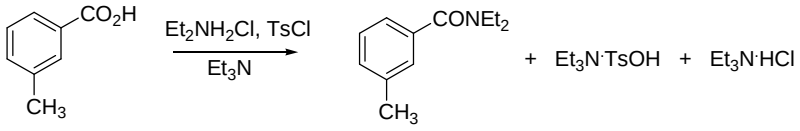
Green Chemistry Analysis

Using the St. Olaf Green Chemistry Assistant (http://fusion.stolaf.edu/gca) you and your partner will generate a **Green Process Analysis Report** for one of two procedures for the synthesis of the insect repellant *N*,*N*-diethyl-*m*-toluamide (DEET). You will then join up with another group to compare the "greenness" of the two procedures. The two procedures are described below.

Method 1:

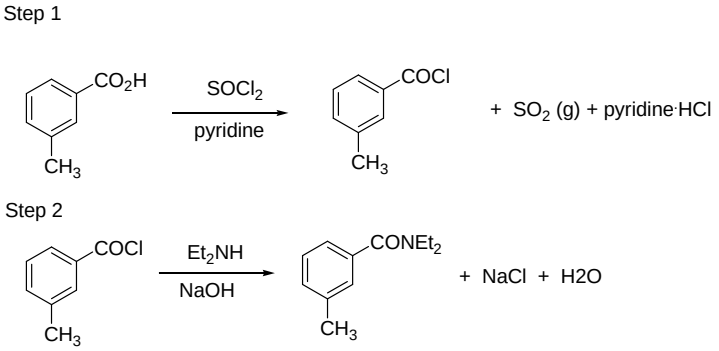


Procedure:

In a small mortar were mixed 1.03 g of a diethylammonium hydrochloride/silica gel mixture (32% w/w diethylammonium hydrochloride), 0.29 g of *p*-toluenesulfonyl chloride (TsCl), and 0.20 g of *m*-toluic acid. The mixture was ground thoroughly using a pestle and then placed in a 6-inch test tube. Triethylamine (0.60 mL) was added by syringe. The mixture was stirred vigorously with a spatula for five minutes.

The solid was extracted three times with 15 mL of diethyl ether. The combined ether extracts were washed three times with 20 mL of 5% aqueous HCl, three times with 20 mL of 5% aqueous NaOH, and once with 30 mL of water. The ether layer was dried over anhydrous magnesium sulfate, and the solvent was removed using a rotary evaporator to give a clear, pale yellow liquid.

Method 2:



Procedure:

To 1.0 mL of dry diethyl ether in a dry 10-mL round bottomed flask were added 2.50 g of *m*-toluic acid, 30 drops of pyridine, and 2.75 mL of thionyl chloride ($SOCl_2$). A reflux condenser fitted with a drying tube was attached, and the solution was stirred at room temperature for 15 minutes. The excess thionyl chloride was then removed at room temperature using a rotary evaporator. The resulting liquid was added dropwise using a Pasteur pipette to a stirred, ice-cold solution of 6.5 mL of diethylamine in 25 mL of 10% NaOH. The solution was stirred for five minutes.

The solution was then extracted twice with 25 mL of diethyl ether. The combined ether extracts were washed first with 20 mL of 10% aqueous HCl and then with 20 mL of water. The ether solution was dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator to give a clear, pale yellow liquid.

Creating the Green Process Analysis Report

Before doing this analysis, read through the GREEN pages of your lab manual. Follow the steps outlined below for the procedure you and your partner have been assigned. Besides the analysis report (which you will turn in by email), answer the questions in your laboratory notebook (or other paper if you do not have a notebook yet).

1. **Balance the overall chemical equation** for the main reaction using just the formulas provided. (For Method 2, there are two steps, with two separate equations.) Balance each equation without worrying about what "Ts" or "Et" mean.

2. Identify the **desired product**.

3. Identify all **coproducts**.

4. Using the *Green Chemistry Search Assistant* (left-hand panel) find the chemical formulas of all reactants and products in the balanced equations. The ChemExper link should be particularly helpful in this regard.

5. Start your Green Chemistry Analysis by entering the **balanced chemical equation** into the Green Chemistry Assistant under Tab 1. When doing this, use chemical formulas and identify the **desired product** with an asterisk. Note the **atom economy**. Explain why the atom economy is not 100%.

6. Enter the **reactant quantities** into the Green Chemistry Assistant using Tab 2. You may have to use the ChemExper link to find density.

7. Check that table. In each step, which reactant is the **limiting reactant**? What is the **theoretical yield**? What is the **experimental atom economy**? -- And why is it lower than the atom economy that you found in (5)?

8. Enter **solvent** information into the analysis using Tab 3a. (*Solvents* in this case include diethyl ether and water.)

9. Enter **other reagent** information into the analysis using Tab 3b. These include everything else used in the reaction. Display the process accounting table by clicking the  icon under the Other Reagents table and note the overall **process mass efficiency**. What does this number signify? Why is it so low?

10. Add **safety information** into the analysis starting with Tab 4a. To begin, you need to assign the correct Chemical Abstracts System (CAS) registry number for each substance you are using. (Ask your instructor how to do this.) Then, under Tab 4b, enter hazard information. You will need to look this up on the web. The MSDS sheet for a substance is an excellent reference for chemical hazard information. Collaborate with other groups to get all this information (Just look up three substances yourself, and share your findings with the others.)

11. Discuss with your partner the safety issues of this procedure. Which reactants or products might pose a hazard? What kind? (Note this in your report.) Is it OK to do this experiment on an open bench top? What protective equipment would you wear when doing this experiment? *Do you think the procedure is inherently safe? Why or why not?*

12. Using Tab 5a, check that the analysis is complete. (Note that no catalysts were used in this reaction.) Add a **title** and **your names**. Leave the scale factor 1. Preview and print your analysis and also save it by sending it to your email accounts (using Tab 5c). Also send it to your lab assistant for grading.

13. Comparing your analysis to that of a group that had the other procedure, consider the two procedures and discuss their relative greenness. Which one is greener? Why do you think so? Which principles of green chemistry do you base your decision on? (State them – don't just give numbers.) How might the better procedure be improved even more?