

***Dyes & Grignard Reactions***  
***Gentian (Crystal) Violet - Malachite Green***  
*Check your assigned product before beginning.*

Colors, dyes and textiles have a long history dating back to about 2500 BC, when it is believed that plant and insect dyestuffs were first used in ancient China. Natural sources were used for dyeing until relatively recently when a synthetic dye was accidentally discovered by a young English chemist, William Henry Perkin (1838-1907). Perkin at the age of 18 had set out to synthesize quinine,  $C_{20}H_{21}N_2O_2$ , by oxidizing allyltoluidine ( $C_{10}H_{12}N$ ). However, he had instead accidentally produced the first synthetic dye, aniline purple, more widely known as mauveine. The actual molecular formula of the dye's principal component is  $C_{26}H_{23}N_4^+ X^-$ ; X = chloride, sulphate, acetate, etc. It is worth noting that molecular structures of only a few compounds were known with any certainty at that time, and Kekule had only recently recognized the structure of benzene.

Perkin set up a factory on a 6-acre site in West London. At the Royal Exhibition of 1862, Queen Victoria made an appearance in a silk gown, which was dyed with mauveine that was made in the late 1850s. She unveiled a "penny lilac" postage stamp thought to have been dyed with the same compound. Curiously, the "correct" structure for mauveine was only determined in 1994, and a complete stereochemical synthesis of quinine was completed by Gilbert Stork in 2001.

The color mauve fell from fashion in the late 1860s, but Perkin discovered other new dyes. It was said that the water in a canal near his factory turned a different color every week, depending on what dyes were being developed at the time.

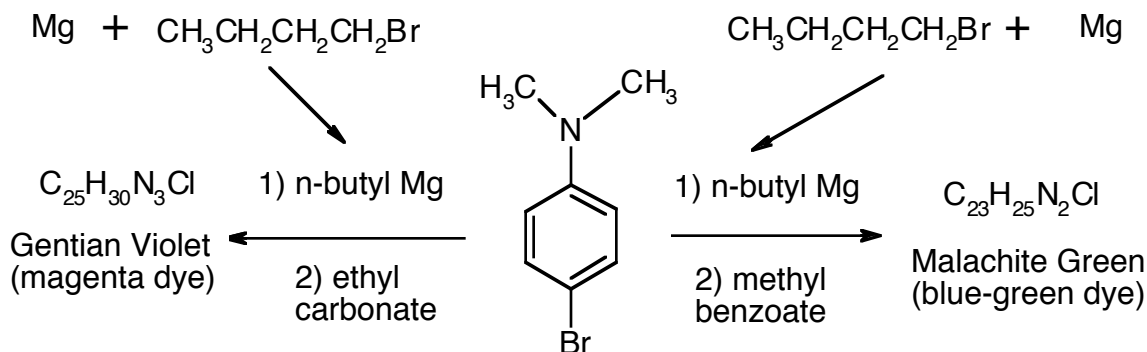
In the textile industry, almost 100 liters of water are used to dye a kilogram of fiber. Today, the aqueous effluent from the dyeing processes must be treated, but most local regulations in the United States allow the water to be returned to its natural source (often a local stream or river) without complete removal of all of the chemicals used in the dyeing process.

Many fibers, such as cotton, nylon, and polyesters, absorb large amounts of water. The dyeing process is very energy intensive because the water that is evaporated has an extremely high heat of vaporization. Besides coloring textiles, dyes have been used as acid-base indicators, histological stains for cells, and as fluorophores in immunoassays.

In this experiment you will be assigned the synthesis of either gentian (crystal) violet or malachite green. Before beginning your synthesis read Experiment 31, Lehman: Grignard reactions and triphenylmethane dyes and complete the following pre-lab questions, data acquisitions and calculations for your assigned reaction in your lab notebook. Include the answers as a separate section after the title. Check on-line for your assigned synthetic compound.

Both procedures involve preparing a Grignard reagent from 4-bromo-N,N-dimethylaniline and reacting it with an ester (methyl benzoate to make Malachite Green or ethyl carbonate to make Crystal Violet). The Grignard reaction requires absolute anhydrous conditions. The procedure is a modification of a normal Grignard reaction. Rather than preparing the desired Grignard reagent directly from 4-bromo-N,N-dimethylaniline, the Grignard is first prepared from n-butyl bromide and then "transferred" to 4-bromo-N,N-dimethylaniline by a process called "transmetalation". The reason for doing this is that the reaction of aryl bromides with magnesium metal is slow but the reaction of alkyl bromides with magnesium metal is fast and the metal transfer is fast.

The product of this reaction will not be isolated nor purified. Product yield will be determined by measuring the visible spectrum and using Beer's Law to calculate the concentration of dye. The product solution will also be used to dye a piece of cloth.



**Pre-lab Questions:** (Include the following in your lab notebook. Follow the standard report format: some of the answers to the questions will be part of your write-up: #3, Data Table: #1 and #2. Show answers to #4 and #5 as a separate section in the notebook. have initialed by Dr. R. before beginning.)

- 1) Using a reference, find the exact structure, molecular formula and molecular weight for your product.
- 2) Find the product's MSDS and consider if it is toxic. If so, how toxic do you think it is?
- 3) Write balanced equations for each of the 4 steps of your reaction:
  - a) formation of the n-butyl bromide Grignard reagent
  - b) transmetalation reaction
  - c) reaction of Grignard reagent with ester
  - d) reaction with HCl

e) What is the stoichiometry of the aniline relative to the ester in your reaction?
- 4) The ester is the limiting reagent. Calculate the mass of ester that you will need in order to react with 0.25g of 4-bromo-N,N-dimethylaniline.
- 5) Normally, an alcohol can be isolated from the reaction of an ester with a Grignard reagent, but in this case the elimination product readily forms at room temperature without heating. The structure of the product is positively charged, having a chloride ion as a counter ion (an anion). Provide a brief explanation for this effect and draw a resonance form of the product where one of the nitrogen atoms has a formal charge of +1 and another resonance form where all of the nitrogen atoms respectively have a formal charge of zero.

**PROCEDURE:**

Equipment preparation: It is essential that all apparatus used during this reaction (until the point where the mixture is added to aqueous HCl) be clean and scrupulously dried.

Dry the following glassware in an approximately 110°C oven for 20-30 minutes after rinsing with acetone:

10 mL pear flask	2 glass vials (but not lids)
reflux condensor	thermometer adapter (with rubber part removed)
glass stirring rod	small magnetic stir bar
two glass Pasteur pipets	

Your drying tube should be filled with fresh Drierite (empty the old Drierite into the used Drierite bottle).

**Caution:** Ethyl ether is extremely flammable and may be harmful if inhaled. Use in fume hoods. Keep away from flames or hot plates, heat guns, or other hot surfaces.  
**Magnesium** can cause dangerous fires if ignited. Keep away from flames and hot surfaces.

**Caution: Crystal violet and malachite green** both stain readily and are somewhat toxic. By-products from the preparation are of unknown toxicity. Avoid contact of the prepared dyes with skin and clothing. Wear gloves when handling the products. Do NOT repeatedly handle the dyed fabric.

**Amounts of reagents below are given for the preparation of malachite green (MG). For crystal violet (CV), use the amounts listed in parentheses. One reagent is different for crystal violet.**

**The reaction:** Weigh into the pear flask 0.08 g (*0.12 g for CV*) of magnesium turnings and 0.5 g (*0.75g for CV*) of 4-bromo-N,N-dimethylaniline. Add the dry stir bar. Attach the reflux condenser topped with the drying tube. Using a heat gun, heat the apparatus to remove any water vapor (the 4-bromo-N,N-dimethylaniline will melt). Cool to room temperature.

In the glass vial, mix 0.4 mL (*0.6 mL for CV*) of n-butyl bromide and 1 mL (*1.5 mL for CV*) of ANHYDROUS ethyl ether. When the apparatus is cool, briefly remove the condenser and add the n-butyl bromide/ether mixture to the reaction flask. Quickly attempt to crush or scratch a little of the magnesium with the stirring rod if possible (don't punch a hole in the flask). Return the condenser/drying tube and begin agitation of the stir bar using the stir motor. The reaction should start on its own. Evidence of starting will be that the heat of the reaction will cause the ether to boil (look for bubbling). For this particular Grignard reaction, the initiation of Grignard formation is also often accompanied by a transient, dark-green color. If the reaction does not start, try warming it with the heat of your hand. Then remove your hand and observe whether the reaction keeps going. Allow the reaction to continue to reflux for at least 20 minutes after it has started, warming it in a warm tap water bath if refluxing slows down towards the end. If the reaction mixture seems to be going dry, 0.5 mL more of anhydrous ether may be added. The solution should be cloudy and the magnesium should almost disappear.

Cool the mixture to room temperature. In the other glass vial, mix 78 microliters of methyl benzoate for malachite green (*80 microliters of ethylcarbonate for crystal violet*) and 0.5 mL (*0.5 mL for CV*) of ANHYDROUS ethyl ether. Add this to the cooled mixture and let the reaction proceed for at least 10 minutes, warming with warm water if needed.

Cool the mixture in ice and transfer it slowly into a beaker containing 2 mL of a 10% aqueous HCl solution. Wait until reaction is completed and transfer to a graduated cylinder, rinsing in any liquid with distilled water. Adjust the mixture to a pH of about 6 and dilute to a total volume of 25 mL. Save about half of the solution in a vial for analysis.

*This experiment was originally reported by D. F. Taber, R. P. Meagley, and D. Supplee. J. Chem. Ed. 73, 1996, 259. The modification using transmetallation was reported by C. Seto and J. Baird at Brown University; <http://www.chem.brown.edu/chem35/Lab2004/Make-upLab-Grignard.pdf>*

#### *Yield Analysis:*

Measure the visible absorbance of the solution on the UV/visible spectrophotometer. Use pipets and volumetric flasks to dilute your solution to an absorbance value in the range of the provided data. Consult the standard curve that will be provided. Using Beer's Law calculate the concentration of your sample and the amount of dye produced in the reaction. This calculation will allow you to calculate the percent yield.

#### *Dyeing Fabric:*

Bring in a piece of plain cloth. Cut it into a square that is approximately  $\sim 25 \text{ cm}^2$ . Immerse the cloth in the reaction mixture for 1-2 minutes. Blot dry with a paper towel and allow to dry in your lab drawer.

**Caution:** Avoid contact with skin and clothing. Wear gloves when handling the products. Do NOT repeatedly handle the dyed fabric.

*Disposal:*

All products must be disposed of in the lab's organic waste container. The dyed cloth can be kept.

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*Post Lab Questions:*

7. Refer to the attached list of criteria for "green chemistry" that follows. Identify those items in the list that might relate to the reaction procedure and/or dyeing process that you just performed. List each item that you think may be pertinent and provide a recommendation for a possible improved alternative for those that you have identified.

***Green Chemistry: Science and Politics of Change***

Martyn Poliakoff, J. Michael Fitzpatrick, Trevor R. Farren, Paul T. Anastas  
*Science*, Volume 297, Number 5582, Issue of 2 Aug 2002, pp. 807-810.

*Green Chemistry Principles*

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g., solvents, separation agents, and so forth) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be developed further to allow for real-time in-process monitoring and control before the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

**Dyes & Grignard Reactions**  
**Gentian (Crystal) Violet**  
*Determining % Yield using Visible Spectroscopy*

Figure 1 shows a beam of light (electromagnetic radiation) before and after it has passed through a solution having a path length,  $b$ , and a concentration,  $c$ . The power of the beam is attenuated (diminished) from  $P_0$  to  $P$  because of the interactions of the photons and the absorbing particles. Transmittance of the solution is the fraction of light that passes through the solution,  $P/P_0$ . In infrared spectroscopy it is often plotted as percent transmission versus frequency ( $\text{cm}^{-1}$ ).

Absorbance ( $A$ ) is expressed as a logarithmic function where the absorbance of a solution increases exponentially as attenuation of the beam becomes larger (less transmittance). Absorbance is directly proportional to the path length,  $b$ , through the solution and the concentration,  $c$ , of the absorbing species shown in the equation:

$A = abc$ , where  $a$  is a proportionality constant called *absorptivity*. If the concentration is expressed in molarity ( $M$ ) and the cell length in centimeters, the absorptivity is called the *molar absorptivity* and given the symbol,  $\epsilon$ . It has also been referred to as the *molar extinction coefficient*.

$A = \epsilon bc$  is known as Beer's Law.

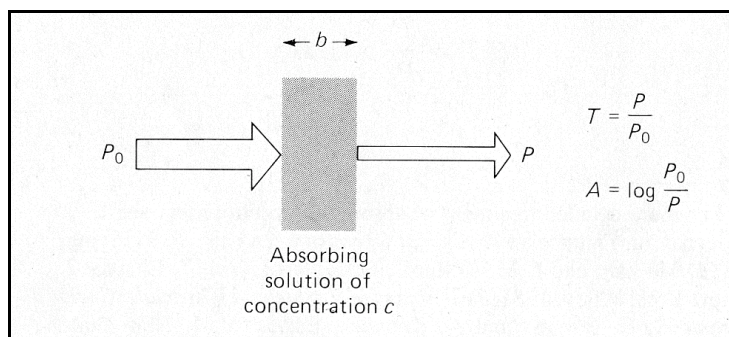


Figure 1

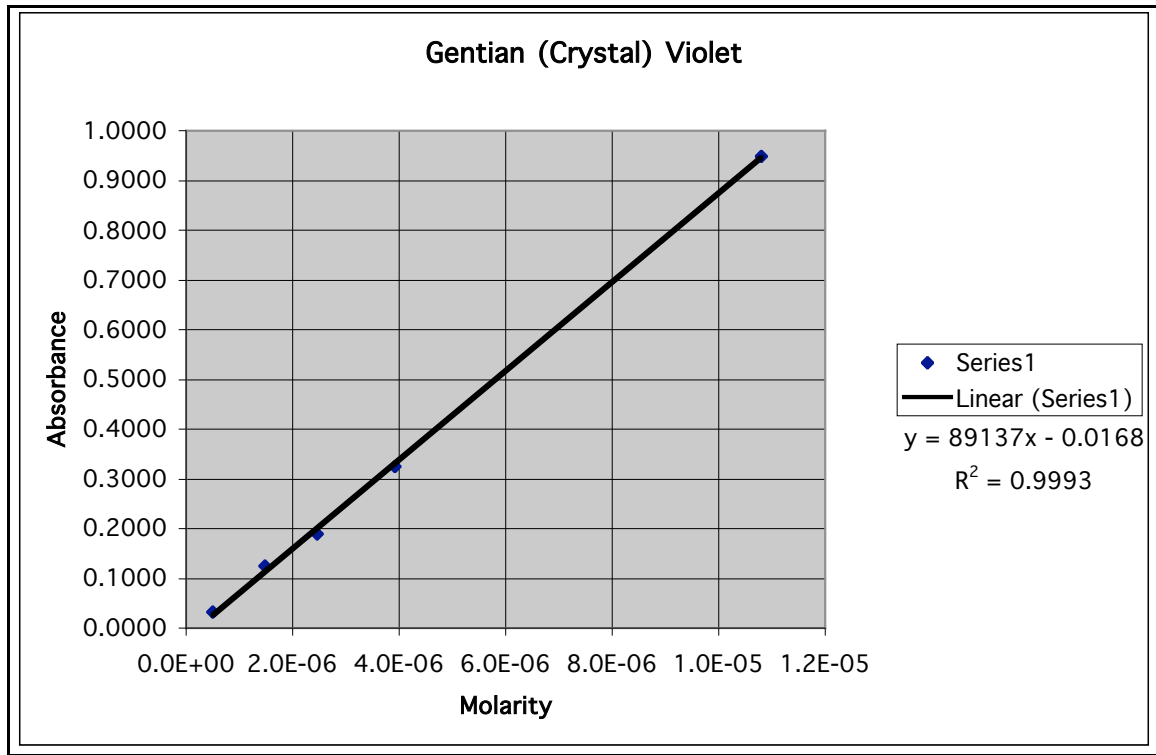
To conclude this experiment, Beer's Law will be used to quantitatively determine the concentration of dye produced in the Grignard reaction. This allows calculation of the total amount of dye produced and the percent yield without actually isolating the dye itself from the solution.

**Visible Analysis Procedure:**

*Gentian (Crystal) Violet:*

Pour the reaction mixture into a 100.00 ml volumetric flask and fill to the line with de-ionized water. Pipet 5 ml from the flask into a clean dry beaker and slowly add base (0.5M NaOH) dropwise to neutralize the excess acid. You will see the solution change from yellow to green-blue to light purple. Stop adding base when the color is purple. Completely transfer the contents of the beaker to a 250 ml volumetric flask rinsing the beaker with de-ionized water and dilute to the mark. Carefully fill a cuvette with the diluted solution and determine its absorbance at 590 nm. If the absorbance is off scale develop a dilution plan to get it on scale consulting the Beer's Law plot below. *(The contents of the 100 ml flask should be discarded in the organic waste container after completing the analysis.)*

Once the absorbance is on scale, using the standard curve below, determine the respective concentration of the reaction solution. From the concentration and the dilution factors, calculate the total amount in grams that were in the reaction mixture and report the percent yield noting the comments following the standard curve. Clearly show your calculations in your report.



**Note:** The standard curve is for a neutral solution,  $\text{pH} \approx 7$ .