

Chem 332
Exam 4
May 22, 2010
Professor Fox

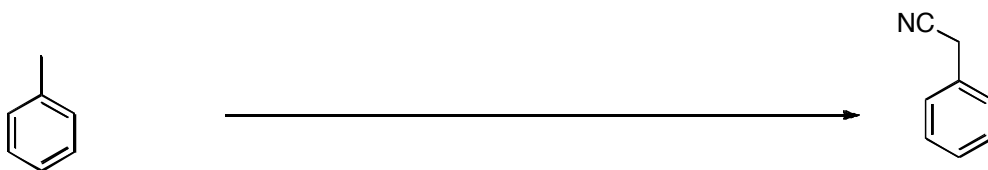
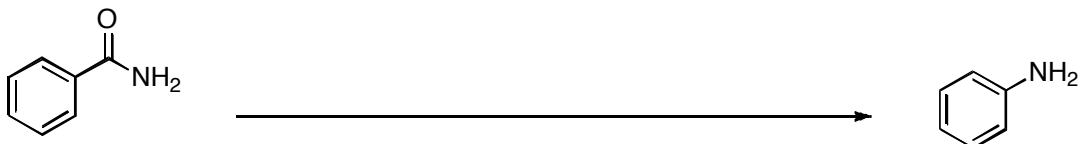
100 points
180 minutes

Your Name_____

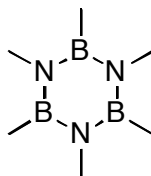
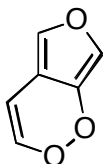
Your Name _____

2 points each

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



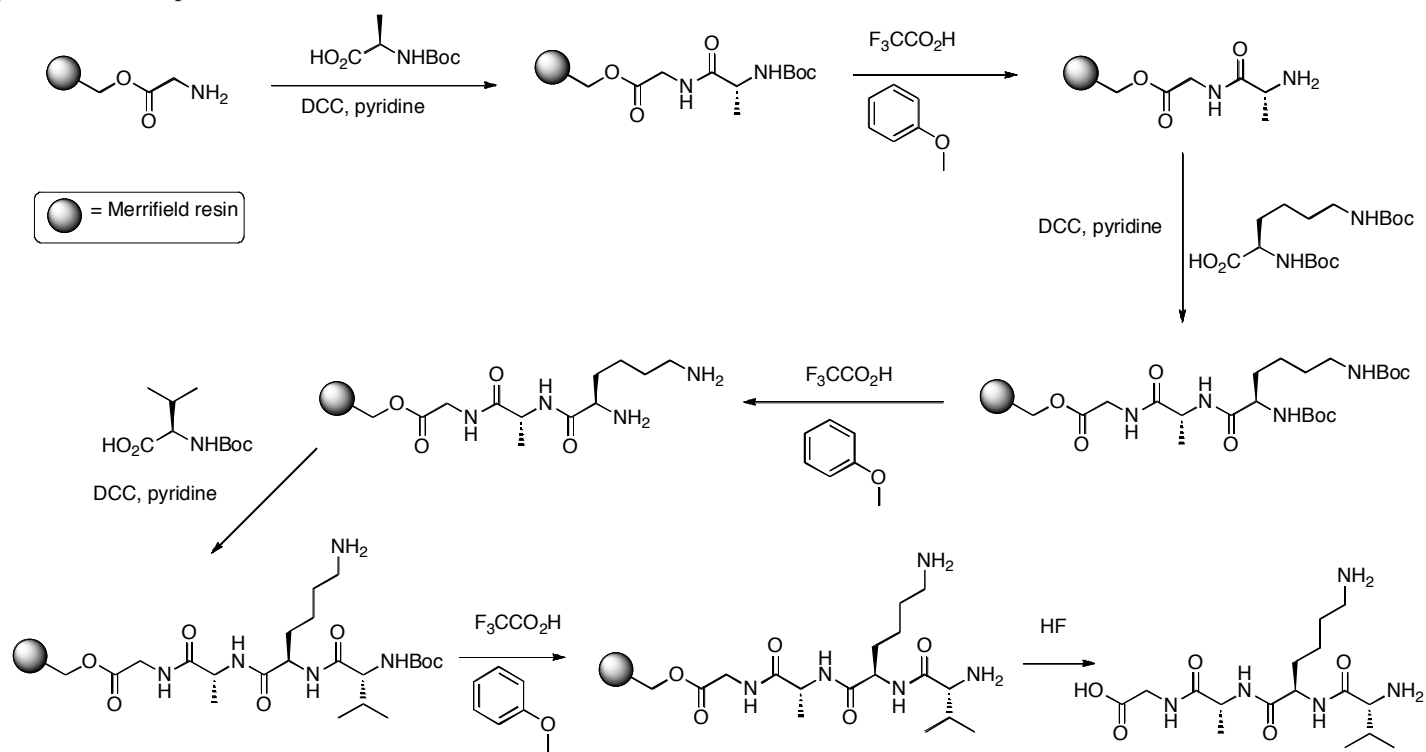
2. Circle the molecules that are aromatic. 2 points each



Your Name _____

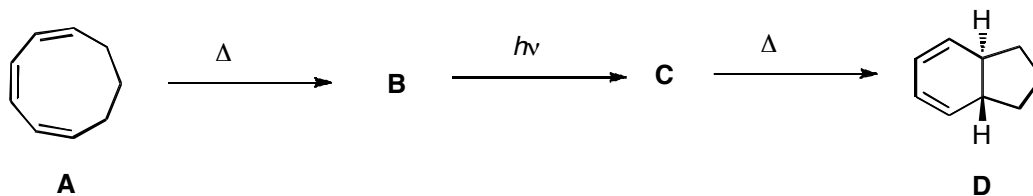
8 points

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



Your Name _____

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



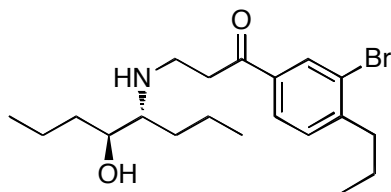
- Provide structures for **B** and **C**, and arrow pushing mechanisms for the formation of **B**, **C** and **D**. (6 pts)
- Use molecular orbital theory to explain the stereoselectivity for the formation of **B**, **C** and **D** (12 pts)

Your Name _____

4. (continued)

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

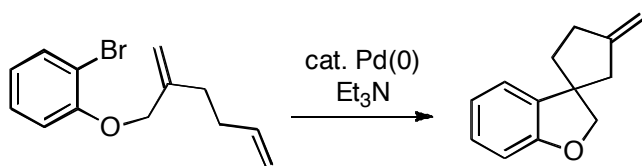


15 points

Your Name _____

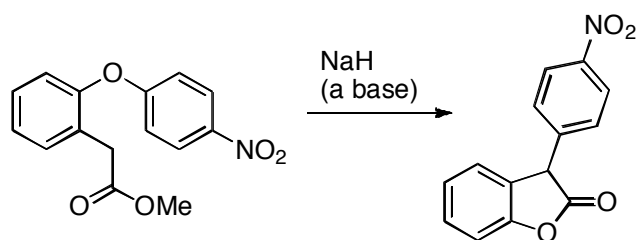
15 points

6. Provide a detailed arrow pushing mechanism.



7. Provide a detailed arrow pushing mechanism.

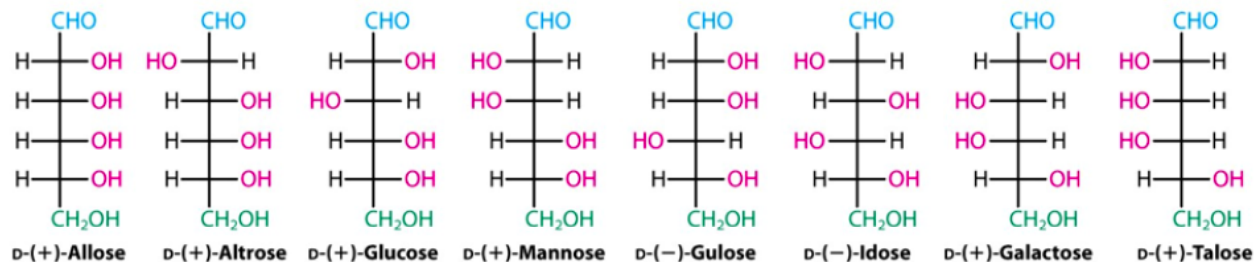
15 points



Your Name _____

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

8 points

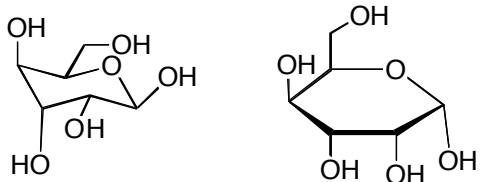


Your Name _____

3 points each

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

(a)



identical (but not meso)

meso

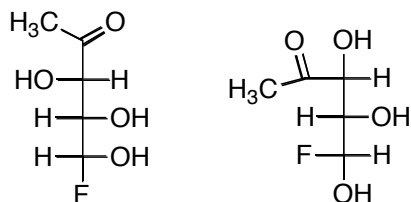
enantiomers

anomers

diastereomers (but not anomers)

these compounds are not stereoisomers

(b)



identical (but not meso)

meso

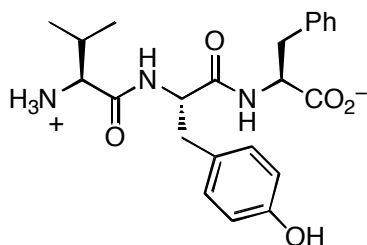
enantiomers

anomers

diastereomers (but not anomers)

these compounds are not stereoisomers

(c) Leu-Tyr-Phe



identical (but not meso)

meso

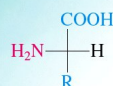
enantiomers

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 (2*S*)-Amino Acids


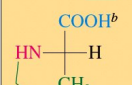
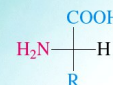

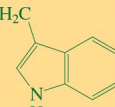

R	Name	Three-letter code	One-letter code	p <i>K</i> _a of α-COOH	p <i>K</i> _a of α- ⁺ NH ₃	p <i>K</i> _a of acidic function in R	Isoelectric point, pI
H	Glycine	Gly	G	2.3	9.6	—	6.0
Alkyl group							
CH ₃	Alanine	Ala	A	2.3	9.7	—	6.0
CH(CH ₃) ₂	Valine ^a	Val	V	2.3	9.6	—	6.0
CH ₂ CH(CH ₃) ₂	Leucine ^a	Leu	L	2.4	9.6	—	6.0
CHCH ₂ CH ₃ (S) CH ₃	Isoleucine ^a	Ile	I	2.4	9.6	—	6.0
H ₂ C- 	Phenylalanine ^a	Phe	F	1.8	9.1	—	5.5
 COOH ^b	Proline	Pro	P	2.0	10.6	—	6.3

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

R	Name	Three-letter code	One-letter code	p <i>K</i> _a of α-COOH	p <i>K</i> _a of α- ⁺ NH ₃	p <i>K</i> _a of acidic function in R	Isoelectric point, pI
Hydroxy containing							
CH ₂ OH	Serine	Ser	S	2.2	9.2	—	5.7
CHOH (R) CH ₃	Threonine ^a	Thr	T	2.1	9.1	—	5.6
H ₂ C- 	Tyrosine	Tyr	Y	2.2	9.1	10.1	5.7
Amino containing							
CH ₂ C(=O)NH ₂	Asparagine	Asn	N	2.0	8.8	—	5.4
CH ₂ CH ₂ C(=O)NH ₂	Glutamine	Gln	Q	2.2	9.1	—	5.7
(CH ₂) ₄ NH ₂	Lysine ^a	Lys	K	2.2	9.0	10.5 ^c	9.7
(CH ₂) ₃ NHC(=O)NH ₂	Arginine ^a	Arg	R	2.2	9.0	12.5 ^c	10.8

Continued

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

R	Name	Three-letter code	One-letter code	p <i>K</i> _a of α-COOH	p <i>K</i> _a of α- ⁺ NH ₃	p <i>K</i> _a of acidic function in R	Isoelectric point, pI
Amino containing (continued)							
H ₂ C- 	Tryptophan ^a	Trp	W	2.8	9.4	—	5.9
H ₂ C- 	Histidine ^a	His	H	1.8	9.2	6.1 ^c	7.6
Mercapto or sulfide containing							
CH ₂ SH	Cysteine ^d	Cys	C	2.0	10.3	8.2	5.1
CH ₂ CH ₂ SCH ₃	Methionine ^a	Met	M	2.3	9.2	—	5.7
Carboxy containing							
CH ₂ COOH	Aspartic acid	Asp	D	1.9	9.6	3.7	2.8
CH ₂ CH ₂ COOH	Glutamic acid	Glu	E	2.2	9.7	4.3	3.2

^aEssential amino acids. ^bEntire structure. ^cp*K*_a of conjugate acid. ^dThe stereocenter is *R* because the CH₂SH substituent has higher priority than the COOH group.