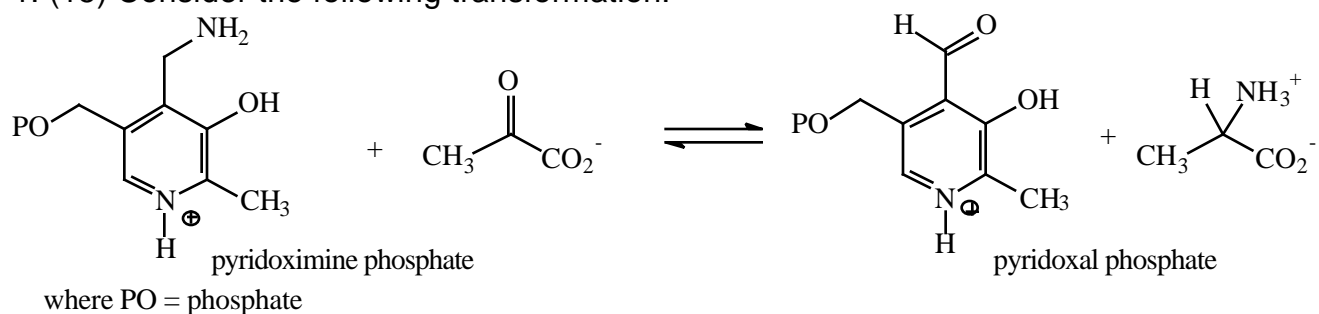


Organic Cumulative Exam March 22, 1997

I. Several recent seminar presentations have dealt with pyridoxal / pyridoxamine chemistry. These compounds are cofactors for a number of enzyme catalyzed transformations. The transamination reaction involved in amino acid synthesis and metabolism is key among them.

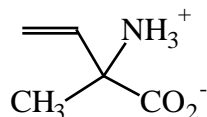
1. (15) Consider the following transformation:



The transformation occurs under enzymatic conditions, by catalysis with metals such as Cu^{++} , or more slowly at acidic pH's. Give a plausible mechanism for the transformation assuming just acid or base catalysis.

2. (5) Speculate on the role of Cu^{++} in the catalysis.

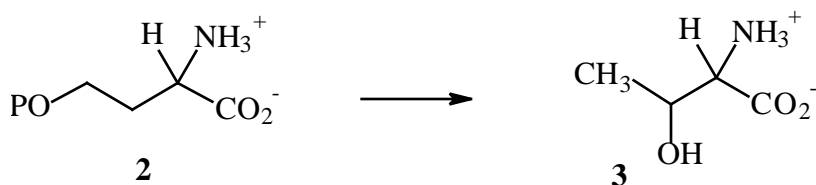
3. (15) Professor Berkowitz presented a seminar focused on α -vinylamino acids, such as **1**. These compounds are known to provide inhibition of enzymes requiring pyridoxal. Using **1** and pyridoxal phosphate, give a mechanism by which inhibition of the reverse of the transformation above might occur.



1

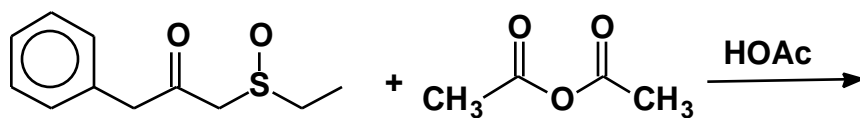
4. (15) Outline a plausible synthesis for racemic **1** from readily available starting materials.

5. (20) Pyridoxal participates in the conversion of homoserine phosphate **2** to threonine **3**. The OH group in threonine comes from water. Using acid and base catalysis give a plausible mechanism for the conversion of **2** to **3**.



II.

1. (10) Use mechanistic rationale to predict the products of the following Pummerer reaction.



2. (20) Kuethe and Padwa (JOC **1997** 62 774-775) present a new heterocycle synthesis as shown below. Give a plausible mechanism for the transformations shown below.

