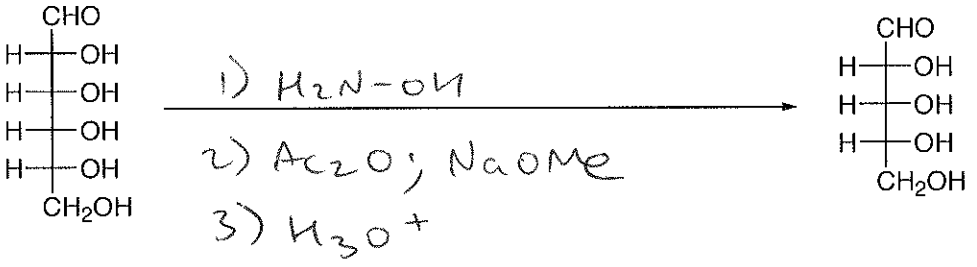
Chem 332
Exam 4
May 29, 2008
Professor Fox

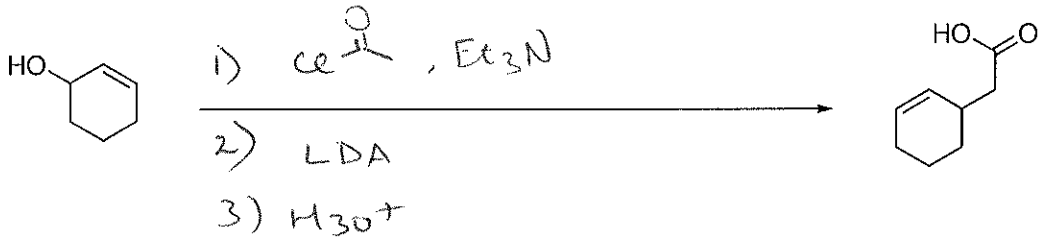
100 points
120 minutes

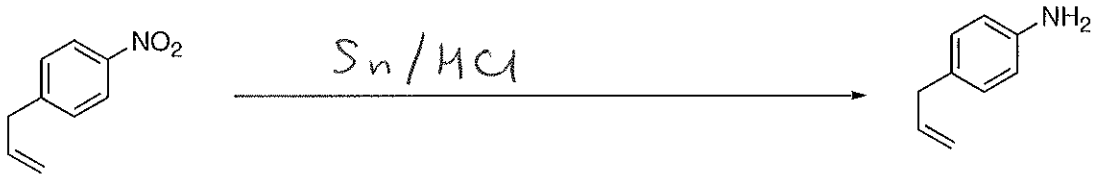
Your Name_____

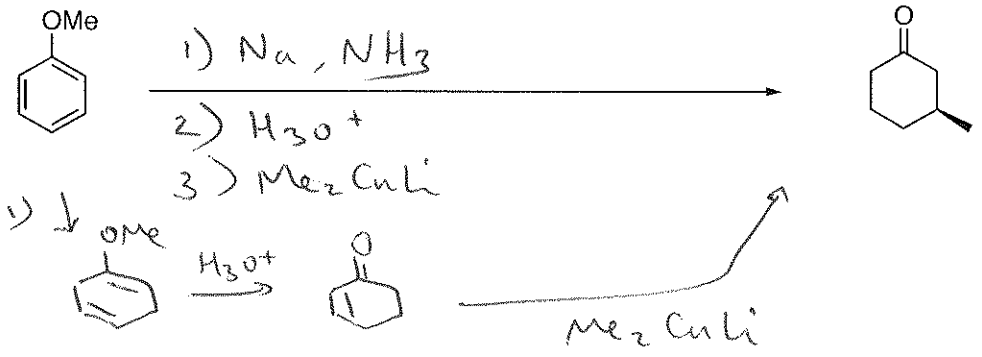
Your Name Key 3 points each

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





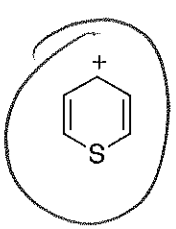


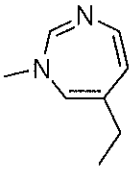


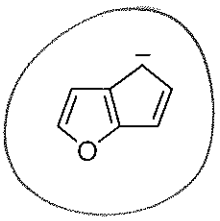
Your Name_____

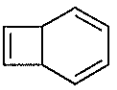
2 points each

2. Circle the molecules that are aromatic.



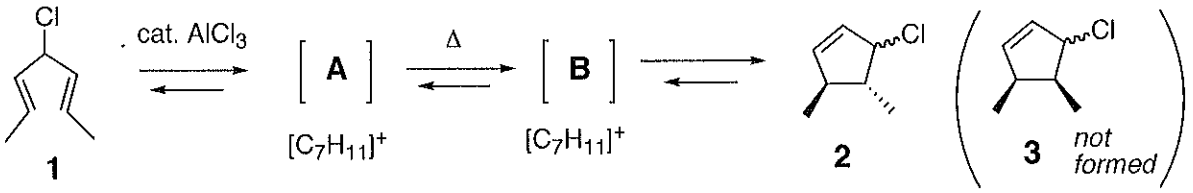






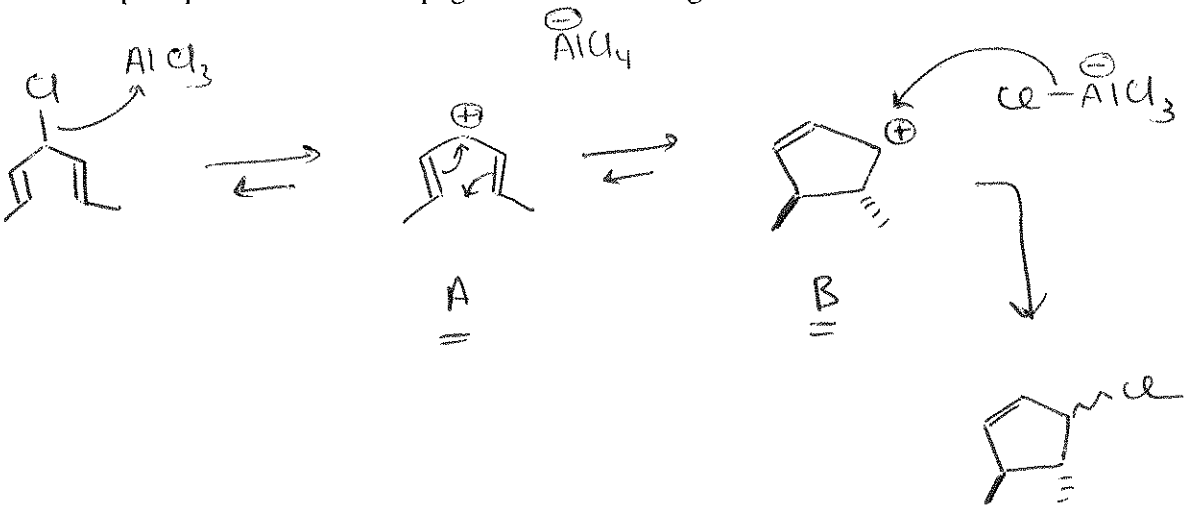
Your Name Key

3 Aluminum chloride ($AlCl_3$) catalyzes the stereoselective transformation of **1** into **2**. Isomeric structures **3** are not formed. The mechanism involves the formation of two carbocation intermediates (**A** and **B**) with the formula C_7H_{11}.



a. Write an arrow pushing mechanism for the conversion of **1** into **2**. Provide structures for intermediates **A** and **B**. 10 points

This is a two part question: read next page before answering



Your Name Key

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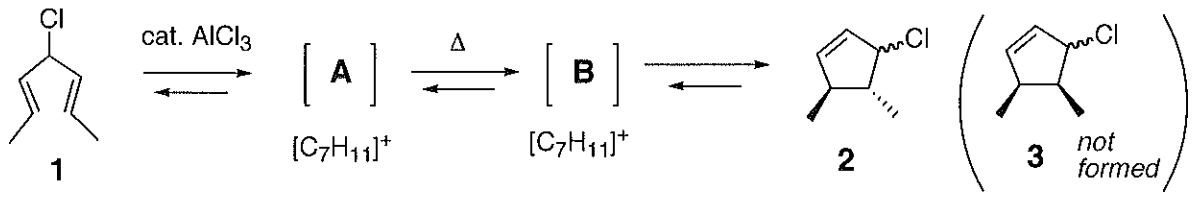
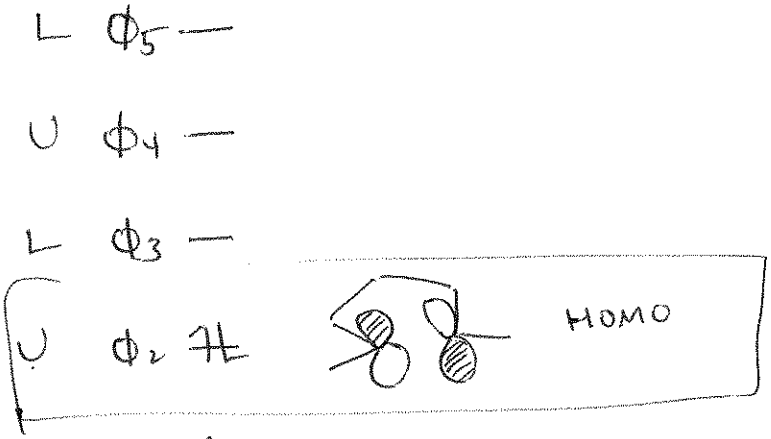


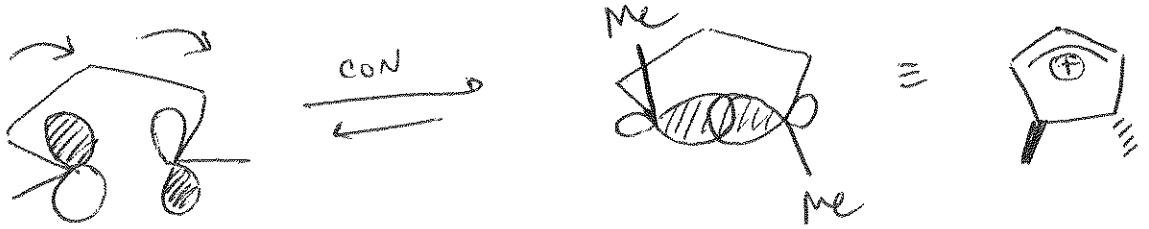
1

b. Explain why **2** is formed stereoselectively, and why **3** is not formed. Explain in detail using an argument that is grounded in molecular orbital theory. HINT: your answer should involve analysis of the interconversion between **A** and **B**. 15 points

A → B is AN ELECTROcyclic Ring Closure involving 4 π electrons.

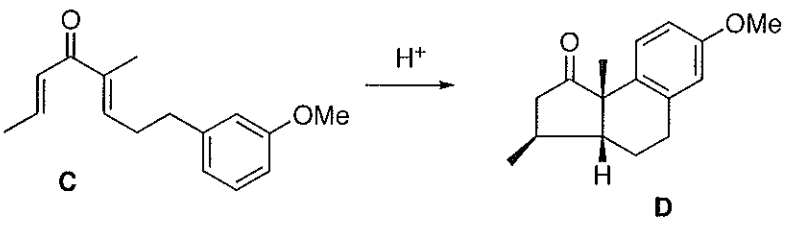


THE HOMO HAS UNLIKE SYMMETRY. The thermal ring closure is CON-ROTATORY & leads to TRANS stereochemistry.



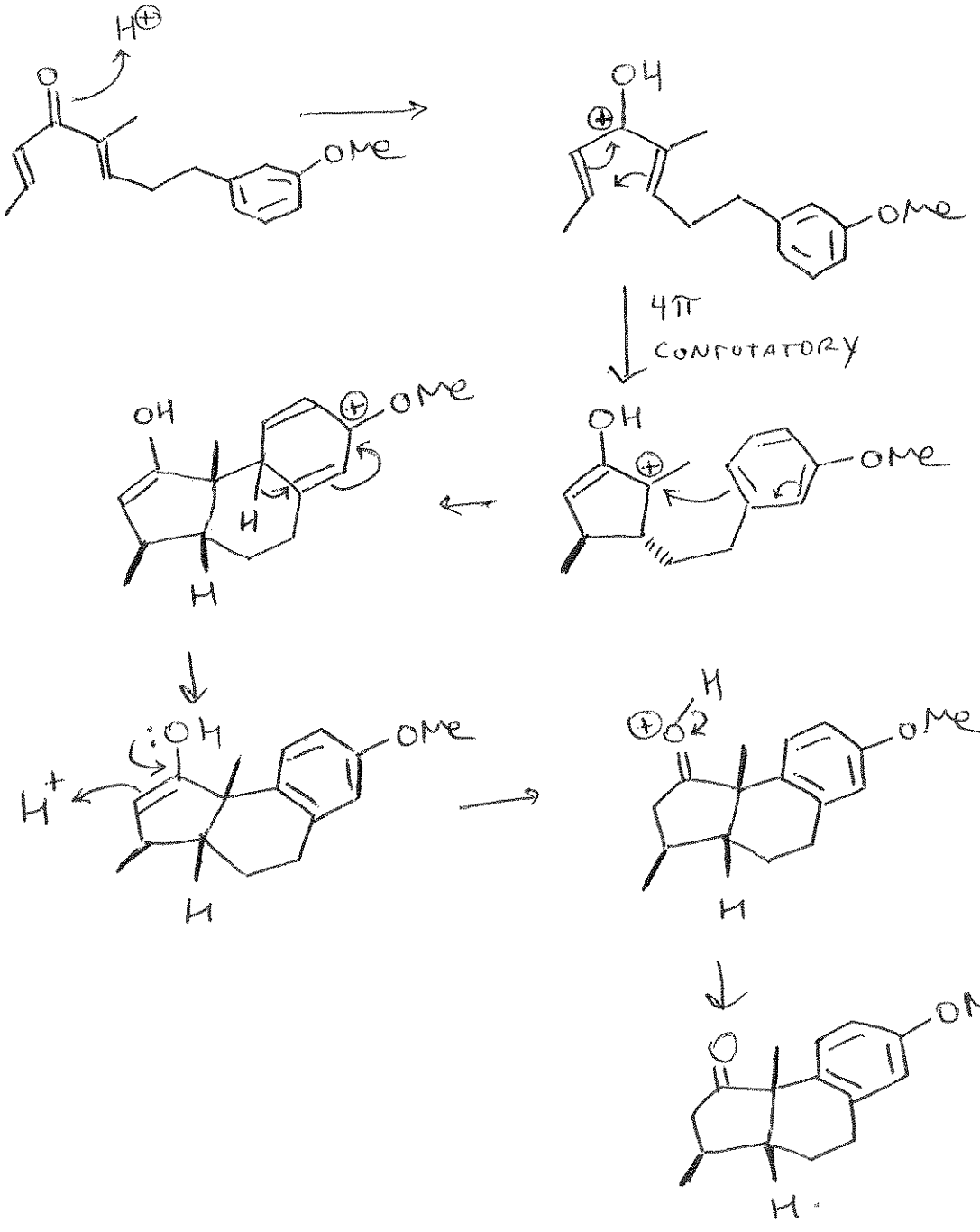
Your Name Key

4. Provide a detailed arrow pushing mechanism for the formation of **D** from **C**



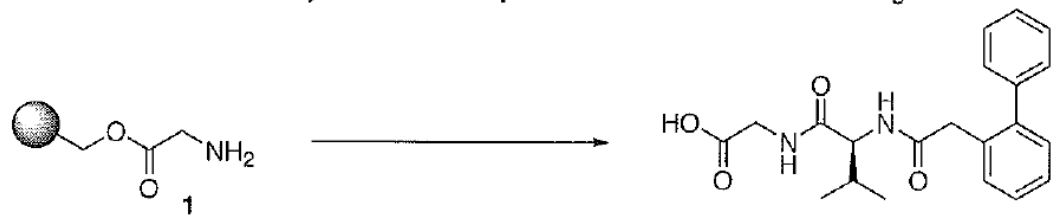
C **D**

17 points



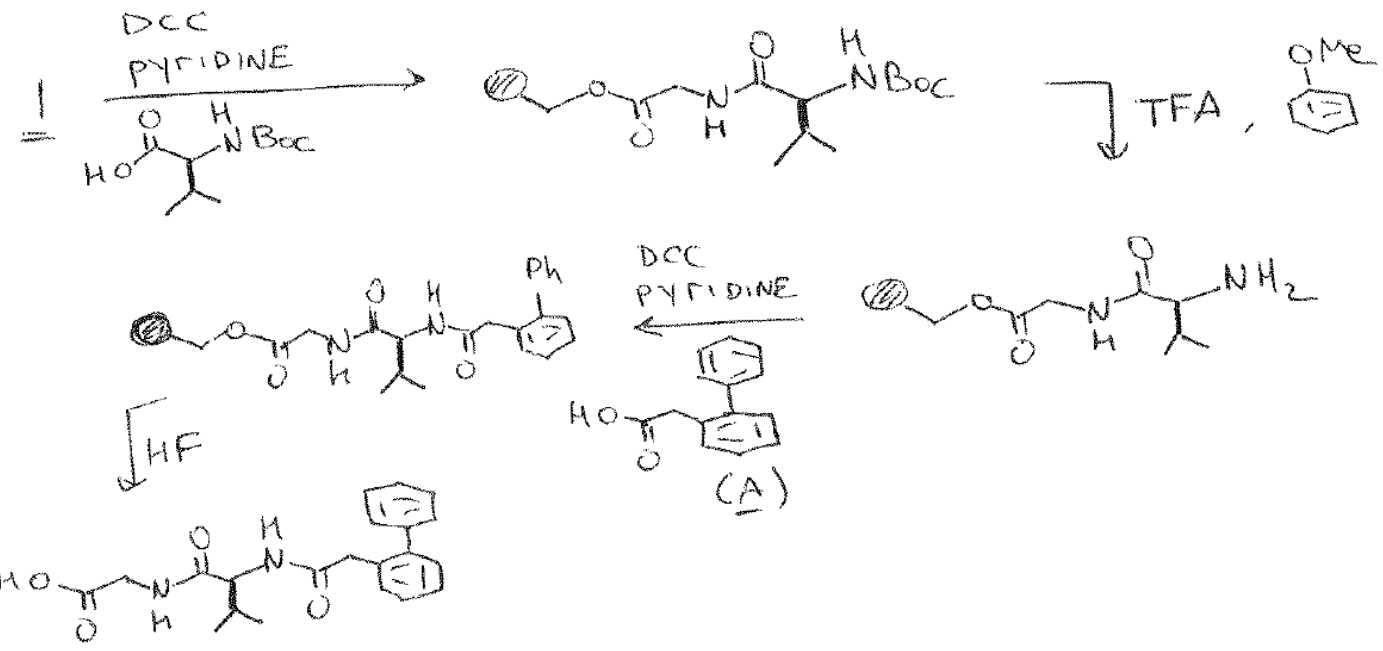
Your Name key

5. Provide a synthesis starting from **compound 1, benzene, toluene** and any other materials that contain less than four carbons. You may also use **BOC-protected amino acids** as starting materials.

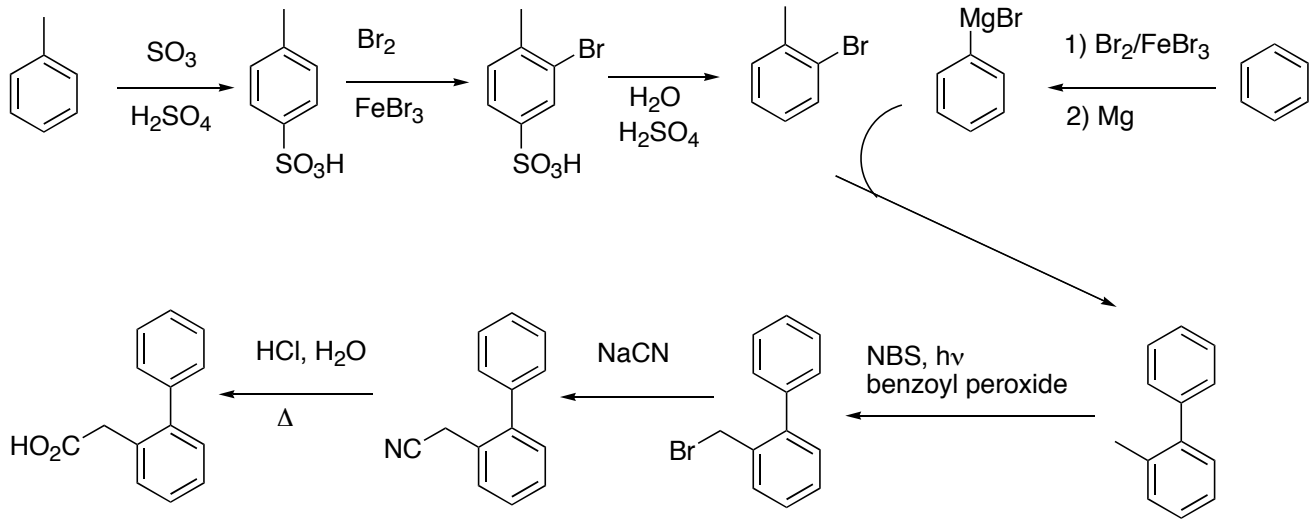


= Merrifield resin

18 points



synthesis of **A**

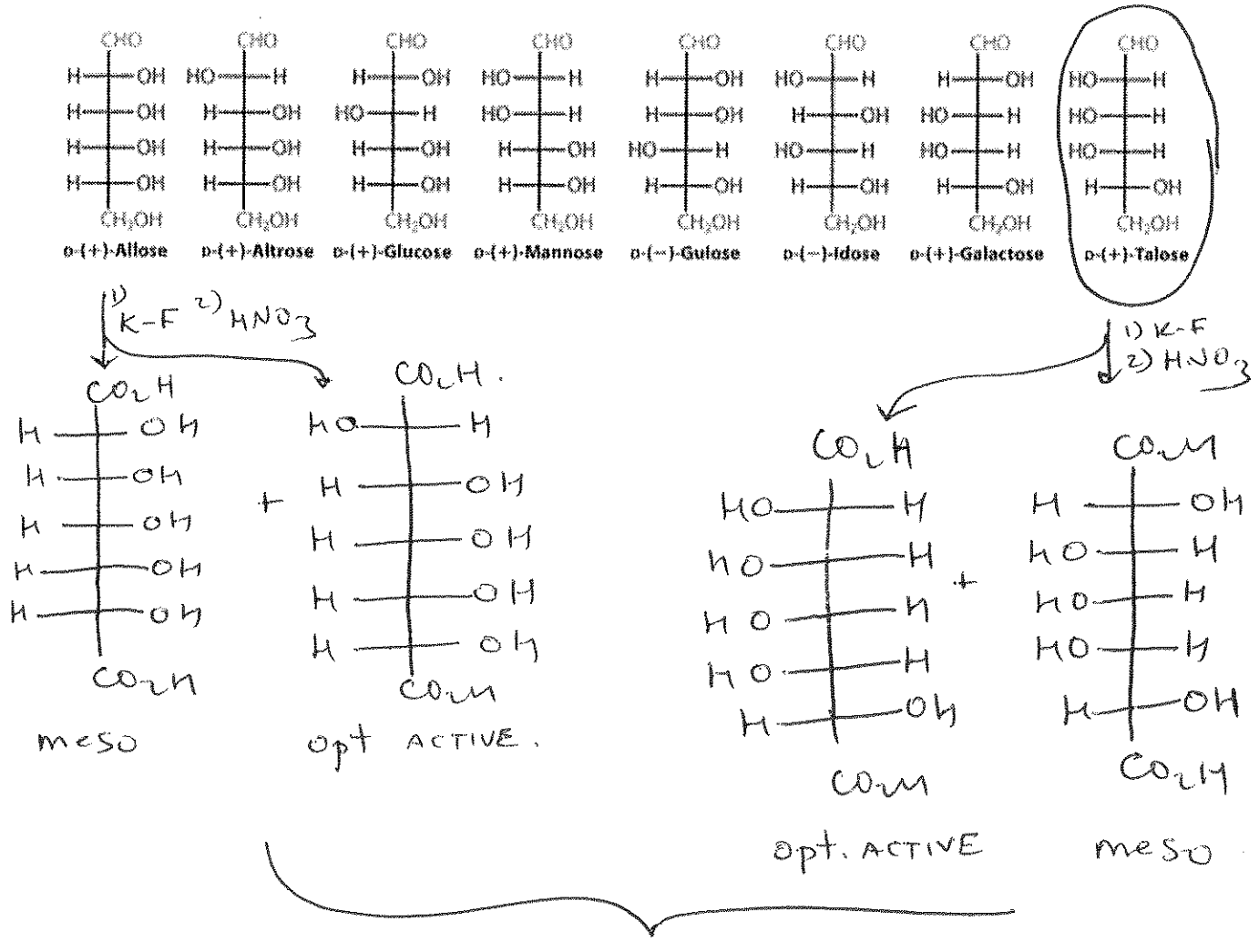


Your Name Key

8 points

6. Kiliani-Fischer synthesis on D-(–)-allose is followed by oxidation by HNO3 to give a mixture of two diacids. One of these diacids is optically active, the other is optically inactive.

Circle the structure of another, naturally-occuring D-aldohexose would give that same, optically active diacid upon sequential Kiliani-Fischer synthesis/ HNO3 oxidation. (NOTE: the optically active diacid is obtained as a mixture with an optically inactive diacid).



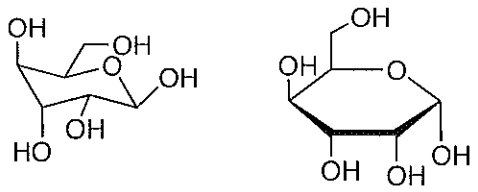
THESE ARE THE SAME.

Your Name key

4 points each

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

(a)



identical (but not meso)

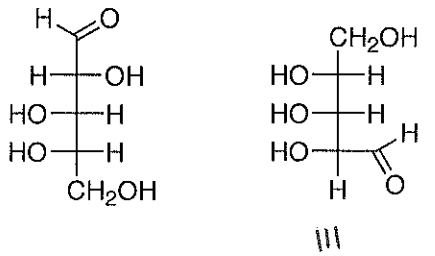
meso

enantiomers

anomers

diastereomers (but not anomers)

(b)



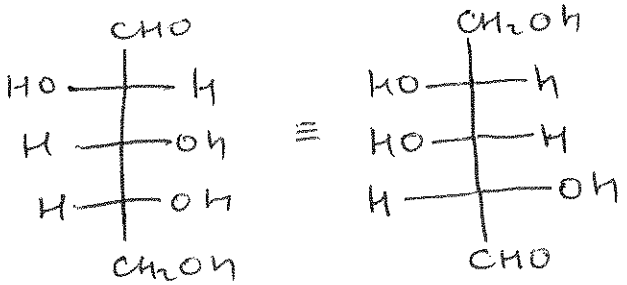
identical (but not meso)

meso

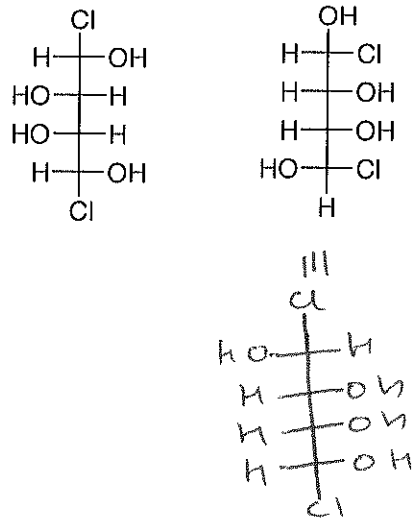
enantiomers

anomers

diastereomers (but not anomers)



(c)



identical (but not meso)

meso

enantiomers

anomers

diastereomers (but not anomers)

Scratch paper