- Organic Synthesis Reductive Amination
- Biosynthesis of Asparagine and Proline not in the textbook, use lecture notes

Mechanisms to Know for AA Synthesis

Reductive Amination

Add arrows to complete this mechanism, adding acids (H^{+}) and bases (:B) when needed



Applied to racemic amino acid synthesis:



• Nucleophilic Acyl Substitution (NAS)



109, Binder

Biosynthesis of Proline



Each step takes place in the active site of an enzyme, which contains all the acids (H^{+}) and bases (:B) necessary to complete each transformation (more on that later). Until then, feel free to use H^{+} and :B as needed.

Always consider physiological pH when drawing intermediates and products.

- Nitrogen is usually protonated (+), sometimes neutral, NEVER (-)
- Carboxylic acids should be deprotonated (-), sometimes protonated / neutral
- Phosphates have 2 (-) oxygen atoms per P
- Alcohols should always be protonated / neutral

Formation and NADH Reduction of Phosphoester



Intramolecular Reductive Amination



109, Binder

Biosynthesis of Asparagine



Hydrolysis of Glutamine

$$0$$
 $HO-H$
 $H_{3}N$ CO_{2} $HO-H$

Phosphate Transfers with ATP

Aspartate

Amide Formation

Mixed Anhydride

H₂N —H (from glutamine hydrolysis)

Exam 1 Overview Anything in the lecture notes or HW is fair game!

- Know functional group structure & name "FG Table" on 109 website
- Structure Property Relationships
 - Link term to definition or figure / scenario
 - Ex. What happens structurally when ethanol boils?
 - Ex. What happens when NaCl dissolves? When sugar dissolves?
- Acid-Base Chemistry
 - Know the **pKa's from lecture 1**, use to predict pKa of new molecule
 - Draw products of acid-base reaction, predict direction of equilibrium

Be ready to draw any the following **mechanisms** given starting materials *and* either the name of mechanism *or* the product(s). **Formal charges** must be clearly represented, where appropriate. The **exact start and end point of arrows** is important! Know **what arrows mean**: bonds broken / formed.

- Electrophilic Addition to Alkenes
- S_N1 & S_N2
- Nucleophilic Addition to Aldehydes & Ketones
- Nucleophilic Acyl Substitution (NAS)
- Aldol & Claisen Condensation Reactions (forward and reverse)
- E1, E2, & E1cB
- Reduction with NADH & Oxidation with NAD+
 - Be able to draw the core structure of NADH if given NAD⁺ & vice versa
- Polyprotic acids: given pKa's, draw all ionic forms over given pH range

Exam 2 material begins with...

- Amino Acid Synthesis
 - Similar or identical to examples in today's notes or HW