Chem 332
Exam 4
May 22, 2010
Professor Fox

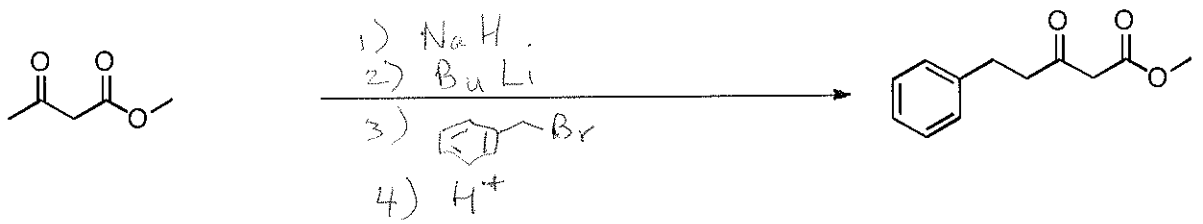
100 points
180 minutes

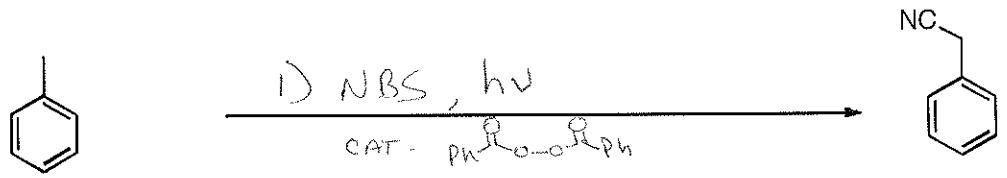
Your Name Key

Your Name_____

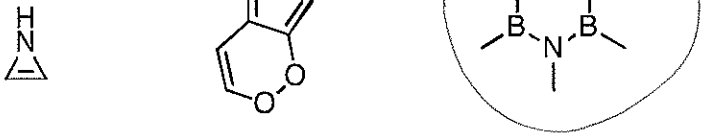
2 points each

1. Provide reagents for the following transformations. There is no limit to the number of carbons that your reagents may contain.

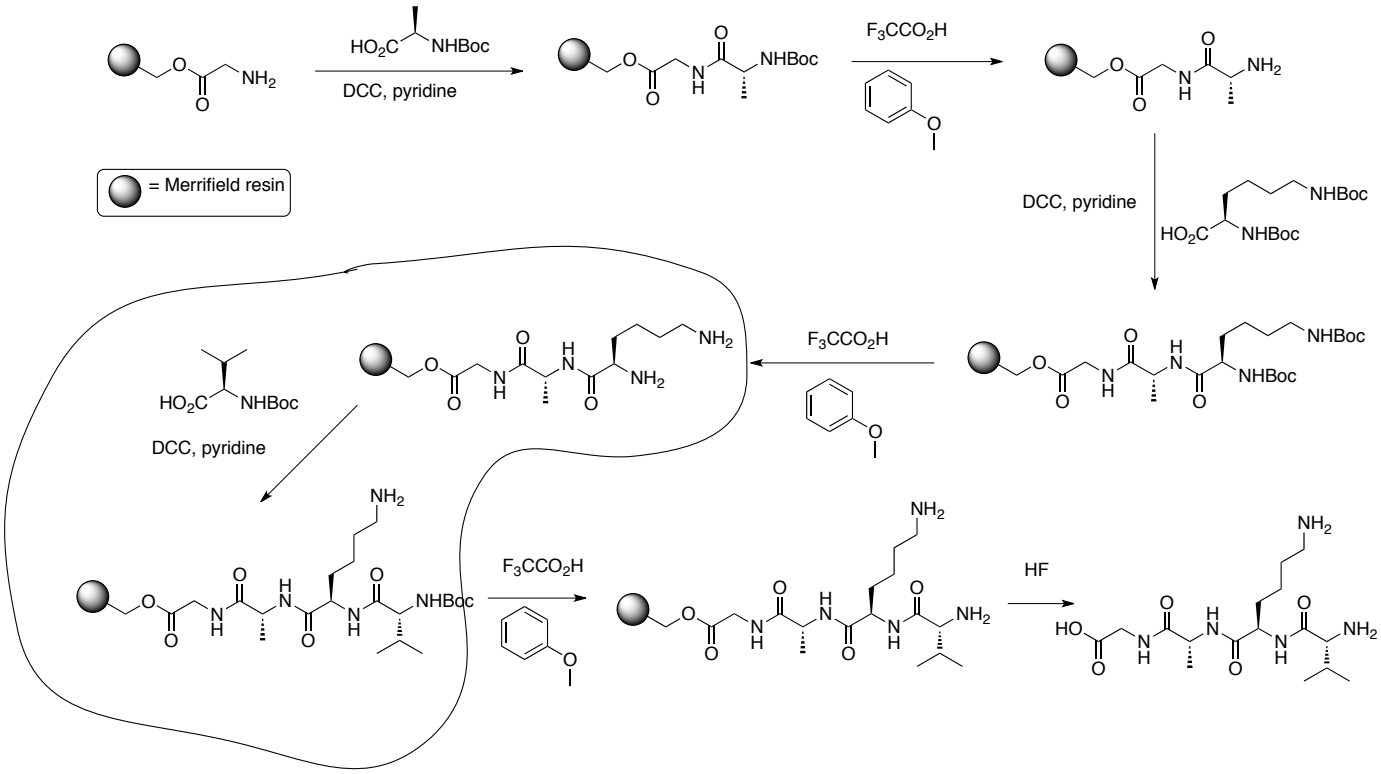




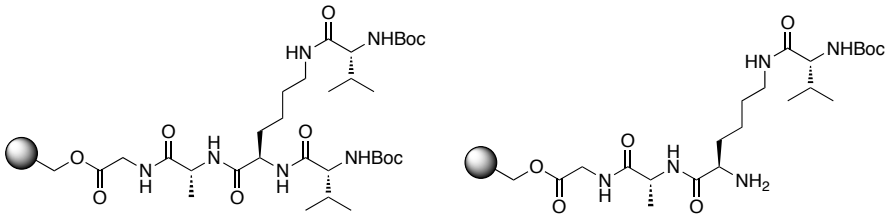
2. Circle the molecules that are aromatic. 2 points each



3. One of the steps in the following synthesis would not proceed in high yield. CIRCLE the problematic step, and describe the problem in the space below in 30 words or less



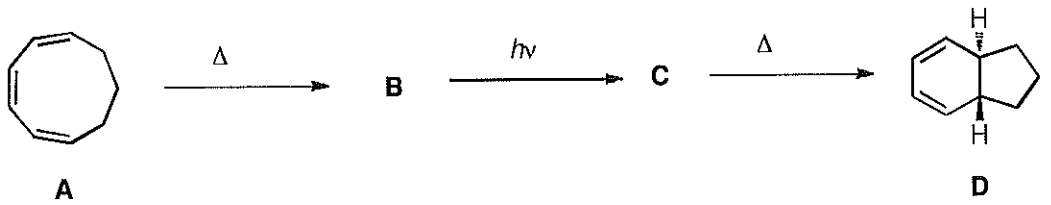
ANSWER: There are two primary amines in the reactant. Thus, this reaction is unselective, and will give the following side products:



Your Name_____

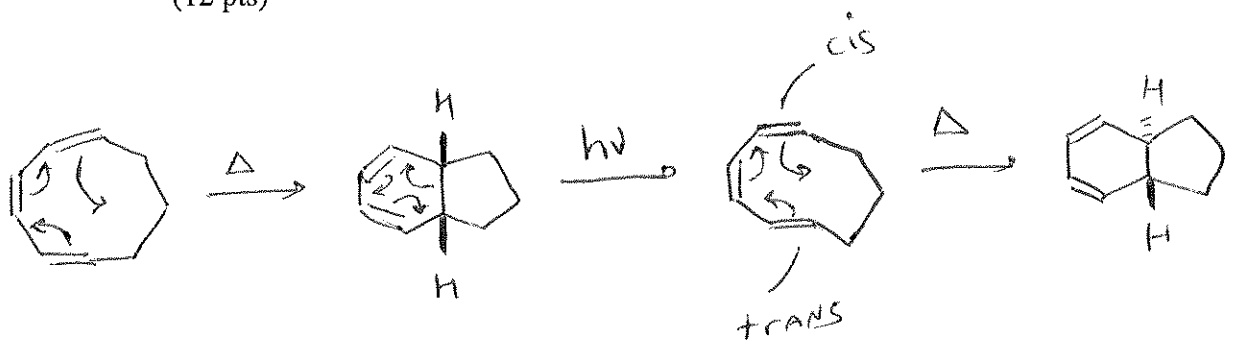
undergoes electrocyclization electrocyclization

4. Upon heating, compound **A** rearranges to isomeric compound **B**. Photochemical reaction of compound **B** produces isomer **C**. Finally, thermolysis of **C** produces isomeric compound **D**.



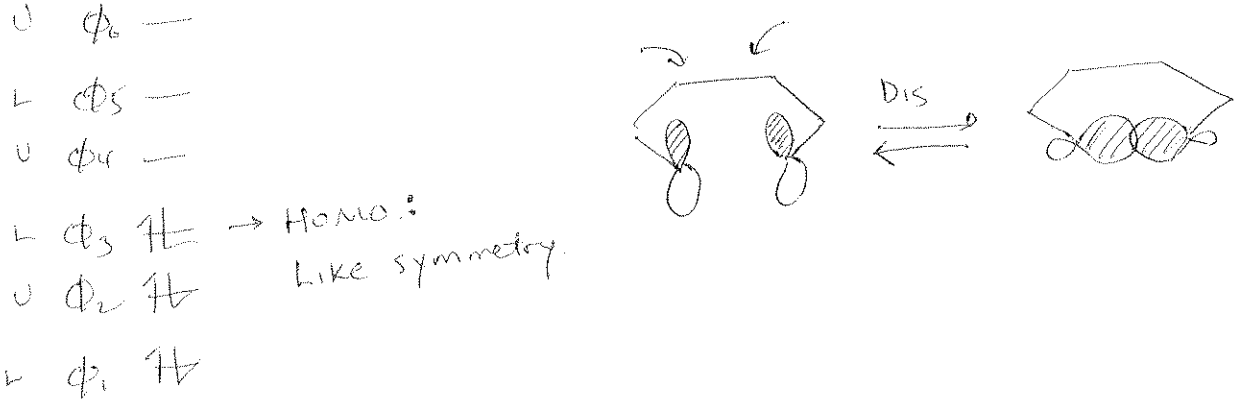
a. Provide structures for **B** and **C**, and arrow pushing mechanisms for the formation of **B**, **C** and **D**. (6 pts)

b. Use molecular orbital theory to explain the stereoselectivity for the formation of **B**, **C** and **D** (12 pts)



These Reactions are all 6 π, 6 e⁻ electrocyclizations

For the thermal reactions: we predict DISROTATION

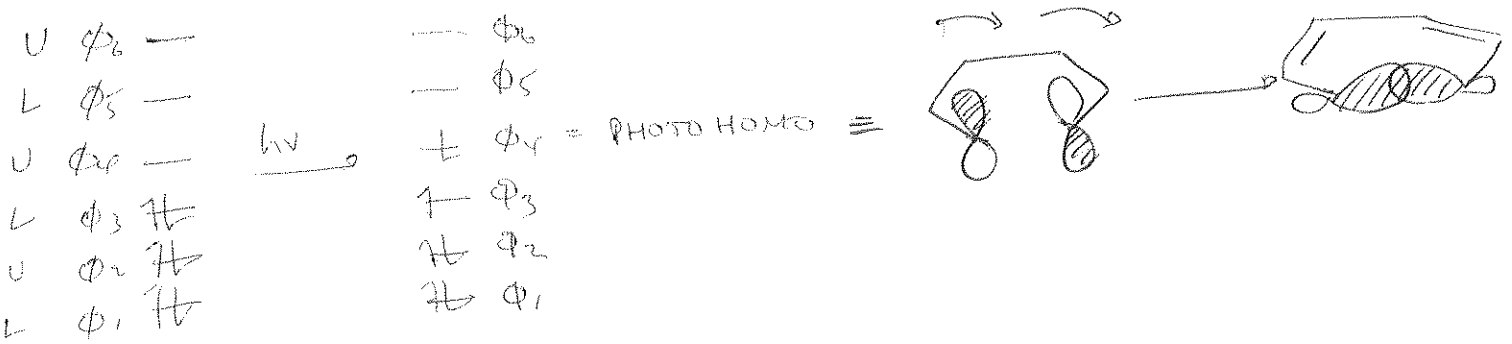


You may use the next page to continue your answer

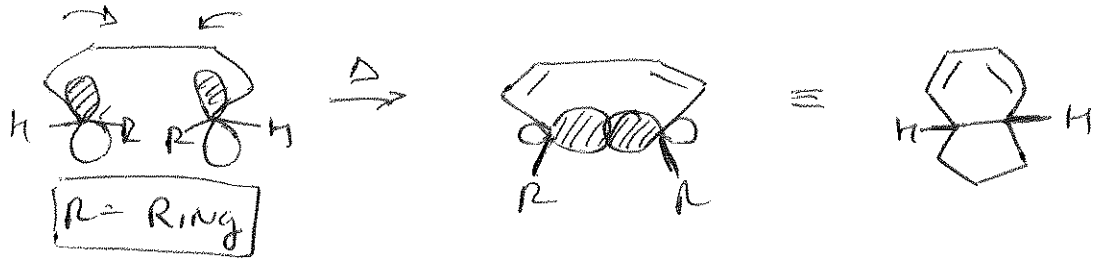
Your Name_____

4. (continued) For the photochemical reactions, we predict

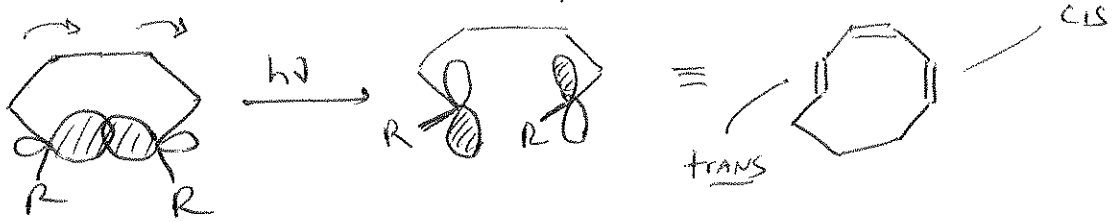
CON - ROTATION



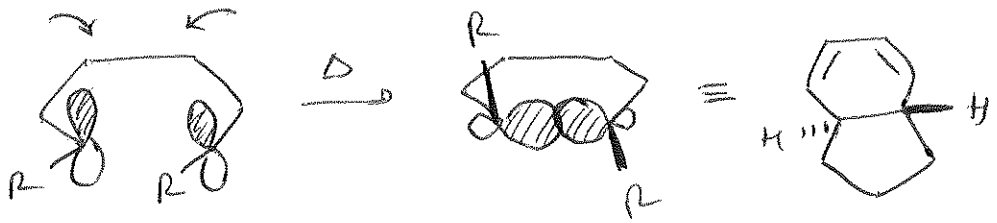
A → B is A DISROTATORY Ring Closing



B → C is a CONROTATORY Ring Opening

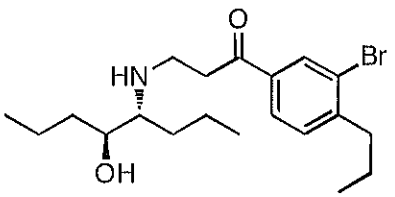


C → D is a DISROTATORY Ring closing

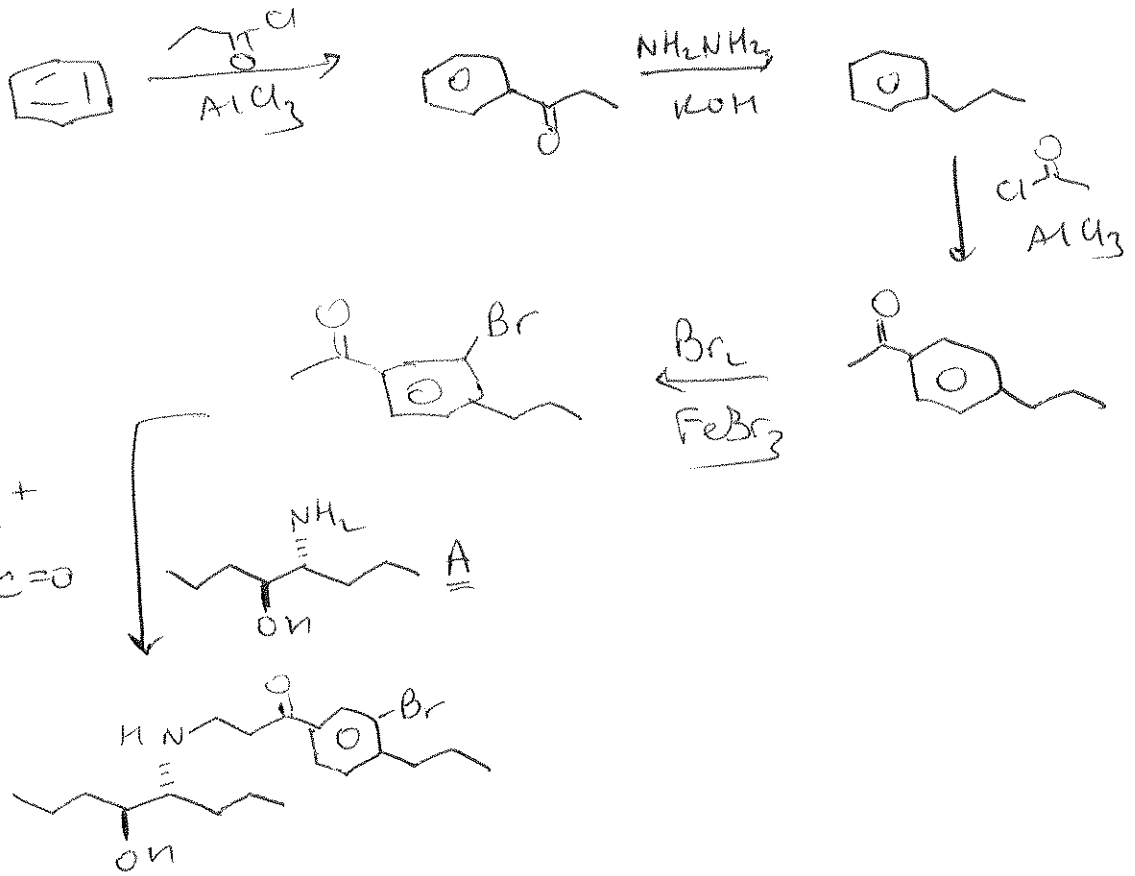


Your Name_____

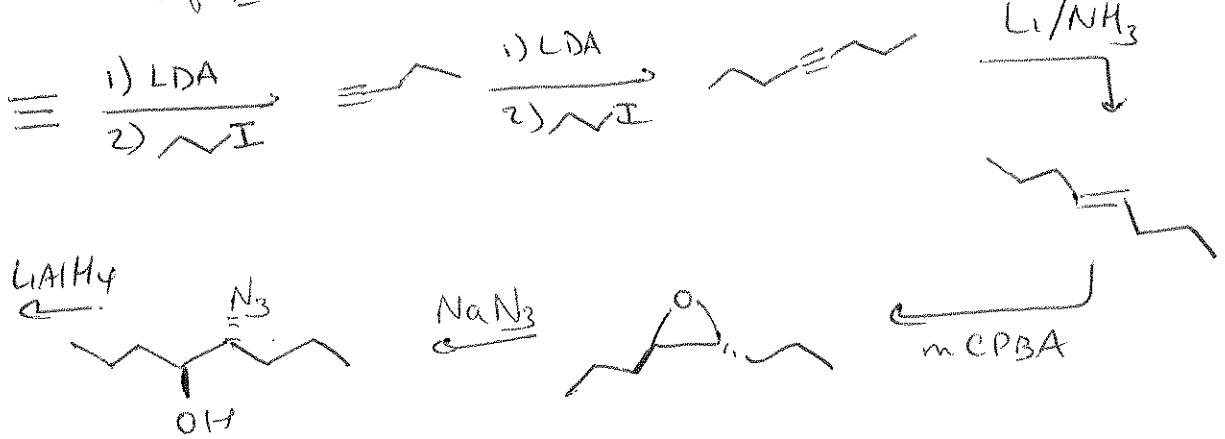
5. Provide a stereoselective synthesis starting with **benzene** and any other materials that contain **three carbons or less.** Any reagents that do not become incorporated into the product (e.g. PPh3) may contain more than three carbons



15 points



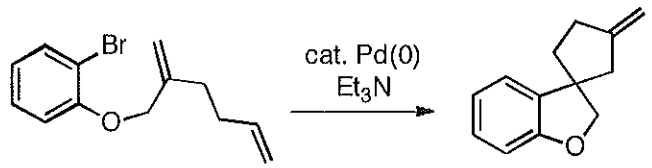
Synthesis of A

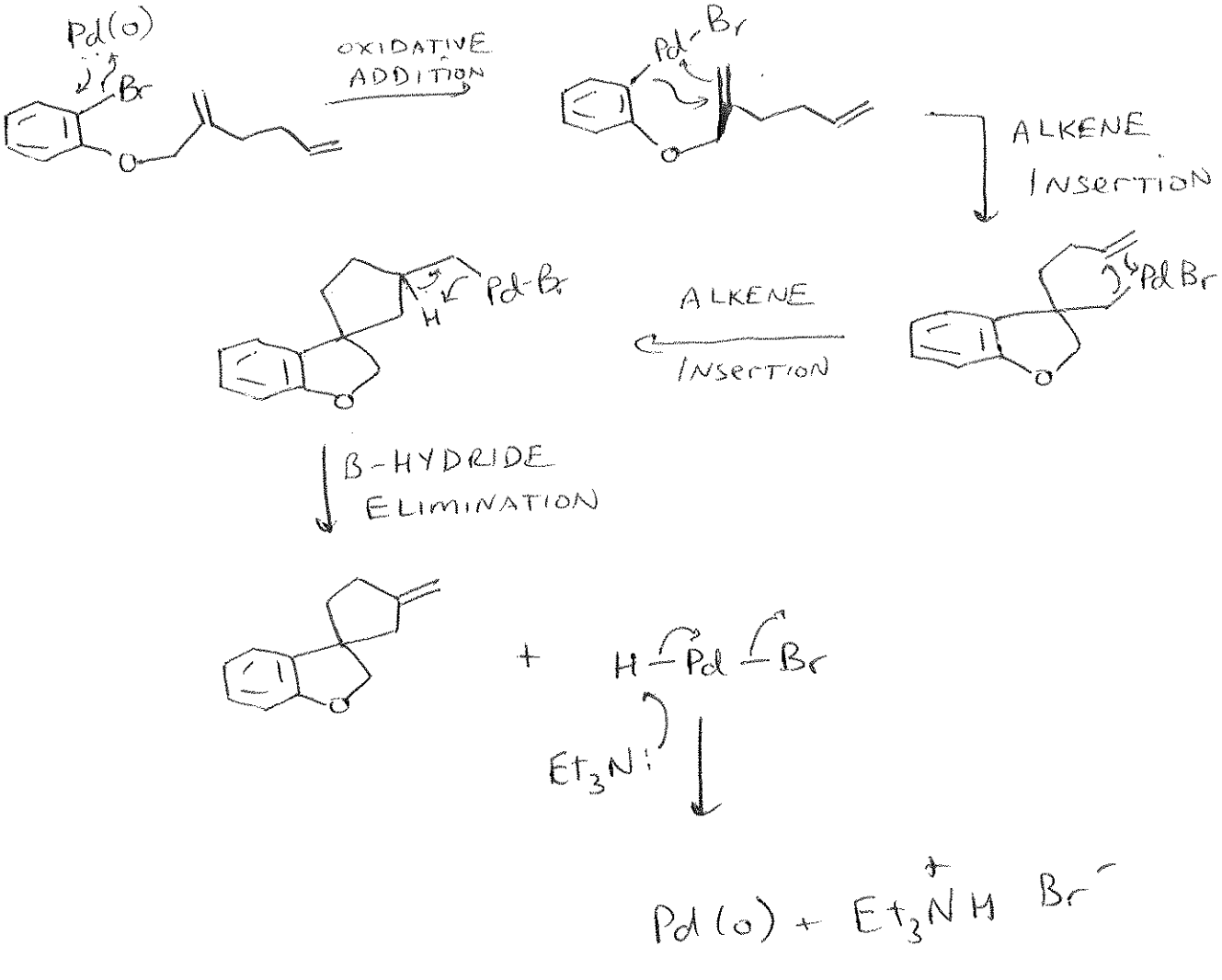


Your Name_____

15 points

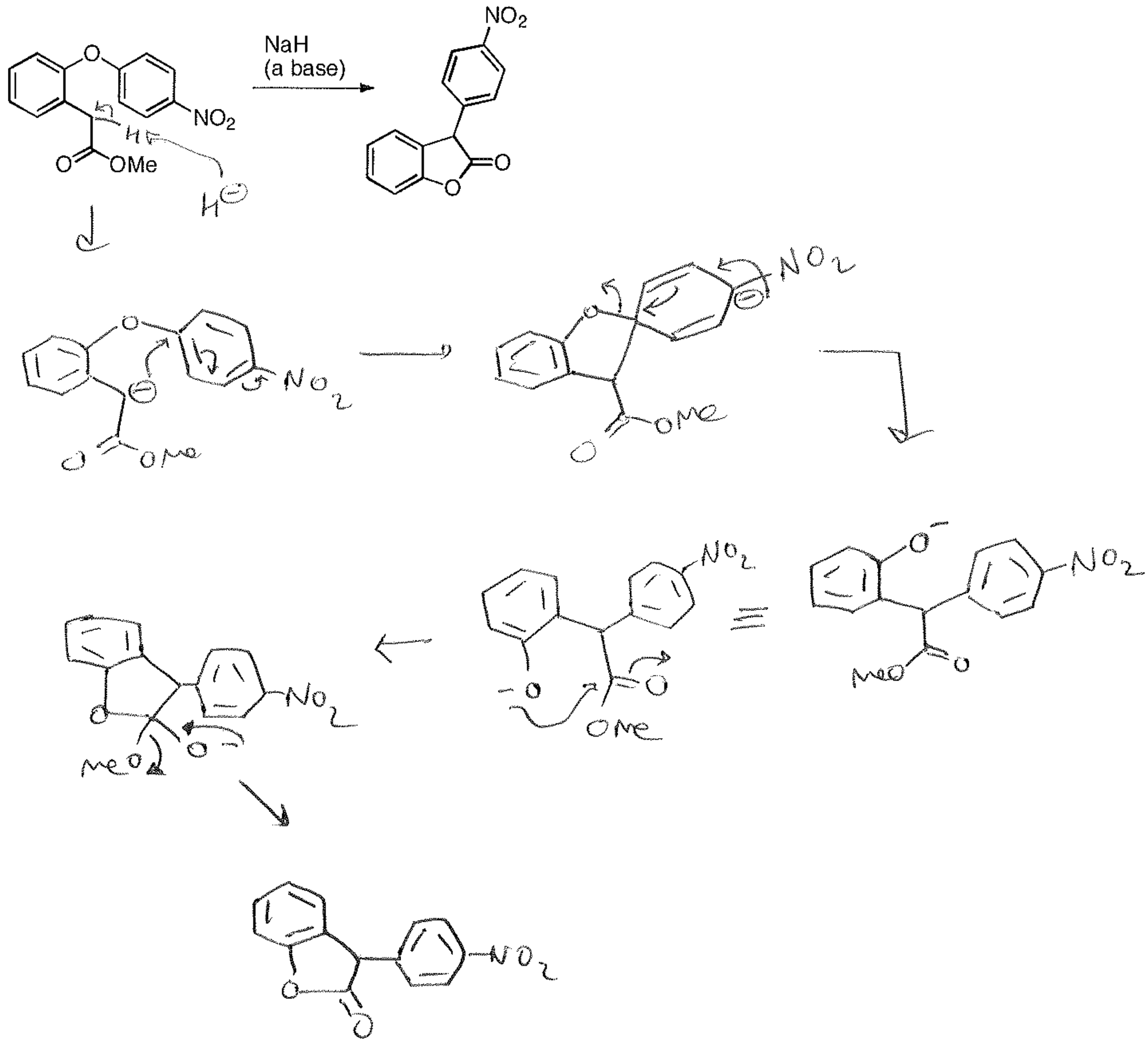
6. Provide a detailed arrow pushing mechanism.





7. Provide a detailed arrow pushing mechanism.

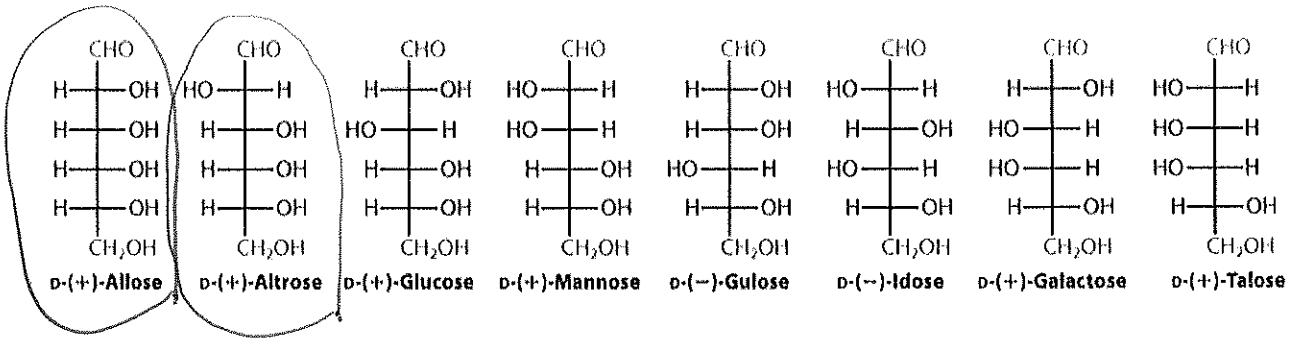
15 points



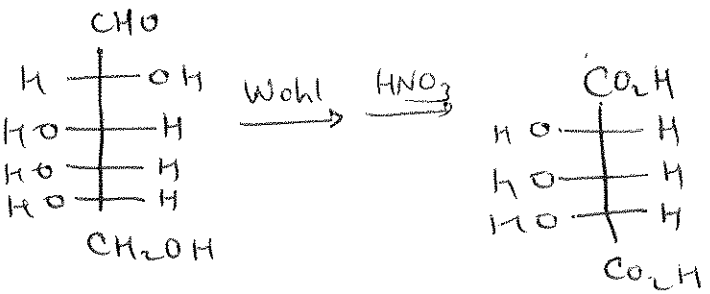
Your Name_____

8. The unnatural sugar (*L*)-Altrose gives a diacid upon sequential Wohl degradation/HNO_3 oxidation. Circle the naturally occuring *(D)*-sugar(s) that give the same diacid upon sequential Wohl degradation/HNO_3 oxidation.

8 points



L-(−)-Altrose

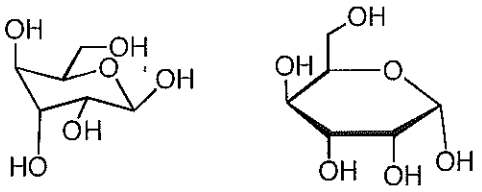


Your Name_____

3 points each

9. Identify each of the following pairs as being identical, meso, enantiomers, anomers, non-anomeric diasteromers. If none of these relationships apply, then indicate that the compounds are not stereoisomers.

(a)



identical (but not meso)

meso

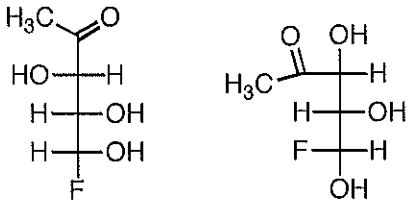
enantiomers

anomers

diastereomers (but not anomers)

these compounds are not stereoisomers

(b)



identical (but not meso)

meso

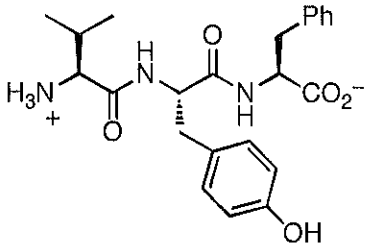
enantiomers

anomers

diastereomers (but not anomers)

these compounds are not stereoisomers

(c) Leu-Tyr-Phe



identical (but not meso)

meso

enantiomers

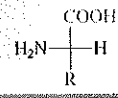
anomers

diastereomers (but not anomers)

these compounds are not stereoisomers

NOTE: the structures of the amino acids are on the following page

TABLE 26-1 Natural (2S) Amino Acids



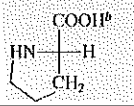
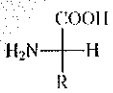
R	Name	Three-letter code	One-letter code	pK_a of α-COOH	pK_a of α-$^+NH_3$	pK_a of acidic function in R	Isoelectric point, p*I*
H	Glycine	Gly	G	2.3	9.6	—	6.0
Alkyl group							
CH_3	Alanine	Ala	A	2.3	9.7	—	6.0
$CH(CH_3)_2$	Valine[a]	Val	V	2.3	9.6	—	6.0
$CH_2CH(CH_3)_2$	Leucine[a]	Leu	L	2.4	9.6	—	6.0
$CHCH_2CH_3$ (*S*) CH_3	Isoleucine[a]	Ile	I	2.4	9.6	—	6.0
	Phenylalanine[a]	Phe	F	1.8	9.1	—	5.5
	Proline	Pro	P	2.0	10.6	—	6.3

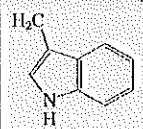
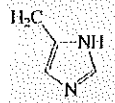
TABLE 26-1 Natural (2S) Amino Acids



R	Name	Three-letter code	One-letter code	pK_a of α-COOH	pK_a of α-$^+NH_3$	pK_a of acidic function in R	Isoelectric point, p*I*
Hydroxy containing							
CH_2OH	Serine	Ser	S	2.2	9.2	—	5.7
$CHOH$ (*R*) CH_3	Threonine[a]	Thr	T	2.1	9.1	—	5.6
	Tyrosine	Tyr	Y	2.2	9.1	10.1	5.7
Amino containing							
CH_2CNH_2 (O)	Asparagine	Asn	N	2.0	8.8	—	5.4
$CH_2CH_2CNH_2$ (O)	Glutamine	Gln	Q	2.2	9.1	—	5.7
$(CH_2)_4NH_2$	Lysine[a]	Lys	K	2.2	9.0	10.5[c]	9.7
$(CH_2)_3NHCNH_2$ (NH)	Arginine[a]	Arg	R	2.2	9.0	12.5[c]	10.8

Continued

TABLE 26-1 Natural (2S) Amino Acids (continued)

R	Name	Three-letter code	One-letter code	pK_a of α-COOH	pK_a of α-$^+NH_3$	pK_a of acidic function in R	Isoelectric point, p*I*
Amino containing *(continued)*							
	Tryptophan[a]	Trp	W	2.8	9.4	—	5.9
	Histidine[a]	His	H	1.8	9.2	6.1[c]	7.6
Mercapto or sulfide containing							
CH_2SH	Cysteine[d]	Cys	C	2.0	10.3	8.2	5.1
$CH_2CH_2SCH_3$	Methionine[a]	Met	M	2.3	9.2	—	5.7
Carboxy containing							
CH_2COOH	Aspartic acid	Asp	D	1.9	9.6	3.7	2.8
CH_2CH_2COOH	Glutamic acid	Glu	E	2.2	9.7	4.3	3.2

[a]Essential amino acids. [b]Entire structure. [c]pK_a of conjugate acid. [d]The stereocenter is *R* because the CH_2SH substituent has higher priority than the COOH group.

Table 26-1 part 3
Organic Chemistry, Fifth Edition