Oakton Community College

Homework Seven
Organic Chemistry II (224) • Prof. Chad Landrie
Spring 2013

Completion (6 pts)		**Name**	
Random Sample(s) (4 pts)		**BID**	
Total (10 pts)		**Section-CRN**	

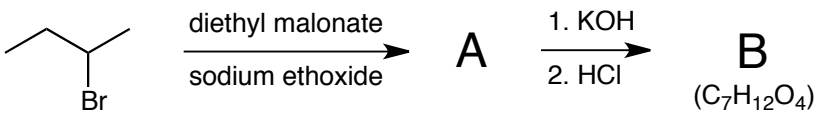
Additional Recommended Problems from McMurray (8th Ed.)	

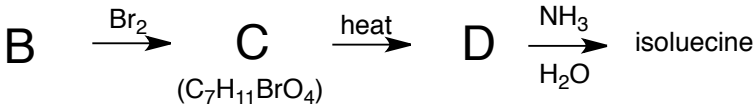
1. Look up the pKa values for isoleucine, then determine the ratio [A–]/[HA] at pH 7. Show all work.

2. At what pH values is [A–] the largest? The smallest? Equal to [HA]?

3. Acrylonitrile (CH_2CHCN) undergoes conjugate addition. Outline a synthesis of β-alanine ($NH_2CH_2CH_2COOH$) that utilizes conjugate addition to acrylonitrile.

4. Draw the structure of intermediates A-D in the synthesis of isoleucine below.





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5. Draw the products of each of the following reactions. Your answer should include all amino acid residues in the starting peptides.

a. Reaction of Leu-Gly-Ser with Sangers's Reagent	b. Hydrolysis of compound in a. in conc. HCl at 100 ºC
c. Treatment of Ile-Glu-Phe with PITC	d. Reaction of Asn-Ser-Ala with benzyloxycarbonyl chloride
e. Reaction of product in d. with *p*-nitrophenol and *N,N'*-dicylohexylcarbodiimide	f. Reaction of product in e. with ethyl ester of valine
g. Hydrogenolysis of product in f with H2 over Pd	h. Reaction of *N-tert*-butoxycarbonylphenylalanylglycine ethyl ester with HBr

6. The imidazole ring of the histidine side chain acts as a proton acceptor in certain enzyme-catalyzed reactions. Draw both potential conjugate acids of histidine and then circle the more stable form. Explain your choice.

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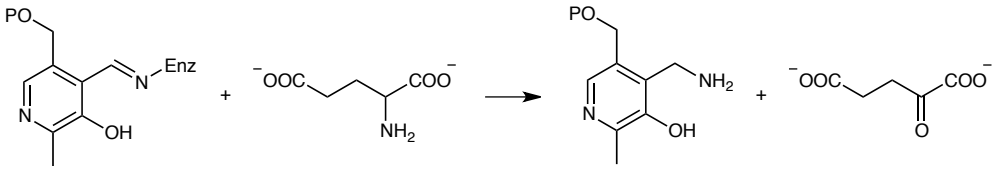
7. Draw the mechanism for transamination of glutamic acid with enzyme-bound pyridoxal phosphate (PLP-E). You may use general-acid or base catalysis as needed. You do not have to draw the mechanism for hydrolysis of imines (I'm assuming you remember this! Review if not.)



enyme-bound pyridoxal phosphate (E-PLP) | glutamic acid | pyridoxamine phosphate (PMP) | α-ketoglutarate

8. Draw the complete mechanism for the deprotection of *N*-benzyloxycarbonylglycine ethyl ester with HBr.

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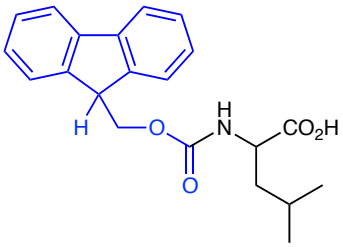
9. Unlike the benzyloxyprotecting group (Z), the 9-fluorenylmethoxycarbonyl (FMOC) is removed under basic conditions (NH_3). **First**, draw all products of this reaction. **Second**, draw a complete mechanism that account for the formation of dibenzofulvene.



10. Phenylalanine was linked with glycine by DCC coupling. Draw (structures, no abbreviations) all four possible dipeptides if these amino acids are not protected.

11. Outline a synthesis of the tripeptide Gly-Val-His. Use appropriate protecting groups in your sequence. You may use solution phase methods or solid-phase synthesis with Merrifield resin.

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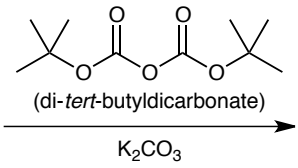
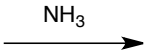
12. Fill in the table below for amino acid protecting groups.

Protecting Group Name and Abbreviation	Protected Alanine (Full structure)	Protecting conditions (Full structure of protecting group)	Deprotection conditions
tert-butoxyl carbonyl (Boc)			
9-fluorenylmethoxycarbonyl (Fmoc)			
Benzyloxycarbonyl (Z or Cbz)			
Ethyl ester (OEt)			
Benzyl ester (OBn or OCH_2Ph)			

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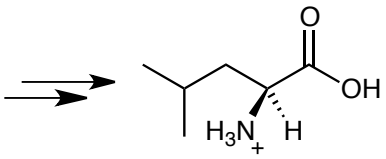
13. Outline a synthesis of the α-amino acid below using each of the methods in the table.



A. Hell-Volhard-Zelinski of carboxylic acids
B. Reductive-Amination of α-ketoacids
C. Strecker Synthesis
D. Acetamidomalonate Synthesis