Midterm Exam 1

Chem 3B, Spring 2018
Friday, February 23, 2018
7:00 – 9:00 pm

Name _____

Student ID _____

You have 120 minutes to complete this exam.

Please provide all answers in the space provided. Work drawn in the margins may not be picked up by the scanner and therefore will not be graded.

The last page of the exam is a table of amino acids and scratch paper. Please tear it off before you begin. It will not be collected, scanned, or graded, so make sure your answers are copied into the appropriate location on your exam.

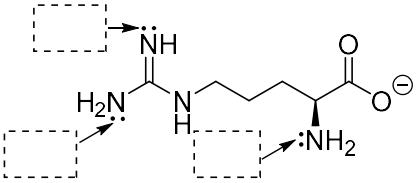
Point values are listed within each question. The exam is worth 200 points total.

Partial Periodic Table

I	II	III	IV	V	VI	VII	VIII
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr
Rb	Sr	In	Sn	Sb	Te	I	Xe

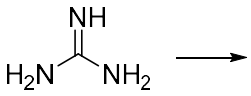
1. Arginine Acid-Base Reactivity.

A. The amino acid arginine is shown below in the "fully deprotonated" protonation state. Fill in each box to label the type of orbital (s, p, sp, sp^2, or sp^3) occupied by each indicated pair of electrons. (6 pt)



"fully deprotonated" arginine structure
(label orbital type for each indicated pair of electrons)

B. The side chain functional group in arginine is called a "guanidine", and its conjugate acid is a "guanidinium ion." Draw two different possible structures of the guanidinium resulting from reaction with acid at different sites of guanidine. Indicate which one is more stable and explain why. (9 pt)



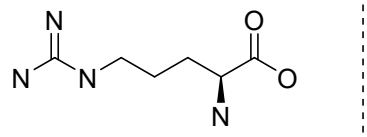
guanidine

A B

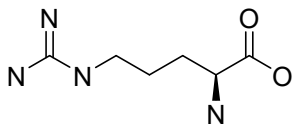
____ is more stable because:

two different possible guanidinium ions

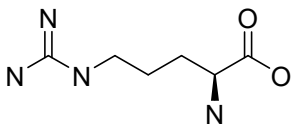
C. The pKa of the guanidinium group in arginine is 12.5. Based on this information, finish the structures below to show the predominant protonation state of arginine at each pH. (9 pt)



Arginine at pH = 0

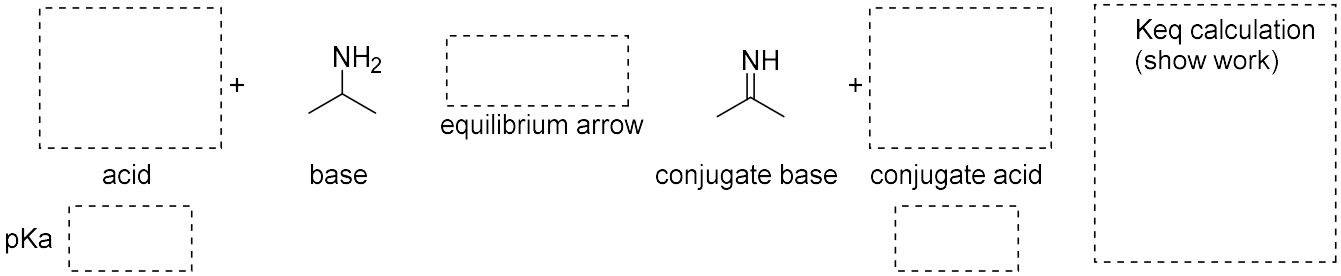


Arginine at pH = 7



Arginine at pH = 11

D. Complete the acid-base reaction scheme and Keq calculation shown below. (15 pt)



acid base equilibrium arrow conjugate base conjugate acid

Keq calculation (show work)

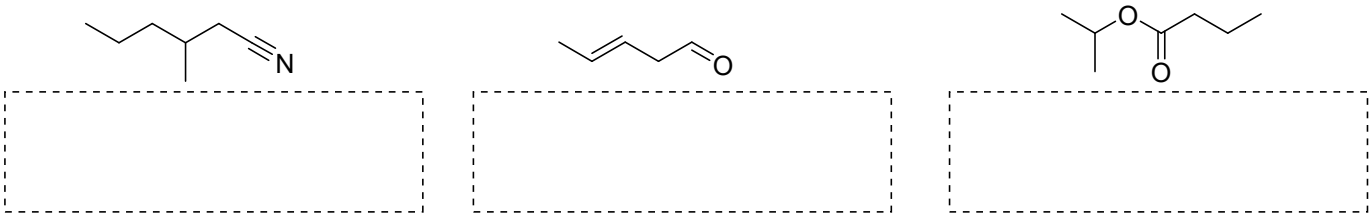
pKa

E. Describe the structure-basicity relationship that is illustrated by each comparison below: (10 words or fewer per box) (2 x 3 = 6 pt)

An **(imine)** or **(amine)** (circle one) is more basic because:	An **(imine)** or **(guanidine)** (circle one) is more basic because:

2. Nomenclature and Functional Groups

A. Write a **systematic name** for each structure below. Used common names for branched substituents. (3 x 4 = 12 pt)



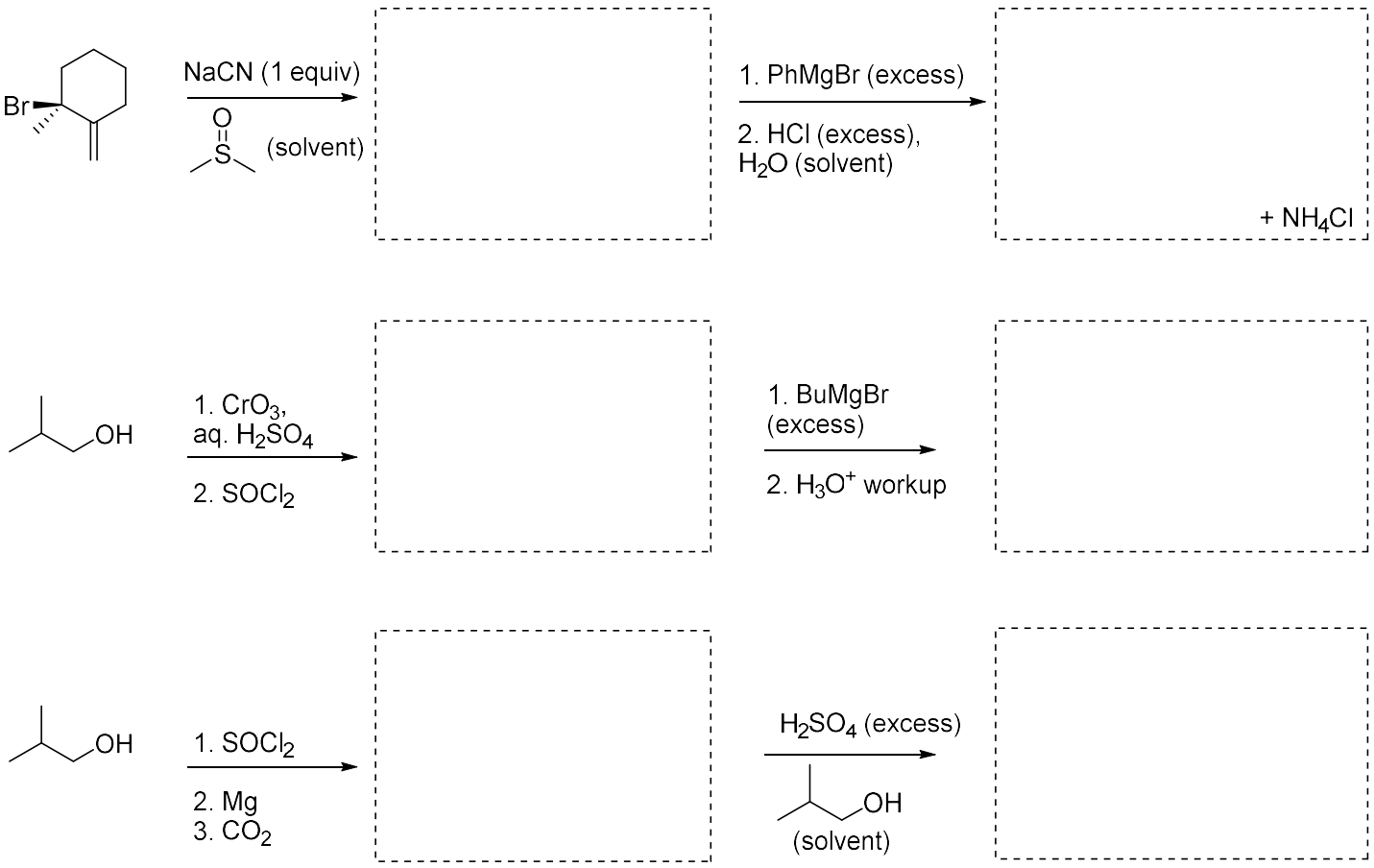
B. Draw a **structure** to match each prompt. (4 + 4 + 6 = 14 pt)

allyl formate

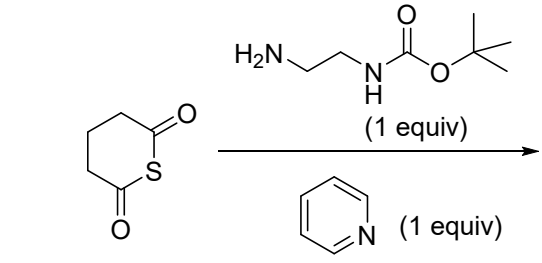
the conjugate base of a thiol

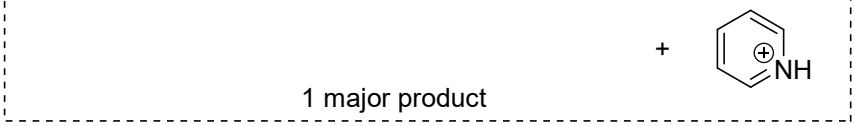
a monounsaturated monoglyceride in its natural geometric configuration

3. Fill in the **missing structures** (**one structure per box)** in the following multistep synthesis schemes. (6 x 4 = 24 pt)

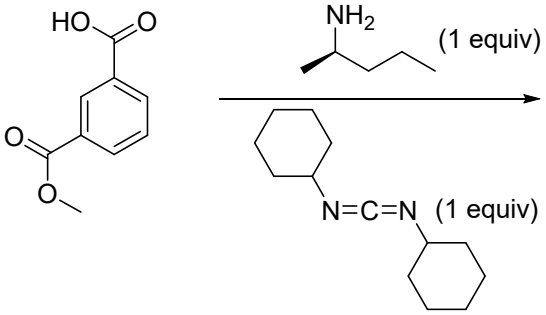


4. **Predict the organic product(s)** from the following reactions. Where relevant, show all stereoisomers. Pay attention to any information given in the product boxes. (5 x 6 = 30 pt)

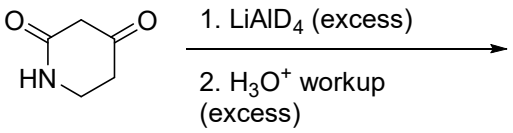




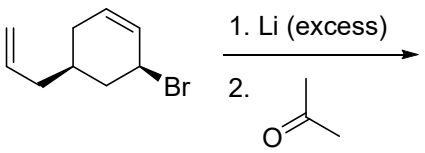
1 major product



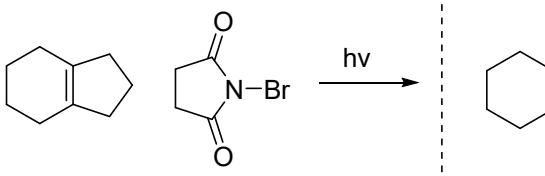
make sure your reaction scheme is balanced

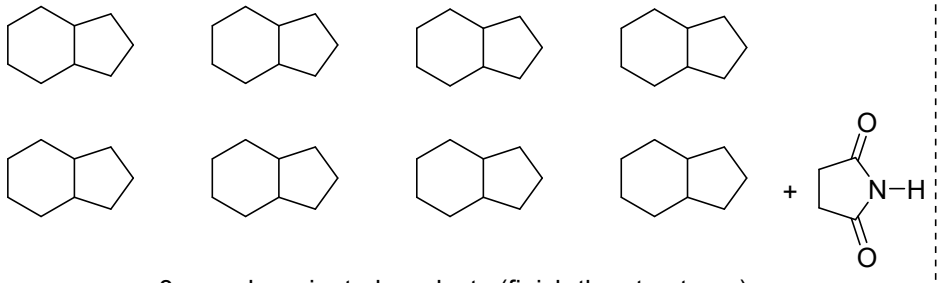


1 major product



4 structures

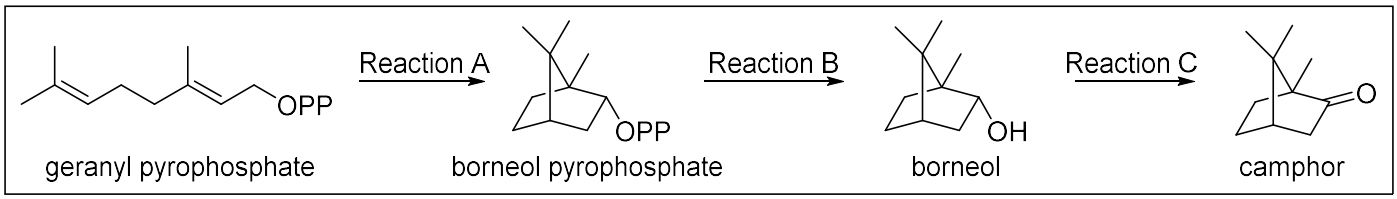




8 monobrominated products (finish the structures)

5. Biosynthesis of Camphor

Camphor is a natural product whose biosynthesis from geranyl pyrophosphate proceeds via three sequential enzyme-catalyzed reactions, as shown in the scheme below.[1]



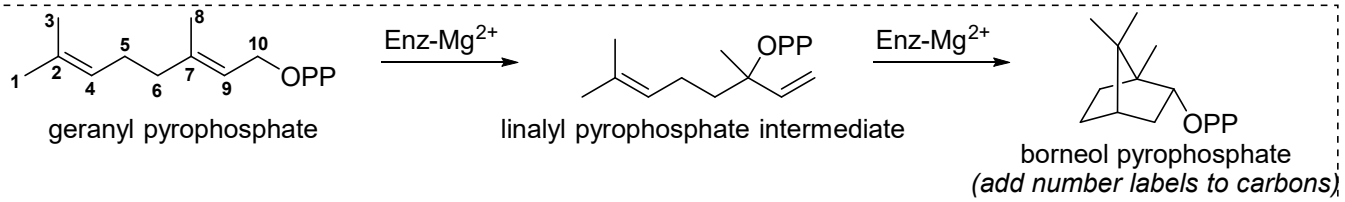
A. What is the **name of the class (family) of natural products** that includes derivatives of geranyl pyrophosphate, including borneol and camphor? Be as specific as possible, including **one** of the following prefixes in the name: (hemi, sesqui, iso, mono, di, or tri) (3 pt)

B. Reaction A is catalyzed by "Enzyme A", which has three Mg^{2+} ions in the active site.

i. **Add numbers to the product** to correspond to the numbers provided on geranyl pyrophosphate.

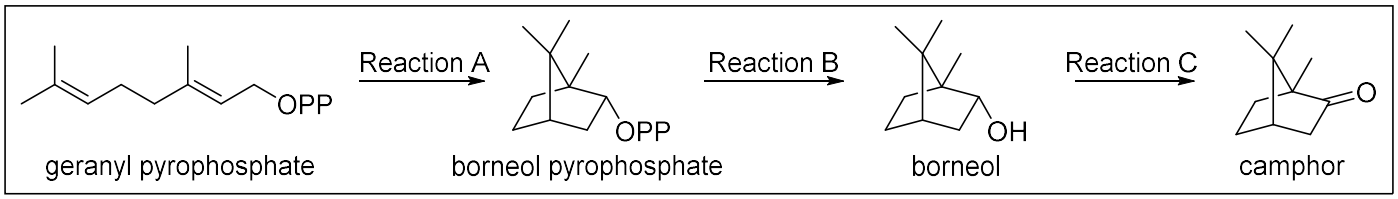
ii. **Draw a curved arrow mechanism** for reaction A. (8 pt)

iii. **Explain why the Mg^{2+} ions** and **linalyl pyrophosphate intermediate** are necessary. (*The intermediate, linalyl pyrophosphate, is formed during the reaction but does not leave the enzyme active site.)* (6 pt)

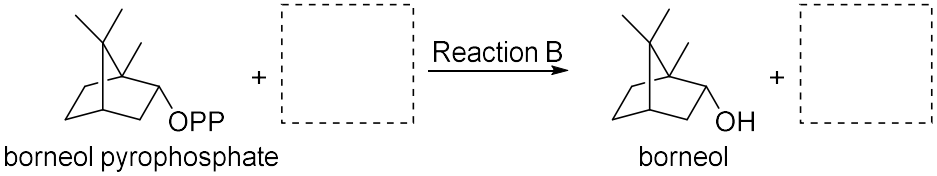


Picture and a few words to explain the role of Mg^{2+} in Enzyme A:	Pictures and a few words to explain why linalyl pyrophosphate is a necessary intermediate in reaction A:

[1] Biochemistry **1985**, *24*, 7077-7085; Chem Rev. **2017**, *117(17),* 11570-11648.



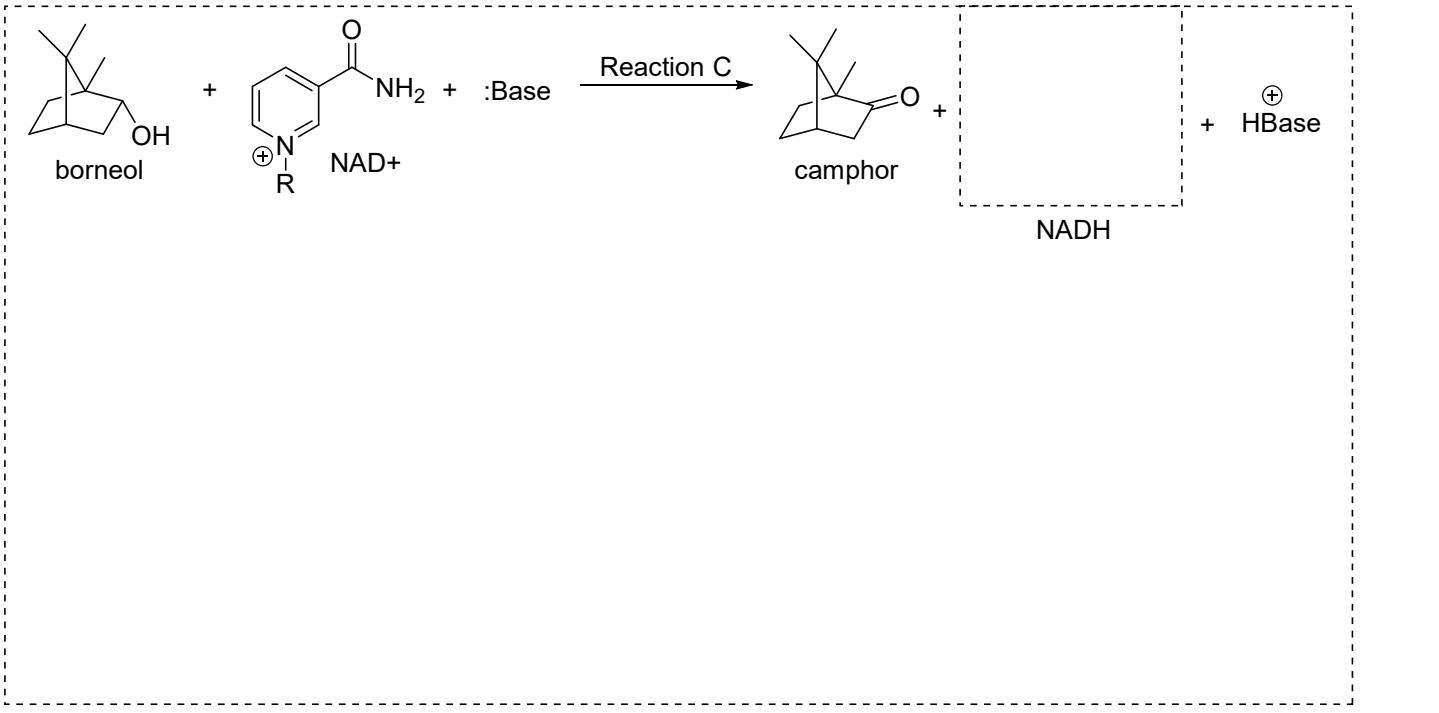
C. Reaction B is catalyzed by a phosphatase enzyme. Fill in the boxes to **balance the reaction scheme**. (3 pt)



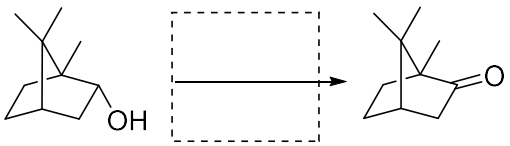
D. Reaction C uses NAD+ as a reactant (drawn in abbreviated form in the scheme below). The reaction proceeds through an alkoxide intermediate

i. Is borneol **oxidized** or **reduced** to make camphor? (3 pt)
ii. Draw the abbreviated **structure of NADH**.
iii. Draw a **curved arrow mechanism** for reaction C. (8 pt)

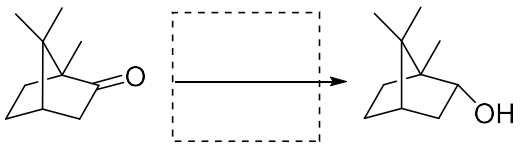
oxidized or reduced?



E. Propose **reaction conditions** to carry out the following reactions in the chemistry lab (not catalyzed by an enzyme). You do not need to take stereochemistry into account in your answer. (2 x 4 = 8 pt)



(not enzyme catalyzed)



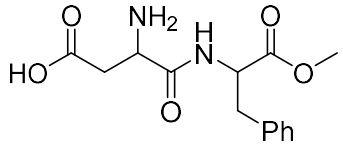
(not enzyme catalyzed)

6. Synthesis of Aspartame

A. Aspartame (Nutrasweet) is a dipeptide-based artificial sweetener that is made from amino acids in their **naturally occurring stereochemical configuration**.

i. Modify (to **wedged or dashed**) **one bond per stereocenter** in the structure. (4 pt)

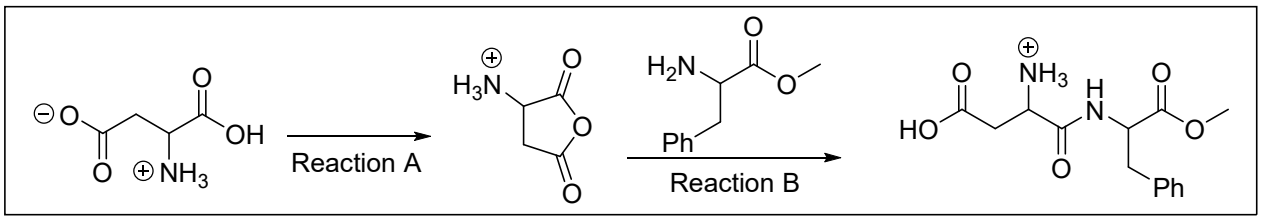
ii. Write a peptide name for aspartame (4 pt) (*Note: an amino acid table is on page 9)*



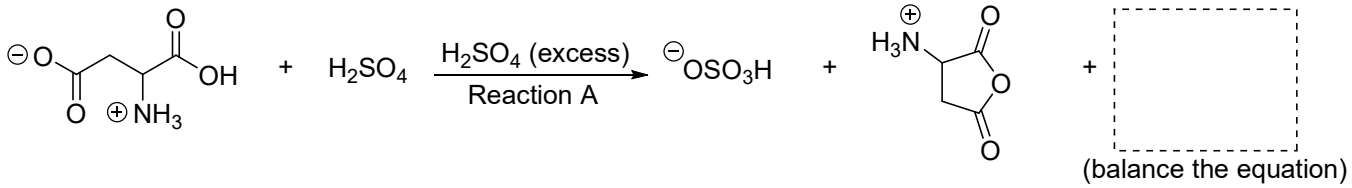
(add stereochemistry)

peptide name of aspartame (using 3-letter codes)

One possible method for the synthesis of aspartame is the following two step reaction sequence.[2]



B. Fill in the product box, then draw a curved arrow mechanism for reaction A. (8 pt)

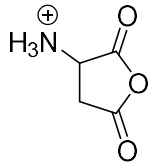


C. In the reaction above, explain why the nitrogen atom **does not** act as a competing nucleophile to create unwanted amide side products. (3 pt)

The nitrogen atom does not act as a competing nucleophile in the reaction above because:

[2] Bulletin of the Chemical Society of Japan **1973** *46:8*, 2611-2612

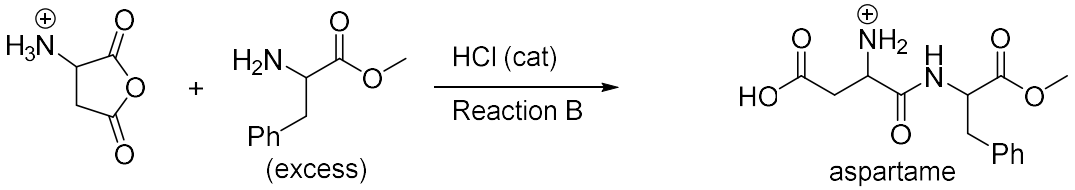
D. Name two functional groups that are present in the cyclic product from Reaction A. (2 x 3 = 6 pt)



Name of one functional group

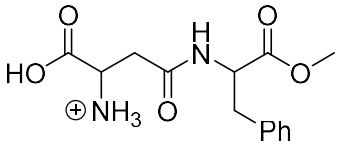
Name of another functional group

E. **Draw a curved arrow mechanism.** If you choose to abbreviate a non-reactive part of a molecule, define your abbreviation by circling and labeling on the original structure (8 pt)



If you choose to abbreviate a non-reactive part of a molecule, define your abbreviation by circling and labeling on the original structure

F. Aspartame is the major product of the reaction above, but the minor side product shown below is also obtained in this reaction. **Explain the observed selectivity** of the reaction. (3 pt)



minor side product from reaction above

The reaction produces more aspartame than the minor side product shown at the left because:

Picture(s) and/or 10 words or fewer

Scratch Paper and Amino Acid Chart

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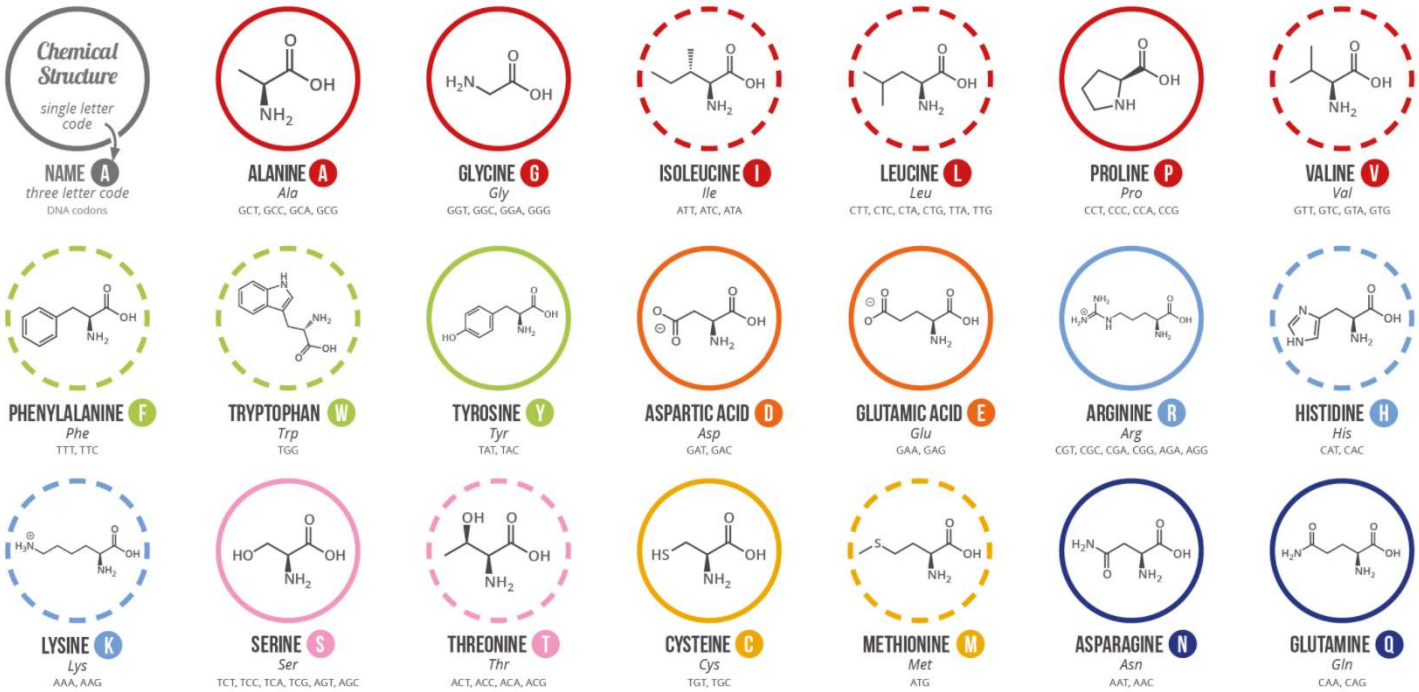

Scratch Paper

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