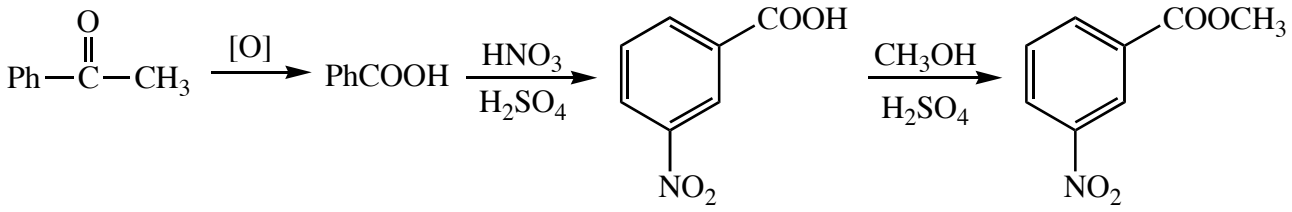
The Oxidation of Acetophenone to Produce Benzoic Acid

AEM – last update July 2017

The oxidation of acetophenone to form benzoic acid is the first step in the three labs that together make up our multistep synthesis project. EACH STEP OF THIS PROJECT WILL BE WRITTEN UP AS SEPARATE LABS, but you will use the products from the early steps as reagents for the subsequent steps. Each product must be carefully characterized (by mp, IR, and/or NMR) before using it in the next step.

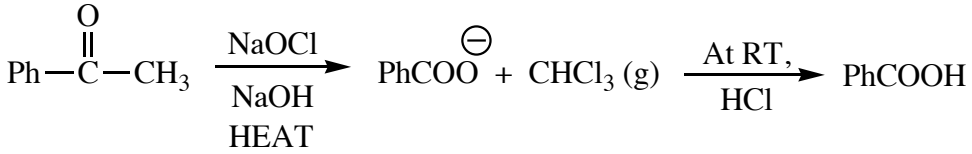
This multi-step synthesis is drawn from a Journal of Chemical Education Article called "**And the Winner is… A Multi-Step Synthesis for the Introductory Organic Course"**. Its reference is S. S. Stradling; C. L. Gage *J. Chem. Ed.* **1985**, *62(12),* 1116-1117. We have chosen only one of the three possible synthetic routes described in this paper for preparing a single substance, methyl *m*-nitrobenzoate. Following the oxidation, we will perform a nitration of the aromatic ring, then finally an esterification of the carboxylic acid. Abbreviated versions of the three reaction steps are given here, with more complete versions of each of the overall reactions given with each lab prompt separately.

All Three Steps of the Multi-Step Reaction Sequence:



Step 1: the Oxidation of Acetophenone to Produce Benzoic Acid

Overall Reaction:



CAUTION! You are using strong base, strong acid, and bleach in this reaction. Some of these caustic materials will be heated, which their danger. Use great care when working with these solutions! Also, the chloroform by-product is an anesthetic and a potential carcinogen; make sure your hoods are working continuously and close the hood sash as much as you can while carrying out the bleach oxidation step.

Two methods can be used for heating this reaction. Your professor will choose which they prefer.

- It can be heated on the lowest setting on your hotplate in the hood; turn on your hotplate to its lowest setting as soon as you get to lab. You do not want to overheat the reaction; gentle heat is important!
- OR it can be heated on a hot water bath (use a metal cake pan) on a hotplate. This method requires a steamy water bath, but keeps the reaction from overheating as much.

REACTION: In a large beaker (at least 400 mL) combine about 2.5 mL of acetophenone (know its mass) with 40 mL of bleach (5% aqueous NaOCl) per gram of acetophenone and 2.5 mL of 10% NaOH (aq) per gram of acetophenone. Warm this mixture using the method chosen by yoru professor for about 30-60 min, stirring with your glass rod about every 5 minutes. During this heating time, the chloroform that is produced should boil out of the mixture. At the beginning of this process, you can observe an oily layer of acetophenone floating on top of the aqueous mixture; at the end of the reaction, the oily phase should no longer be visible since it has reacted to form product. If you still have a significant oily layer after heating for 30 minutes, consult your professor.

WORK-UP: Once the oily layer has disappeared, the oxidation is complete. Remove from the heat, and slowly add 1 mL of acetone to destroy any excess bleach and then cool in an ice bath to RT. Slowly add conc. HCl with a pipet, with stirring, until a significant amount of precipitate has formed. When you cannot detect more precipitate forming, mix well and check that the pH of the liquid is 2-3 or less; if not, continue to add HCl until that is so. Cool the mixture in an ice bath to complete crystallization of the benzoic acid product and isolate this product by suction filtration. Wash the product really well with water, and then let it air dry on the aspirator for a while. It can then further dry in your lab drawer until the next lab period.

When the product is completely dry, obtain its mass and calculate the theoretical and percent yield for your reaction. Check its purity by mp, IR, and/or NMR, as directed by your professor. The product is usually of sufficient purity to use for the next step, but if that is not the case, you can recrystallize it from water.

CLEAN UP: Combine all the various filtrates, check the pH of the mixed solution, neutralize as needed, and flush down the drain with lots of water.