Experimental Procedures

Experiment: 1 **Date: 19/03/2020;**
Lab No: 4 **Time: 9:00a.m. to 1:00p.m.**

Preparation of N,N-dimethyl-4-nitrosoaniline

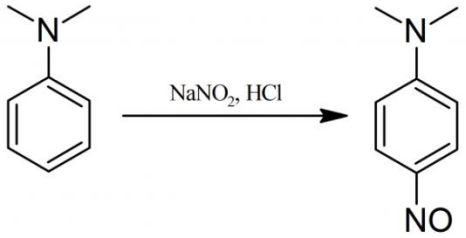

Figure 1 synthesis of N,N-dimethyl-4-nitrosoaniline

Chemicals Required:

N,N-dimethylaniline	:5gm
Hydrochloric acid	:25ml
Sodium nitrite	:3gm
Sodium Hydroxide	:1.7gm

Procedure:

5gm of N,N-dimethylaniline is dissolved in 25ml of concentrated hydrochloric acid, and ice added till the temperature reaches below 0°C. 3gm of sodium nitrite, dissolved in a small quantity of water, is slowly added, the reaction mixture is stirred and the temperature is not allowed to rise above 8-10° C. The N,N-dimethyl-4-nitrosoaniline hydrochloride separates out, and, after standing, is filtered, washed with a little dilute hydrochloric acid, and dried yielding yellow needles with melting point 177°C. N,N-dimethyl-4-nitrosoaniline hydrochloride is converted to N,N-dimethyl-4-nitrosoaniline base by treating with stereochemical amount of NaOH.

M.P. 85-87°C

Yield: 5.37gm (87%)

Experiment: 2 **Date: 23/03/2020;**
Lab No: 5 **Time: 9:00a.m. to 1:00p.m.**

Preparation of Aspirin

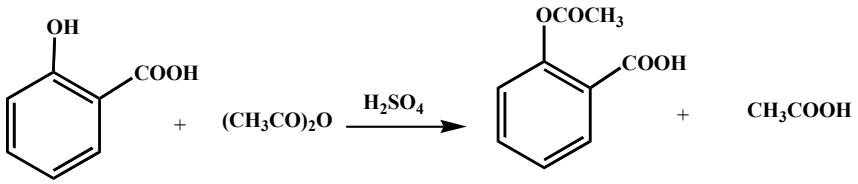

Figure 2 synthesis of Asprin (acetylsalicylic acid)

Chemicals Required:

Salicylic acid	:2.0gm
Acetic anhydride	:5mL
Suphuric Acid	:5drops
Aaturated Aq. sodium bicarbonate solution	:25mL
Hydrochloric Acid	:3.5mL

Procedure

Place 2.0gm (0.015 mole) of salicylic acid in a 125-mL Erlenmeyer flask. Add 5mL (0.05 mole) of acetic anhydride, followed by 5 drops of conc. H_2SO_4 (*use a dropper,* H_2SO_4 *is highly corrosive*) and swirl the flask gently until the salicylic acid dissolves. Heat the flask gently on the steam bath for at least 10 minutes. Allow the flask to cool to room temperature. If acetylsalicylic acid does not begin to crystallize out, scratch the walls of the flask with a glass rod. Cool the mixture slightly in an ice bath until crystallization is completed. The product will appear as a solid mass when crystallization is completed. Add 50mL of water and cool the mixture in an ice bath. Do not add the water until crystal formation is complete. Vacuum filter the product using a Buchner funnel. You can use some of the filtrate to rinse the Erlenmeyer flask if necessary. Rinse the crystals several times with small portions (5mL) of cold water and air dry the crystals on a Buchner funnel by suction until the crystals appear to be free of solvent. Test this crude product for the presence of unreacted salicylic acid using the ferric chloride test. Record the weight of the crude solid which probably contains water. Stir the crude solid with 25mL of a saturated aqueous sodium bicarbonate solution in a 150

mL beaker until all signs of reaction have ceased (evolution of ceases). Filter the solution through a Buchner funnel to remove any insoluble impurities or polymers that may have been formed. Wash the beaker and the funnel with 5 to 10 mL of water. Carefully pour the filtrate with stirring, a small amount at a time, into an ice cold HCl solution (*ca* 3.5mL of conc. HCl in 10 mL of water) in a 150-mL beaker and cool the mixture in an ice bath. Make sure that the resulting solution is acidic (blue litmus paper) and that the aspirin has completely precipitated out. Filter the solid by suction and wash the crystals 3X with 5 mL of *cold* water each. Remove all the liquid from the crystals by pressing with a clean stopper or cork. Air dry the crystals and transfer them to a watch glass to dry. Test a small amount of the product for the presence of unreacted salicylic acid using the ferric chloride solution. When the product is completely dry, weigh the product, determine its melting point (lit mp 135-136 °C) and calculate the percentage yield. Dissolve the final product in a minimum amount (no more than 2-3 mL) of *hot* ethyl acetate in a 25 mL Erlenmeyer flask. Make sure that the product is completely dissolved while gently and continuously heating on a steam bath. Cool the solution to room temperature and then in a ice-bath. Collect the product by vacuum filtration and rinse out of the flask with a few milliliters of cold petroleum ether. When the product is completely dry, weigh its weight, determine its melting point (lit mp 135 °C) and calculate the percentage yield of this recrystallized product.

M.P. 135°C

Yield: 2.0gm (76.5%)

Experiment: 3 **Date: 26/03/2020;**
Lab No: 4 **Time: 9:00a.m. to 1:00p.m.**

Preparation of Methyl Orange

In this experiment you will prepare methyl orange, an azo dye that forms beautiful orange crystals and is used as an acid-base indicator. The anion form is yellow and the acid form is red. You will synthesize methyl orange from sulfanilic acid and N,N-dimethylaniline using a diazonium coupling reaction just like the one you saw in the previous experiment in the nitrous acid test for primary aromatic amines. The overall reaction is shown in figure 3.

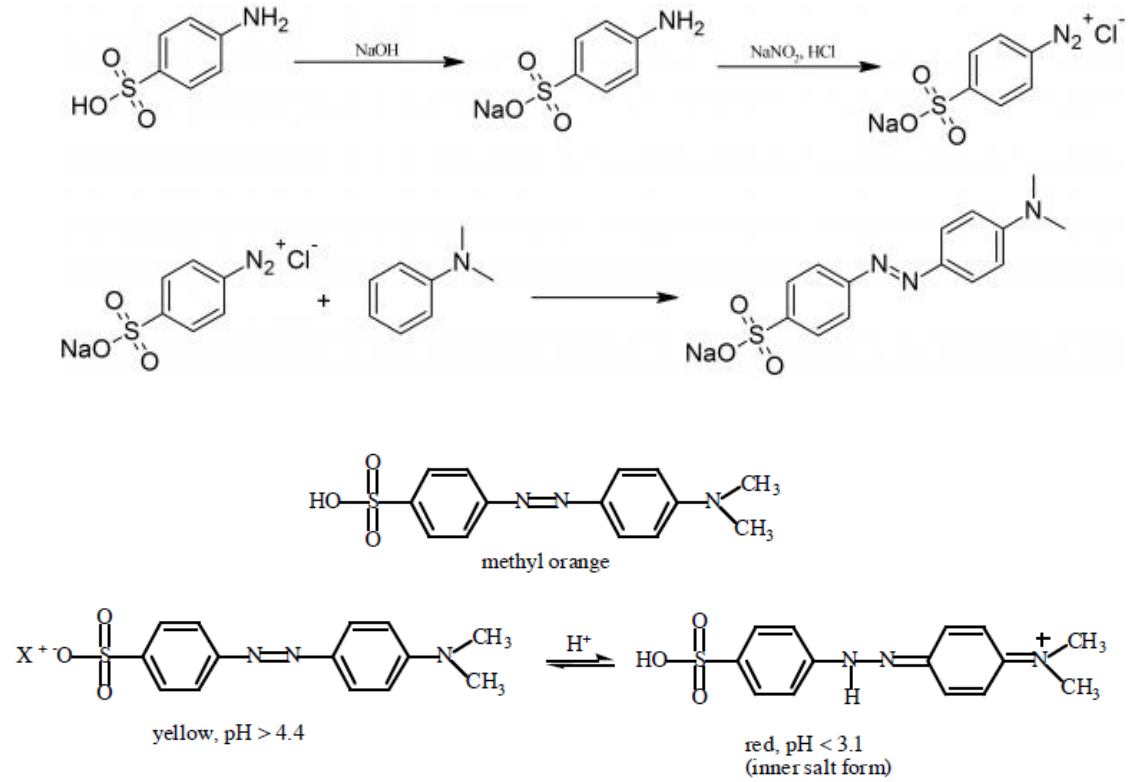

Figure 3 synthesis of methyl orange

Chemicals Required:

Sulfanilic acid	:1.73gm
N,N-dimethyl aniline	:1.21gm
Sodium nitrite	:700mg
Sodium carbonate	:1.05-1.10gm
95% Ethanol	:3.0mL

Procedure:

Dissolve 1.73gm (0.010 mole) of sulfanilic acid (anhydride) in about 50 ml of a solution of sodium carbonate containing 0.010 to 0.0125 moles of sodium carbonate in a 125 ml Erlenmeyer flask. The solution is prepared by the stockroom and its strength is indicated on the bottle, but you must calculate the exact amount needed. Warm the mixture slightly to speed up dissolution. Test one drop of the solution to make sure it is alkaline. If not, add a small amount (1-2 mL) sodium carbonate solution and check the pH again. Then add 0.010 moles sodium nitrite and cool to 25 °C (room temperature). Put 40 g of ice in a 400 mL beaker and add enough hydrochloric acid of a 6M or a 12 M solution in order to provide a total of 0.030 mol HCl in your beaker. Add the sulfanilate solution prepared above in a fine stream while stirring continuously. Keep this solution cold in the ice bath at all times. It now contains your diazonium salt, which will decompose if it becomes warm. It is only partially soluble in the aqueous solution and will precipitate as a bluish-greenish solid. Prepare a solution of N,N-dimethylaniline 1.21gm (0.010 mol) in 0.010 mol of acetic acid in a 25 ml Erlenmeyer flask. Now add the dimethylaniline acetate solution slowly with constant stirring to the suspension of the diazonium salt. A dull, reddish-purple mass should appear. Now, very slowly add about 30 mL of 1.0 M sodium hydroxide solution with constant stirring. Add the NaOH a few mL at a time. The addition should take 10-15 minutes. The actual coupling reaction does not occur until you add the NaOH. The reaction takes place best at about pH 7. Keep adding the NaOH until the solution becomes basic (blue to litmus.) If the sodium hydroxide is added too quickly, then free dimethylaniline will separate out as an oily phase. This then leaves an equivalent amount of the diazonium salt unreacted. This excess salt decomposes to brown tar on warming to room temperature and contaminates the otherwise beautiful crystalline orange dye. At the end of the coupling reaction a yellow-orange or golden color should be observed. The product will now be recrystallized from the reaction mixture. Heat the reaction mixture to boiling using your tripod and Bunsen burner. Everything should dissolve and the solution should be clear (though it will be highly colored). If all the material does not dissolve when the solution is heated to boiling, add more water as needed. Then, allow it to cool slowly to room temperature to crystallize and then place the flask in an ice bath to get it as cold as possible. Remember: do not stir or shake the solution when it is cooling. Allow the crystals to form in an undisturbed flask. They will be much purer and larger if they form slowly in a motionless flask. Filter the crystals by suction filtration, rinse them with 10–15 ml cold water and allow them to dry. Calculate the percent yield and turn in your crystals in a vial along with your Organic Yield Report Sheet. Do not attempt to take the melting point of your methyl orange as it decomposes on heating. In order

to observe the beautiful color change that occurs with our orange indicator dye, dissolve a small amount of the methyl orange in 2-3 mL of 95% ethanol and add 5% HCl a few drops at a time until you see the color change.

Yield: 1.82gm (81%)

Experiment: 4 **Date: 30/03/2020;**
Lab No: 5 **Time: 9:00a.m. to 1:00p.m.**

Preparation of 3-Acetamidocoumarin (3-Acetamido-*2H*-chromen-2-one)

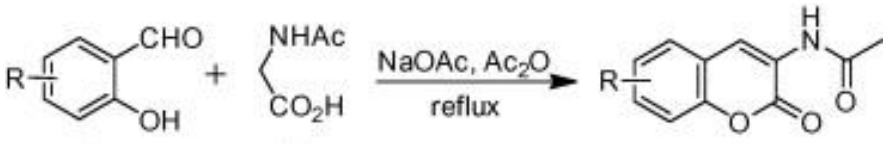

Figure 4 synthesis of 3-Acetamidocoumarin

Chemicals Required:

Salicylaldehyde	:6.10gm
N-acetylglycine	:5.85gm
Anhydrous sodium acetate	:16.40gm
Acetic anhydride	:25mL

Procedure:

A mixture of salicylaldehyde (6.10 g, 50.0 mmol), *N*-acetylglycine (5.85 g, 50.0 mmol), anhydrous sodium acetate (16.40 g, 200.0 mmol) and acetic anhydride (25.0 mL) was heated at 110-120 ºC for 3.0 h. The resulting brown solution was allowed to cool to room temperature and it solidified completely. Ice-cold water was added to the brown solid and the mass was broken up with a spatula. The resulting mixture was suction filtered and the solids were washed 2-3 times with cold water. The resulting solid was air dried, triturated with ethyl acetate, suction filtered and air dried again to afford 3-acetamidocoumarin as a pale yellow solid.

M.P. 195-196 °C

Yield: 4.59 g (46%).