

Department of Chemistry
SUNY/Oneonta

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

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.

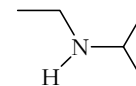
You have 90 minutes. Good luck!

Explanations are in red type.

Answers are highlighted in red.

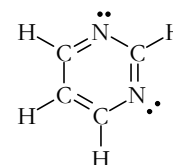
1. The amine shown to the right is a _____ amine.

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



Two carbons are attached to the nitrogen.

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. Choice (d) is incorrect. Choices (b) and (c) would add electrons to a ring that is already aromatic (6 π -electrons). These electrons would be forced into antibonding π -orbitals.

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.

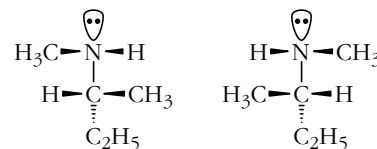
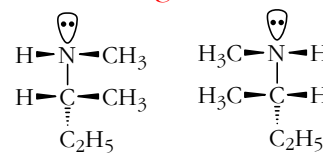
(b) Under ordinary conditions it is possible to isolate 2 stereoisomeric forms of this compound in the laboratory.

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.



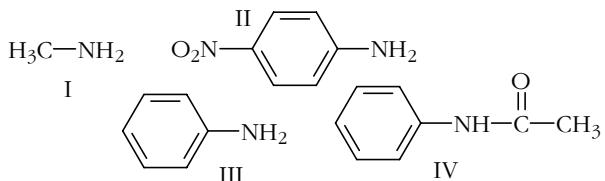
At room temperature tetrahedral nitrogen rapidly inverts its configuration – the unshared pair of electrons passes through the nitrogen and comes out the other side, then repeats the process in the reverse direction – over and over. Consequently, an open chain nitrogen cannot hold its configuration long enough for one to isolate stereoisomers based on its tetrahedral geometry. The only chiral center here that leads to the molecule being chiral is the stereogenic carbon.

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

Owing to their zwitterionic form amino acids have high melting points and even higher boiling points. Diethylamine is an associated liquid and pentane is non-polar.

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



- (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.

IV is the least basic; it is an amide, not an amine. I is most basic; aliphatic amines are usually much more basic than aromatic ones. III is more basic than II because the ring of II holds an electron withdrawing group making the unshared pair of electrons on the amine nitrogen less available for sharing.

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.

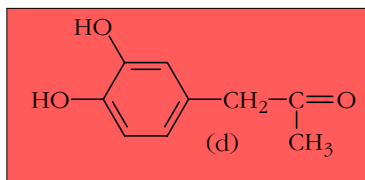
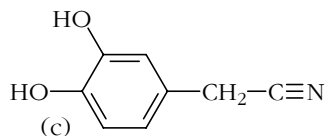
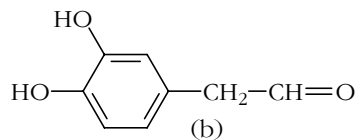
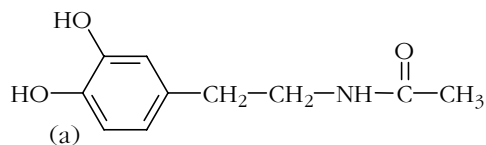
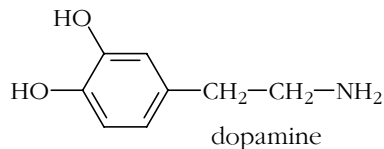
(a) the alkyl amines, (b) the protonated alkyl amines, (c) the aryl amines, (d) the protonated aryl amines.

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.

Hydrolysis of diazonium salts leads to phenols.

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.



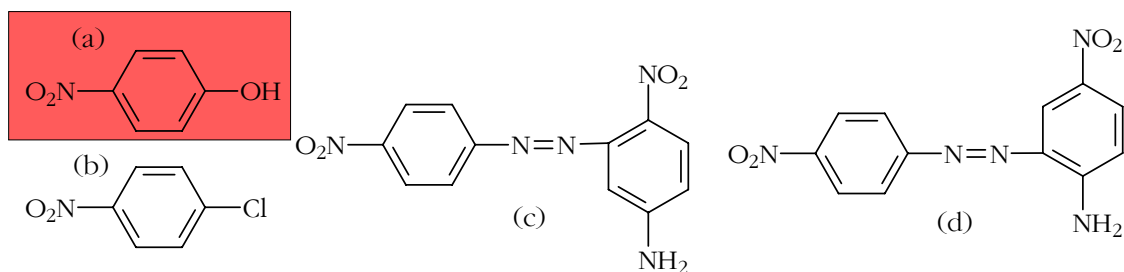
Dopamine can be formed from (a) by hydrolysis of the amide, from (b) by reductive amination using ammonia, and from (c) by reduction using, say, lithium aluminum hydride. It could be made from (d) but not in a simple way. Starting with (d) one could use the haloform reaction to convert the methyl ketone to (3,4-dihydroxyphenyl)-acetic acid. The acid could be converted to an ester which could then be reduced with DIBAL to give the aldehyde. The aldehyde could then be reductively aminated with ammonia.

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^o, 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?



Diazonium salts react with water to form phenols.

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 .

Butanol is oxidized to butanoic acid. Butanoic acid is converted to the acid chloride.

The acid chloride is converted to the amide. The Hoffmann rearrangement converts the amide to an amine having one less carbon (the carbonyl carbon is lost).

(b) PBr_3 , then NaN_3 , then H_2/Pt .

Butanol is converted to 1-bromobutane. The Br is replaced by N_3 ; this is then reduced to the butylamine.

(c) PBr_3 , then $NaCN$, then $LiAlH_4$, then H_2O .

Butanol is converted to 1-bromobutane. The Br is replaced by CN. The triple bond of the CN is reduced to a single bond. Since CN was added to 4 carbons, there are now five carbons – pentylamine.

(d) PBr_3 , then Mg, then CH_3NH_2 .

Butanol is converted to 1-bromobutane. This is converted to the Grignard reagent, butylmagnesium bromide. A proton on an oxygen or nitrogen is acidic enough to cause butylmagnesium bromide to form butane.

(e) $K_2Cr_2O_7$, then $CH_3NH_2/NaBH_3CN$.

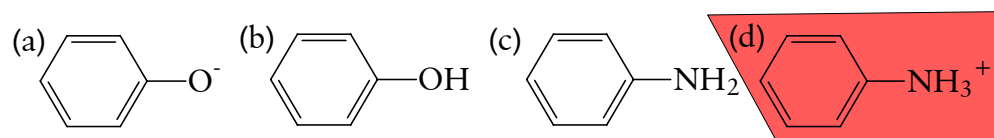
This doesn't make much sense.

11. Which of the following general methods could you use to synthesize Ph-CH(CH₃)NH₂?

(I) ammonolysis of an alkyl halide, This is not a good method owing to the substrate being a secondary halide and the possibility of forming secondary and tertiary amines, but it could be used. (II) reductive amination of a ketone, Reductive amination of acetophenone would give this product. (III) reduction of a nitrile, Reduction of a -CN always gives a -CH₂NH₂ group, not a structural feature of this compound. (IV) Hofmann rearrangement of an amide. α -Methy- α -phenylacetamide would work here.

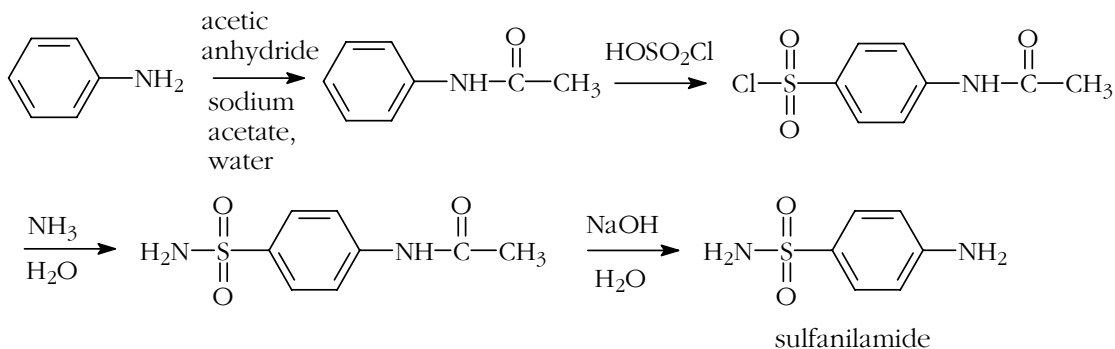
(a) I-IV, (b) I-III, (c) II-IV, (d) I, II, IV, (e) I, III, IV

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

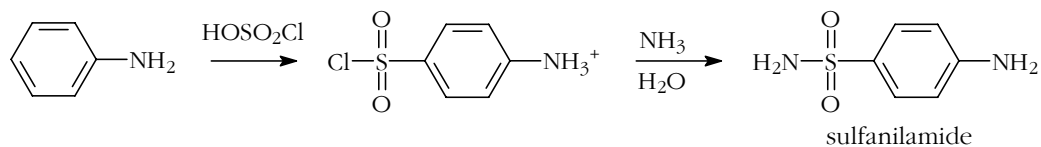


The -NH₃⁺ group is powerfully deactivating.

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



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.



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.

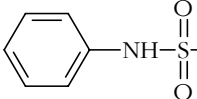
(a) The acetyl group blocks the positions ortho to the nitrogen so substitution by the chlorosulfonyl group does not occur there.

When sulfuric acid sulfonates aniline, sulfanilic acid results. The amino and sulfonic acid groups are para to each other, so sulfonation of the ortho positions is not much of an issue in this case.

(b) The presence of the acetyl group avoids protonation of the $-NH_2$ group, which would lead to chlorosulfonyl substitution meta to the nitrogen.

When sulfuric acid sulfonates aniline, the amine group has already been protonated to form the $-NH_3^+$ group. This group is meta directing when the reaction is an electrophilic substitution where the product is the result of kinetic control. In this case the product is the result of thermodynamic control and the para isomer is the most stable, even though it is not the one formed most quickly.

(c) The presence of the acetyl group avoids reaction between the $-NH_2$ group of aniline

and chlorosulfonic acid to form  Yup.

(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 quaternary ammonium salts. (e) None of the previous answers is correct. Proline is a secondary amine; the others are primary.

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. The zwitterionic form is deprotonated in the basic solution.

- (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.
It just is.
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.
The other answers involve at least one interaction that is mainly involved in tertiary structure.
23. An Edman degradation performed on the pentapeptide Ala-Gly-Pro-Glu-Ile would result in the formation of a phenylthiohydantoin and
The N-terminal residue is clipped off to form the phenylthiohydantoin.
(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?

The idea is to protect (render unreactive) the ends of the amino acids that you don't want to react together to form a peptide bond – these would be the amino of Phe and 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.

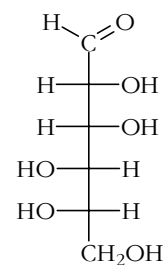
26. Hemoglobin consists of of an association of four globins (and their attached hemes). This aspect of hemoglobin is referred to as its

- (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

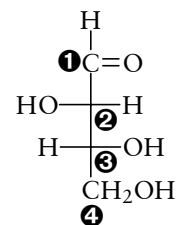


28. With regard to the mannose shown in question #27, to which family of sugars does this molecule belong.

- (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

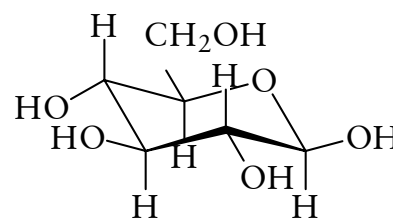


30. The glucose molecule shown to the right below is

(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