(\text{CH}_2)_4\text{NH}_2$, from pentanoic acid, $\text{CH}_3(\text{CH}_2)_4\text{COOH}$, in good yield. You may use any other materials you need.

(b) Make phenol from benzene. You may use any other materials you need.

(c) Make para red from acetanilide. You may use any other materials you need.



Para Red

2. **PROTEINS AND POLYPEPTIDES.**

(a) The disulfide linkage in a polypeptide, RS-SR', can be reduced to produce two thiols, RSH and R'SH, by adding a large excess of HSCH₂CH₂OH.

(i) Complete the equation for this reaction:



(ii) How is this reaction involved in determining the sequence of amino acid residues in proteins where disulfide bridges exist, *eg* insulin?

(b) Distinguish between simple and conjugated proteins.

(c) Describe three types of interaction/bonding that are responsible for the tertiary structure of proteins.

(1)

(2)

(3)

Part I (100)_____

Part II

1. (15)_____

2. (10)_____

Total (125)_____

PLEASE RETURN THE PENCIL YOU BORROWED.