Pre-Laboratory Exercises **Name_____________________**

Unit 1M: Introduction to Organic Synthesis I
Preparation of benzyltriphenylphosphonium bromide (Last updated 08/18/04)

This assignment is due <u>at the beginning</u> of your recitation section one week before the day that you are scheduled to perform this experiment. It is in your best interests to complete these exercises as far in advance as practical. It is not in your best interests to wait until the day you have lab.

To receive a satisfactory grade your answers must be presented clearly. Looks count. Do your preliminary work on scrap paper. You can find data about the physical properties of the compounds in question in an Aldrich catalog, copies of which are available in rooms 152 and 363 of the Science building.

Consider the following excerpt from a procedure for the preparation of benzyltriphenylphosphonium <u>chloride</u>, $C_6H_5CH_2P^+(C_6H_5)_3\ Cl^-$:

Place 2.2 g of triphenylphosphine into a 100 mL round bottom flask containing a magnetic stir bar. Transfer 1.44 mL of benzyl chloride to the flask and add 8 mL of toluene. Reflux the mixture for 1.5-2 hours. Stir the mixture during this period.

Figure 1 summarizes some of the calculations that a chemist would make while planning this procedure. Using these examples for reference, answer questions 1-3. Since most of the experiments in this course are done on a millimolar scale, it is useful to calculate masses in milligrams (mg). However, since the balances weigh in grams (g) you will want to develop the ability to convert g to mg and vice versa. To that end, some of the problems require answers in both units. Show your work for all problems.

Figure 1
Sample Calculation for Problem 1*

PPh_3 MW = 262.29 g/mol

$$\frac{2.2\ \text{g}}{262.29\ \text{g/mol}} = 0.0084\ \text{mol}$$

$$\frac{8\ \text{mL}}{1000\ \text{ml/L}} = 0.008\ \text{L}$$

$$\frac{0.0084\ \text{mol}}{0.008\ \text{L}} = 1.05\ \text{M}$$

$$\frac{PPh_3}{C_6H_5CH_2Cl} = \frac{0.0084}{0.0125} = 0.67$$

$C_6H_5CH_2Cl$ MW = 126.59 g/mol
d = 1.100 g/mL

1.44 mL x 1.100 g/mL = 1.584 g

$$\frac{1.584\ \text{g}}{126.59\ \text{g/mol}} = 0.0125\ \text{mol}$$

$$\frac{0.0125\ \text{mol}}{0.008\ \text{L}} = 1.56\ \text{M}$$

* **Note-**Chemists use several abbreviations to represent the phenyl ring. The three most common are C_6H_5, Ph, and the Greek letter phi, ϕ. Thus triphenylphosphine may be abbreviated as $(C_6H_5)_3P$, Ph_3P, and ϕ_3P.

1. The procedure for the preparation of benzyltriphenylphosphonium bromide, $C_6H_5CH_2P^+(C_6H_5)_3\ Br^-$, allows you to use between 0.90 and 1.05 mmol of triphenylphosphine, Ph_3P. What is the equivalent mass range that you should use? Record your answers to 3 significant figures.

   0.90 mmol = ________ mg

   0.90 mmol = ________ g

   1.05 mmol = ________ mg

   1.05 mmol = ________ g

2. The procedure also calls for you to use 5±1 mL of toluene. Calculate the minimum and maximum molarities of the solutions you would obtain by using these mass and volume ranges.

   Minimum molarity = _______ M

   Maximium molarity = ______ M

3. For each mmol of Ph_3P that you use, you are supposed to use 1.05 mmol of benzyl bromide, $PhCH_2Br$. In other words, Ph_3P is the **limiting reagent** in this reaction. Calculate the number of mmol, the mass (in g and mg), and the volume (in mL and µL) of $PhCH_2Br$ that you should use for 0.95 mmol and 1.05 mmol of Ph_3P.

   For 0.95 mmol of Ph_3P:

   Use ________ mmol of $PhCH_2Br$

   Use ________ mg of $PhCH_2Br$

   Use ________ g of $PhCH_2Br$

   Use ________ mL of $PhCH_2Br$

   Use ________ µL of $PhCH_2Br$

For 1.05 mmol of Ph_3P:

Use ________ mmol of $PhCH_2Br$
Use ________ mg of $PhCH_2Br$

Use ________ g of $PhCH_2Br$

Use ________ mL of $PhCH_2Br$

Use ________ µL of $PhCH_2Br$

As the scheme shown in Figure 2 indicates, the theoretical yield of benzyltriphenylphosphonium chloride from the procedure described above is 3.26 grams. The second equation is an abbreviation of the first, where Ph stands for a phenyl ring, C_6H_5, and the (1) before each compound is a reminder of the stoichiometry of the reaction; the reactants combine in a 1/1 molar ratio, which, when you use 2.2 g of the limiting reagent is equivalent to an 8.39×10^{-3} mol/8.39×10^{-3} mole ratio, as the third equation indicates.
Use these examples to help you with the calculations required to answer questions 4-7 below.

Figure 2
Sample Calculation for Problem 4

$$\underset{126.6\ g/mol}{C_6H_5CH_2Cl} + \underset{262.3\ g/mol}{P(C_6H_5)_3} \longrightarrow \underset{388.9\ g/mol}{C_6H_5CH_2\overset{+}{P}(C_6H_5)_3\ Cl^-}$$

$$(1)\,PhCH_2Cl + \underset{2.2\ g}{(1)\,PPh_3} \longrightarrow (1)\ PhCH_2\overset{+}{P}Ph_3\ Cl^-$$

$$\frac{2.2\ g}{262.3\ g/mol} = 8.39 \times 10^{-3}\ \text{mol of } PPh_3$$

$$8.39 \times 10^{-3}\ PhCH_2Cl + 8.39 \times 10^{-3}\ PPh_3 \longrightarrow 8.39 \times 10^{-3}\ PhCH_2\overset{+}{P}Ph_3\ Cl^-$$

$$8.39 \times 10^{-3}\ \text{mol} \times 388.9\ g/mol = 3.26\ \text{g of } PhCH_2\overset{+}{P}Ph_3\ Cl^-$$

4. What is the theoretical yield of $C_6H_5CH_2P^+(C_6H_5)_3\ Br^-$ that would be formed in the reaction of 1.03 mmol of Ph_3P with a 5% excess of $PhCH_2Br$?

________ g

________ mg

5. Assume that the student running the reaction described in question 4 obtained 0.376 g of product. What was the percentage yield of the product?

________ %

6. Assuming that your preparation of $C_6H_5CH_2P^+(C_6H_5)_3\ Br^-$ will proceed in 100% yield, what mass of Ph_3P should you use in order to prepare 0.500 g of $C_6H_5CH_2P^+(C_6H_5)_3\ Br^-$?.

mass = _________ g

7. Assuming that your preparation of $C_6H_5CH_2P^+(C_6H_5)_3\ Br^-$ will proceed in 90% yield, what mass of Ph_3P should you use in order to prepare 0.500 g of $C_6H_5CH_2P^+(C_6H_5)_3\ Br^-$?

mass = _________ g