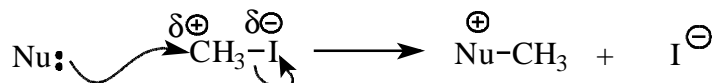
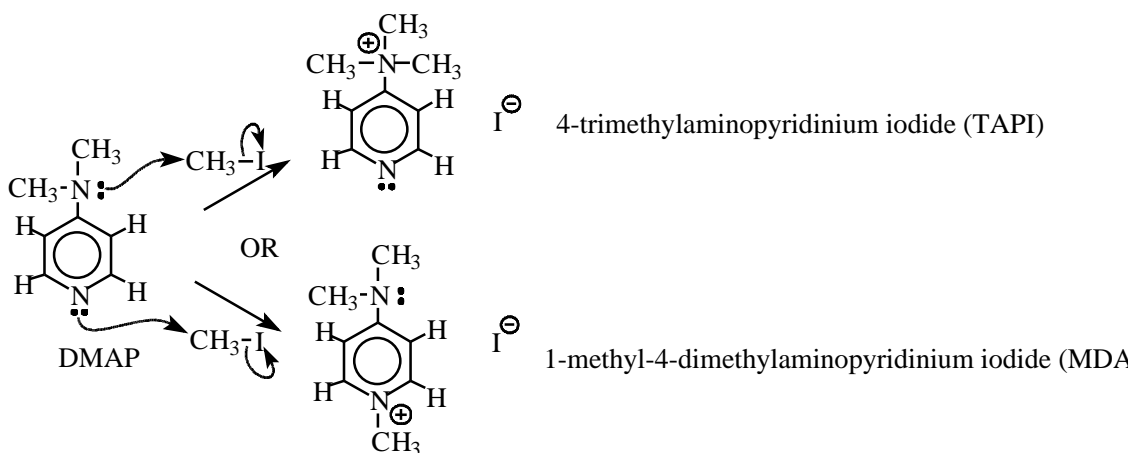


WHICH NITROGEN? Reaction of a Nucleophile  
*Adapted from Leslie Hull, J. Chem. Ed. 2001, 78, 420-421*

The electrons in the C-I bond of iodomethane ( $\text{CH}_3\text{-I}$ ) are unsymmetrically distributed causing the carbon atom to possess a partial positive charge. This positive charge makes that carbon atom susceptible to attack by and bond formation to nucleophiles.



Now suppose that there are two nucleophilic sites in the same molecule. The one that reacts fastest with iodomethane and similar compounds will be the site whose nonbonded electron pair are most available for donation to another atom. We will examine the relative nucleophilicities of the nitrogen sites in 4-dimethylaminopyridine (DMAP). This will be accomplished by simply allowing the reaction to occur, then isolating and identifying the product.



LABORATORY PROCEDURE:

**CAUTION: DMAP and iodomethane (methyl iodide) are both health hazards absorbed through the skin. Wear gloves while preparing the reaction mixture.**

Set up a reflux apparatus using a 5 mL round-bottomed flask fitted with a West condenser and heated by a sand bath with a minimum amount of sand. Weigh *directly* into the flask 1.0 mmol (0.122 g) of 4-dimethylaminopyridine (DMAP); add a boiling stone and 2.0 mL of methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), swirling until the DMAP dissolves. Now add 1 mmol (0.142 g, 62  $\mu\text{L}$ ) of methyl iodide. Attach the condenser and heat to reflux for 30 minutes.

After refluxing, remove the heat and cool the flask briefly in an ice bath. Isolate the solid that is formed by vacuum filtration, rinse the flask out into the suction funnel with two 3-mL portions of  $\text{CH}_2\text{Cl}_2$  and then continue pulling air through the crystals for two minutes to dry them. Determine the mass of the crystals and obtain their proton NMR spectrum in  $\text{D}_2\text{O}$ . Use the mass to calculate the percent yield of the reaction and use the NMR spectrum to identify the product as directed in the post-lab questions.

*\*Adapted from Leslie Hull, J. Chem. Ed. 2001, 78, 420-421*

PRELAB QUESTIONS:

1) Based on the following information which nitrogen in DMAP would you expect to be the better nucleophile? Explain your answer using a **drawing** of the molecule as described below.

The nitrogen atom in the ring is planar  $sp^2$  hybridized with one electron donated to the pi cloud of the planar ring through its remaining p-orbital. Its nonbonded electron pair is located in one of the hybrid orbitals, extends out in the plane of the ring and is not involved in the bonding of the molecule.

The nitrogen atom with the methyl groups is also  $sp^2$  hybridized and planar even though that would not have been predicted using VSEPR. Its *nonbonded* electron pair is not actually nonbonding since the two electrons are in a p-orbital that is lined up with and has a strong bonding interaction with the carbon atom p orbitals of the ring.

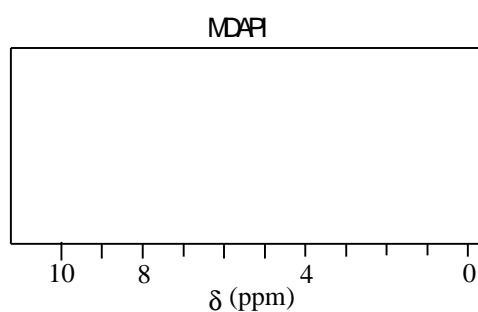
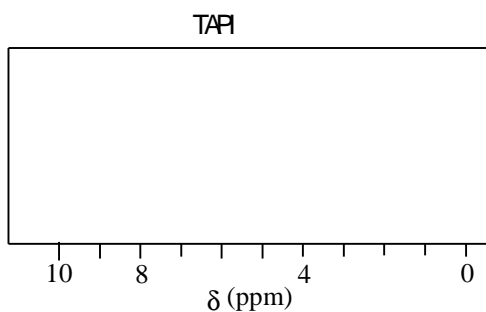
2) Iodomethane and DMAP are potential hazards. How do they gain entry into your body? How is this avoided?

3) Why is the proton NMR spectrum run in heavy water ( $D_2O$ ) instead of regular water.

4) How many NMR signals should be produced in the  $^{13}C$  NMR spectrum of each of the potential products? Remember that atoms in each unique molecular environment produce a different NMR signal.

5) How many NMR signals should be produced in the  $^1H$  NMR spectrum of each of the potential products?

5) Hydrogen atoms on the pyridine ring absorb at 6-9  $\delta$  and methyl hydrogen atoms absorb at 1-4  $\delta$ . Use this information to sketch the spectra that you anticipate for each. The size of each signal is proportional to the number of hydrogen atoms that produce it.



## POSTLAB QUESTIONS:

### 1) Percent yield:

- a) Calculate the molar quantities of DMAP and  $\text{CH}_3\text{I}$  you used in this reaction.
- b) Which is the limiting reagent, DMAP or  $\text{CH}_3\text{I}$ ?
- c) Calculate the molecular weight of the product formed by your reaction. Remember that the iodide anion is present in the crystals and must be included in the molecular weight.
- d) What is the mass of the maximum amount of this product that can be produced from the amounts of reagents you used? This is called the theoretical yield.
- e) Use the calculated theoretical yield and the measured actual yield to calculate the percent yield obtained in your experiment.

### 2) Interpretation of the NMR spectrum:

- a) How many signals are present in the  $^{13}\text{C}$  spectrum of your compound? Based on this evidence which of the products was formed by the reaction?
- b) Measure the integration for each of the  $^1\text{H}$  signals and use this to assign signals to specific hydrogen atoms in the product molecule.

3) Based on what we know about the behavior of molecules and ions, we would expect that the more stable of the two ions would be formed by the reaction. This is generally the ion in which the electrical charge is most widely distributed. The position of the electrical charge for the ion produced in this experiment can be represented by a series of resonance structures in which the charge is distributed around the ring as well as on to the other nitrogen atoms. Draw these resonance structures.