AIM: To prepare and submit benzocaine from p- nitrobenzoic acid.

REFERENCES: Vogel's Textbook of Practical Organic Chemistry by Brian S. Furniss, Antony J. Hannaford, Peter W. G. Smith & Austin R. Tatchell; Fifth Edition; Page No. 896.

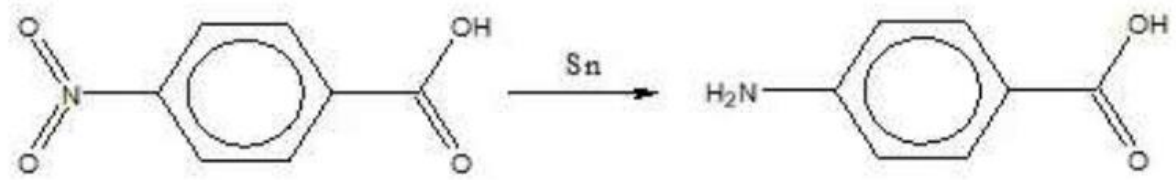
REQUIREMENTS:

Chemicals: p-Nitrobenzoic acid, Tin powder, Conc. HCl, Conc. Ammonia, Celite (filter aid), Glacial acetic acid, Prepared p-aminobenzoic acid, Absolute ethanol, Sodium carbonate.

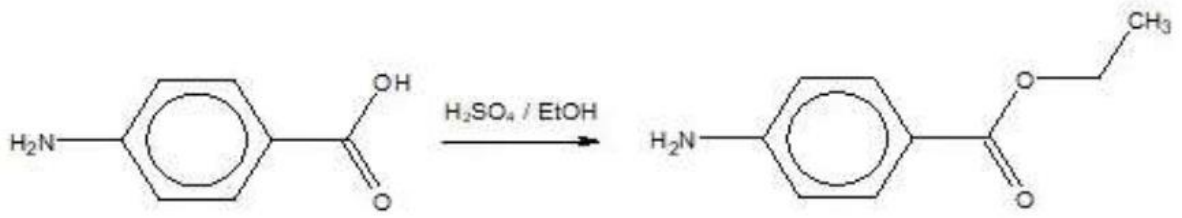
Apparatus: RBF, Reflux condenser set, Gas inlet tube, Beaker, Buchner funnel, Measuring cylinder, Filter paper, Litmus paper, etc.

PRINCIPLE: In step 1 common reduction of aromatic para-nitrobenzoic acid by tin and hydrochloric acid to para-aminobenzoic acid and in step 2 esterification of para-aminobenzoic acid by sulphuric acid and ethanol to benzocaine occurs called Fischer esterification. Reaction:

Step 1:



Step 2:



PROCEDURE:

Step 1: Preparation of p-aminobenzoic acid:

Place 15 g (0.09 mol) of p-nitrobenzoic acid in a 1-litre round-bottomed flask fitted with a reflux condenser. Introduce 35 g (0.295 mol) of powdered tin and 75 ml of concentrated hydrochloric acid. Heat the mixture gently until the reaction commences, and remove the

flame. Shake the flask frequently and take care that the insoluble acid adhering to the sides of the flask is transferred to the reaction mixture: occasional gentle warming may be necessary. After about 20 min, most of the tin will have reacted and a clear solution remains. Allow to cool somewhat and decant the liquid into a 1-litre beaker; wash the residual tin by decantation with 15 ml of water, and add the washings to the contents of the beaker. Add concentrated ammonia solution (d 0.88) until the solution is just alkaline to litmus and digest the suspension of precipitated hydrated tin oxide on a steam bath for 20 min. Add 10 g of filter-aid ('Celite'), stir well, filter at the pump and wash with hot water. Transfer the filter cake to a beaker, and heat on a water bath with 200 ml of water to ensure extraction of the product and refilter. Concentrate the combined filtrate and washings until the volume has been reduced to 175-200 ml: filter off any solid which separates. Acidify the liquid to litmus with glacial acetic acid and evaporate on a water bath until crystals commence to separate; cool in ice, filter the crystals at vacuum pump and dry in the steam oven. The yield of p-aminobenzoic acid, m.p. 192 °C, is 9.5 g (77%).

Step 2: Preparation of ethyl p-aminobenzoate (esterification of p-aminobenzoic acid): Place 80 ml of absolute ethanol in a 250 ml two-necked flask equipped with a double surface reflux condenser and a gas inlet tube. Pass dry hydrogen chloride through the alcohol until saturated; the increase in weight is about 20 g; remove the gas inlet tube, introduce 12 g (0.088 mol) of p-aminobenzoic acid, and heat the mixture under reflux for 2 hours. Upon cooling, the reaction mixture sets to a solid mass of the hydrochloride of ethyl p-aminobenzoate. However, it is better to pour the hot solution into 300 ml of water (no hydrochloride separates) and carefully add solid sodium carbonate to the clear solution until it is neutral to litmus. Filter off the precipitated ester at the pump and dry in the air. The yield of ethyl p-aminobenzoate, m.p. 91 °C, is 10 g (69%). Recrystallization from rectified (or methylated) spirit does not affect the m.p.

Calculation of yield:

Here limiting reagent is p-nitrobenzoic acid; hence yield should be calculated from the amount taken.

The molecular formula of p-nitrobenzoic acid = C7H5NO4

The molecular formula of Benzocaine = C9H11NO2

The molecular weight of p-nitrobenzoic acid = 167 g/mole

Molecular weight of Benzocaine = 165 g/mole

Theoretical yield:

167 g p-nitrobenzoic acid forms 165 g Benzocaine

Therefore, 15 g p-nitrobenzoic acid will form …….? (X) g Benzocaine

X = (165 × 15)/167 = 14.82 g

Theoretical yield = 14.82 g

Practical yield = ————- g

% Yield = (Practical Yield) / (Theoretical Yield) × 100

RESULT: Benzocaine was synthesized and the percentage yield was found to be……..%