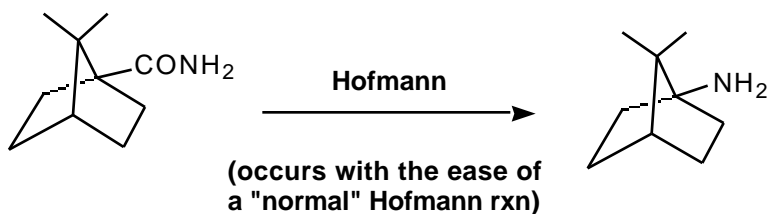
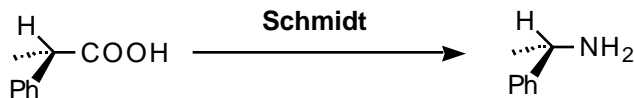
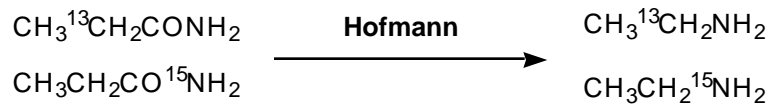
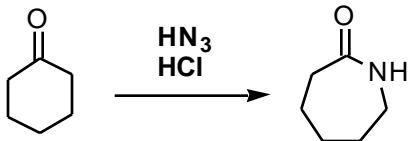




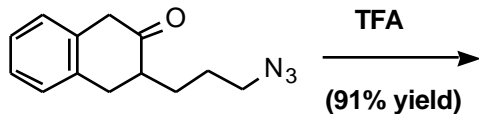
4. What did the experiments shown below tell early researchers about the mechanism of the Schmidt and Hofmann rearrangements? (What alternate mechanism(s) do these observations rule out?) (6 pts)



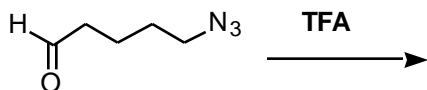
5. Now for a different Schmidt reaction: the Schmidt reaction of ketones. The major product resulting from addition of hydrazoic acid to cyclohexanone is shown below. Suggest a mechanism for this Schmidt Reaction. (7pts)



6. A Schmidt Reaction utilizing ALKYL azides has recently been developed independently by Aube and Pearson. Aube's version is shown below. Predict the product and propose a mechanism for its formation. (10pt)



7. In the intramolecular Schmidt Reaction utilizing alkyl azides, aldehydes behave differently than ketones. The reaction shown below yields two products each with molecular formulas of  $\text{C}_5\text{H}_9\text{NO}$ . Spectroscopic evaluation reveals that one contains an aldehyde group and the other an amide. Suggest what the two major products are and rationalize their formation with mechanisms. (6pt)

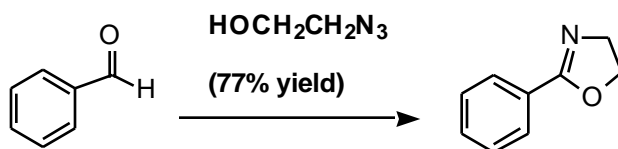


8. Aube expressed surprise (*JACS* **1995**, *117*, 10449) that the Schmidt reaction of alkyl azides was not developed until the 1990s, given that the "standard" Schmidt reaction has been widely used for a very long time. To explain the longstanding lack of interest in this area he suggested that the early attempts at carrying out intermolecular Schmidt reactions with alkyl azides which were quite unsuccessful must have discouraged further work. Early unsuccessful attempts involved intermolecular addition of alkyl azides to ketones. Aube notes that he and Pearson have succeeded in their recent attempts largely because intramolecular Schmidt reactions are much more facile than intermolecular versions.

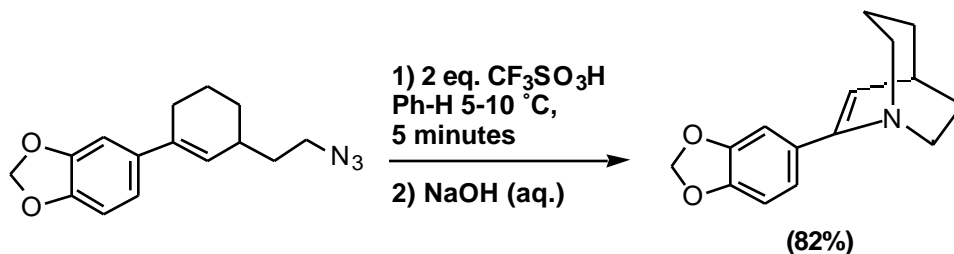
a) Suggest why the intramolecular Schmidt Reaction of Alkyl Azides is more facile than intermolecular versions. (4 pts)

b) Aube's group has also shown that the intermolecular Schmidt Reaction of alkyl azides can proceed if titanium tetrachloride is used as a catalyst (again, in explaining why this interesting reaction lay undiscovered for so long, he notes that in the 1950's the use of titanium tetrachloride was not all that common - so early researchers did not attempt titanium tetrachloride-catalyzed version of this reaction). What is the general role of  $\text{TiCl}_4$ ? (3 pts)

c) In the old literature there is one example of a high-yielding Schmidt reaction using an alkyl azide. The successful reaction uses hydroxyethyl azide. The reaction with ethyl azide does not work. Given what we now know about this general reaction, suggest why the reaction with hydroxyethyl azide works. Show a mechanism (5 pts)



10. Pearson's group has developed related Schmidt-type chemistry (*J. Heterocyclic Chem.* **1996**, *33*, 1489). For our final question, let's take a quick look at Pearson's chemistry.



Suggest a mechanism for this transformation (7 pts).