





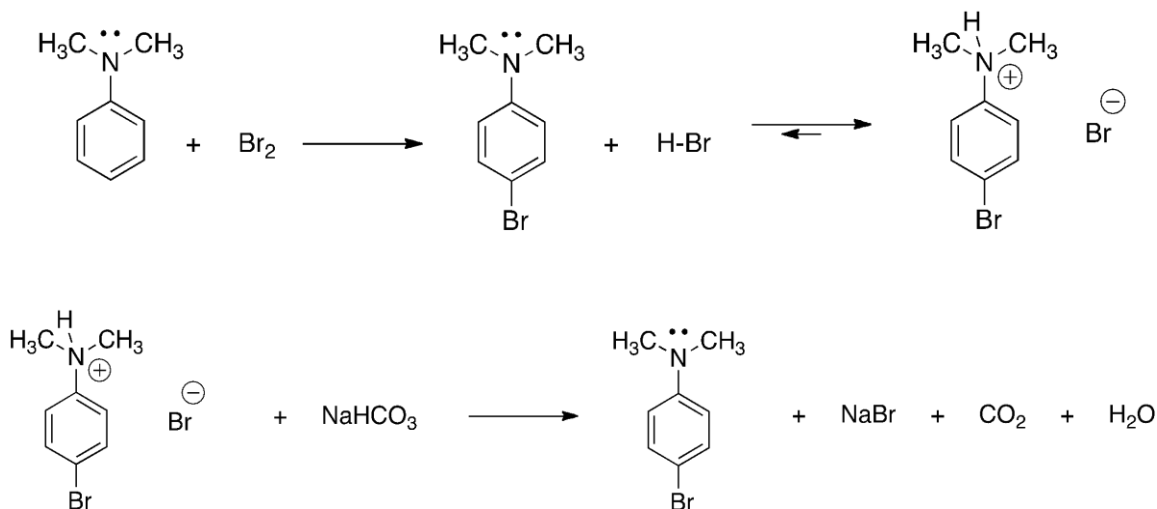
CH 2280 Bromination of *N,N*-Dimethylaniline (Electrophilic Aromatic Substitution)

Reference: *Bruice, P.Y.*, Seventh Edition, Chapter 19

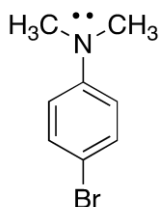
Materials

From the Chemicals Hood:	From the Stockroom (Blue Bin):
N,N-Dimethylaniline	1" stirbar 
Dichloromethane	Stirbar retriever 
1 M Br ₂ in dichloromethane solution	
Saturated sodium bicarbonate solution	
Magnesium sulfate	
Ethanol	
Saturated sodium bisulfite aqueous solution	250 mL separatory funnel with stopcock 
	Glass stopper 

Electrophilic Aromatic Substitution (EAS) is usually accomplished only through the use of an acid (e.g. Bronsted or Lewis) catalyst. It can be seen that when an “activating” (electron-donating by resonance) group is present on an aromatic ring, no catalyst is necessary. This is the case in this experiment.



In this experiment you will have the task of preparing and identifying a monobrominated product from this reaction. This will be your starting material for the “Colorful Grignard Reaction” later in the semester.



mp 54-55 °C
(Acros, 99%)

Caution!

Elemental bromine is toxic and causes burns. It is a strong oxidizer. If spilled on skin, rinse with water and wash with soap and water. Neutralize spills on surfaces by reacting with aqueous sodium bicarbonate.

Procedure

Add 7.0 mL of *N,N*-dimethylaniline and 50 mL of dichloromethane (CH_2Cl_2 , DCM) to a 400-mL beaker. Place the beaker in an ice-water bath. Add a magnetic stir bar and thermometer. Turn on the stirring motor.

Add 1.1 equivalents of a solution (~1 M) of bromine (Br_2) in DCM (already prepared in the hood) portion-wise with a plastic disposable pipet. The orange color of the bromine solution should dissipate during addition. At the same time, vapor may appear above the surface of the reaction solution. After the color leaves, add another 5 mL of bromine solution.

After addition of bromine is completed the color of the solution may still be orange. This is expected because you used an excess of bromine. Keep the reaction in the ice bath and add an aqueous solution of saturated sodium bicarbonate **SLOWLY** and **CAREFULLY**, with vigorous stirring. The reaction of bicarbonate with the hydrogen bromide side product will cause bubbling and foaming! Try to keep the bubbling and foaming froth from escaping the beaker.

After you have slowly (portion-wise) added 150 mL of bicarbonate solution, check the pH of the solution with pH paper. If the solution is still acidic, keep adding bicarbonate, 10 mL at a time.

When the solution has been neutralized you will notice that there are two layers in the beaker. Carefully pour these two layers through a funnel into a 250-mL separatory funnel. Remove the bottom layer (the organic layer) into a clean, dry 250-mL Erlenmeyer flask. If you have too much liquid you may have to do this in two steps.

Add enough magnesium sulfate (white solid in the balance room) to cover the bottom of the flask containing the organic solution and swirl occasionally to dry the organic solution. This should require about five minutes. A dry solution is clear to look through and not cloudy. The white solid should be loose, not clumped (think of a snow globe, that's what you want). When you have determined the water has been removed from the organic layer, filter through fluted filter paper or carefully decant the organic layer away from the magnesium sulfate into a clean, dry and pre-weighed 250-mL Erlenmeyer flask. Put a wooden stick (from the side shelf) into the flask and evaporate the dichloromethane on a steam bath. When bubbling has ceased, remove the flask from the steam bath and allow it to cool. Crystallization should occur. Weigh the flask with crystals in it to determine your crude yield.

Crystallize your product with ethanol:

Add 10 mL of ethanol and a wooden stick to the flask and place it on the steam bath. Heat the solution until the entire solid has dissolved in the solvent. Be careful to turn off the steam while manipulating the rings, you could get burned!

After the solid has dissolved, remove the flask from the steam bath and allow it to cool.

Crystallization will occur. After cooling enough that the flask is not too hot to touch, cool it further in an ice-water bath. Also cool ~50 mL of ethanol in an ice-water bath. Allow both flasks to cool for 15 minutes. Filter the crystals by vacuum and rinse them with the cold ethanol.

Continue to draw air through the solid for several minutes and break up any chunks to maximize surface area. Transfer the solid onto a clean, dry watch glass and store them in your desk drawer until the next lab period. You will use it in the “Colorful Grignard” experiment later in the semester.

Next Period: Weigh your dried product and characterize it by the usual analytical techniques (IR, NMR & mp). Compare your spectra data with the spectra for this compound on the CH 2280 website.

Waste Disposal

The aqueous layer from the separatory funnel should be poured into the **Base** Waste container. The filtrate from the recrystallization can be poured into the liquid **Halogenated** Waste container.