EXPERIMENT 6
DYES & DYEING

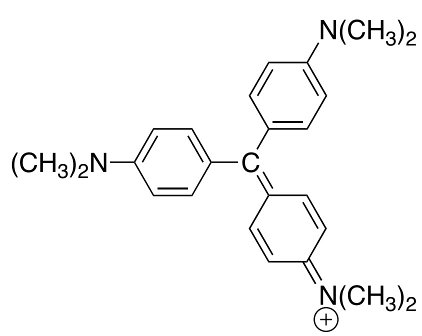
PART 1: GRIGNARD SYNTHESIS OF TRIPHENYLMETHANE DYES: CRYSTAL VIOLET AND MALACHITE GREEN

Reading Assignment: ***Smith*** sections 20.9–20.10, 20.13.

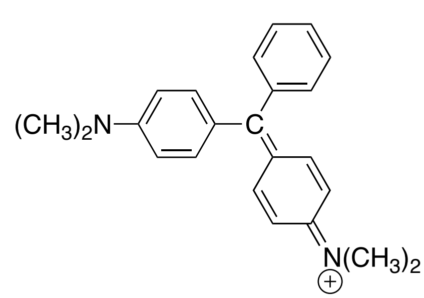
Pre-lab Questions:

1) Anhydrous conditions are essential for the success of a Grignard reaction. To illustrate this point, calculate the mass of water it would take to completely destroy the *p*-dimethylaminophenylmagnesium bromide that you will synthesize. What is the volume of this amount of water, and what are the products of this hydrolysis reaction?
2) What is the role of the iodine?

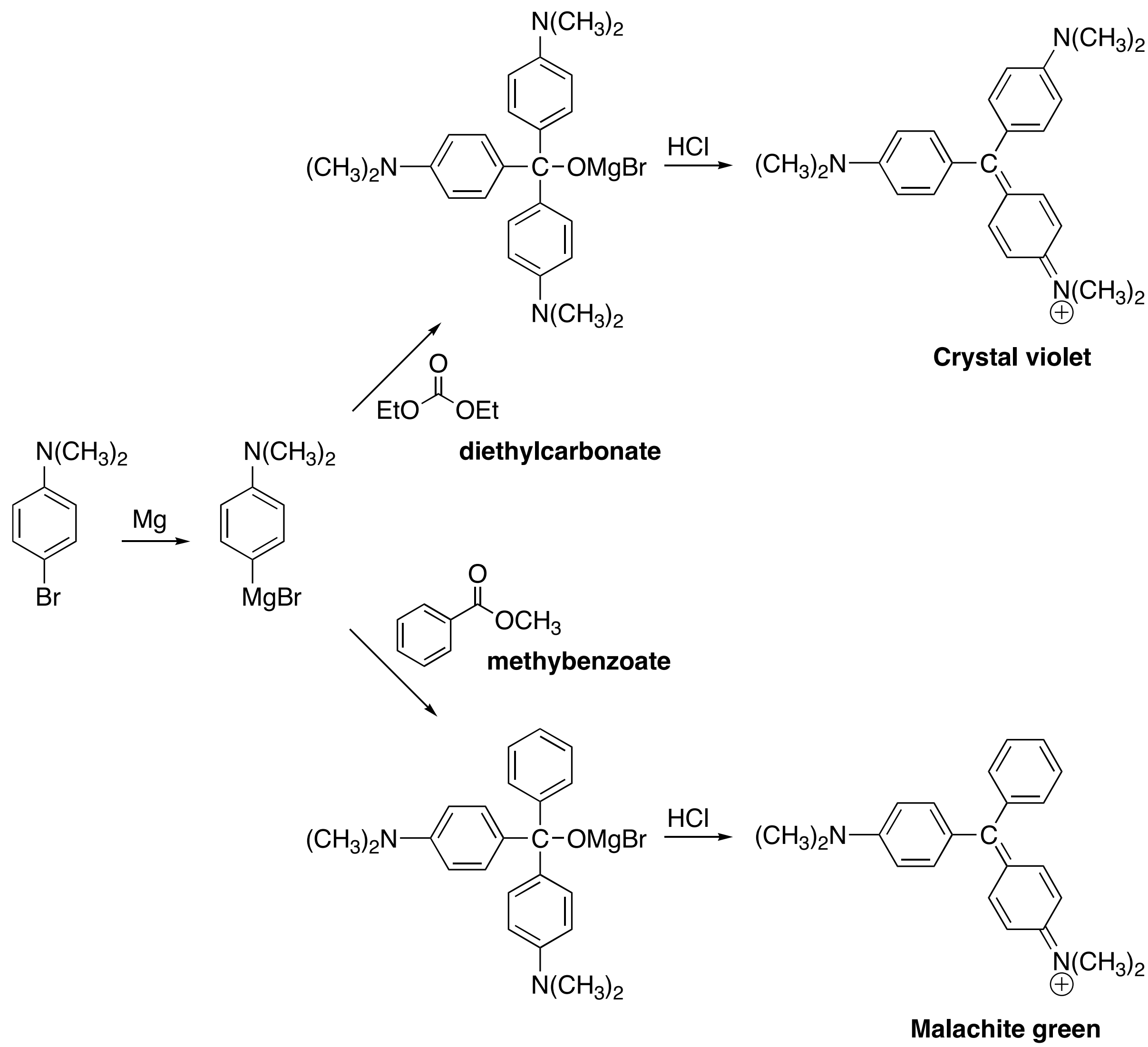
In **Part 1** of Dyes and Dyeing, you will be using a Grignard synthesis to prepare one of two triphenylmethane dyes, crystal violet, and malachite green. Crystal violet is formed by the Grignard reaction between *p*-dimethylaminophenylmagnesium bromide and diethylcarbonate. Malachite green is formed by treating the same Grignard reagent with methylbenzoate. An important aspect of both malachite green and crystal violet is their extensive conjugation, which is responsible for the colors of these two dyes. The positive charge is extensively delocalized onto all three aromatic rings, and the *para*-dimethylamino groups.



Crystal violet

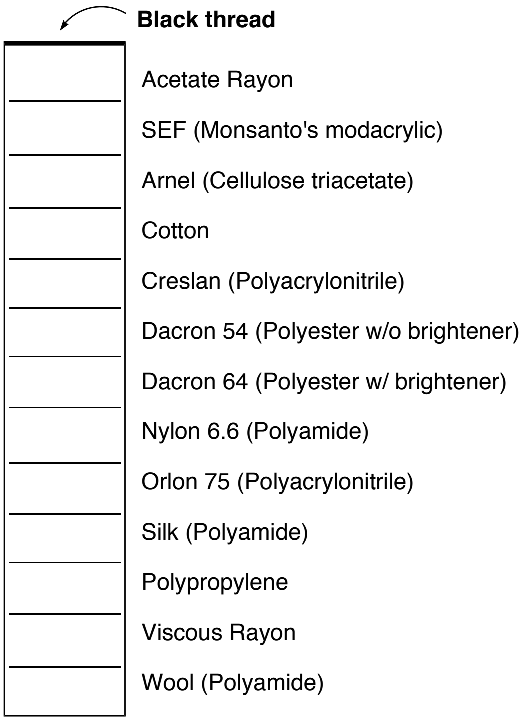


Malachite green

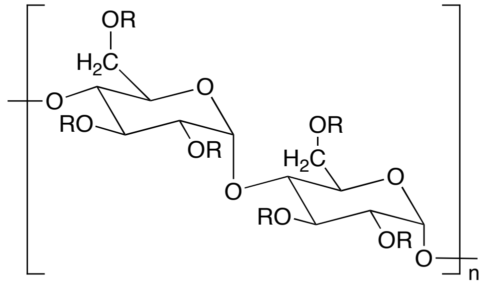


Onnce you synthesize your malachite green or crystal violet dye, you will be dyeing a special fabric called Multifiber Fabric 43. It includes 13 different fibers woven into small strips, so that you can see how the dyes take to different fibers. Because the fibers contain different functional groups, there will be a great variation in intensity and hue among the different fibers.

Multifiber Fabric 43

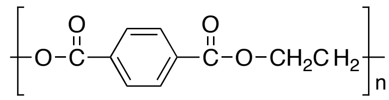


Polymeric Structure for Natural and Man-made Fibers

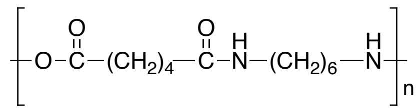


Cellulose (cotton, R=H)

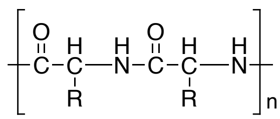
Acetylated Cellulose (Rayon, R=OAc)



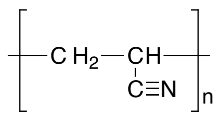
Polyester (Dacron, PET)



Nylon 6.6



Silk, Wool (R varies w/ amino acid present)



Polyacrylonitrile

Procedure:

You will work in a 2-person team. One student will synthesize malachite green, and the other will synthesize crystal violet.

****All aminobenzenes are potentially toxic****

Make sure you look up the SDS for 4-bromo-*N,N*-dimethylaniline and upload it to the SDS folder in ELN.

The SDS for 4-bromo-*N,N*-dimethylaniline Contains the following information:

This compound is harmful is swallowed, in contact with skin, or if inhaled.

\- - - - - - - - - - - FIRST-AID MEASURES- - - - - - - - - - - -

IN CASE OF EYE CONTACT, IMMEDIATELY FLUSH EYES WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES.

IN CASE OF SKIN CONTACT, IMMEDIATELY WASH SKIN WITH SOAP AND COPIOUS AMOUNTS OF WATER.

IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.

IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS. CALL A POISON CONTROL CENTER.

WASH CONTAMINATED CLOTHING BEFORE REUSE.

Part 2: Grignard Synthesis of Crystal Violet or Malachite Green

The Grignard reagent is *very* water sensitive. All glassware used for this experiment ***must be dry***. Prepare a drying tube filled with anhydrous calcium chloride. Take a 25 mL round bottom flask, magnetic stirring bar, and reflux condenser from the drying oven and assemble your glassware while hot! *The stockroom may have already placed hot glassware into a dessicator and allowed it to cool, in which case, get glassware from the dessicator and assemble quickly*. Place the reflux condenser on the round bottom and the drying tube on top of the reflux condenser and secure with Keck clips. When the apparatus has cooled to room temperature, add 1.25 g of 4-bromo-*N,N*-dimethylaniline, 13 mL anhydrous THF, 0.20g magnesium turnings *(break one or two magnesium turnings in half before adding to expose fresh metal surface)*, and 1 or 2 small crystals of iodine. Work quickly so that minimal amounts of air *(which contains a lot of water, especially on rainy days)* enters the system. After attaching water line to the condenser, swirl the reaction mixture, then heat in a 70° - 75°C water bath. Maintain a gentle reflux for 30 minutes, swirling the flask every 5 minutes during the heating period. The initial dark color fades and is replaced by a grayish solution typical of Grignard reagents. Cool the reaction flask in a beaker of tap water until it reaches room temperature.

For malachite green: Weigh 0.105 g of methyl benzoate into a small Erlenmeyer flask. Add 0.5 mL anhydrous THF to the vial.

For crystal violet: Weigh 0.15 g diethyl carbonate into a small Erlenmeyer flask. Add 0.5 mL of anhydrous THF to the vial.

Remove the condenser. Using a Pasteur pipette, add the ester solution drop-wise to the reaction flask with stirring. After the addition is complete, replace the condenser and heat the reaction mixture under reflux for 5 minutes. Swirl the flask occasionally while heating it. Cool the flask to room temperature.

Dyeing test samples

Put on gloves before starting the dye synthesis. Pour the reaction mixture into a 100 mL beaker. VERY Slowly add 2.5 mL 5% HCl solution to the beaker with stirring; some bubbling will occur as the residual magnesium reacts with the acid.

Dip a fabric test strip into the dye solution, and leave it in for at least 1 minute. Remove the sample, rinse it with tap water into another beaker, and blot dry. The dye solution is very concentrated, so intense color should be produced on some of the fiber types in the test strip, depending on how well the particular type of fiber accepts the dye. Record the types of fabrics you tested, and describe any variations in intensity observed for the different fibers. Compare you results with those of another student who synthesized the alternative dye.

Allow the samples to dry and attach them to your report. Keep them in a small plastic bag because the dye may rub off an anything the samples touch.

Cleanup: the dye solution should be poured into the waste container labeled "Dye Solution." Dye stains on glassware can be removed with a few milliliters of 6M HCl, followed by washing with water. Neutralize the acid washings with sodium carbonate before pouring them into the container for aqueous inorganic waste. DO NOT PLACE CLEANED GLASSWARE BACK INTO DESSICATOR! The stockroom will take care of baking cleaned glassware for the next lab section.

Post-lab Questions:

1) Why does it require three moles of the Grignard reagent for each mole of ester in the synthesis of crystal violet, but only two moles of the Grignard reagent are required for each mole of ester in the synthesis of malachite green?
2) What precipitate formed when the ester was added to a solution of your Grignard reagent?
3) Your dyed fabric will likely smell a little like mothballs. This is due to a small amount of N-N-dimethyl aniline that is a side-product of the reaction. How is N,N-dimethyl aniline formed, and how would you change the reaction conditions to prevent this side-product from forming?