Experiment 4 - Oxidation of Acetophenone

OBJECTIVE

- to demonstrate a simple application of the "Iodoform" reaction
- to illustrate that common household chemicals can be important reagents
- to utilize simple test tubes to run a reaction

INTRODUCTION

The haloform reaction is characteristic for methylketones as well as for alcohols (e.g. ethanol, 2-propanol), that can be oxidized to methyl carbonyl compounds.

The iodoform test is commonly used as a test for the **CH_3—CO group**. The group to which the CH_3—CO group is attached can be aryl, alkyl and hydrogen.

In this experiment you will explore a variant of the haloform reaction, using bleach as the oxidizing agent.

Mechanism of the Classic Iodoform Reaction

Step 1: First, an acid-base reaction. Hydroxide functions as a base and removes the acidic α-hydrogen, giving the enolate.

Step 2: The nucleophilic enolate reacts with the iodine giving the halogenated ketone and an iodide ion.

Step 3: Steps 1 and 2 repeat twice more yielding the trihalogenated ketone.

Step 4: The hydroxide now reacts as a nucleophile at the electrophilic carbonyl carbon, with the **C═O** becoming a **C—O** single bond and the oxygen is now anionic.

Step 5: Reform the favorable **C═O** and displace a leaving group, the trihalomethyl system which is stabilized by the 3 halogens. This gives the carboxylic acid.

Step 6: An acid-base reaction. The trihalomethyl anion is protonated by the carboxylic acid, giving the carboxylate and the haloform (trihalomethane).

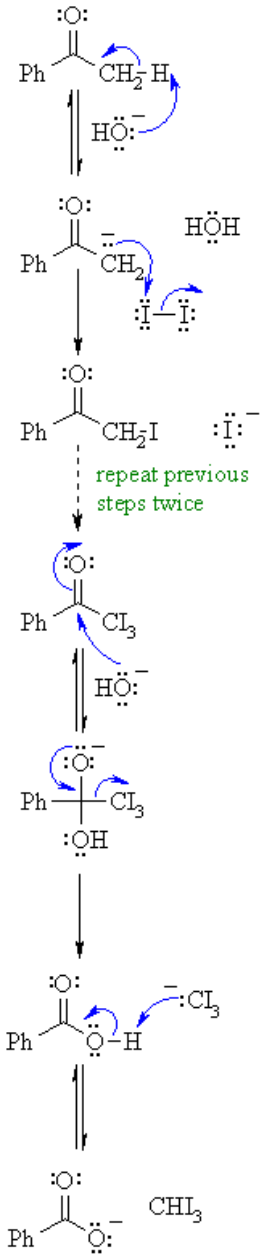

Figure 1

PRE-LAB

Complete the pre-lab assignment in WebAssign.

EQUATION

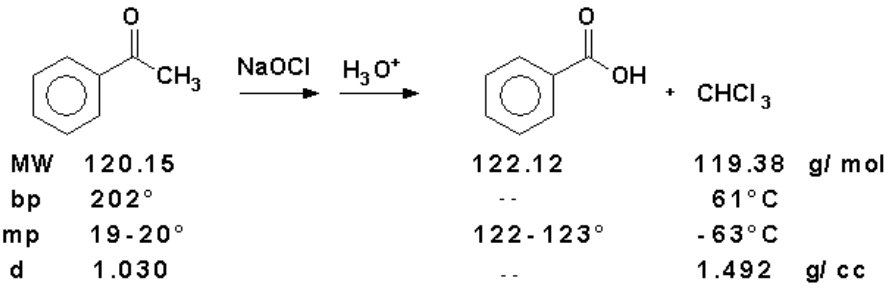

Figure 2

PROCEDURE

Using a dispensing pipet, carefully add 180 μL of acetophenone to a clean 6" Test Tube. Measure 6.3 mL of household bleach (e.g., "CLOROX"^{TM}) in a 10 mL graduated cylinder and carefully add it to the same test tube, followed by 0.5 mL of 10% NaOH. Heat the reaction mixture in a water bath (**$\sim$75°C**) for 20 minutes. During the heating, frequently shake the test tube to ensure mixing of the reagents.

While the solution is being heated, weigh out about 45.0 mg of sodium sulfite. After the solution has reacted for 20 min., carefully add the sodium sulfite to destroy any unreacted bleach (NaOCl). Shake this mixture for 5 min.

Extract the mixture with a 1.5 mL portion of diethyl ether using your calibrated Pasteur pipet to transfer the ether into and out of the test tube.

CAUTION: Diethyl ether is a highly flammable solvent!

Stopper the test tube with a cork, and carefully shake for *about* 10 seconds. Carefully remove the cork and allow the layers to separate.

Repeat the extraction with two additional 1.5 mL portions of ether. Discard the combined ether extracts in the "Organic Waste" in the hood.

The remaining aqueous layer in the test tube is cooled in an ice bath and acidified by the dropwise addition of concentrated HCl. After the addition of each drop or two of HCl, check the pH in the test tube using a glass rod to transfer a drop to pH paper. STOP as soon as pH is below 3.

Collect the thick white precipitate on a Hirsch Funnel. Wash the test tube with 1 mL of *ice-cold* tap water and pour the washing through the solid on the filter. Allow the crystals to dry, and determine the melting point, the actual yield, and the percentage yield.

Waste Disposal

The ether from the extraction may be carefully evaporated in the hood under a stream of nitrogen. The aqueous washings may be adjusted to a pH between 5.5 and 10.5 by the addition of 5% $NaHCO_3$ and then washed down the drain in a stream of cool water.

IN-LAB QUESTIONS

Download and print the worksheet. You will use this worksheet to record your answers to the In-Lab questions.

Questions

Record the following data.

Question 1: Amount of acetophenone used _____ mL, _____ g, _____ mol

Question 2: Theoretical Yield of Benzoic acid _____ mol, _____ g

Question 3: Actual Yield _____

Question 4: Percentage Yield _____

Question 5: Show your calculations.

Question 6: Melting Point of Product _____ (observed), _____ (reported)

