

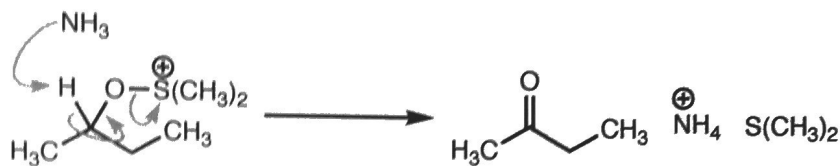
PRACTICE EXAM 1 | CHEM 2313

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Multiple-choice Questions

Choose the best answer among the choices provided. Mark your choices clearly in pencil on your Scantron sheet **and** circle your choices below.

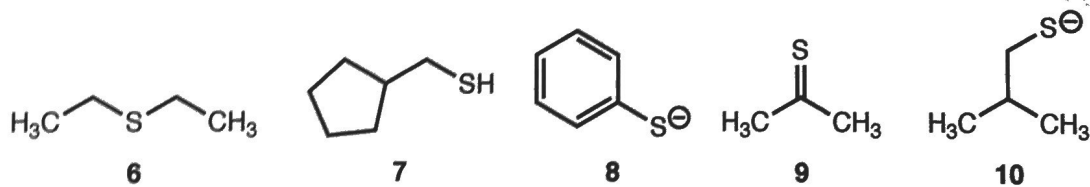
1. What elementary step is depicted in the figure below?



- a. Beta-elimination ([E_β])
 - b. Bimolecular elimination ([E₂])
 - c. 1,2-Rearrangement ([1,2R])
 - d. Bimolecular nucleophilic substitution ([S_N2])
 - e. Nucleophilic addition to a polarized pi bond ([A_{dN}])
2. What localized MO interaction is depicted in the figure below?

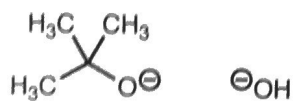


- a. $\sigma \rightarrow \sigma^*$
 - b. $\pi \rightarrow \sigma^*$
 - c. $n \rightarrow \sigma^*$
 - d. $\sigma \rightarrow a$
 - e. $\pi \rightarrow a$
3. Which of the following molecules is the strongest base?

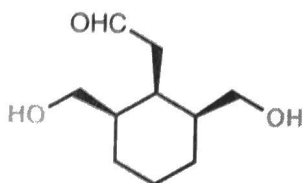


- a. 6
- b. 7
- c. 8
- d. 9
- e. 10

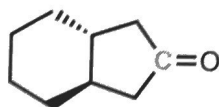
4. What stability factor is most relevant in comparing the basicities of the anions below?



- a. Electronegativity of charge-bearing atom(s)
 - b. Resonance delocalization of charge
 - c. Hybridization of lone-pair-bearing atoms
 - d. Inductive effect
 - e. Steric effect
5. What is the stereotopic relationship between the groups highlighted in blue below?




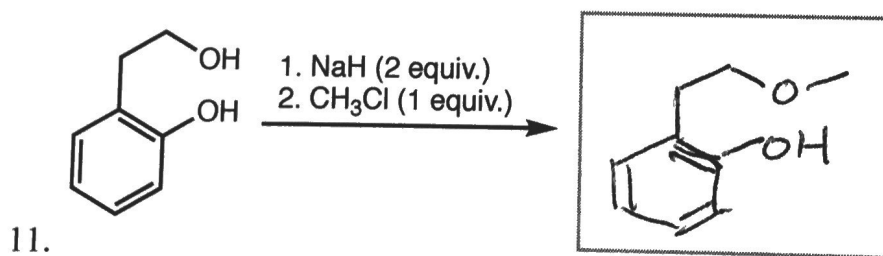
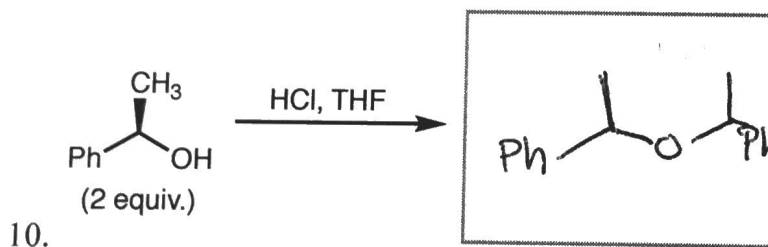
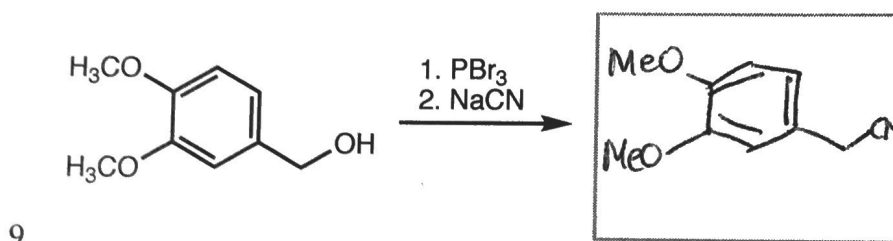
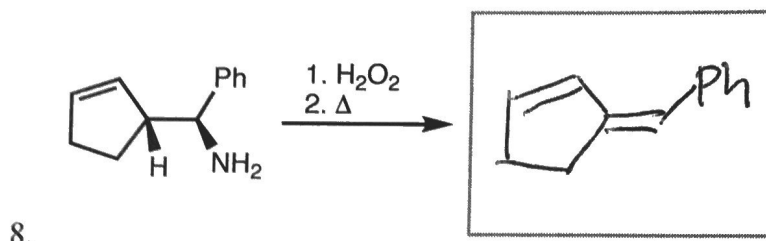
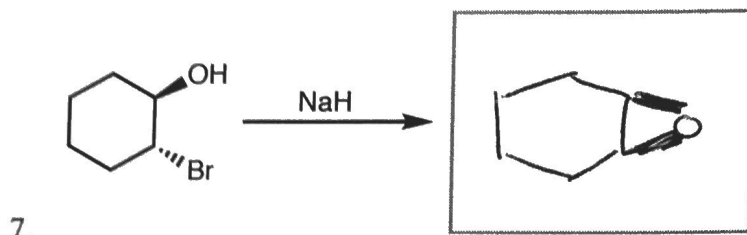
- a. Homotopic
 - b. Enantiotopic
 - c. Diastereotopic
 - d. Constitutionally heterotopic
 - e. Prochiral
6. What is the stereotopic relationship between the faces of the carbonyl carbon highlighted in blue below?



- a. Homotopic
- b. Enantiotopic
- c. Diastereotopic
- d. Constitutionally heterotopic
- e. Prochiral

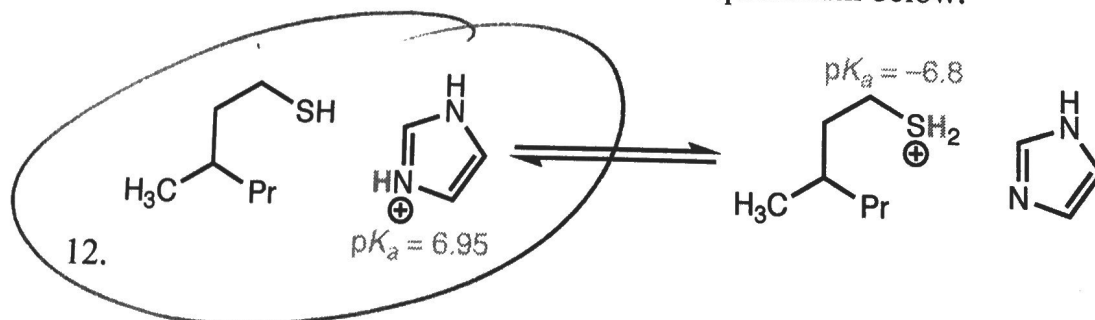
Predict the Products

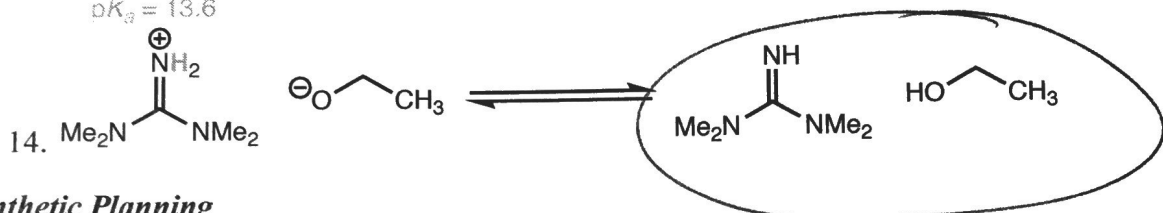
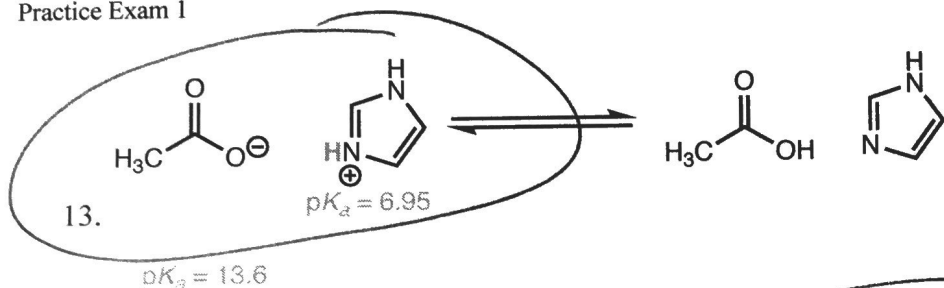
Provide the major organic product for each reaction or sequence of reactions below. Clearly indicate the configurations of all stereocenters, using a wavy bond () to indicate a mixture of configurations.



Acid-base Equilibria

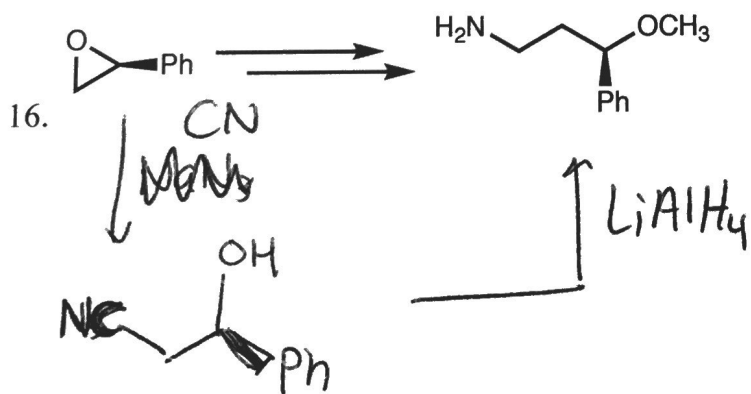
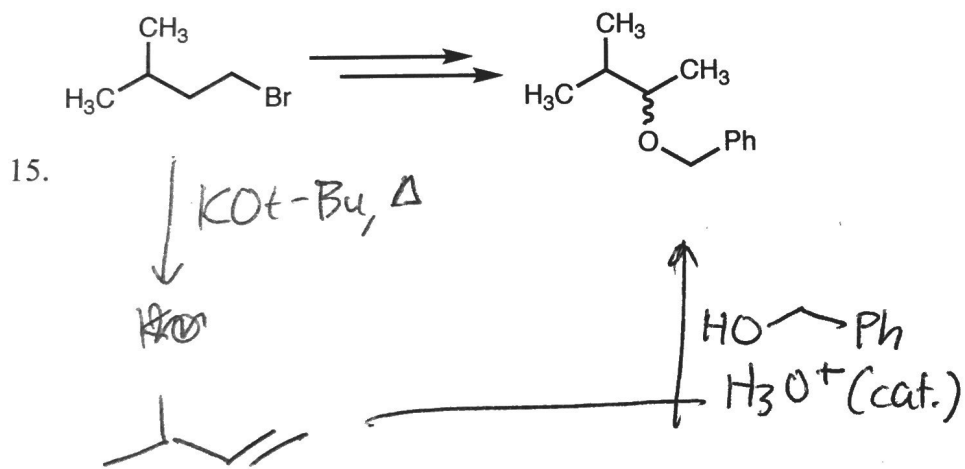
Clearly circle the favored side of each acid-base equilibrium below.

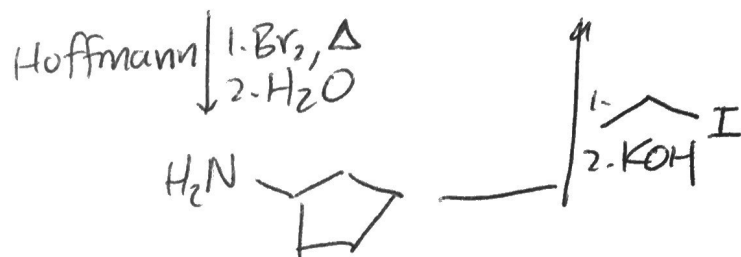
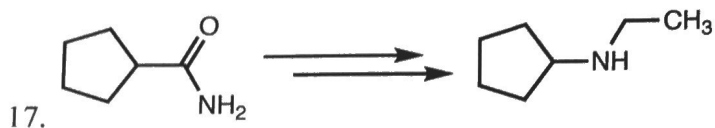




Synthetic Planning

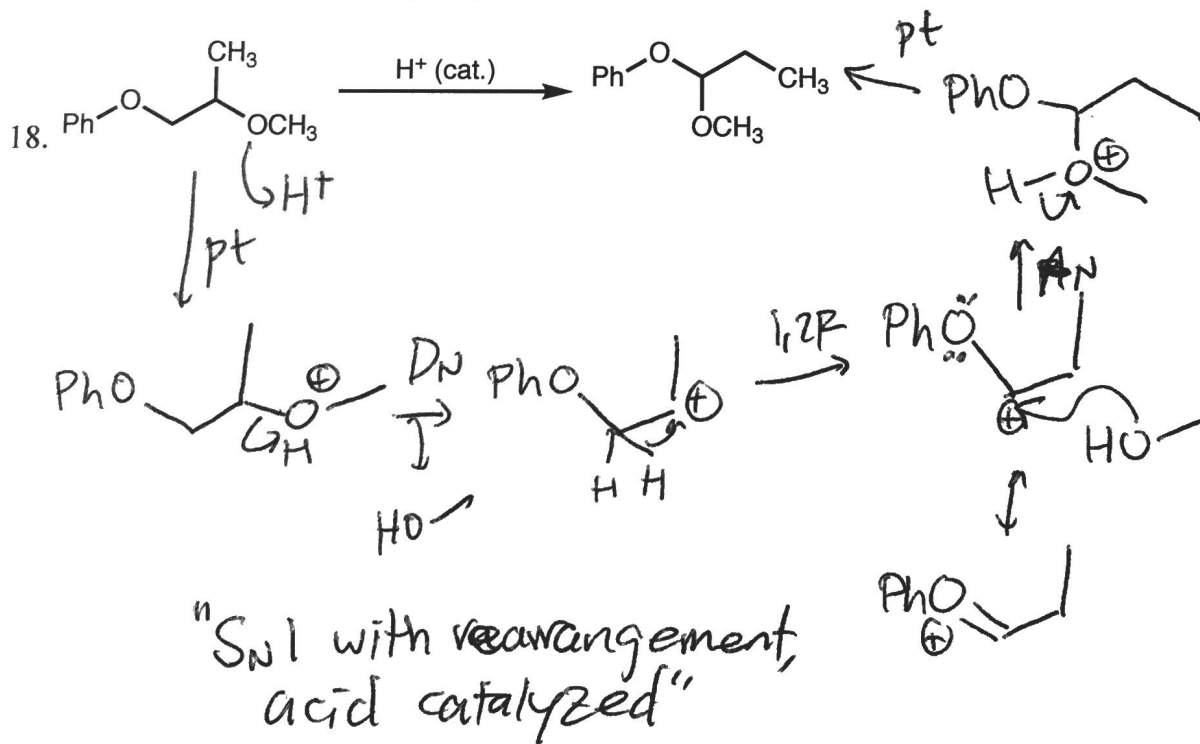
Of the three problems below, **choose two** and provide a sequence of reagents that will accomplish the desired transformation. Include all isolated synthetic intermediates, but do not draw curved arrows or any reactive intermediates.





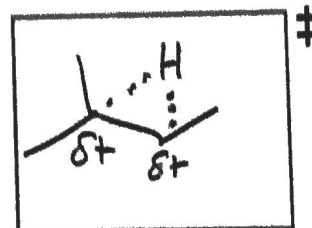
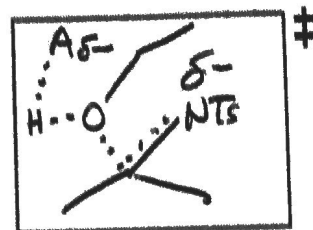
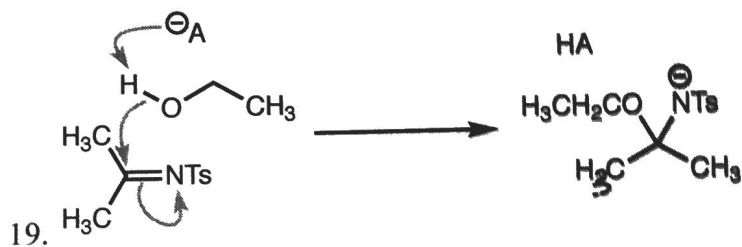
Reaction Mechanisms

Draw a complete mechanism for each reaction including curved arrows and all reactive intermediates. Valid resonance forms should be drawn, but drawing the best resonance form is not necessary. Each step should be one of the ten elementary steps or a valid combination thereof.



Drawing Transition States

Each problem below shows an elementary step with curved arrows. Draw a transition state for the step including all partial bonds and partial charges.



CHEM 2313 EXAM 02

Name KEY

Having read the Georgia Institute of Technology Academic Honor code, I understand and accept my responsibility as a member of the Georgia Tech community to uphold the Honor Code at all times.

Signature _____

There are 6 sections on 8 pages; the pages are numbered. Write all answers legibly and draw all structures clearly with sensible bond angles. Blank pages for scratch work and supplemental tables are included at the end of this exam.

Only pencil, paper, and a model kit are permitted—no electronic devices, including cell phones and calculators.

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<i>Section</i>	<i>Score</i>
I. Multiple-choice Questions	20 /20
II. Predict the Products	20 /20
III. Provide the Reagents	10 /10
IV. Short-answer Questions	12 /12
V. Synthetic Planning	18 /18
VI. Reaction Mechanisms	20 /20
<i>Total</i>	/100

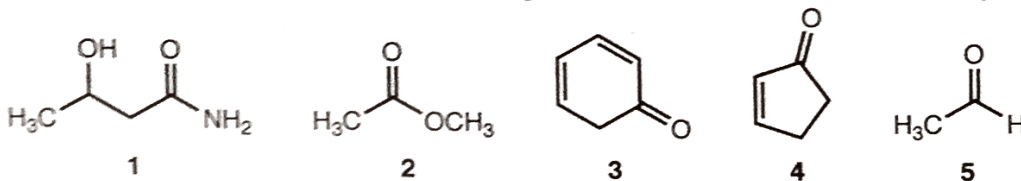
Multiple-choice Questions (20 points; 2 points each)

Choose the best answer among the choices provided. Mark your choices clearly in pencil on your Scantron sheet **and** circle your choices below.

1. Which of the following best describes the key mechanistic steps in the reaction of an acyl chloride and an alcohol to form an ester?

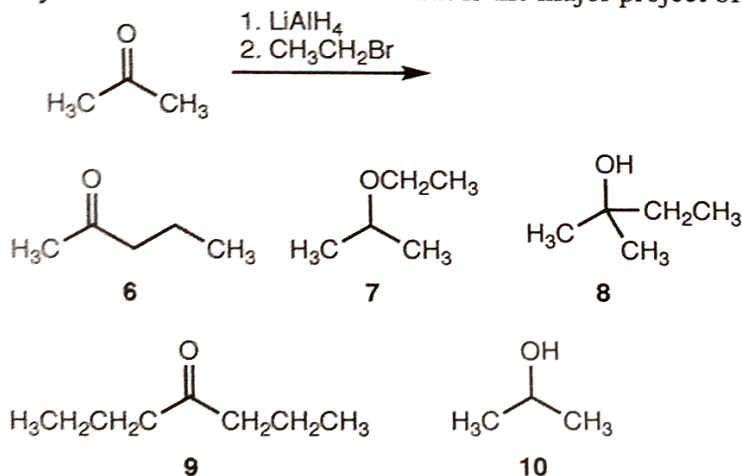
- a. Beta-elimination followed by nucleophilic addition
- b. Nucleophilic addition followed by beta-elimination
- c. Substitution (S_N2) followed by beta-elimination
- d. Substitution (S_N2)
- e. Substitution (S_N1)

2. For which of the following carbonyl compounds is the enol form most heavily favored?



- a. 1
- b. 2
- c. 3
- d. 4
- e. 5

3. A student performed a reduction of acetone with lithium aluminum hydride, but quenched with ethyl bromide instead of acid. What is the major product of this process?

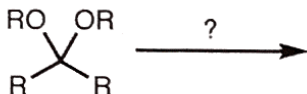


- a. 6
- b. 7
- c. 8
- d. 9

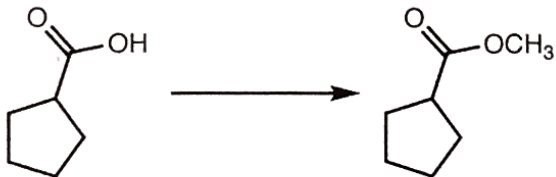
e. 10

4. Which of the following statements *best* explains why an ester is less acidic than an aldehyde?
- The alkoxy group of the ester is more sterically bulky than hydrogen.
 - The alkoxy group of the ester is more inductively electron withdrawing than hydrogen.
 - The ester lacks a hydrogen bound to the carbonyl carbon, but the aldehyde has one.
 - The ester lacks a carbonyl group, but the aldehyde has one.
 - The alkoxy oxygen donates electrons to the carbonyl group, but hydrogen is a much poorer electron-donating group.
5. Which of the following choices correctly lists carboxylic acid derivatives from *most to least* reactive in hydrolysis reactions (nucleophilic acyl substitution with H₂O)?
- Acyl chlorides > esters > amides
 - Acyl chlorides > amides > esters
 - Amides > acyl chlorides > esters
 - Esters > amides > acyl chlorides
 - Esters > acyl chlorides > amides

6. Under which of the following conditions will an acetal react?



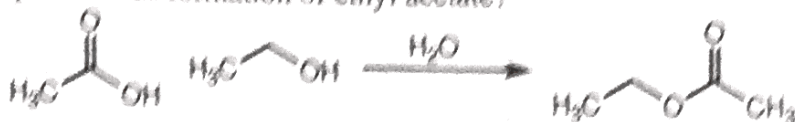
- PhMgBr
 - CH₃Li
 - H₃O⁺, H₂O
 - (*t*Bu)₂CuLi
 - NaOCH₃, HOCH₃
7. Which of the following is the *best* set of reagents to perform the reaction shown below?



- CH₃MgBr
 - H₂SO₄ (cat.), CH₃OH
 - NaOCH₃
 - CH₃OH, NH₃
 - CH₃I, H₂SO₄
8. Which of the following is *not* an electron-donating group?
- OCH₃

- b. $-\text{NH}_2$
- c. $-\text{CHO}$
- d. $-\text{N}(\text{CH}_3)_2$
- e. $-\text{NHCOCH}_3$

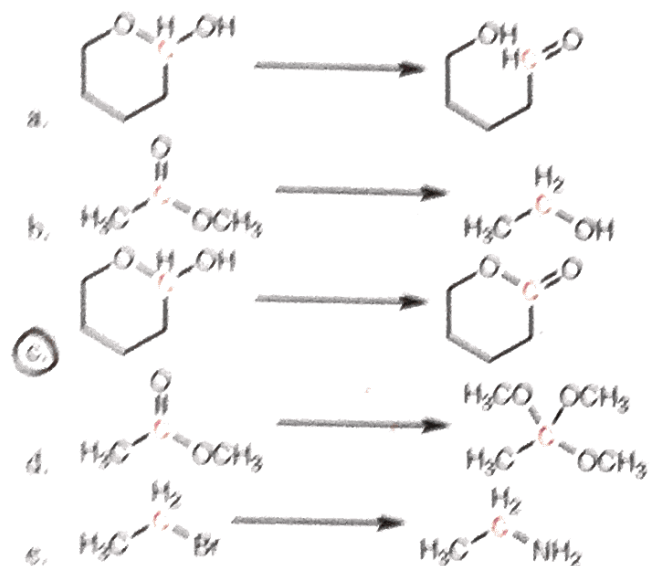
9. Imagine you are working with a mixture of ethanol, acetic acid, and water in a closed flask containing a small amount of acid. Which of the following interventions would promote the spontaneous formation of ethyl acetate?



- I. Adding ethanol
- II. Removing acetic acid
- III. Removing water
- IV. Lowering the pH of the mixture

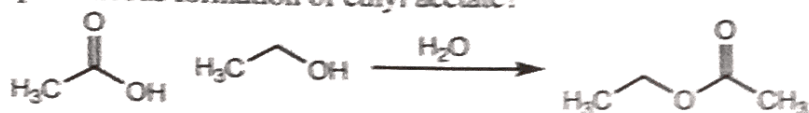
- a. I only
- b. IV only
- c. I and II
- d. I and III
- e. I, III, and IV

10. Which of the following transformations represents an oxidation at the indicated carbon?



- b. $-\text{NH}_2$
- c. $-\text{CHO}$
- d. $-\text{N}(\text{CH}_3)_2$
- e. $-\text{NHCOCH}_3$

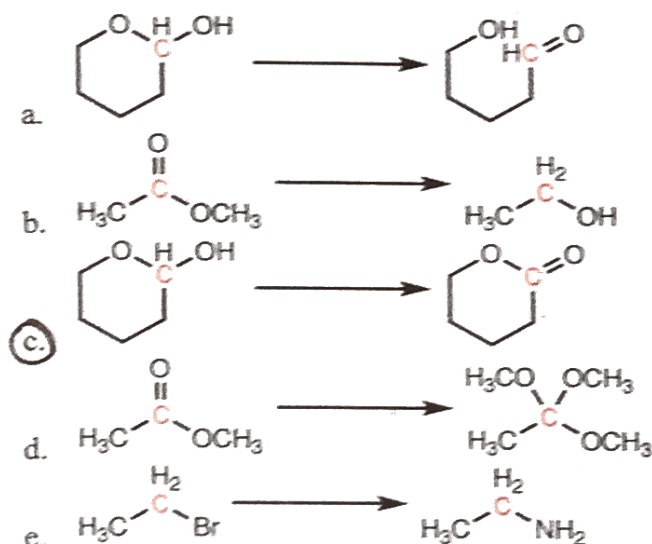
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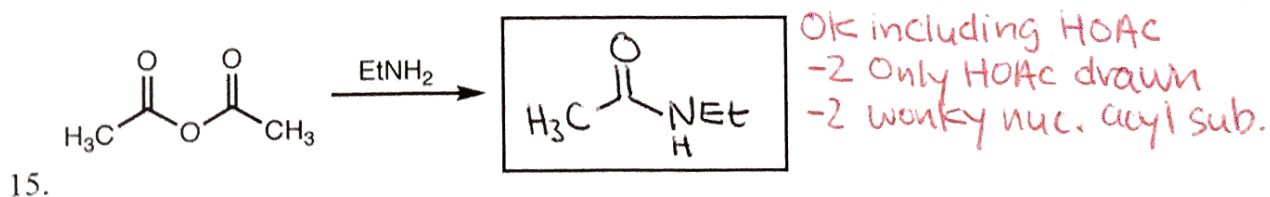
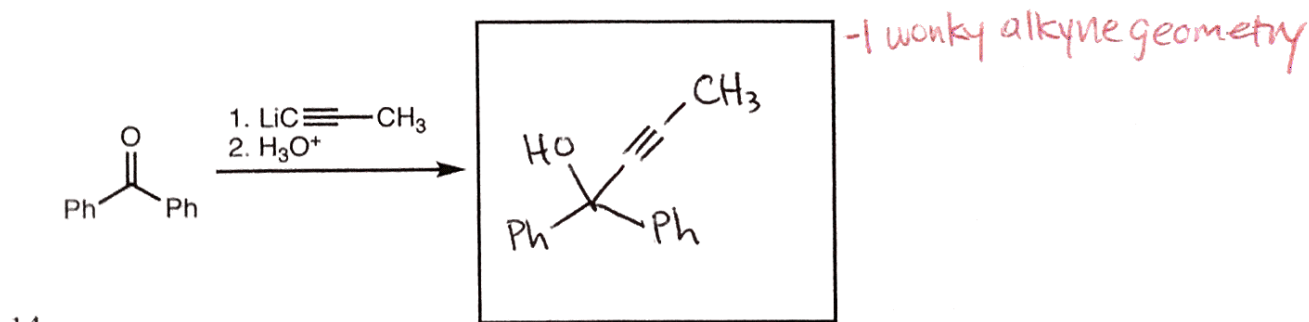
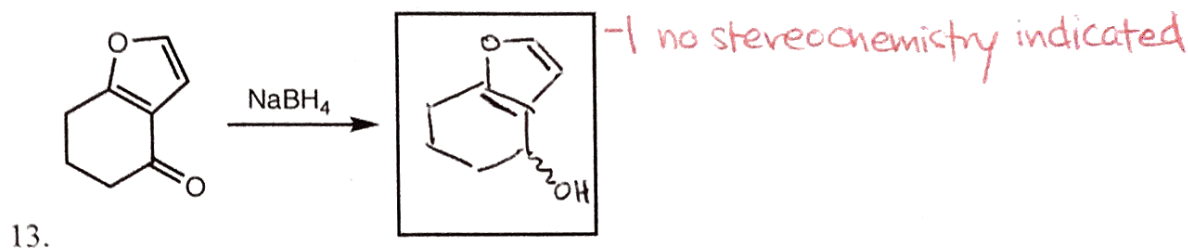
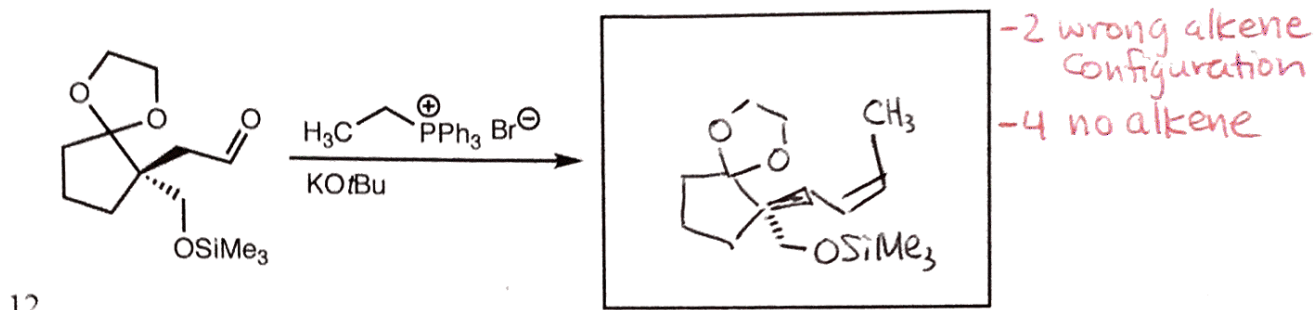
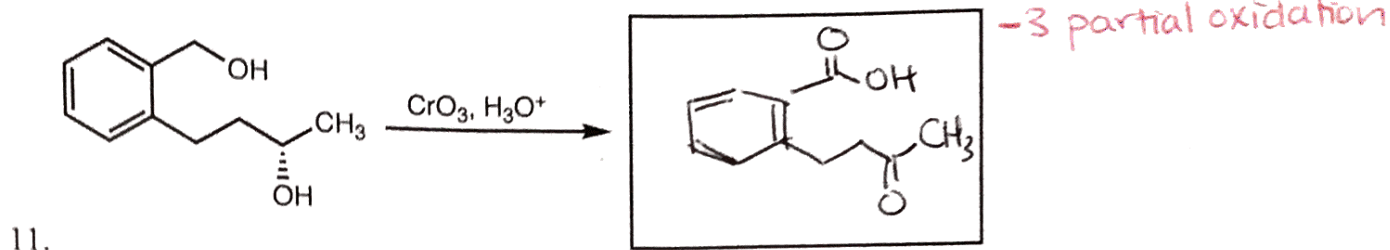
- a. I only
- b. IV only
- c. I and II
- d. I and III
- e. I, III, and IV

10. Which of the following transformations represents an oxidation at the indicated carbon?



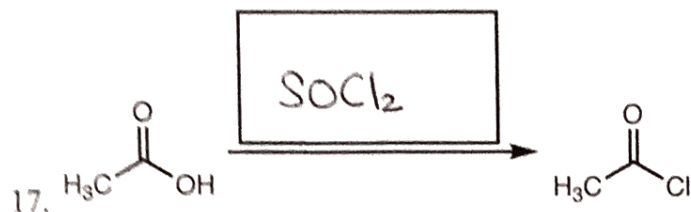
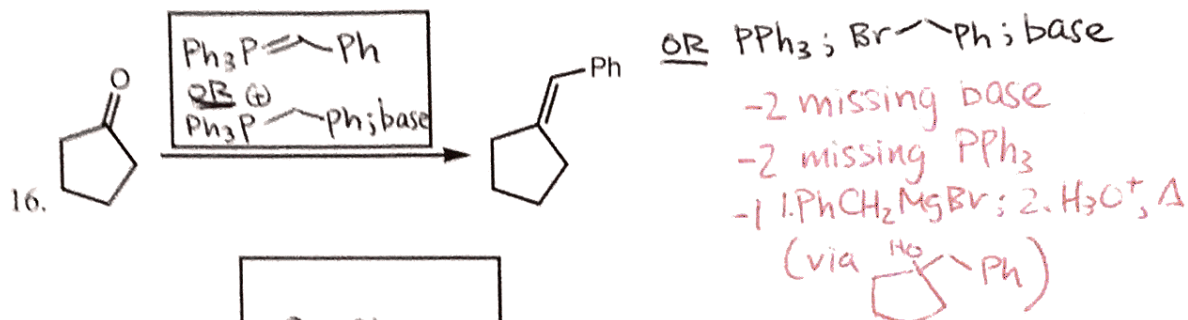
Predict the Products (20 points; 4 points each)

Provide the major organic product for each reaction or sequence of reactions below. Clearly indicate the configurations of all stereocenters, using a wavy bond (\sim) to indicate a mixture of configurations.



Provide the Reagents (10 points; 5 points each)

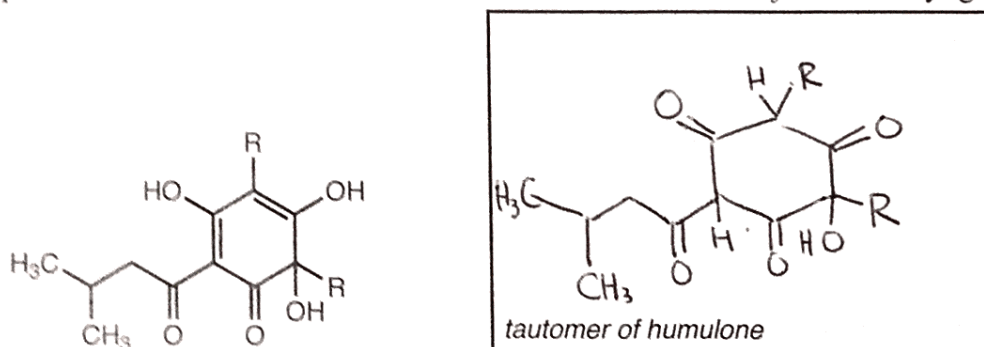
Provide the set of reagents necessary to complete the transformation shown. For reactions that require sequential addition, use numbers ("1. ...; 2. ...") to indicate the order of addition.



Short-answer Questions (12 points; 4 points each)

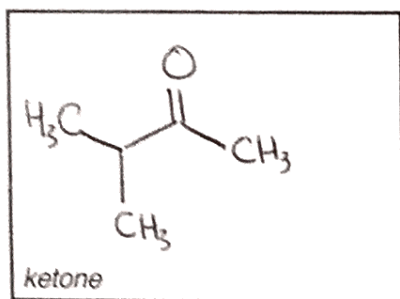
For each question below, provide the requested structure or mechanism.

18. Humulone is a bittering compound present in hops. An abbreviated structure of humulone is provided below. Draw a tautomer of humulone that contains *four* carbonyl groups.



OK NO stereochemistry
 -1 per missing carbonyl
 -2 everything switched

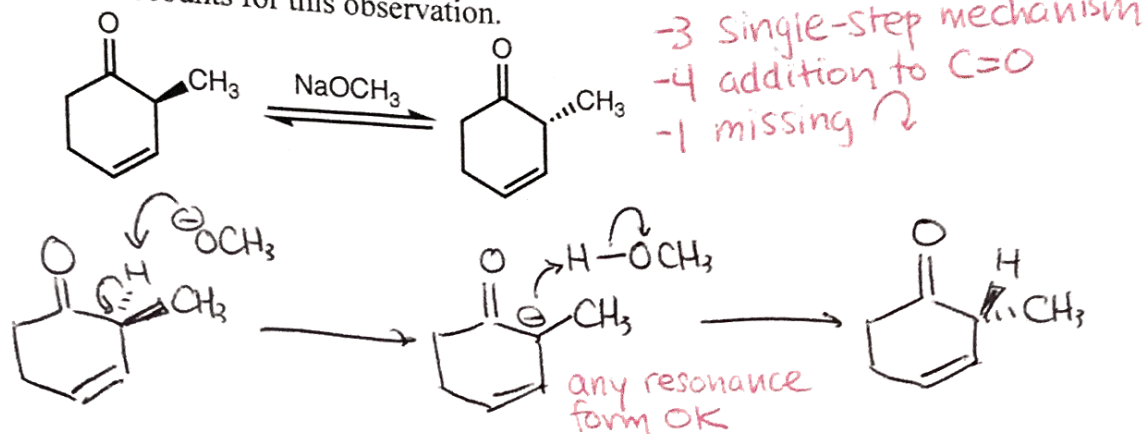
19. Draw the structure of a ketone that will give different products upon treatment with LDA or NaOCH_3 followed by methyl iodide.



or any ketone w/ distinct sets of α -hydrogens with different substitution patterns.

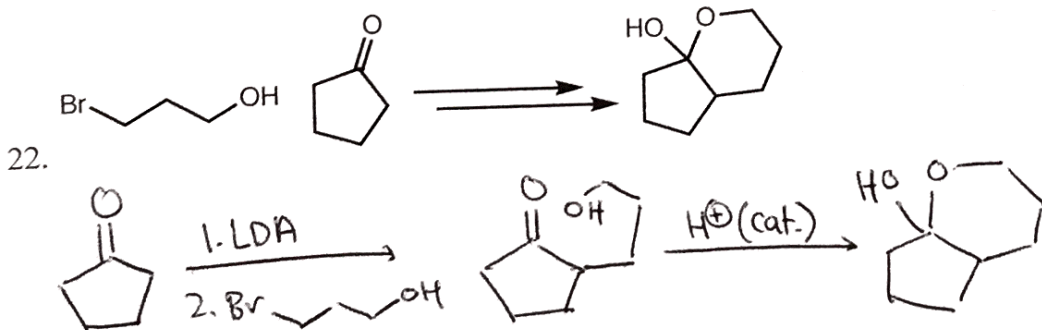
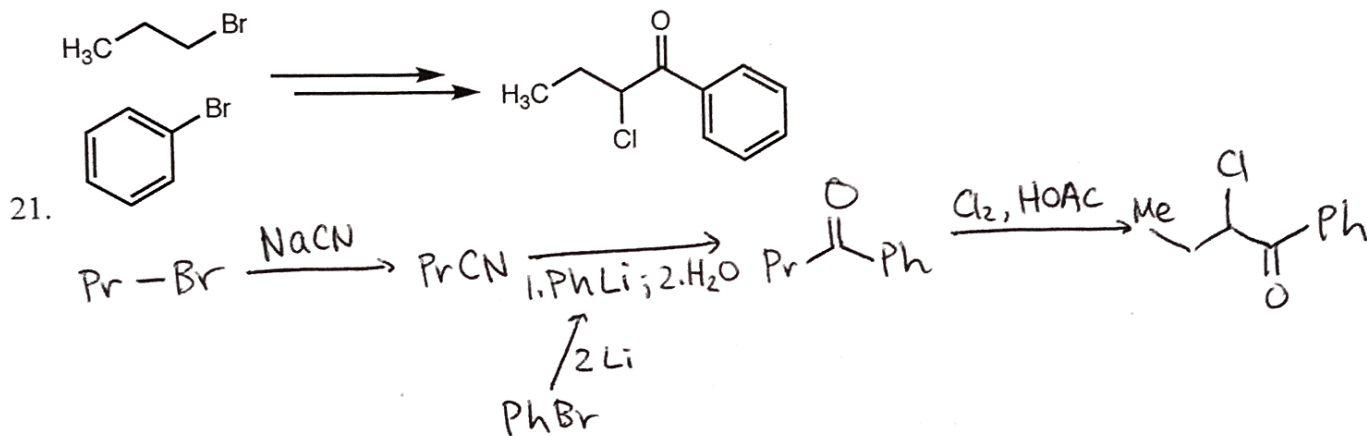
-1 ester
 -2 one set of α -hydrogens

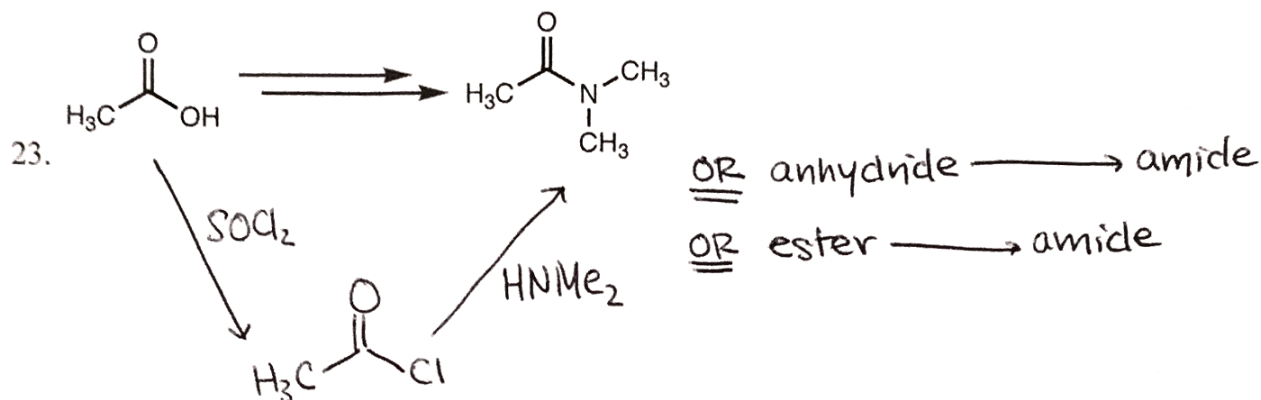
20. The carbonyl compound below was prepared as a single stereoisomer, but quickly lost its optical activity when placed in solution with sodium methoxide. Draw a mechanism with curved arrows that accounts for this observation.



Synthetic Planning (18 points; 9 points each)

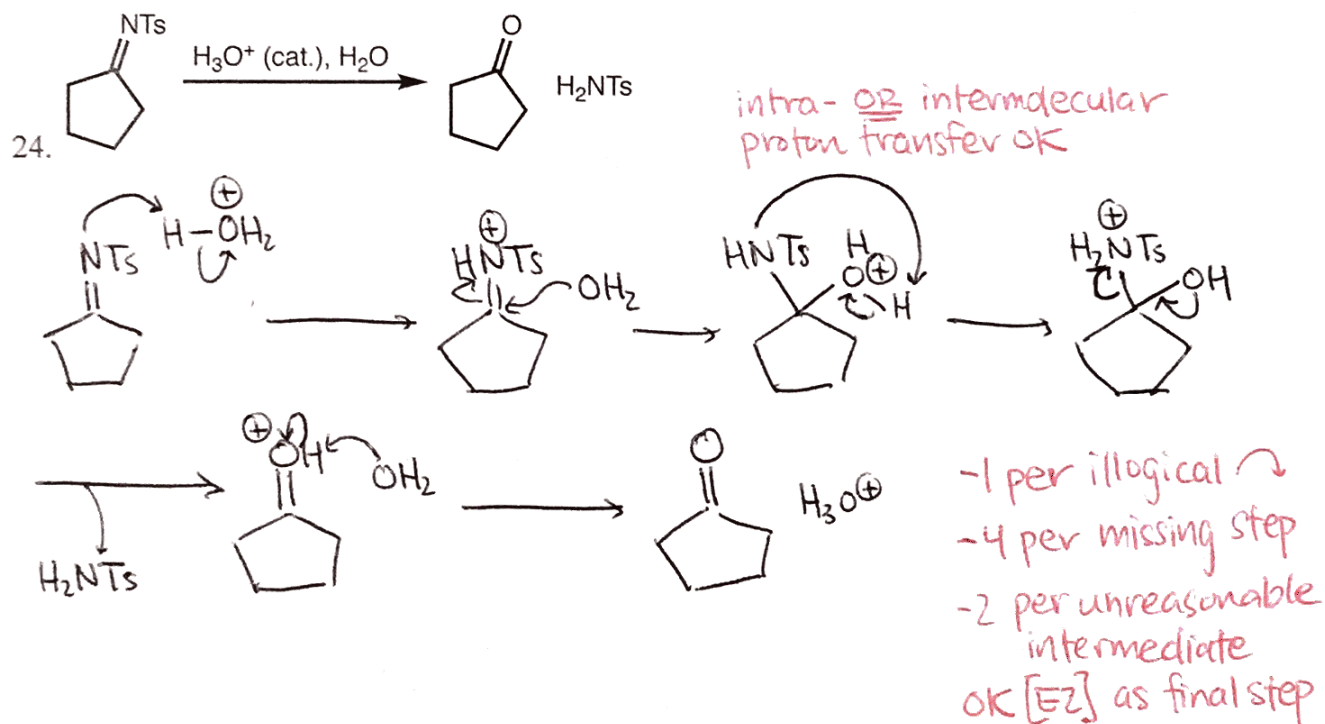
Of the three problems below, *choose two* and provide a sequence of reagents that will accomplish the desired transformation. Include all isolated synthetic intermediates, but do not draw curved arrows or any reactive intermediates.





Reaction Mechanisms (20 points)

Draw a complete mechanism for each reaction including curved arrows and all reactive intermediates. Valid resonance forms should be drawn, but drawing the best resonance form is not necessary. Each step should be one of the ten elementary steps or a valid combination thereof.

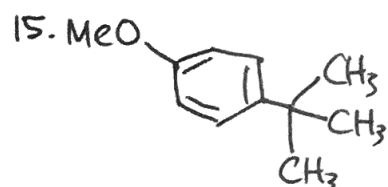
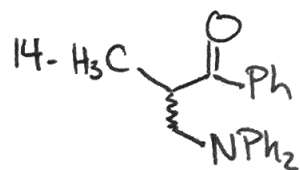
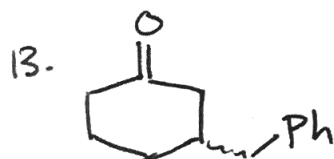
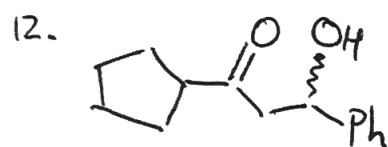
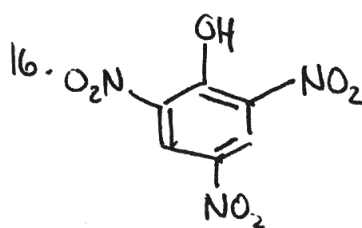
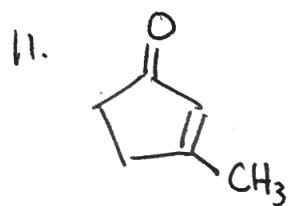


Exam 03 Key - CHEM 2313

Multiple-choice

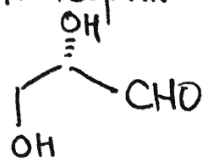
1. E
2. A
3. B
4. D
5. B
6. E
7. C
8. A
9. B
10. A

Predict the Products



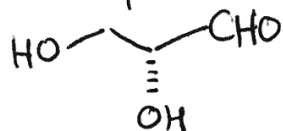
Short-answer I

17. nucleophile:



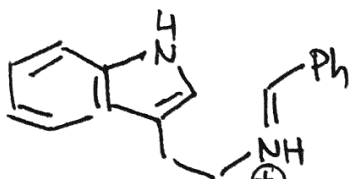
L-glyceraldehyde

electrophile:



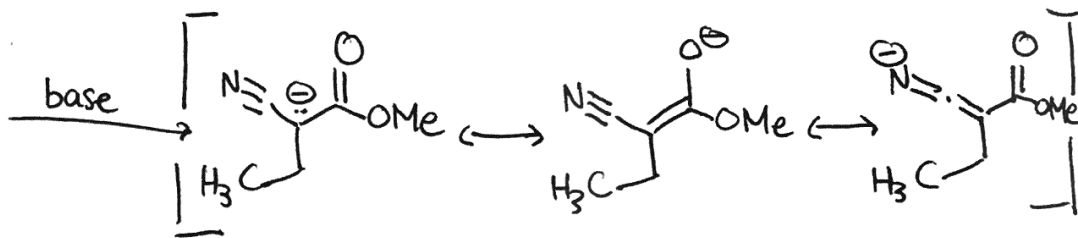
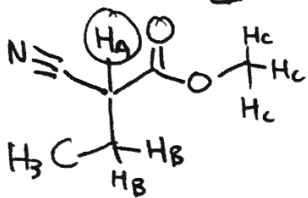
D-glyceraldehyde

18.

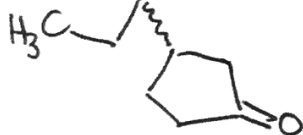


Short-answer II

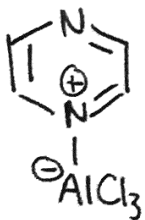
19.



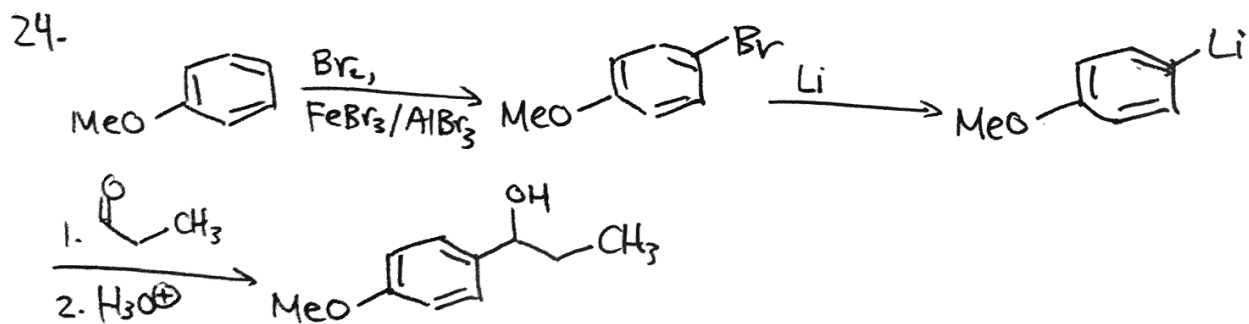
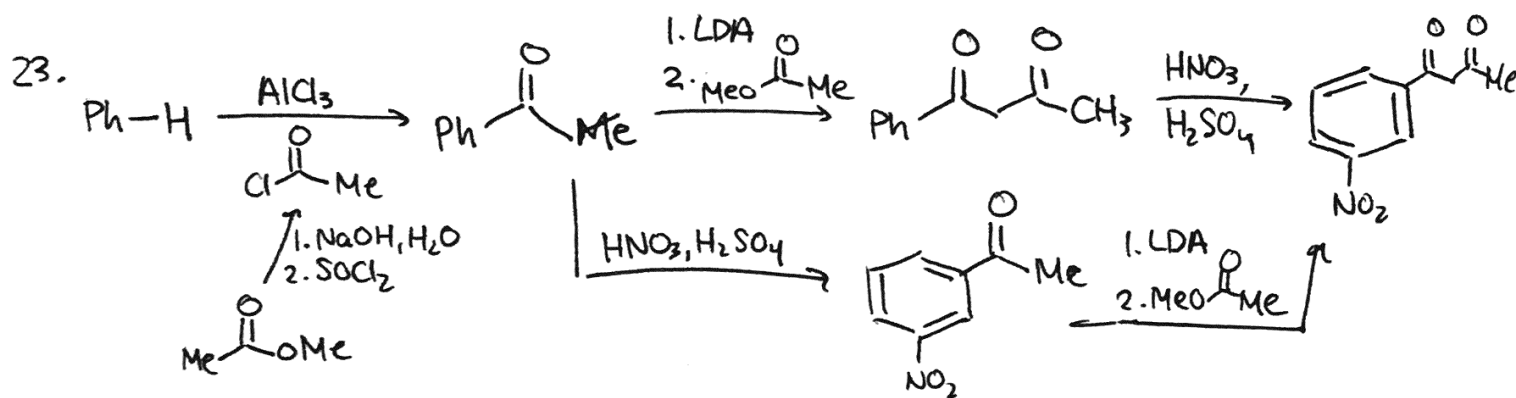
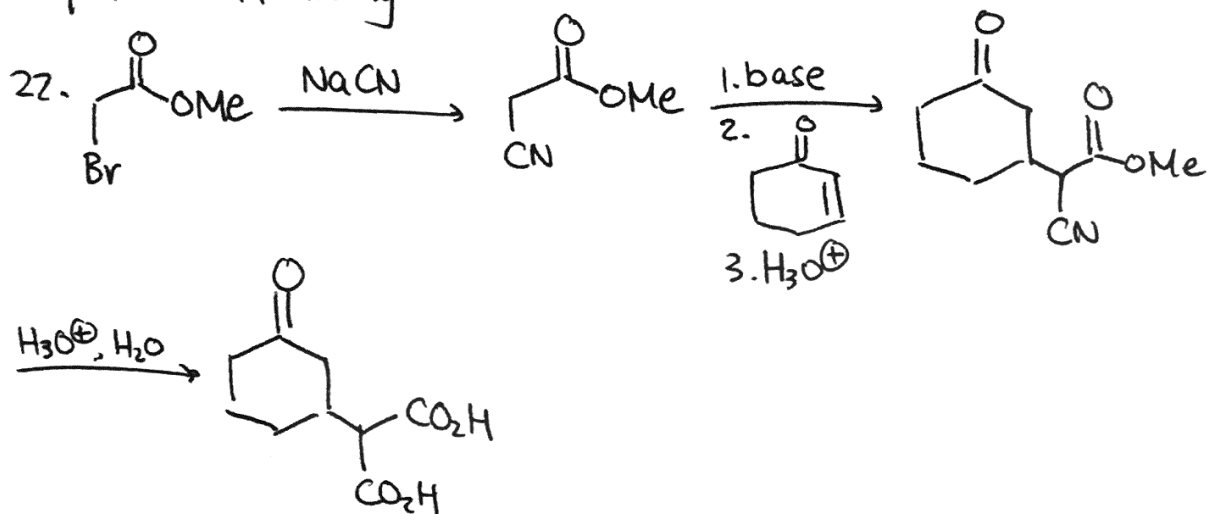
20. NC-CO₂Me (or enolate)



21.

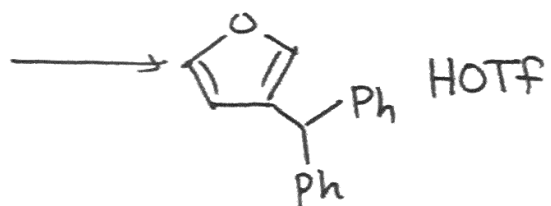
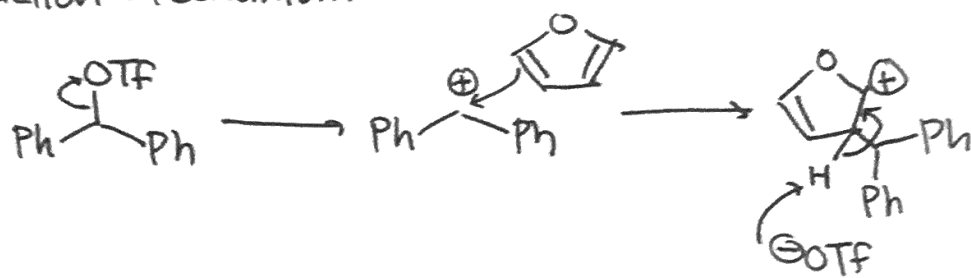


Synthetic Planning



Reaction Mechanism

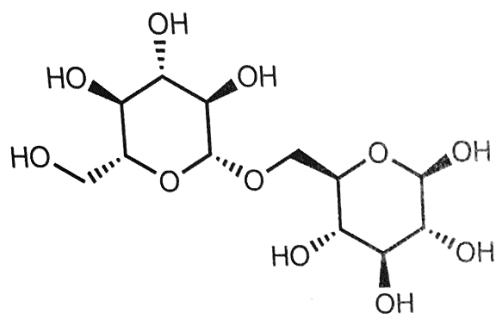
25.



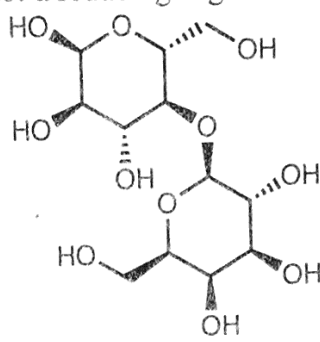
Multiple-choice Questions (20 points; 2 points each)

Choose the best answer among the choices provided. Mark your choices clearly in pencil on your Scantron sheet **and** circle your choices below.

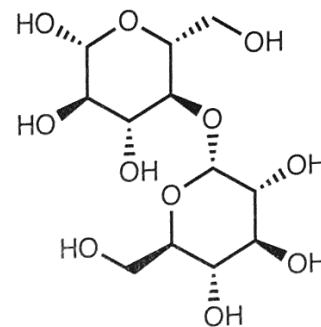
1. Which of the following disaccharides is *not* a reducing sugar?



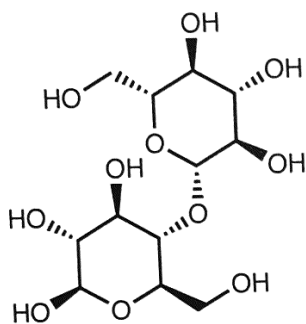
gentiobiose



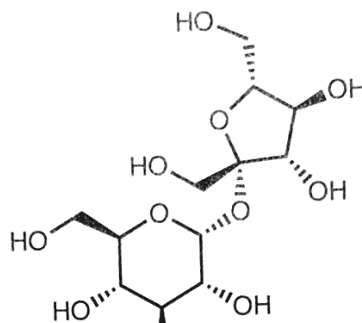
lactose



maltose



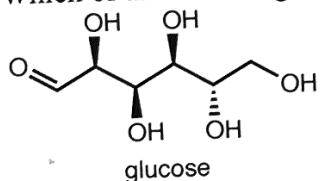
cellobiose



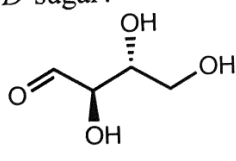
sucrose

- a. Gentiobiose
- b. Lactose
- c. Maltose
- d. Cellobiose
- e. Sucrose

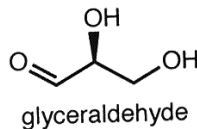
2. Which of the following is a *D*-sugar?



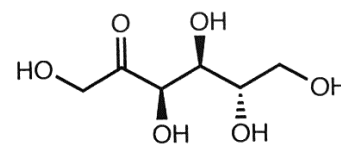
glucose



erythrose



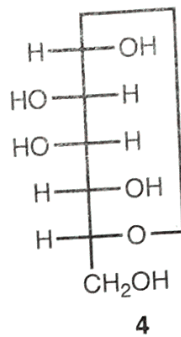
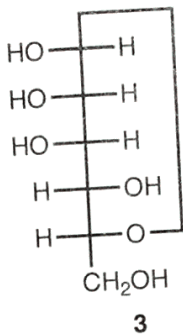
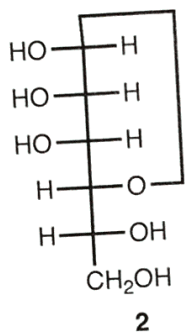
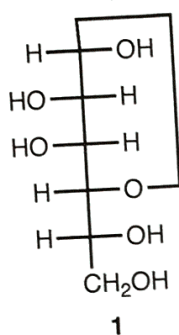
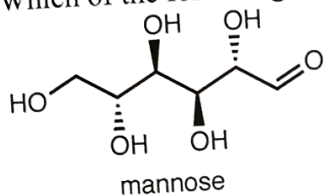
glyceraldehyde



fructose

- a. Glucose
- b. Erythrose
- c. Glyceraldehyde
- d. Fructose
- e. The answer cannot be determined from the information provided.

3. Which of the following Fischer projections represents the α -pyranose form of *D*-mannose?



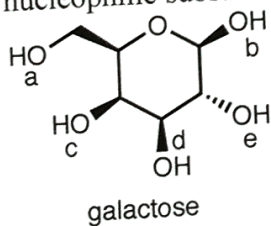
- a. 1
- b. 2
- c. 3
- d. 4

e. The answer cannot be determined from the information provided.

4. Which of the following reaction classes best characterizes the hydrolysis of polysaccharides to form monosaccharides?

- a. Oxidation/reduction
- b. Addition
- c. Elimination
- d. Substitution
- e. Rearrangement

5. In the presence of catalytic acid and ethanol, which of the following hydroxyl groups undergoes nucleophilic substitution?



- a. -OH_a
- b. -OH_b
- c. -OH_c
- d. -OH_d
- e. -OH_e

6. Which of the following amino acids has a nonpolar side chain?

- a. Serine
- b. Glycine
- c. Arginine
- d. Threonine
- e. Cysteine

7. Which of the following statements regarding protein structure is *true*?

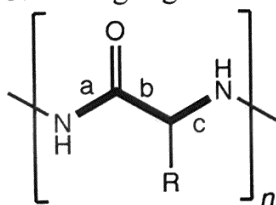
- a. Nonpolar residues tend to cluster in the center of proteins while polar residues tend to be found on the periphery.
- b. Ionic interactions are responsible for holding amino acid residues close to one another in alpha-helices.
- c. Proteins always consist of a single polypeptide chain.
- d. It is more favorable entropically for oil to dissolve in water than it is for the two phases to separate, because the distribution of molecules is more random in the former case.
- e. Most of the surface area of a protein is associated with the active site.

8. A sequence of reactions leading to a dipeptide is described below. Select the answer choice that correctly describes the structure(s) of the product(s). The *N*-terminus is designated “H₂N-” and the *C*-terminus is designated “-OH.”

Valine (Val) is treated with Boc₂O + DMAP followed by DCC, then serine (Ser) is added. The resulting protected dipeptide is treated with trifluoroacetic acid to remove the Boc group.

- a. H₂N-Ser-Val-OH
- b. H₂N-Ser-Ser-OH
- c. H₂N-Val-Val-OH
- d. H₂N-Val-Ser-OH
- e. The process described would lead to a statistical mixture of all four possible dipeptides.

9. A generic polypeptide is shown below with three of the backbone bonds labeled and highlighted. Of the highlighted bonds, which are capable of free rotation?



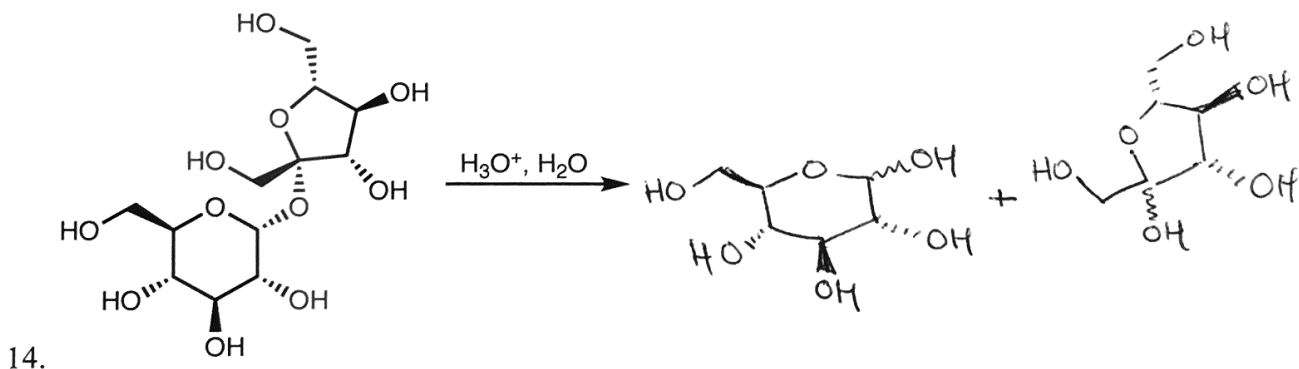
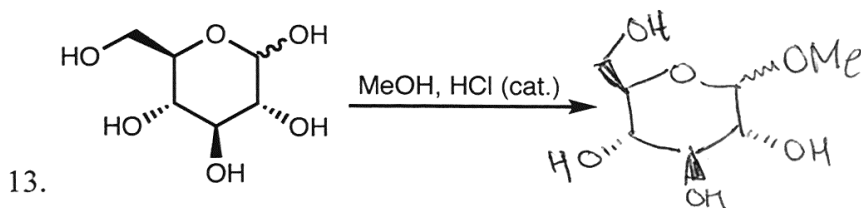
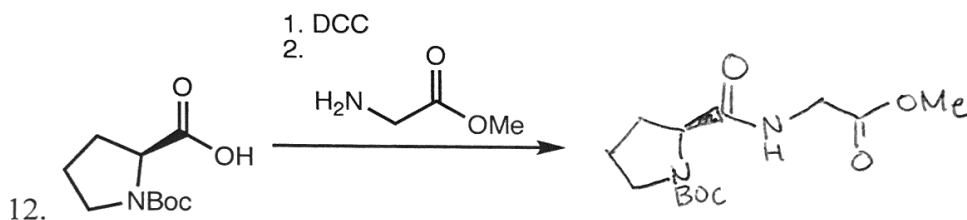
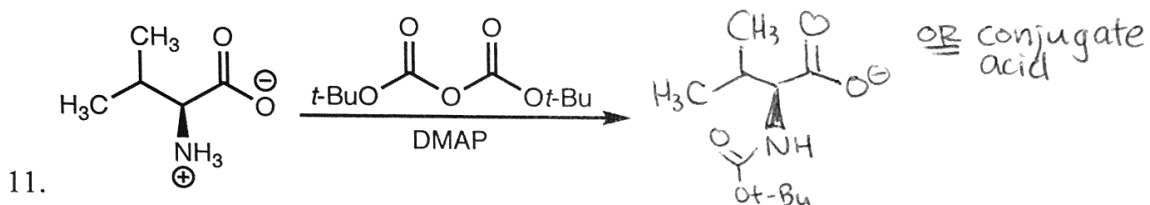
- a. Bond (a) only
- b. Bond (b) only
- c. Bond (c) only
- d. Bonds (a) and (c)
- e. Bonds (b) and (c)

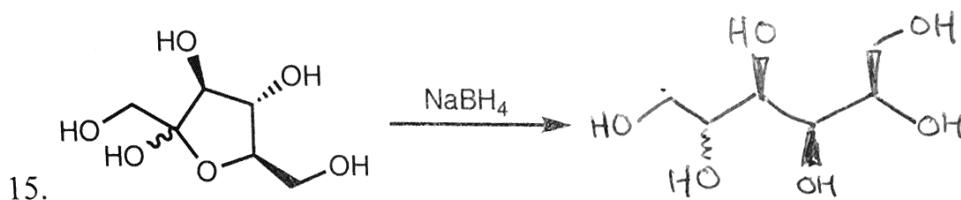
10. Which of the following amino acids is *most likely* to serve as one of the catalytic residues in an enzyme?

- a. Leucine
- b. Histidine**
- c. Valine
- d. Glycine
- e. Alanine

Predict the Products (20 points; 4 points each)

Provide the major organic product for each reaction or sequence of reactions below. Clearly indicate the configurations of all stereocenters, using a wavy bond (\sim) to indicate a mixture of configurations.

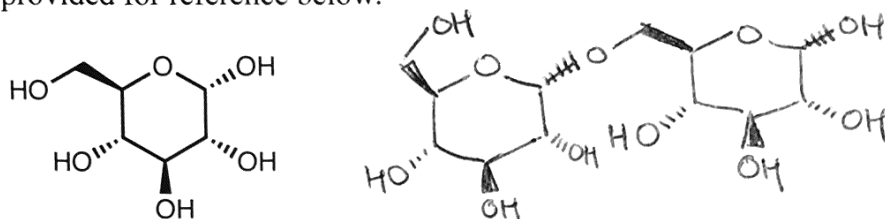




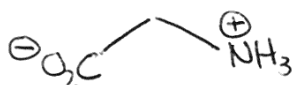
Short-answer Questions (30 points; 5 points each)

For each question below, provide the requested structure, mechanism, or explanation.

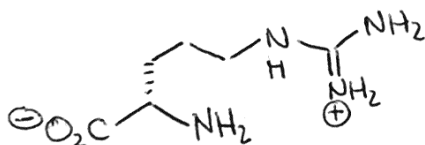
16. The enzyme α -amylase catalyzes the cleavage of $\alpha(1 \rightarrow 4)$ linkages in polysaccharides. When amylase operates on the branched polysaccharide amylopectin, it cleaves all of the $1 \rightarrow 4$ linkages, leaving only disaccharides containing $\alpha(1 \rightarrow 6)$ glycosidic bonds. Draw the structure of these disaccharides, which consist of glucose monomers. The structure of α -D-glucose is provided for reference below.



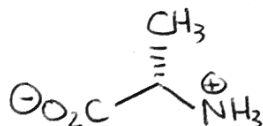
17. Provide the structure of the dominant ionization state of the amino acid glycine at a pH of 5.3. See the reference table at the end of the exam.



18. Provide the structure of the dominant ionization state of the amino acid arginine at a pH of 9.4. See the reference table at the end of the exam.



19. Provide the structure of the dominant ionization state of the amino acid alanine at a pH of 7.4.

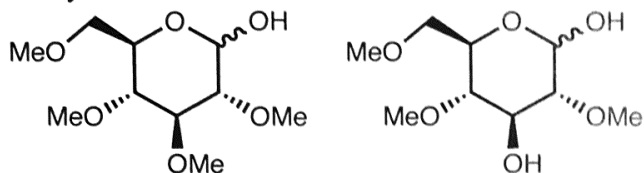


20. Reductions of aldoses to polyols using sodium borohydride go to completion even though the cyclic forms of aldoses (which are unreactive toward NaBH_4) are heavily favored. Explain why this reaction works despite the fact that the open-chain form is disfavored.

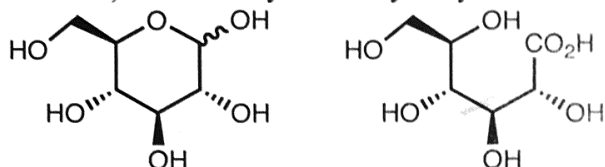
The small amount of open form present is consumed by NaBH_4 , causing more open form to form (based on Le Châtelier's Principle). This new open form is then consumed, etc. until no starting material remains.

Analysis of a Disaccharide (10 points)

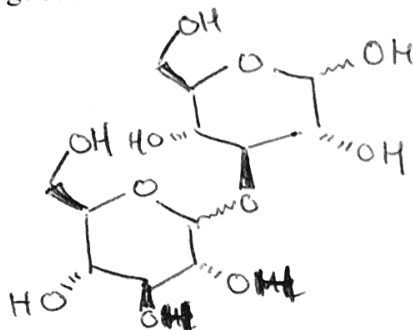
21. Exhaustive methylation of an unknown disaccharide followed by acidic hydrolysis afforded the methylated monosaccharides below.



In a separate series of reactions of the unknown disaccharide, weak oxidation (using aqueous bromine) followed by acidic hydrolysis afforded the products below.



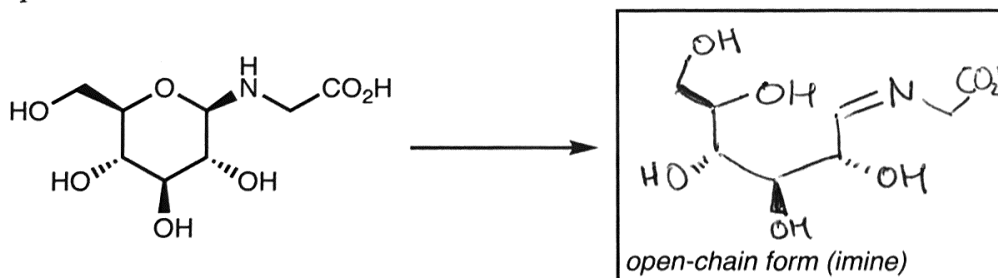
Draw the structure of the unknown disaccharide, using wavy bonds to indicate locations where configuration is ambiguous.



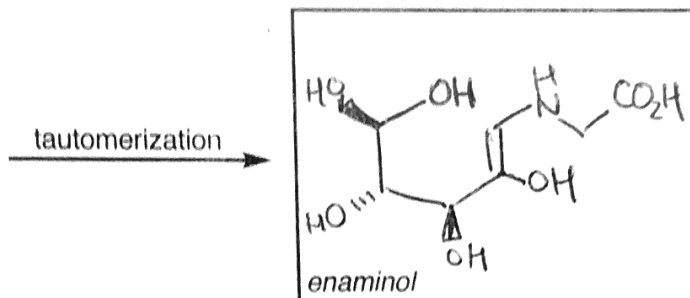
Reaction Mechanism (20 points; 5 points each)

Glycosylamino acids undergo a reaction called the *Amadori rearrangement* under strong heating in water (e.g., under cooking conditions). The problems in this section explore its mechanism.

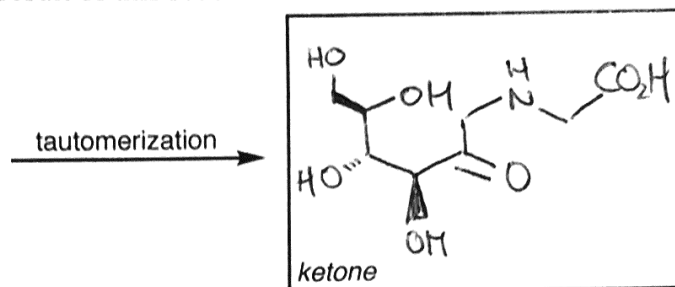
22. The first stage of the mechanism involves ring opening of the glycosylamino acid. Draw the open-chain form of the molecule shown.



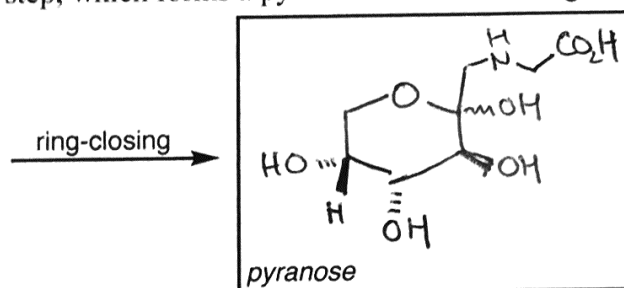
23. The next stage of the mechanism involves tautomerization of the open-chain form. Draw the product of tautomerization, an “enaminol.”

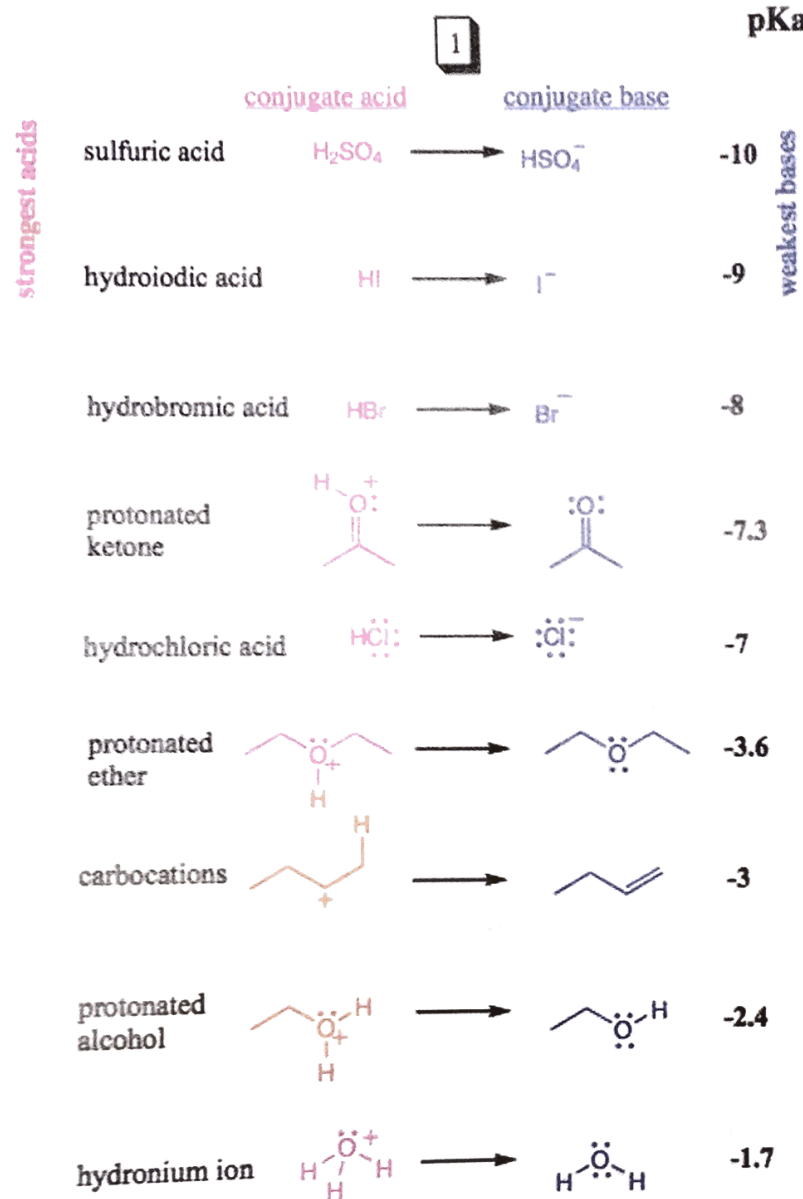


24. The enaminol intermediate then tautomerizes in a *different* way to afford a ketone. Draw the result of this second tautomerization.

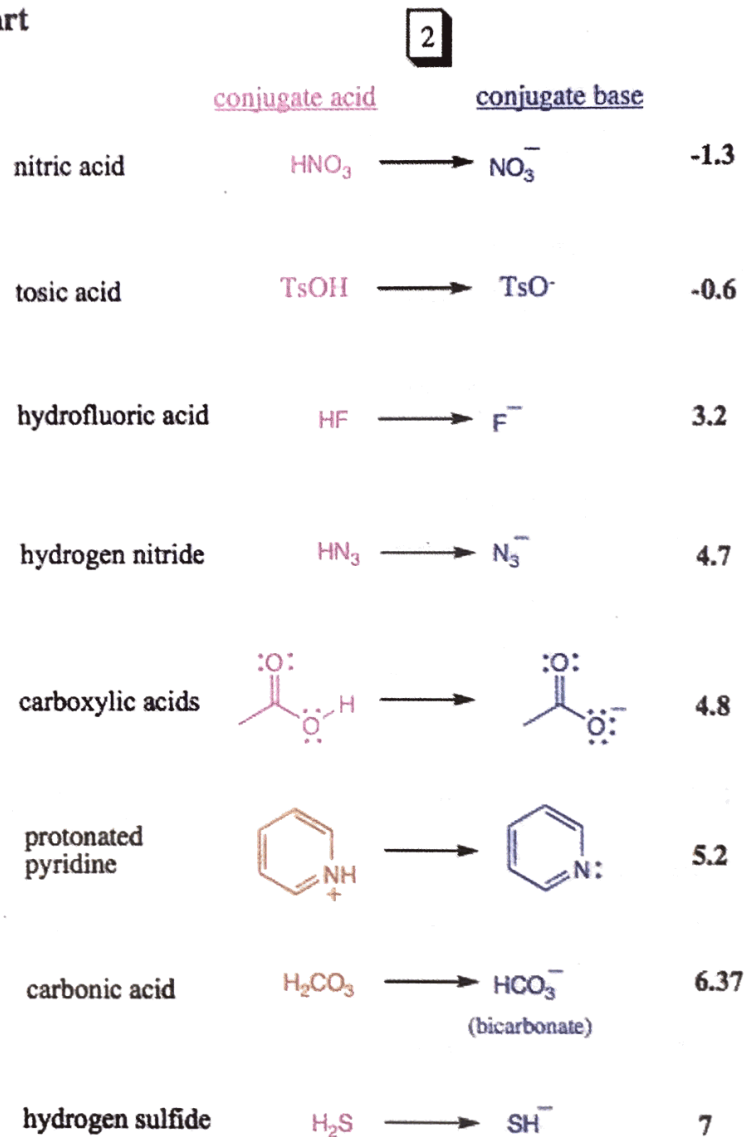


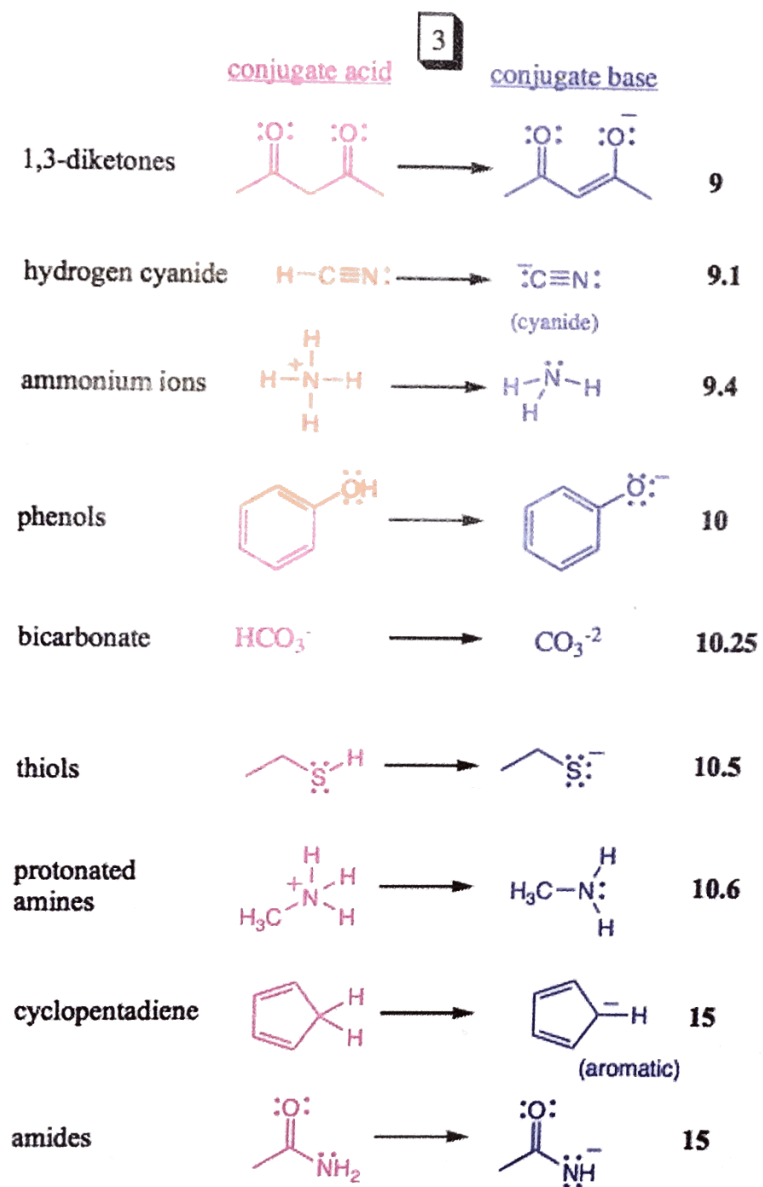
25. Finally, the ketone undergoes ring-closing to afford a cyclic hemiacetal. Draw the product of this step, which forms a pyranose. Indicate ambiguous configuration at the anomeric carbon.



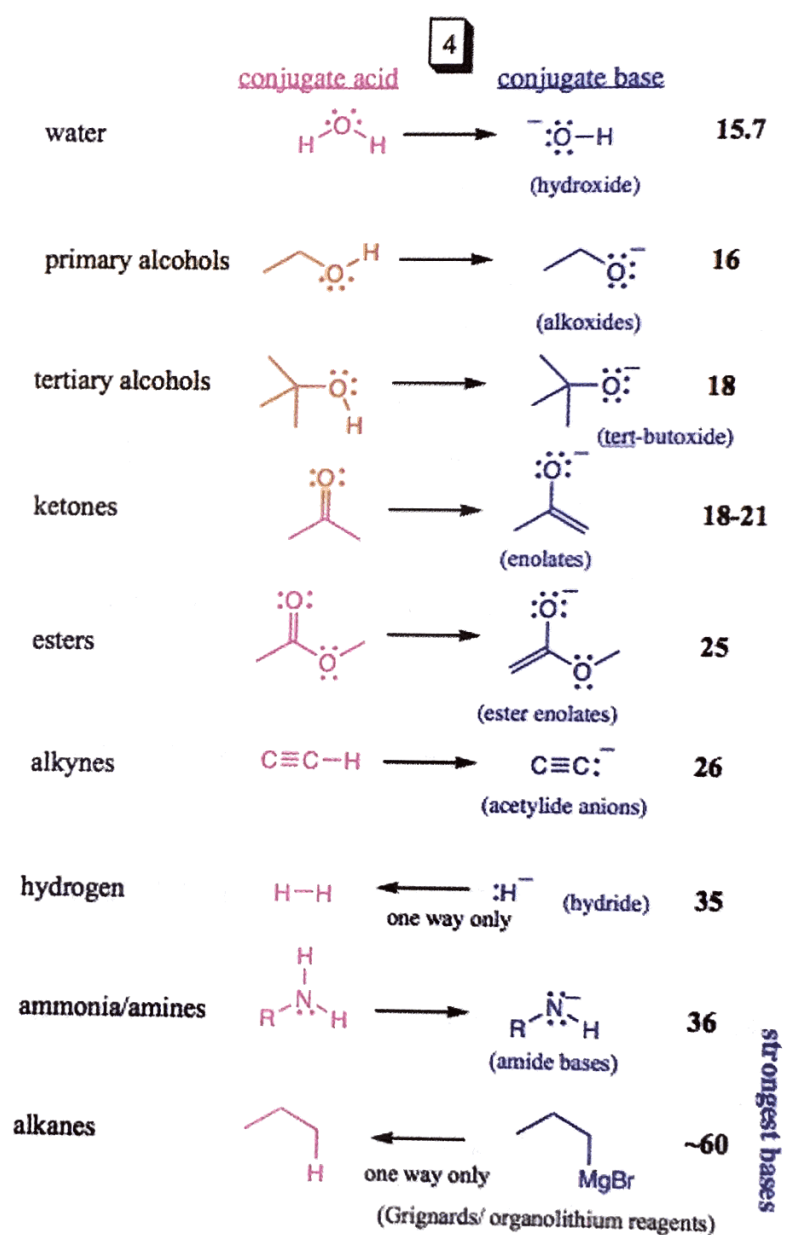


pKa Chart

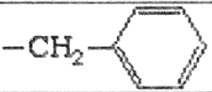
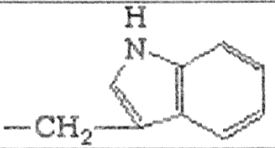

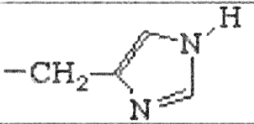
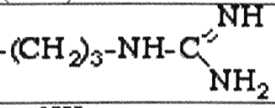
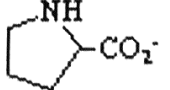




weakest acids



strongest bases

Amino Acid	R	-NH ₃ ⁺	-CO ₂ H	Side chain	pI
Glycine, Gly	-H	9.78	2.35	–	5.97
Alanine, Ala	-CH ₃	9.87	2.35	–	6.02
Valine, Val	-CH(CH ₃) ₂	9.74	2.29	–	5.97
Leucine, Leu	CH ₂ CH(CH ₃) ₂	9.74	2.33	–	5.98
Isoleucine, Ile	CH(CH ₃)CH ₂ CH ₃	9.76	2.32	–	6.02
Phenylalanine, Phe		9.31	2.20	–	5.48
Tryptophan, Trp		9.41	2.46	–	5.88
Tyrosine, Tyr		9.21	2.20	10.46	5.65
Histidine, His		9.33	1.80	6.04*	7.58
Serine, Ser	CH ₂ OH	9.21	2.19	–	5.68
Threonine, Thr	CH(CH ₃)-OH	9.10	2.09	–	6.53
Methionine, Met	CH ₂ CH ₂ SCH ₃	9.28	2.13	–	5.75
Cysteine, Cys	CH ₂ SH	10.70	1.92	8.37	5.14
Aspartic Acid, Asp	CH ₂ CO ₂ H	9.90	1.99	3.90	2.87
Glutamic Acid, Glu	CH ₂ CH ₂ CO ₂ H	9.47	2.10	4.07	3.22
Asparagine, Asn	CH ₂ CONH ₂	8.72	2.14	–	5.41
Glutamine, Gln	CH ₂ CH ₂ CONH ₂	9.13	2.17	–	5.65
Lysine, Lys	(CH ₂) ₄ NH ₂	9.06	2.16	10.54*	9.74
Arginine, Arg		8.99	1.82	12.48*	10.76
Proline, Pro		10.64	1.95	–	6.10

* Refers to the conjugate acid.