CHEMISTRY 3331, Spring 2005
Professor Walba
Third Hour Exam, April 14

scores:

1) 20

2) 20

3) 20

4) 20

5) 20

100

CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.

Name (printed): Key

Signature: _____

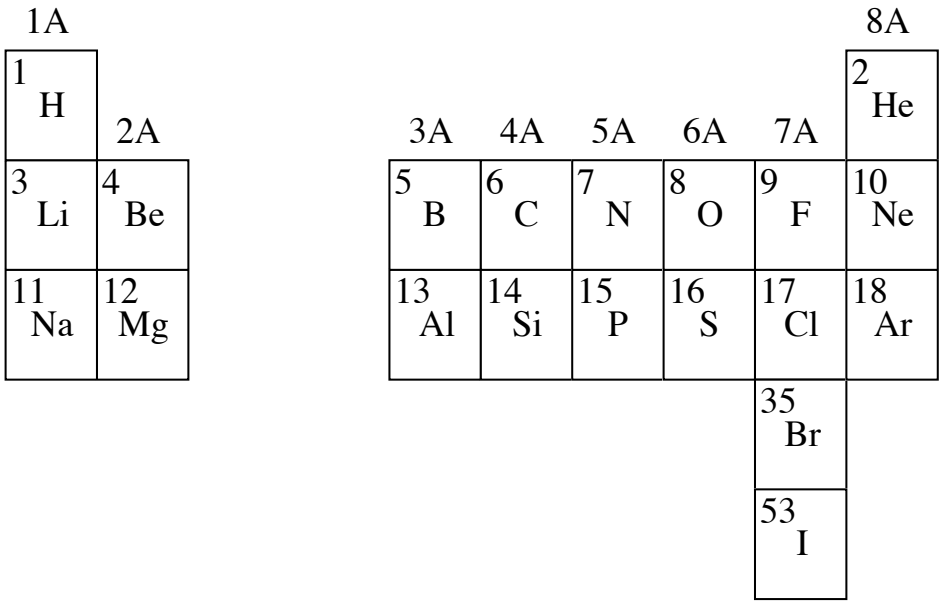
Recitation TA Name: _____

Recitation day and time: _____

This is a closed-book exam. The use of notes, models, calculators, scratch paper, or any other paraphernalia will not be allowed during the exam. Please put all your answers on the test. Use the backs of the pages for scratch.

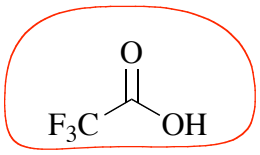
PLEASE read the questions very carefully!

Partial Periodic Table



Name:_____

1) (20 pts) a) Trifluoroacetic acid (**1**) and acetic acid (**2**) both turn litmus paper red. But, one of them is a much stronger Brønsted acid than the other. Circle the stronger acid.



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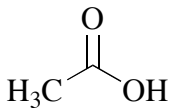
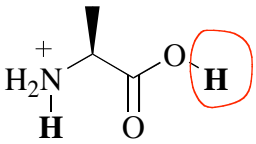


2

b) Briefly explain your answer for part a) above.

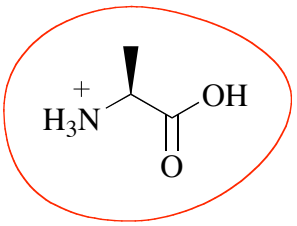
Inductive delocalization of charge in the TFA conjugate base makes the TFA a stronger acid.

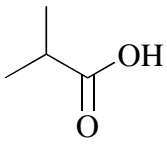
c) Alanine ammonium salt (**3**), has two possible acidic protons, indicated in bold. Circle the more acidic proton.



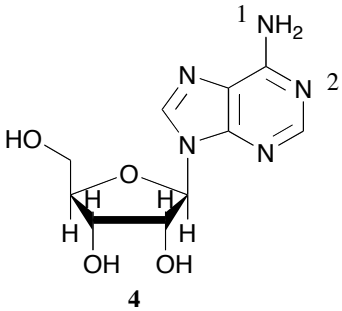
3

d) For the following pair of structures, circle the stronger acid.





e) Adenosine (**4**) has many basic nitrogen atoms. Focusing on N1 and N2, which of these is the stronger base?



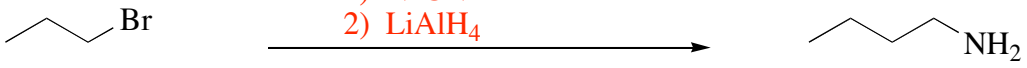
4

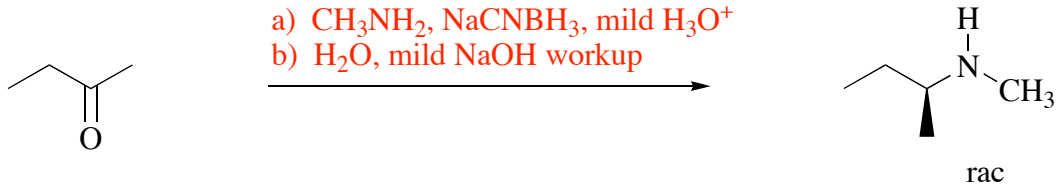
N2

Page 2 of 7 Total points for this page:

Name:_____

2) (20 pts) Propose a synthesis for each of the following amines from the starting material given. You may use any organic or inorganic reagents. More than one step may be required. Ignore stereochemistry for this question.

a) 

b) 

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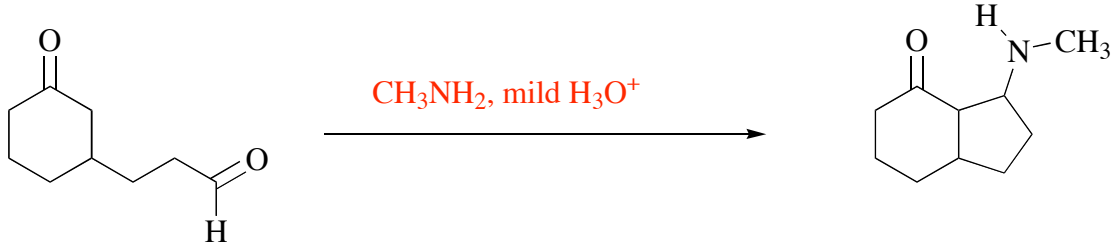
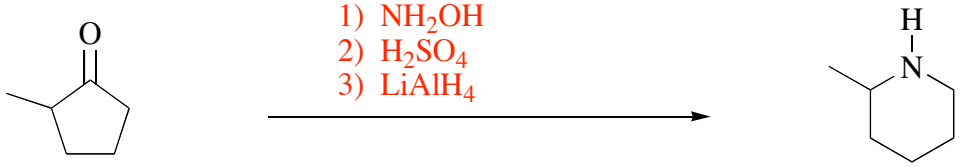
c) 

d) 

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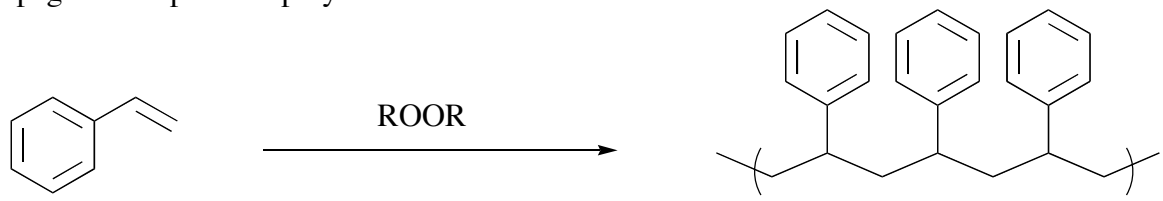
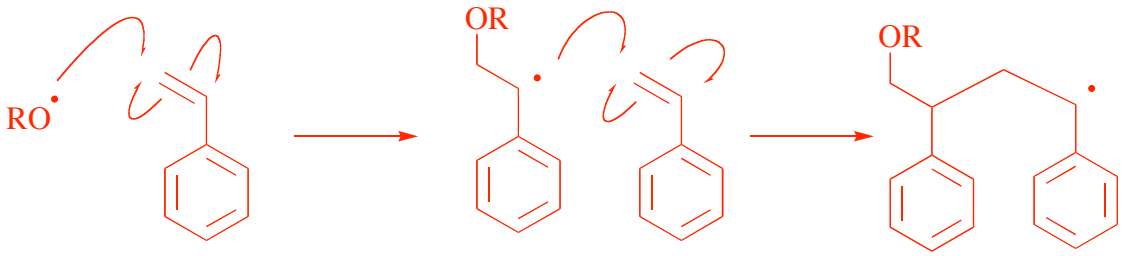
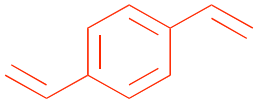
3) (20 pts) When styrene (**1**) is treated with a peroxide (ROOR), polystyrene results (the structure of the polymer is indicated by **2** using three monomer units). Give arrow-pushing mechanisms for the initiation step and one propagation step in this polymerization reaction.



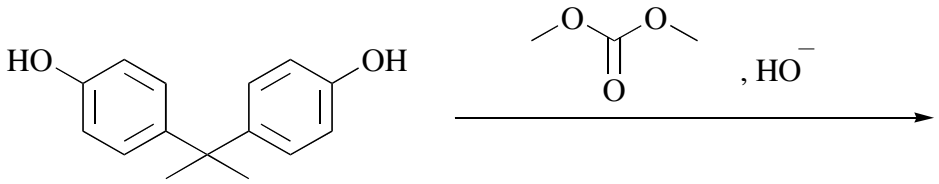
1 **2**



b) In order to make the polystyrene stronger, a cross-linker is often added to the reaction mixture shown in part a. Suggest a structure of a good cross-linker for this reaction.



c) When bis-phenol A **3** is mixed with dimethylcarbonate and hydroxide catalyst, a polymer is formed. Give the structure of this polymer showing three monomer units (as I did for polystyrene in part a).



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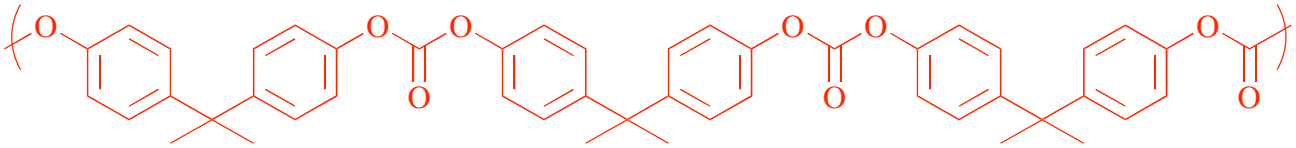

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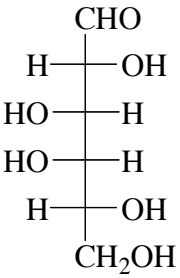
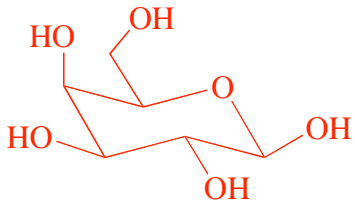
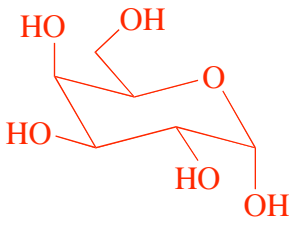
4) (20 pts) a) Draw a perspective chair "cyclohexane" structure for both α and β anomers of D-galactopyranose. Draw your structures carefully, and please leave out the H atoms.

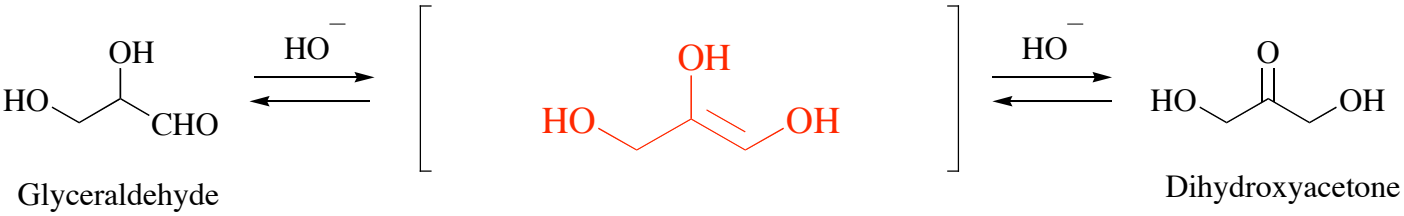


D-Galactose





b) The aldose glyceraldehyde (racemic), forms an equilibrium mixture containing the ketose dihydroxyacetone in the presence of hydroxide, as indicated in the equation below. This equilibration involves a key neutral (i.e. not charged) intermediate, which is present in very small concentration at equilibrium. Give the structure of the intermediate.

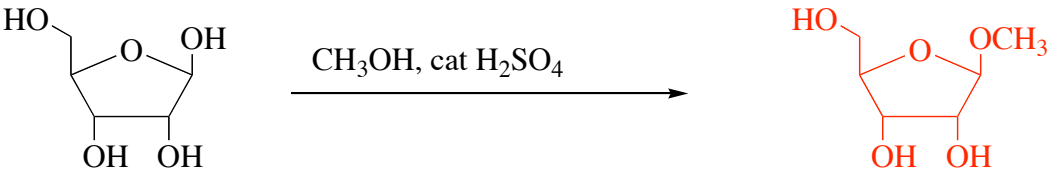


Glyceraldehyde

Neutral intermediate

Dihydroxyacetone

c) When treated with catalytic sulfuric acid in methanol solvent, β-D-ribofuranose (**1**) gives a mixture of products with molecular formula $C_6H_{12}O_5$. Give the structure of any one of these products using a Haworth projection to show the structure and stereochemistry.



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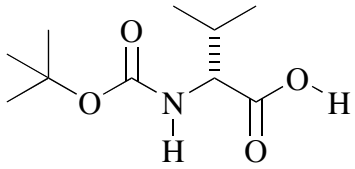
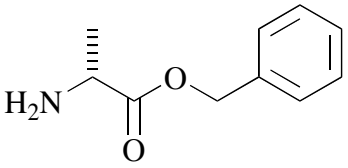
5) (20 points) a) Boc-valine (**1**) reacts with the benzyl ester of alanine (**2**) in the presence of dicyclohexylcarbodiimide to give a protected dipeptide **3**. Carefully draw the complete structure of compound **3** showing stereochemistry using wedges and dashes.

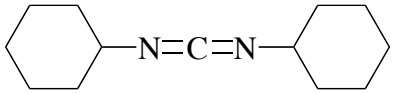


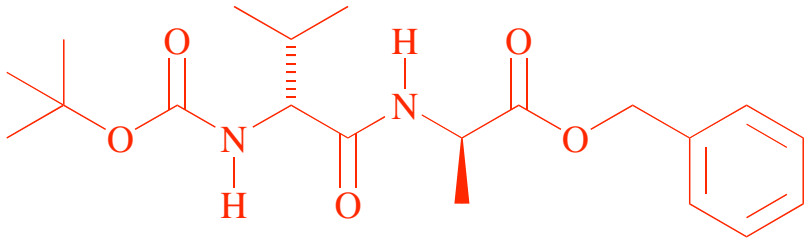
Boc-Valine (**1**)

+



Alanine benzyl ester (**2**)





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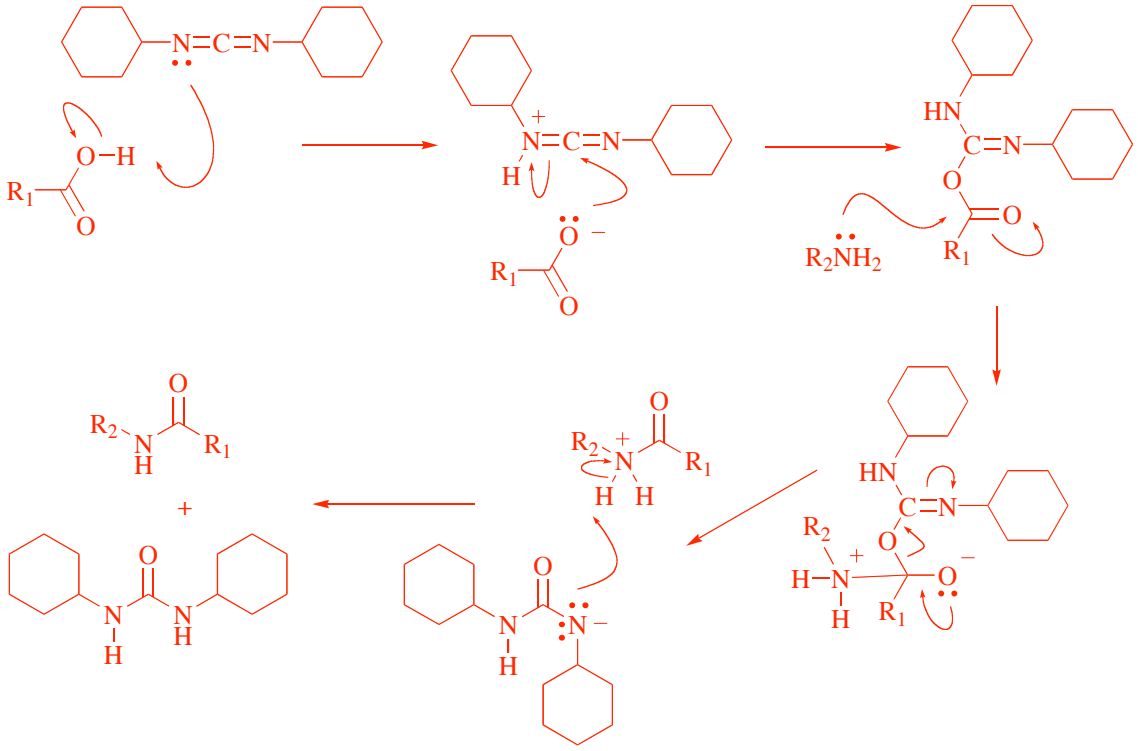
5) – continued

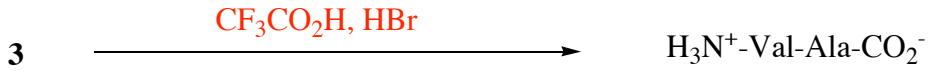
b) Propose an arrow-pushing mechanism for the formation of compound **3**. In your mechanism, use the abbreviated structures shown below to represent starting materials **1** and **2**.

Boc-Valine (**1**) = R_1CO_2H

Alanine benzyl ester (**2**) = R_2NH_2



c) Give reagents for removal of the protecting groups from the protected dipeptide **3** to give $^{+}NH_3$-Val-Ala-CO_2^{-}.



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