Department of Chemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #4 - May 5, 2003

INSTRUCTIONS —

This examination 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.

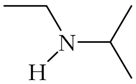
On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your OSC student (or Social Security) number, course number (30032201) and the test number (04); darken the appropriate bubbles under the entries, making dark black 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 are worth 3.03 points each.

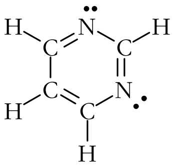
You have 90 minutes. Good luck!

1. The amine shown to the right is a _______ amine.



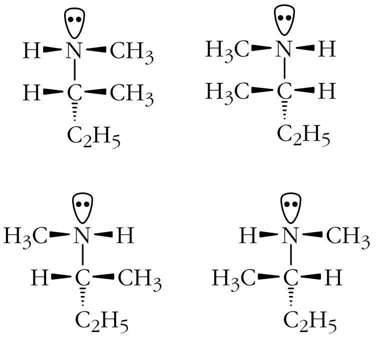
(a) primary, (b) secondary, (c) tertiary, (d) quarternary,
(e) primary-secondary, (f) secondary-tertiary, (g) primary-tertiary.

2. Pyrimidine, shown to the right, is a biologically important heterocyclic aromatic amine. Which of the following statements is correct concerning the electronic structure of pyrimidine?



(a) The structure, as shown, is correct; each nitrogen holds an unshared pair of electrons.
(b) The structure, as shown, is incorrect; one of the nitrogens holds an unshared pair of electrons, but the other nitrogen actually donates the pair shown as unshared to the aromatic π-electron system of the ring.
(c) The structure, as shown, is incorrect; both of the nitrogens donate the electron pairs shown as unshared to the aromatic π-electron system of the ring.
(d) The structure as shown is incorrect; it does not have the correct number of electrons.

3. Consider N-methyl-*sec*-butylamine and select the correct statement from those below.



(a) Under ordinary conditions it is possible to isolate 4 stereoisomeric forms of this compound in the laboratory. These isomers are shown to the right.
(b) Under ordinary conditions it is possible to isolate 2 stereoisomeric forms of this compound in the laboratory. The isomers are enantiomers.
(c) Under ordinary conditions it is possible to isolate 2 stereoisomeric forms of this compound in the laboratory. The isomers are diastereomers.
(d) This compound is achiral.

4. Diethylamine (I), glycine (II) and pentane (III) all have about the same molecular weight, yet their boiling points are different. Based on their structures, rank them in order from highest boiling point to lowest boiling point (highest boiling point first).

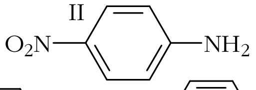
(a) I > II > III, (b) III > II > I, (c) II > I > III, (d) III > I > II, (e) II > III > I, (f) I > III > II

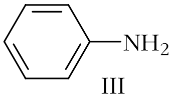
5. Arrange the compounds shown to the right in order of decreasing basicity (most basic first).

$H_3C—NH_2$

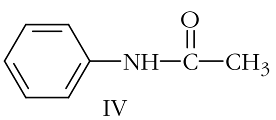
I

II





III



IV

(a) I>II>III>IV, (b) IV>III>II>I,
(c) IV>II>III>I, (d) III>II>I>IV,
(e) I>III>II>IV, (f) None of the above answers is correct.

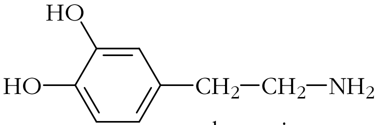
6. The difference in basicity between alkyl amines and aryl amines can be explained by resonance structures that can be drawn for _______ but not for the other species.

   (a) the alkyl amines, (b) the protonated alkyl amines, (c) the aryl amines, (d) the protonated aryl amines.

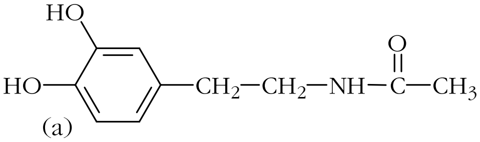
7. Which of the following is not a method of synthesizing amines?

   (a) reduction of nitriles, (b) reduction of amides, (c) hydrolysis of amides, (d) hydrolysis of diazonium salts, (e) reduction of nitro compounds, (f) reductive amination of aldehydes and ketones.

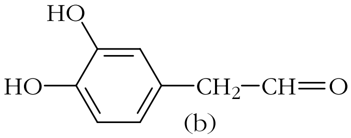
8. Which of the following compounds would *not* be a good starting material for a *simple* (one or two step) synthesis of the neurotransmitter dopamine.



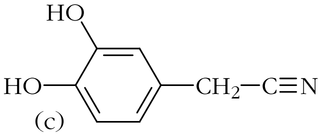
dopamine



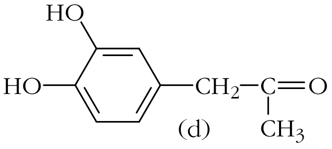
(a)



(b)



(c)

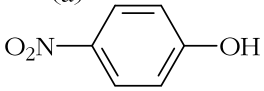


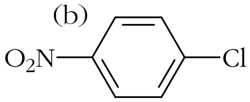
(d)

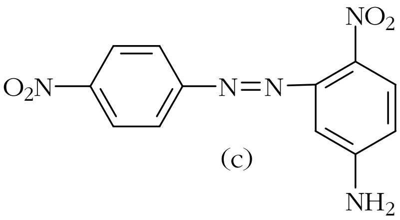
9. In the laboratory, recently, you synthesized para red. You did this by reacting *p*-nitroaniline with excess hydrochloric acid to form its salt. You then reacted this mixture with aqueous sodium nitrite to form the diazonium salt. You then allowed this diazonium salt to react with 2-naphthol to form the dye. The instructions told you to keep the solution of diazonium salt cold and use it quickly to react with the 2-naphthol:

> "To the vigorously agitated suspension of p-nitroaniline hydrochloride, maintained at 5 - 10°, add as quickly as possible a cold solution of 0.86 g (0.013 mole, a 20% excess) of sodium nitrite in 2 - 3 ml of water. Swirl the flask until most of the p-nitroaniline hydrochloride dissolves (about 3 minutes) and allow it to stand a few minutes to complete the diazotization. Proceed at once to the next step.
>
> "Pour the solution of diazotized p-nitroaniline all at once into the chilled alkaline solution of 2-naphthol."

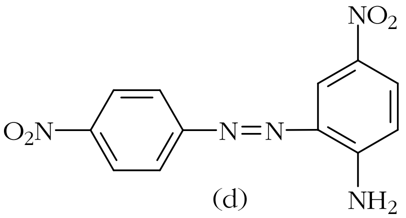
The diazonium salt was kept cold (and used right away) to prevent it from forming an unwanted byproduct. Which of the following compounds is that byproduct?

(a)


(b)




(c)



(d)

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

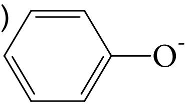
(a) $K_2Cr_2O_7/H_2SO_4$, then $SOCl_2$, then NH_3, then Br_2 and KOH.
(b) PBr_3, then NaN_3, then H_2/Pt.
(c) PBr_3, then NaCN, then $LiAlH_4$, then H_2O.
(d) PBr_3, then Mg, then CH_3NH_2.
(e) $K_2Cr_2O_7$, then $CH_3NH_2/NaBH_3CN$.

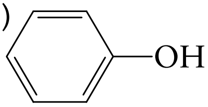
11. Which of the following general methods could you use to synthesize Ph-$CH(CH_3)NH_2$?

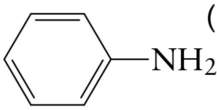
(I) ammonolysis of an alkyl halide, (II) reductive amination of a ketone, (III) reduction of a nitrile, (IV) Hofmann rearrangement of an amide.

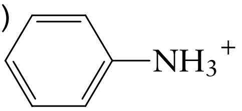
(a) I-IV, (b) I-III, (c) II-IV, (d) I, II, IV, (e) I, III, IV

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

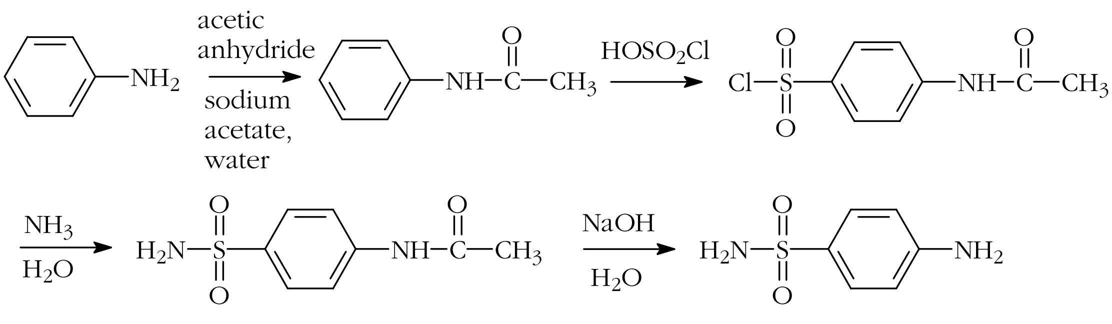
(a)


(b)


(c)


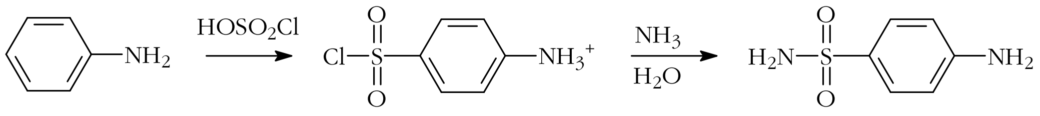
(d)


13. Consider the synthesis of sulfanilamide from aniline shown below.



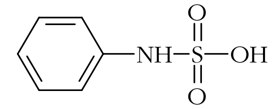
sulfanilamide

The acetyl group is attached to the amine group in the first step of the synthesis and removed in the last step. If the acetyl group were not present when the chlorosulfonic acid is employed in the second step, the synthesis of sulfanilamide would not be successful. In other words the reaction sequence below does not work well.



sulfanilamide

What is the purpose of the acetyl group?
Hint: Try to remember the details of the reaction between aniline and sulfuric acid to get at the answer here. As far as attack on the ring goes, chlorosulfonic acid and sulfuric acid would be expected to behave in a similar way.

(a) The acetyl group blocks the positions ortho to the nitrogen so substitution by the chlorosulfonyl group does not occur there.
(b) The presence of the acetyl group avoids protonation of the -NH_2 group, which would lead to chlorosulfonyl substitution meta to the nitrogen.
(c) The presence of the acetyl group avoids reaction between the -NH_2 group of aniline and chlorosulfonic acid to form  .

(d) (a) and (b).

14. Of the 20 amino acids that are commonly found in polypeptides and proteins

(a) all are α-amino acids. (b) all are β-amino acids. (c) nineteen are α-amino acids and one is a β-amino acid. (d) ten are α-amino acids, eight are β-amino acids, and two are γ-amino acids.

15. Of the 20 amino acids that are commonly found in polypeptides and proteins

(a) nineteen are D-amino acids. (b) nineteen are L-amino acids.
(c) nineteen are R-amino acids. (d) nineteen are S-amino acids.
(e) nineteen occur as racemic mixtures.

16. Of the 20 amino acids that are commonly found in polypeptides and proteins

(a) all are primary amines. (b) all are secondary amines. (c) all are tertiary amines.
(d) all are quarternary ammonium salts. (e) None of the previous answers is correct.

17. When alanine (pI = 6.01) is dissolved in water at pH = 6 the species present in greatest concentration is the

(a) zwitterionic form. (b) anionic form. (c) cationic form.
(d) non-zwitterionic, non-ionic form.

18. When alanine (pI = 6.01) is dissolved in water at pH = 10

(a) the concentration of the anionic form will be greater than the cationic form.
(b) the concentration of the cationic form will be greater than the anionic form.
(c) the concentration of the cationic and anionic forms is equal.
(d) nothing can be said about the relative amounts of cationic and anionic forms based on this information.

19. The amidomalonate method of synthesis of amino acids is based on

(a) the Hell-Volhard-Zelinski reaction. (b) the Sandmeyer reaction.
(c) the acetoacetic ester synthesis. (d) the malonic ester synthesis.

20. Amino acid analysis of the polypeptide angiotensin II shows the presence of eight different amino acids in equimolar amounts: Arg, Asp, His, Ile, Phe, Pro, Tyr, and Val. Partial hydrolysis of angiotensin II with dilute hydrochloric acid yields the following fragments: (1) Asp-Arg-Val-Tyr, (2) Ile-His-Pro, (3) Pro-Phe, (4) Val-Tyr-Ile-His. What is the primary structure of angiotensin II?

(a) Arg-Asp-His-Ile-Phe-Pro-Tyr-Val, (b) Val-Tyr-Pro-Phe-Ile-His-Asp-Arg,
(c) Asp-Arg-Val-Tyr-Ile-His-Pro-Phe, (d) Phe-Pro-His-Ile-Tyr-Val-Arg-Asp,
(e) None of the above answers is correct.

21. The Merrifield technique for synthesizing polypeptides differs from previous techniques in that it employs

(a) DCC (dicyclohexylcarbodiimide) to form peptide bonds between amine and carboxylic acid groups.
(b) the t-butoxycarbonyl (BOC) group to protect the amine group.
(c) a polymer to which the polypeptide is attached throughout its synthesis.
(d) L-amino acids.

22. Which of the following phenomena are most important in determining the secondary structure of proteins?

(a) hydrophobic interactions and salt bridges, (b) hydrogen bonding and disulfide bridges, (c) hydrophobic interactions and disulfide bridges, (d) hydrogen bonding and the double bond character of the peptide (or amide) bond.

23. 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.

24. 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?

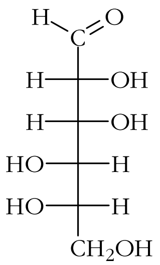
25. Consider the two pentapeptides, I and II, shown below:
I: Val-Leu-Phe-Thr-Ser II: Ser-Thr-Phe-Leu-Val

Select the statement below that correctly identifies their relationship.
(a) The amino acids are joined in reverse order in I and II. In I Val is the N-terminus and Ser is the C-terminus. In II Ser is the N-terminus and Val is the C-terminus. All the amino acids are in the L-family.
(b) The amino acids are joined in reverse order in I and II. In I Val is the C-terminus and Ser is the N-terminus. In II Ser is the C-terminus and Val is the N-terminus. All the amino acids are in the L-family.
(c) I is the mirror image of II. In I Val is the N-terminus and Ser is the C-terminus. In II Ser is the C-terminus and Val is the N-terminus. The amino acids in I are in the L-family; the amino acids in II are in the D-family.
(d) I is the mirror image of II. In I Val is the C-terminus and Ser is the N-terminus. In II Ser is the N-terminus and Val is the C-terminus. The amino acids in I are in the L-family; the amino acids in II are in the D-family.

26. Hemoglobin consists of of an association of four globins (and their attached hemes). This aspect of hemoglobin is referred to as its

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

27. Select the terms that will correctly characterize mannose, which is shown to the right in Fisher projection.



I: monosaccharide, II: disaccharide, III: pentose, IV: hexose, V: aldose, VI: ketose.

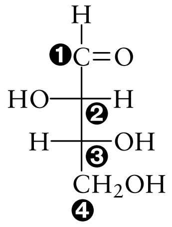
(a) I, III, V, (b) II, IV, VI, (c) I, IV, V, (d) II, III, V, (e) I, III, VI

28. With regard to the mannose shown in question #27, to which family of sugars does this molecule belong.

(a) α, (b) β, (c) D, (d) L

29. Select the correct R/S designations for the two chiral centers in the threose molecule shown in Fisher projection to the right.

(a) 2R, 3R, (b) 2R, 3S, (c) 2S, 3R, (d) 2S, 3S

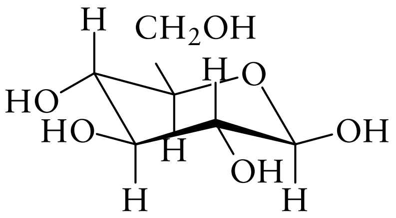


30. The glucose molecule shown to the right below is

(a) the α-anomer, (b) the β-anomer,
(c) the α-epimer, (d) the β-epimer.

31. The glucose molecule shown to the right is a

(a) hemiacetal and a furanose.
(b) hemiacetal and a pyranose.
(c) acetal and a furanose.
(d) acetal and a pyranose.



32. If the glucose molecule shown to the right above is treated with excess CH_3I and Ag_2O which of the OH groups will be methylated.

(a) All of them.
(b) All of the ones directly attached to the ring, but not the CH_2OH in the back.
(c) None of the ones directly attached to the ring; only the CH_2OH in the back.
(d) Only the OH attached to the ring carbon that is attached to the oxygen that is part of the ring.

33. Ordinary table sugar is

(a) glucose, (b) mannose, (c) sucrose, (d) amylose, (e) lyxose