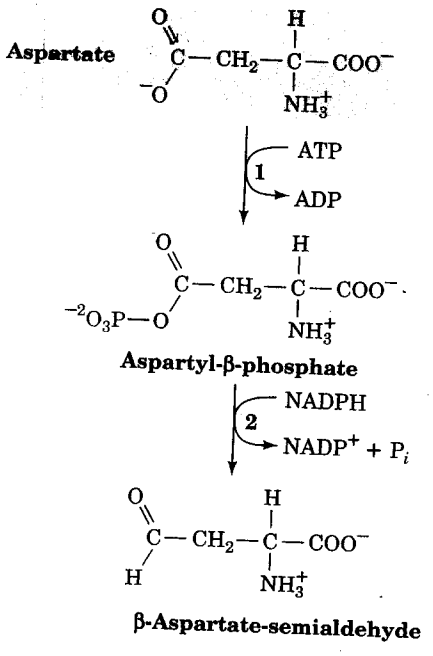
Name_____

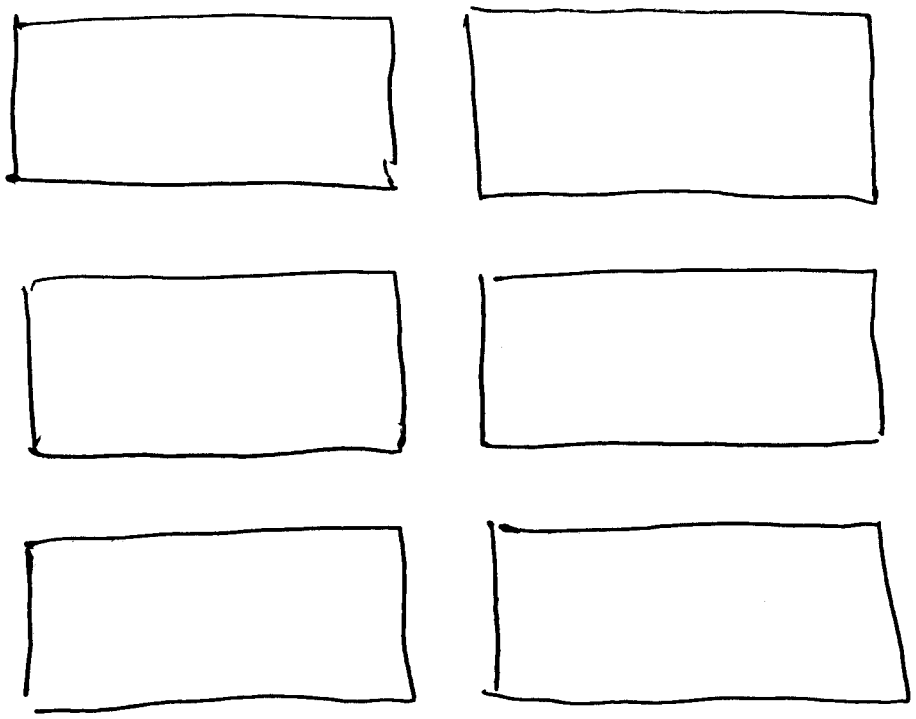
Chemistry 153CH - Spring 2004
Midterm #2 - Monday May 24th
Total of 90 points - make sure you have all 4 pages!

1. (26 points total) Let's make some essential amino acids! We didn't discuss the detailed pathways of essential amino acid synthesis in plants and microorganisms, but I assured you all came from molecules we had seen before in chemical pathways not too dissimilar from what we had seen.

For example, in bacteria, lysine, threonine, and methionine are all made from aspartate beta-semialdehyde in the reactions shown below.

Asp/Thr/Lys pathway **Gluconeogenesis** **Proline/Arginine synthesis**

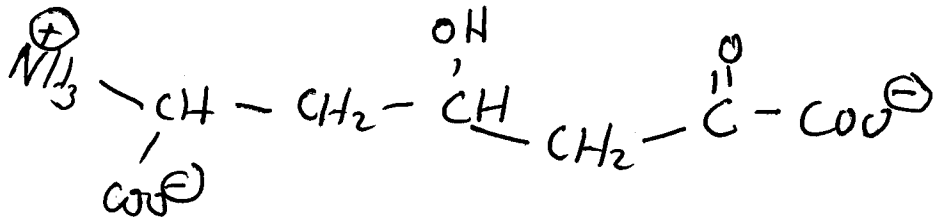




Fill in the **names** and the **structures** of the corresponding compounds involved in the mechanistically similar pathways that we have seen in gluconeogenesis and in the pathway of proline and arginine synthesis. Use **arrows** to indicate the normal overall direction of each step in the pathway listed. Show **cofactors** and **other substrates and products** as in the example.

2. (28 points total) And even more essential amino acids!

To make lysine from L-aspartic acid beta-semialdehyde, some cells react pyruvate with it to linearly extend the amino acid side chain to give the product shown below.

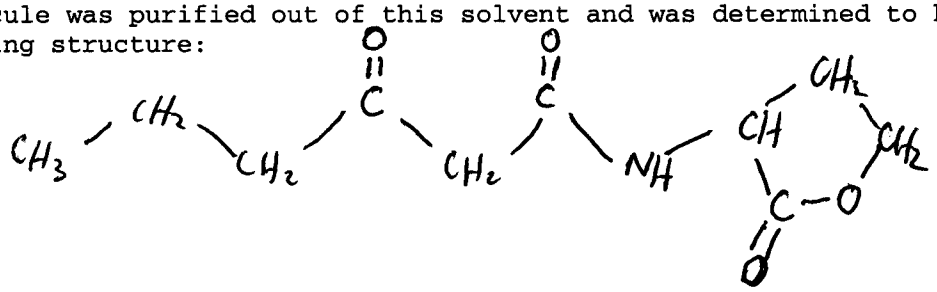


(a) (10 points) Write out the mechanism of this reaction, using appropriate arrows to show electron movements. **Draw resonance forms** for the portions of the substrates that demonstrate how they react here.

(b) (18 points) Based on the reactions you have seen in this course, suggest a series of steps that will bring this intermediate to lysine. You **need not** show mechanisms but do indicate the possible participation of any cofactors and indicate all substrates and products. Draw the full structures of all intermediates on the pathway; for cofactors and other substrates and products, you can simply name them.

3. (19 points)

Extracts were made of rat liver cells with a solvent of hexane:2-propanol (3:2). A molecule was purified out of this solvent and was determined to have the following structure:



(a) (3 points) Based on its extraction properties, what general class of biomolecule is this?

(b) (16 points) Describe a possible pathway for its synthesis from an intermediate of fatty acid biosynthesis and S-adenosylmethionine. Indicate the mechanism using appropriate arrows to show electrons movements and give the **full structures** of all substrates, products, and intermediates.

4. (17 points total).

We have learned that humans with deficiency of vitamin B12 can accumulate methylmalonyl-CoA. We mentioned that this compound could lead to the production of branched chain fatty acids that could be eventually incorporated into membrane phospholipids.

(a) (9 points) Write out a reaction in which methylmalonyl-CoA can be incorporated instead of malonyl-CoA into a fatty acid chain in fatty acid synthase. Give the structures of methylmalonyl-CoA, an appropriate intermediate in the synthase reaction, and the product of the incorporation step. Use appropriate arrows to indicate electron movements.

(b) (8 points) Write out the structure of the final product of fatty acid synthesis where one molecule of methylmalonyl-CoA has participated in the reaction you have drawn above. At what position in the longest carbon chain is the branch in your structure? (Number from the carboxylate carbon as #1). At what other carbon positions in the final product of fatty acid synthase can branches also occur at?