

Department of Chemistry & Biochemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #4 - May 2, 2005

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 number, and
- > course number (30032201);

darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

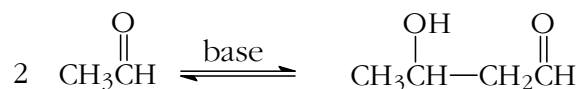
You may use a set of molecular models but no other aids during the exam.

Answer all questions. Each question is worth 3.79 points.

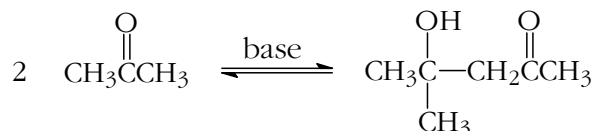
You have 50 minutes. Good luck!

1. The reaction shown to the right is an example of a(n)

- (a) Claisen condensation.
 (b) aldol reaction.
 (c) demerol reaction.
 (d) Knoevenagel reaction.
 (e) Diels-Alder reaction.



2. The reaction shown to the right does not give as good a yield as the similar reaction shown in question #1. A reasonable explanation for this would be that



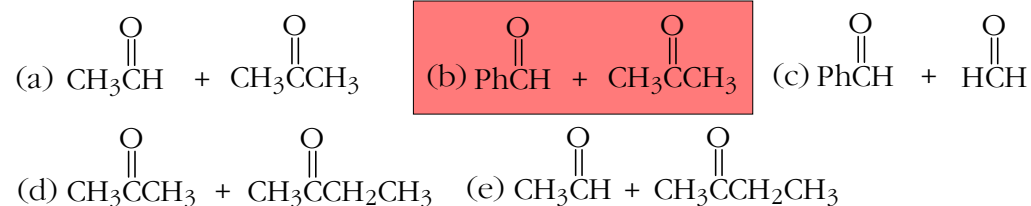
- (a) the aldehydic proton is more acidic than the methyl protons.
 (b) the product formed from acetone undergoes a subsequent reaction, thus reducing the yield.
 (c) a steric factor is involved as a result of the intermediate (and product) being more crowded in these reactions and the ketone case is worse than the aldehyde in this respect.
 (d) the ketone has 6 acidic hydrogens while the aldehyde has only 3.
 (e) Trick question, dude! Like, this reaction gives a better yield than the one in question #1.

3. Which of the following describe common situations encountered with aldol reactions?

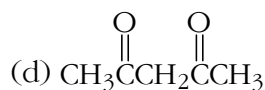
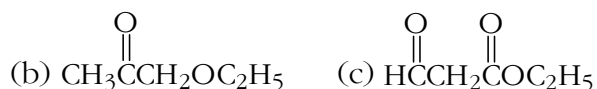
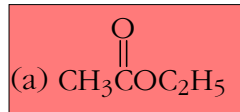
- (I) Product and reactant are in an equilibrium which may favor reactant.
 (II) Product undergoes a spontaneous dehydration, producing a conjugated enone.
 (III) Product undergoes a spontaneous dehydration, producing a non-conjugated enone.
 (IV) Product undergoes a spontaneous reduction, producing a diol.

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

4. Which of the following pairs of compounds would be the most reasonable choice for an attempt at a "mixed" or "crossed" aldol condensation?

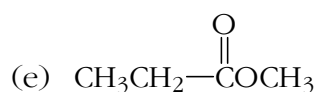
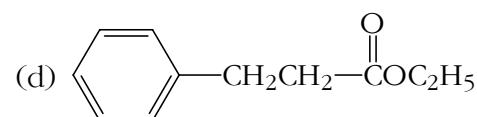
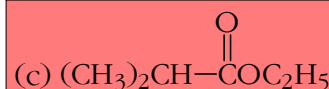
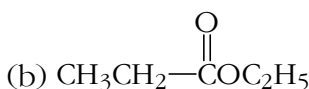
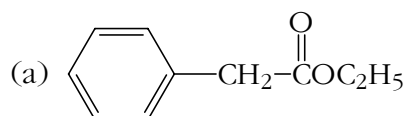


5. To prepare acetoacetic ester (ethyl acetoacetate), which of the following compounds could you use in a Claisen condensation?

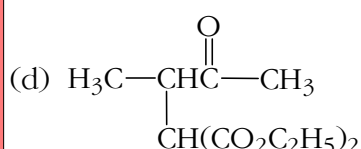
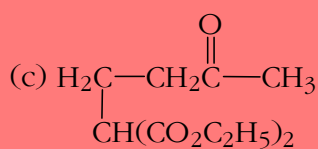
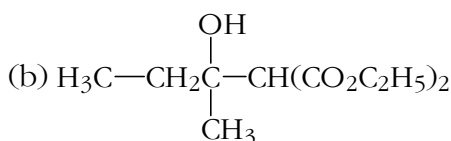
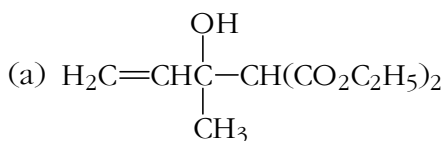
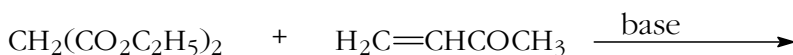


(e) none of these answers is correct

6. Which of the following compounds would not give a good yield in a Claisen condensation?



7. Select the product that is formed in the following Michael addition.

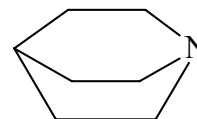


(e) none of these products is formed

8. A frequent aim of synthesis is to make larger molecules from smaller ones. Which of the following syntheses does *not* accomplish this?

(a) aldol reaction, (b) Claisen condensation, (c) Grignard synthesis, (d) Hoffmann elimination reaction, (e) Diels-Alder reaction

9. Quinuclidine, shown to the right, is a _____ amine.



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

10. 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 _b of amine	4	6	10

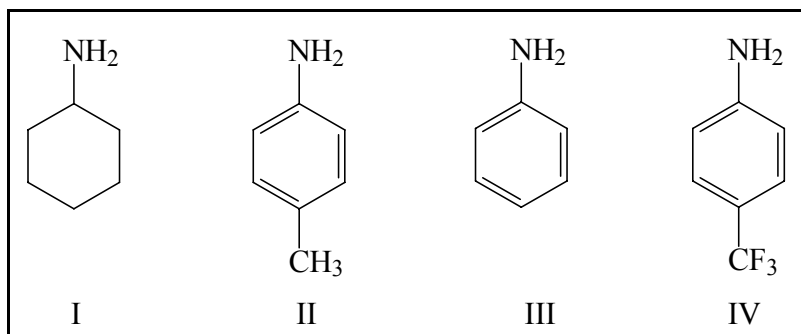
(a) X > Y > Z, (b) Z > Y > X, (c) Y > X > Z, (d) Z > X > Y.

11. If an amine, R₃N:, has a pK_b of 5, the pK_a of its conjugate acid, R₃N⁺-H, is

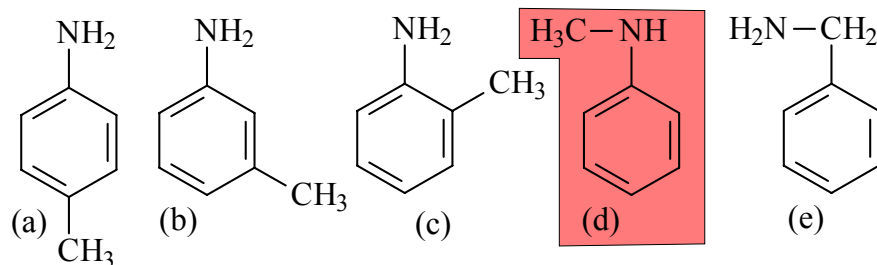
(a) 5, (b) -5, (c) 9, (d) -9, (e) none of the previous answers is correct

12. 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



13. Which of the following compounds is N-methylaniline?

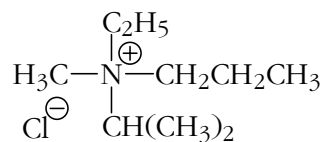


14. Select the major product of the following reaction.

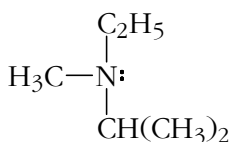


(a) CH₂=C(CH₃)-N(CH₃)₂, (b) (CH₃)₂C(CN)-N(CH₃)₂,
 (c) (CH₃)₂C=N(CH₃)₂ CN⁻, (d) (CH₃)₂CH-N(CH₃)₂,
 (e) None of the above answers is correct.

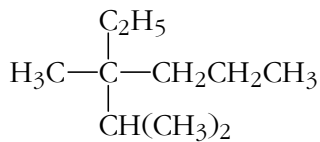
15. For which of the following compounds would it ordinarily be impossible to resolve enantiomers?



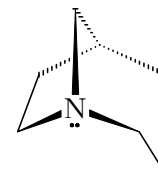
I



II



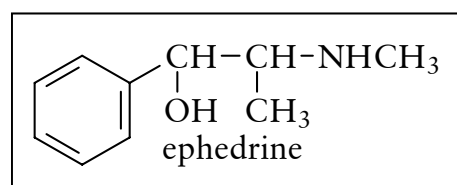
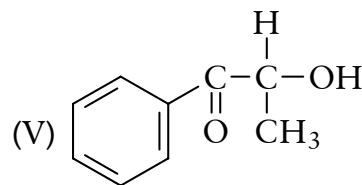
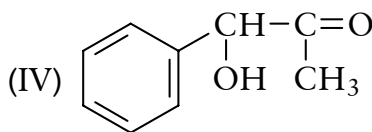
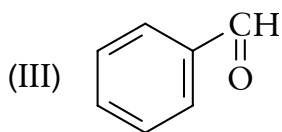
III



IV

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

16. Ephedrine, which is used in the treatment of bronchial asthma, can be synthesized by reductive amination. Which of the following compounds would be employed in this synthesis?

(I) CH_3NH_2 (II) $\text{CH}_3\text{CH}_2\text{NHCH}_3$ 

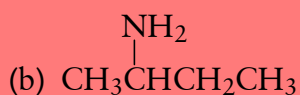
(a)

- I&III, (b) I&IV, (c) I&V, (d) II&III, (e) II&IV, (f) II&V

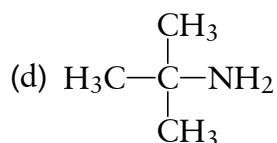
17. Aniline is much less basic than cyclohexylamine. This difference in basicity can be explained by resonance stabilization of

- (a) aniline, (b) protonated aniline (the anilinium cation), (c) cyclohexylamine, (d) protonated cyclohexylamine (the cyclohexylammonium cation)
(e) Bogus question, dude! Resonance has nothing to do with this.

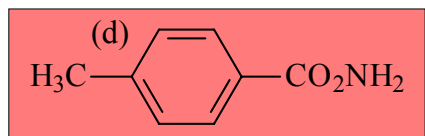
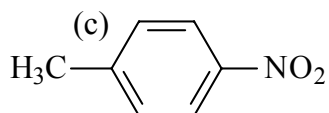
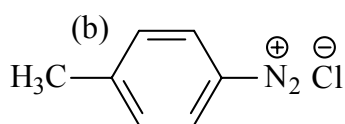
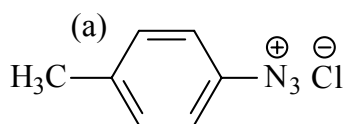
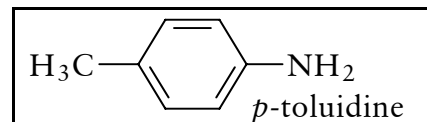
18. Select *sec*-butylamine.

(a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ 

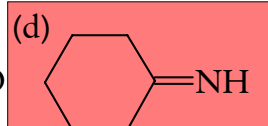
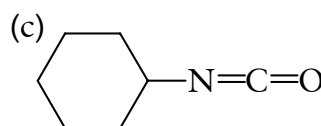
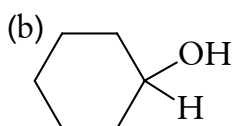
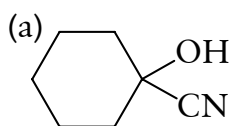
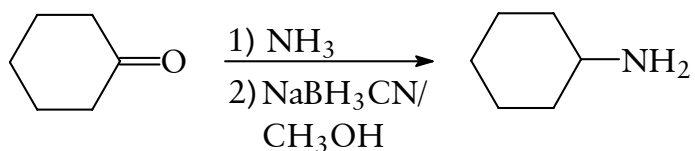
(c) $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{CHCH}_2\text{NH}_2 \\ \diagup \\ \text{H}_3\text{C} \end{array}$



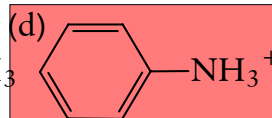
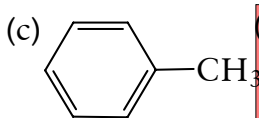
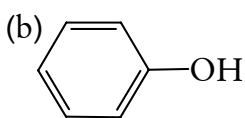
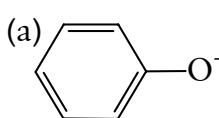
19. What organic starting material would you use to prepare *p*-toluidine by a Hofmann rearrangement?



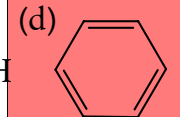
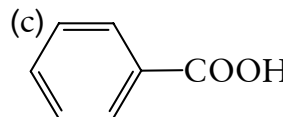
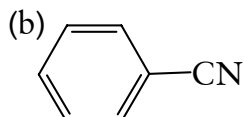
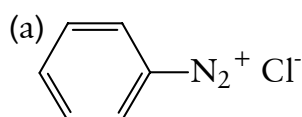
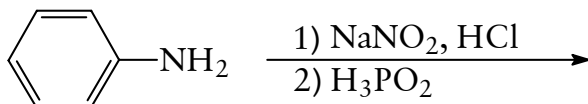
20. Which of the following is an intermediate in the reaction shown?



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



22. Select the major product of the following reaction.



23. 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



24. 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 ₂ COOH]	3.0	+	-	dnm	dnm
lysine [-(CH ₂) ₄ NH ₂]	10.5	-	+	-	+

(e) None of the above answers is correct.

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

- (a) Almost all belong to the L-family of chiral compounds related to L-glyceraldehyde.
 (b) In neutral aqueous solution the zwitterionic form will predominate over the form in which none of the atoms carries a formal charge.
 (c) Each has a characteristic isoelectric point, at which point it will be most soluble in aqueous solution.
 (d) They form salts with both strong acids and strong bases.

26. Sickle cell anemia is caused by

- (a) mosquitoes. (b) malaria. (c) a mutation involving one amino acid residue in the β -globins of hemoglobin. (d) a mutation involving the hemes in hemoglobin.

27. 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.

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

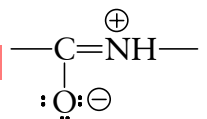
- (a) the amino and carboxyl group of Phe?
 (b) the amino and carboxyl group of Gly?
 (c) the amino group of Phe and the carboxyl of Gly?
 (d) the amino group of Gly and the carboxyl of Phe?

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

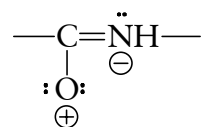
- (a) hydrogen bonds. (b) peptide bonds. (c) disulfide bridges.
 (d) hydrophobic interactions. (e) Velcro.®

30. 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.

31. Linus Pauling is credited with being the first to describe how polypeptide chains in protein molecules arrange themselves in helical patterns (α -helix) or pleated sheets (β -pleated sheet) 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.

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.