Chem 332
Exam 4
May 22, 2009
Professor Fox

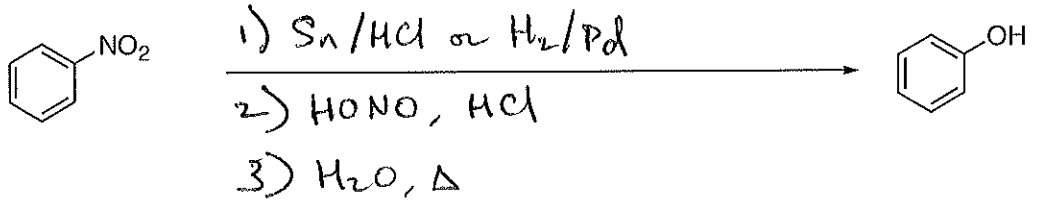
100 points
120 minutes

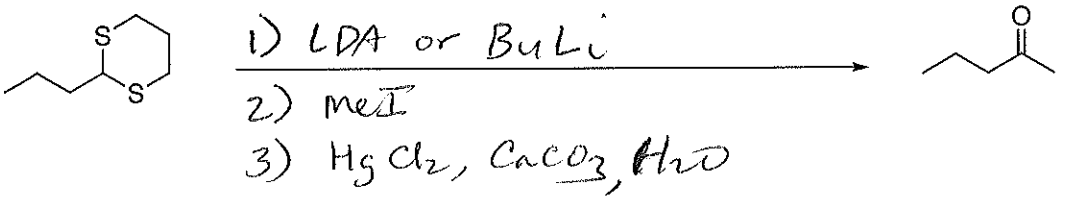
Your Name_____

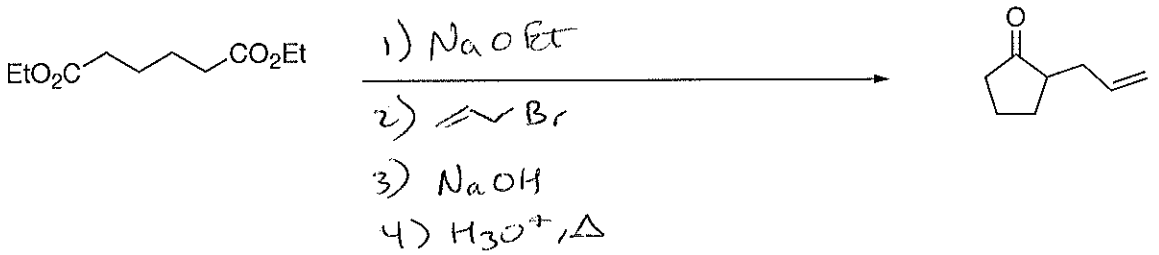
Your Name Key

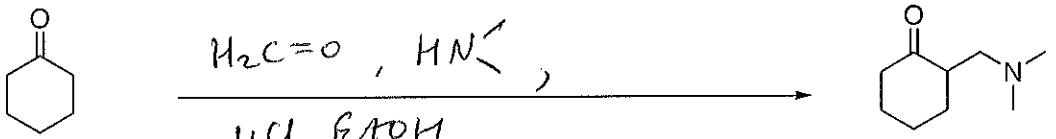
1. Provide reagents. More than one step may be necessary. You do not need to provide mechanisms

2.5 points each

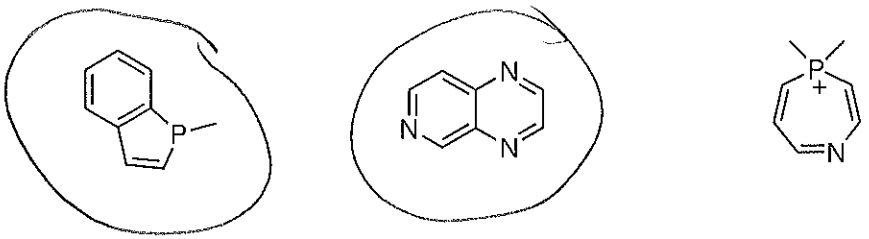






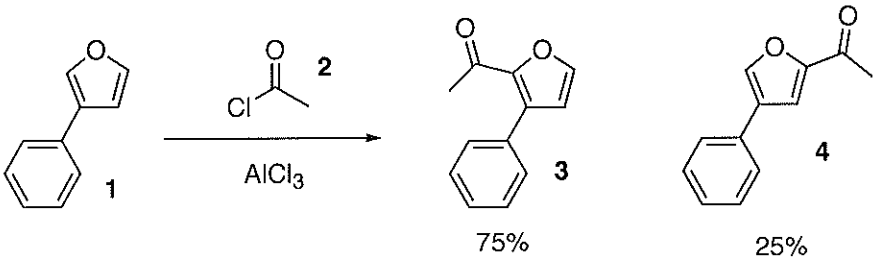


2. Circle the molecules that are aromatic. 2 points each



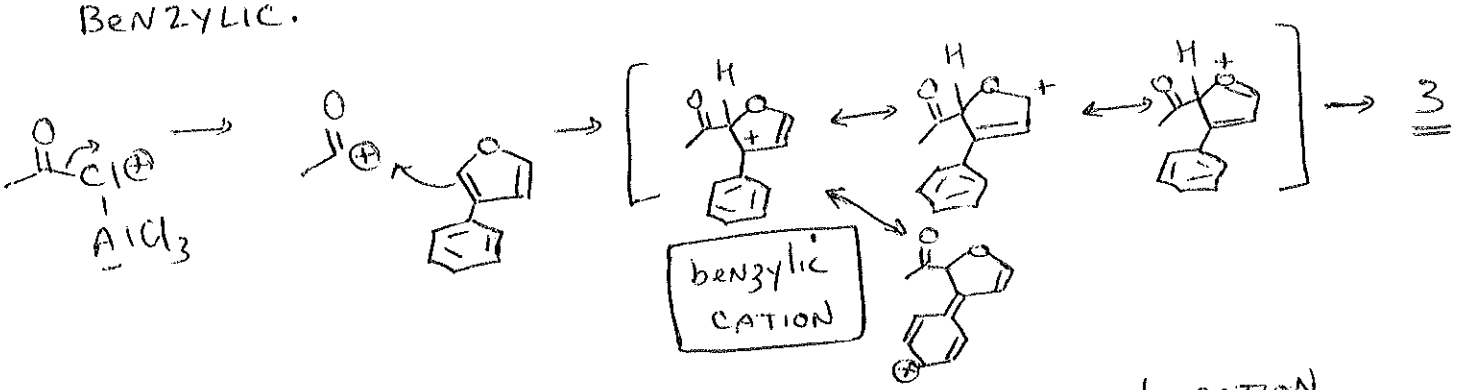
Your Name Key

3. Explain why the $AlCl_3$ catalyzed reaction of **1** with acetylchloride (**2**) gives **3** as the major product,with **4** as a minor product. You should include chemical structures that support your answer. A corrrect answer will explain the relative stability of the intermediates leading to each product.

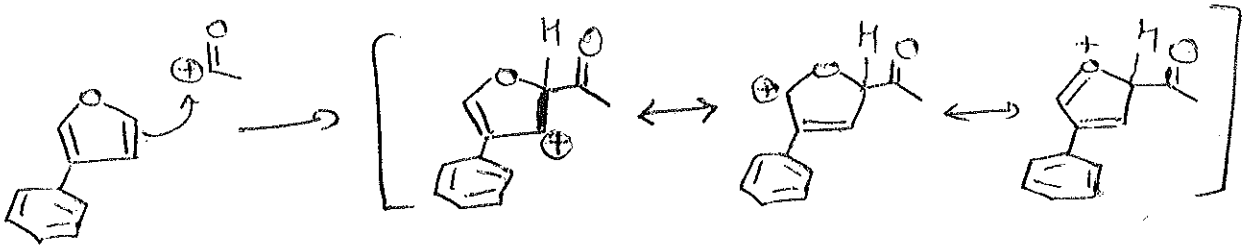


15 points

The acylium ion from 2 is formed. THE REACTION TO PRODUCE 3 proceeds VIA A CARBOCATION THAT, IN ADDITION TO ALLYLIC RESONANCE STABILIZATION & OXONIUM STABILIZATION, IS ALSO BENZYLIC.



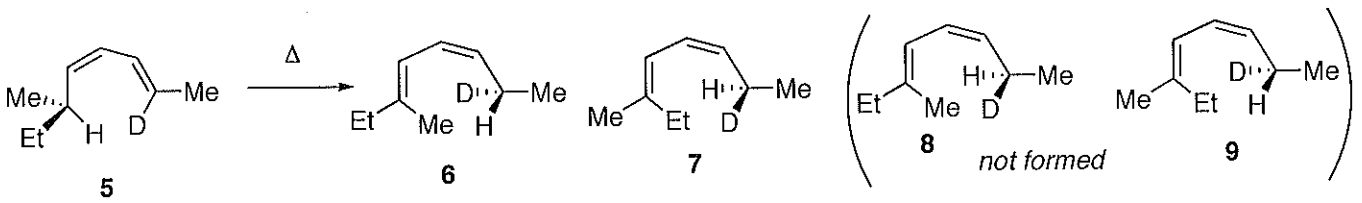
THE REACTION TO FORM 4 proceeds VIA A CARBOCATION THAT IS LESS STABLE BECAUSE IT IS NOT BENZYLIC



CATION IS NOT CONJUGATED to the BENZENE RING

Your Name key

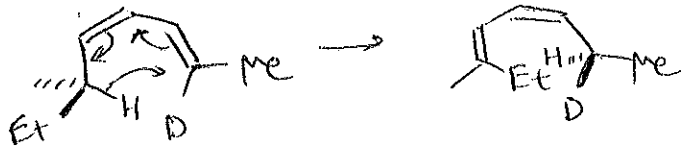
4. Upon heating, compound **5** rearranges to give **6** and **7**, but isomeric compounds **8** and **9** are not formed.



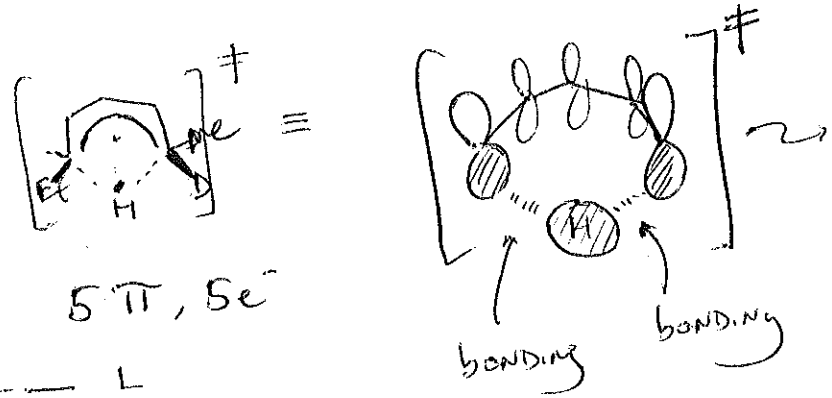
a. Provide an arrow pushing mechanism for the formation of **6** or **7**. (3 pts)

b. Provide a molecular orbital representation for the transition state for the rearrangement. HINT: your answer requires you to identify the HOMO of the pi system, and indicate how the symmetry of this HOMO is reflected in the transition state. (7 pts)

a.



b. Transition State for a Sigmatropic [1,5] hydride shift



5 π, 5e⁻

in the TS, the ends of the 5 π system have like symmetry.

ϕ_5 — L

ϕ_4 — U

ϕ_3 — L ≡ Like symmetry.

ϕ_2 — U

ϕ_1 — L

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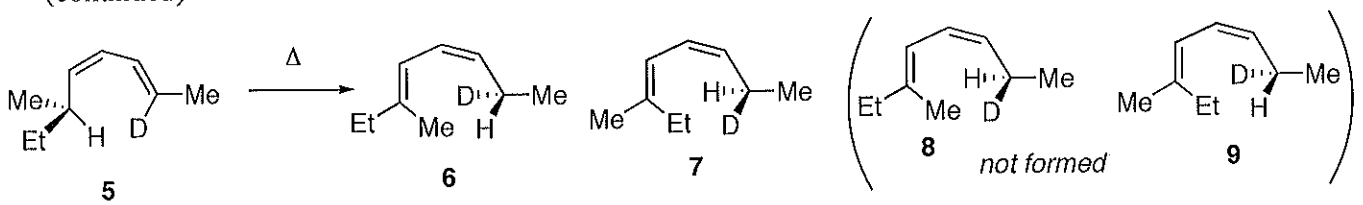
Your Name Key

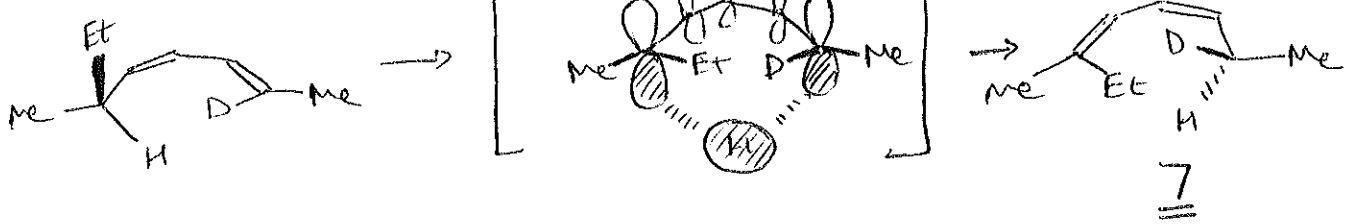
4. Upon heating, compound **5** rearranges to give **6** and **7**, but isomeric compounds **8** and **9** are not formed.

(continued)

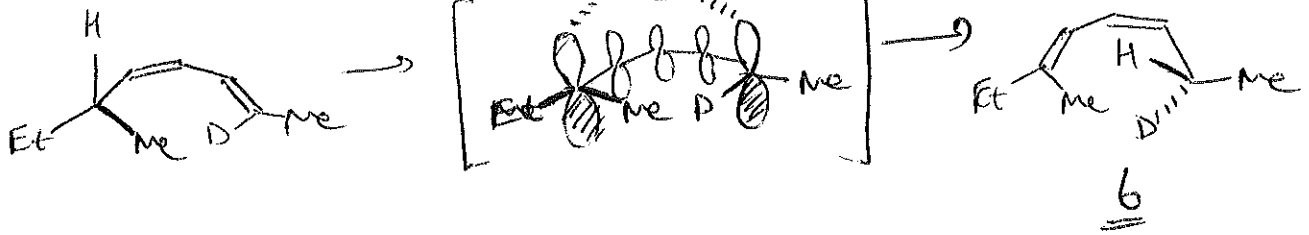


c. Explain why ONLY **6** and **7** are formed, ~~but not **8** and **9**~~. Use your transition state analysis from part B to support your answer. (8 pts)

HYDRIDE SHIFT ON THE "BOTTOM" FACE LEAD STEREOSELECTIVELY to 7.

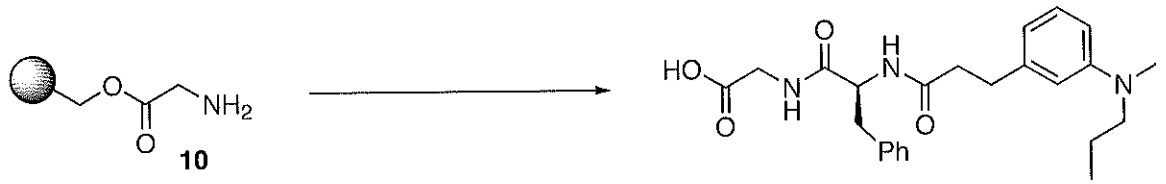


HYDRIDE SHIFT ON THE "TOP" FACE LEADS STEREOSELECTIVELY to 6.



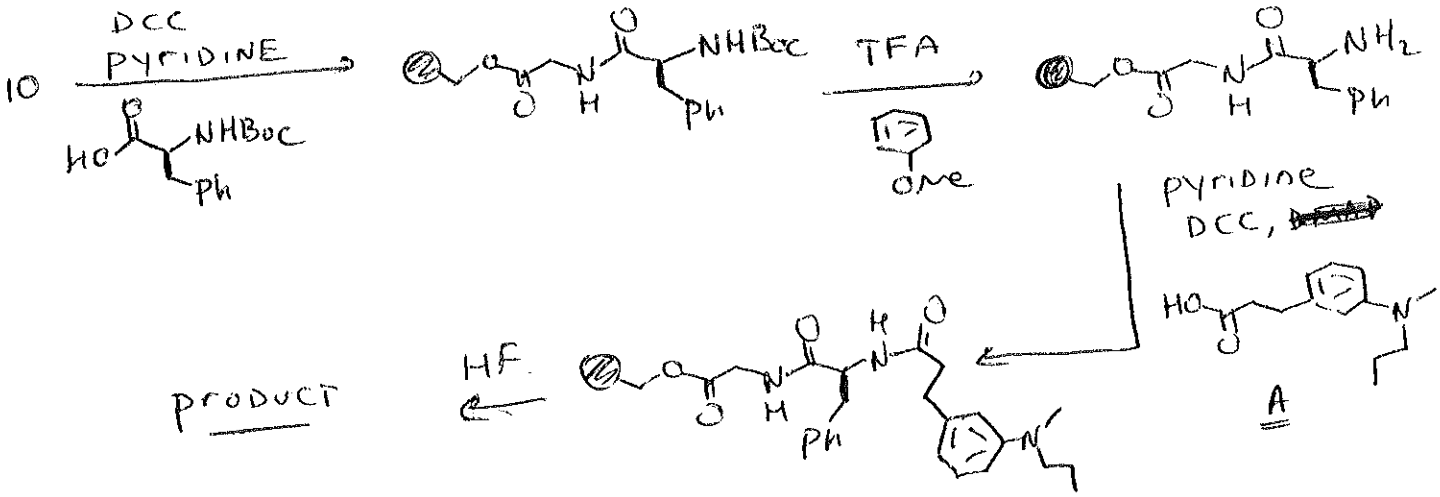
Your Name Key

5. Provide a synthesis starting from **compound 10, benzene** and any other materials that contain less than four carbons. You may also use **BOC-protected amino acids** as starting materials.

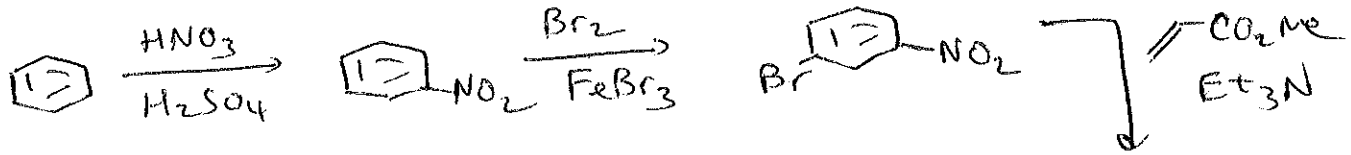


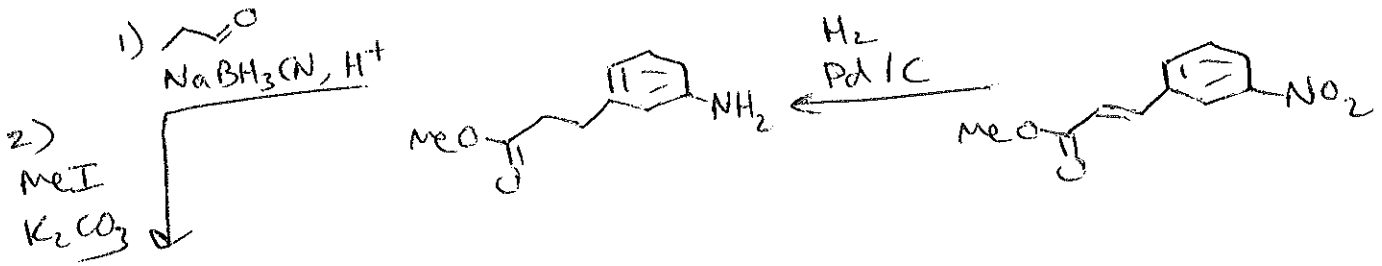
= Merrifield resin

17 points



Synthesis of A



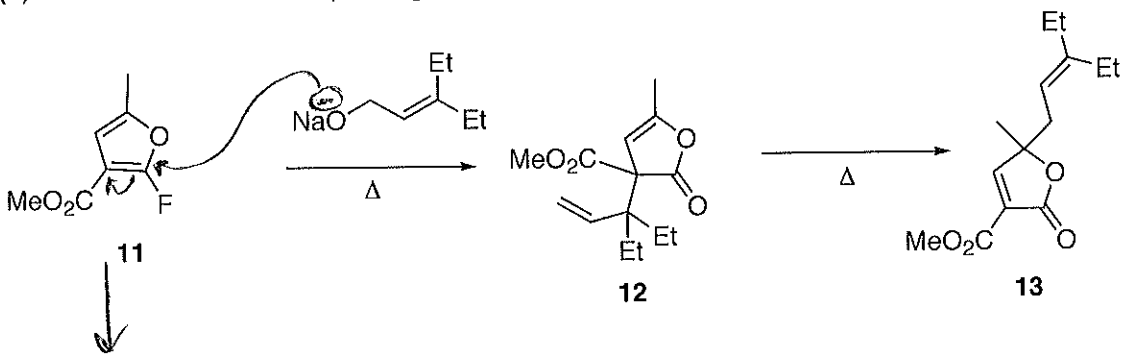


Your Name key .

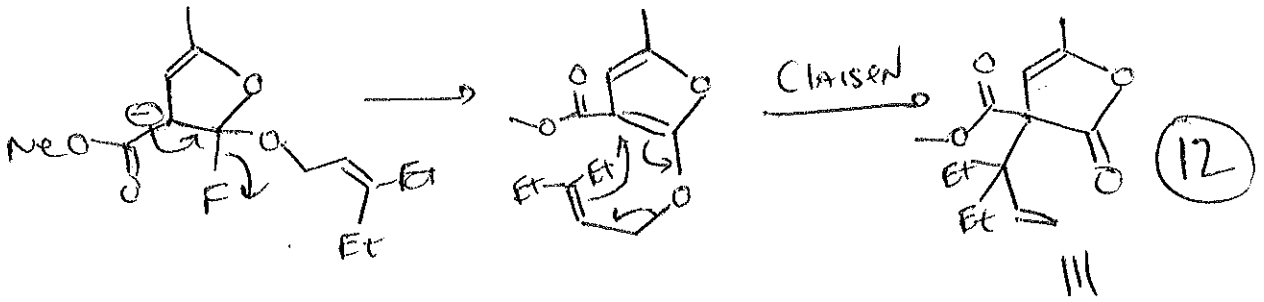
17 points

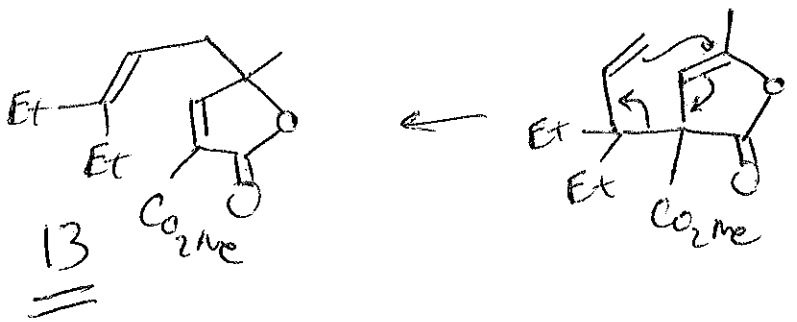
6 (a) Provide a detailed arrow pushing mechanism for the conversion of **11** into **12**

(b) Provide a detailed arrow pushing mechanis for the conversion of **12** into **13**



11 **12** **13**

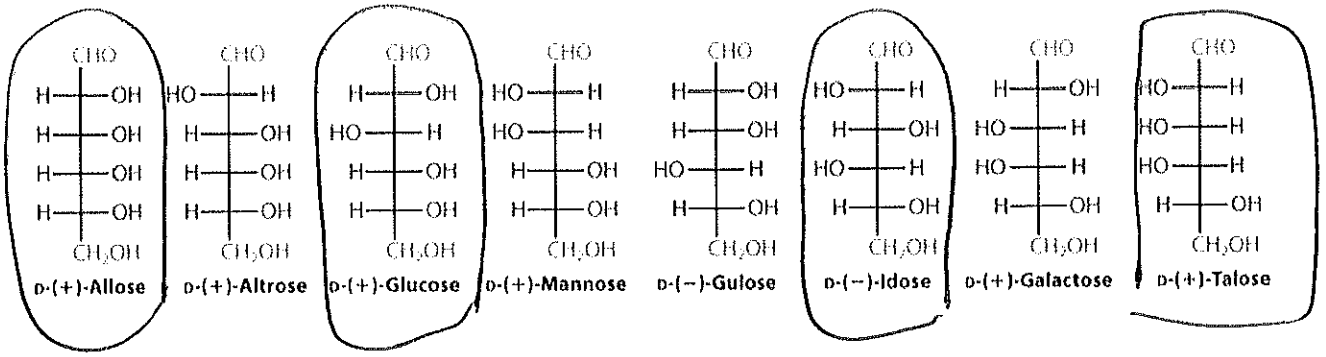




Your Name key

7. Circle the D-aldohexoses that upon sequential Kiliani-Fischer synthesis/HNO3 oxidation will give one optically active 7-carbon diacid and one optically inactive 7-carbon diacid.

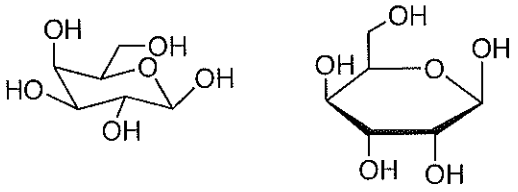
8 points



Your Name Key

3 points each

8. Identify each of the following pairs as being idential, meso, enantiomers, anomers, or non-anomeric diasteromers

(a) 

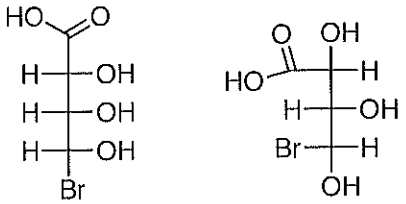
identical (but not meso)

meso

enantiomers

anomers

diastereomers (but not anomers)

(b) 

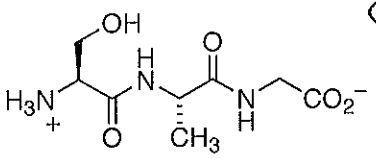
identical (but not meso)

meso

enantiomers

anomers

diastereomers (but not anomers)

(c) Ser-Ala-Gly 

identical (but not meso)

meso

enantiomers

anomers

diastereomers (but not anomers)

Scratch paper