

CH 2280

Procedure for Metal/Acid Reduction of Nitro Compounds

Materials

From the Chemicals Hood:		From the Stockroom (Blue Bin):
Week one:	Week two:	1" stirbar
<i>m</i> -Nitroacetophenone	3-(1-hydroxyethyl)aniline	Stirbar retriever 
Granular tin	3-(1-hydroxyethyl)nitrobenzene	
Concentrated hydrochloric acid	3-aminoacetophenone	
30% (10 M) sodium hydroxide solution	Dichloromethane	
	97% dichloromethane/3% methanol solution	

Introduction

Sn/HCl is a source of electrons (a reducing agent) and protons. A proposed mechanism for this reaction is fifteen steps (counting every arrow pushing electrons)!

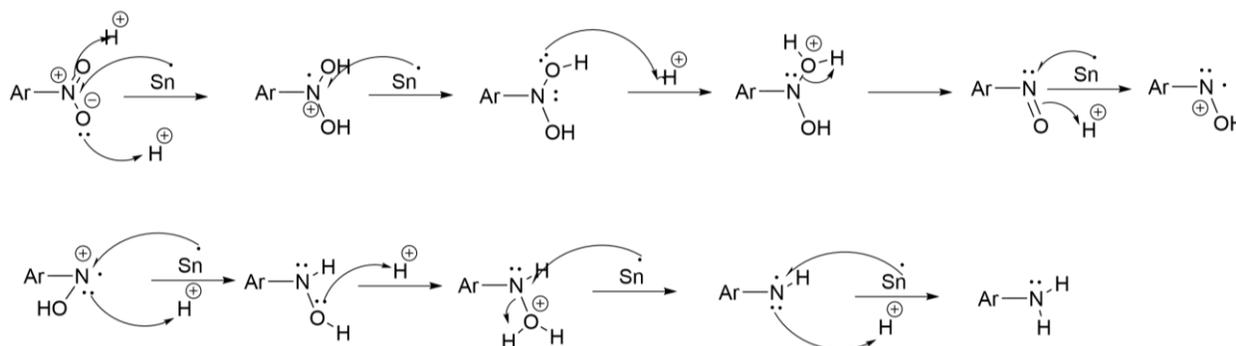


Figure 1. Proposed mechanism for tin/HCl reduction of nitro compounds.

Safety

Concentrated HCl is a corrosive highly reactive acid. Handle with extreme caution. If any spills on you, wash the affected area under running water for five minutes and notify your instructor. Watch carefully for drips and runs on the outside surface of reagent bottles and graduated cylinders when you pick them up. Apply sodium bicarbonate solution to the area.

Be sure to consult the MSDs in the stockroom for any compound you deal with, if you wish.

Procedure

In a 125 mL Erlenmeyer flask containing a one-inch magnetic stir bar add 2.0 g of *m*-nitroacetophenone and 4.0 g of granular tin. Take the closed bottle of concentrated HCl from the dispensing hood to your own work area and dispense 40 mL into a 150 mL beaker. Add the acid **SLOWLY, WITH CARE** (add one "squirt" of the plastic disposable pipet at a time) while continuing the magnetic stirring. If reaction foams, wait for it to subside, then continue addition of acid.

After addition of the acid is completed, stir and warm (set the digital temperature to 100 °C) on the hot plate for 30 min or until most of the tin has dissolved (whichever happens first). Cool in an ice-water bath for 10 min, and then add 30% (10 M) NaOH **SLOWLY, WITH CARE** (add one “squirt” from the plastic disposable pipet at a time) until the pH is about 10 (this will precipitate the amine but also tin salts). This will require ~48 mL of 30% NaOH.

To remove the tin salts, heat the solution (set the digital temperature on the hot plate to 200 °C with magnetic stirring) for 10 min. The amine (your product) will dissolve, leaving SnO as a solid which can be gravity filtered while hot, and washed with hot water. Thoroughly heat an inverted stemless funnel on the steam bath. Heat approximately 25 mL of water to boiling on the hot plate while the product mixture is being heated; do not let the water boil for an extended time or an appreciable volume will evaporate. Set up a gravity filtration apparatus using the hot funnel and a fluted filter paper. Wet the paper with the boiling water, then pour the hot product mixture through the filter paper. Use your second 125 mL Erlenmeyer flask as the receiving flask. Use Erlenmeyer tongs or blue “hot hands” to hold the hot flask(s) and beaker as necessary.

The filtrate is cooled to room temperature, then in an ice-water bath and allowed to crystallize. This is, in effect, a recrystallization of the product from water. Filter the solid using vacuum. Rinse the crystallized product four times with 5 mL of ice-cold water. Allow your product to dry until the next laboratory period at which time weigh it and analyze by IR, NMR, TLC and mp. Record those results in your notebook.

Compare your data with those of 3-(1-hydroxyethyl)aniline, 3-(1-hydroxyethyl)nitrobenzene, and 3-aminoacetophenone. Original spectra of these compounds are available on the CH 2280 website and authentic commercial samples are available in the balance room for mp and TLC comparison. The TLC solvent is 97% dichloromethane/3% methanol. It has been prepared and is in the hood.

The product of this reaction will be used in the next reaction (reduction with NaBH₄/EtOH).

Disposal

The filtrate can be disposed of in the “Base Waste” bottle in the hood. The tin salts should be placed in the “Tin Waste” bottle. The TLC solvent and solutions should be disposed of in the “Halogenated Waste” bottle.