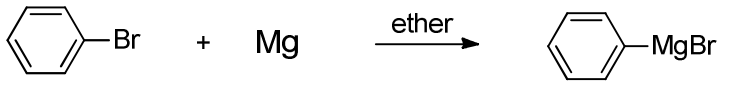
Experiment 21

Grignard Dyes: Preparation of a Triarylmethane Dye by the Grignard Reaction

Study Questions

1) A student planned to react bromobenzene and magnesium to form phenylmagnesium bromide in the molar amounts given below. As he set up his glassware, he did not notice a small amount of water (0.5 mL) in his separatory funnel. He put the magnesium and ether in the round bottom flask and the bromobenzene in the separatory funnel. While he was forming his Grignard reagent he noticed a substantial amount of white solid precipitating in his reaction flask.



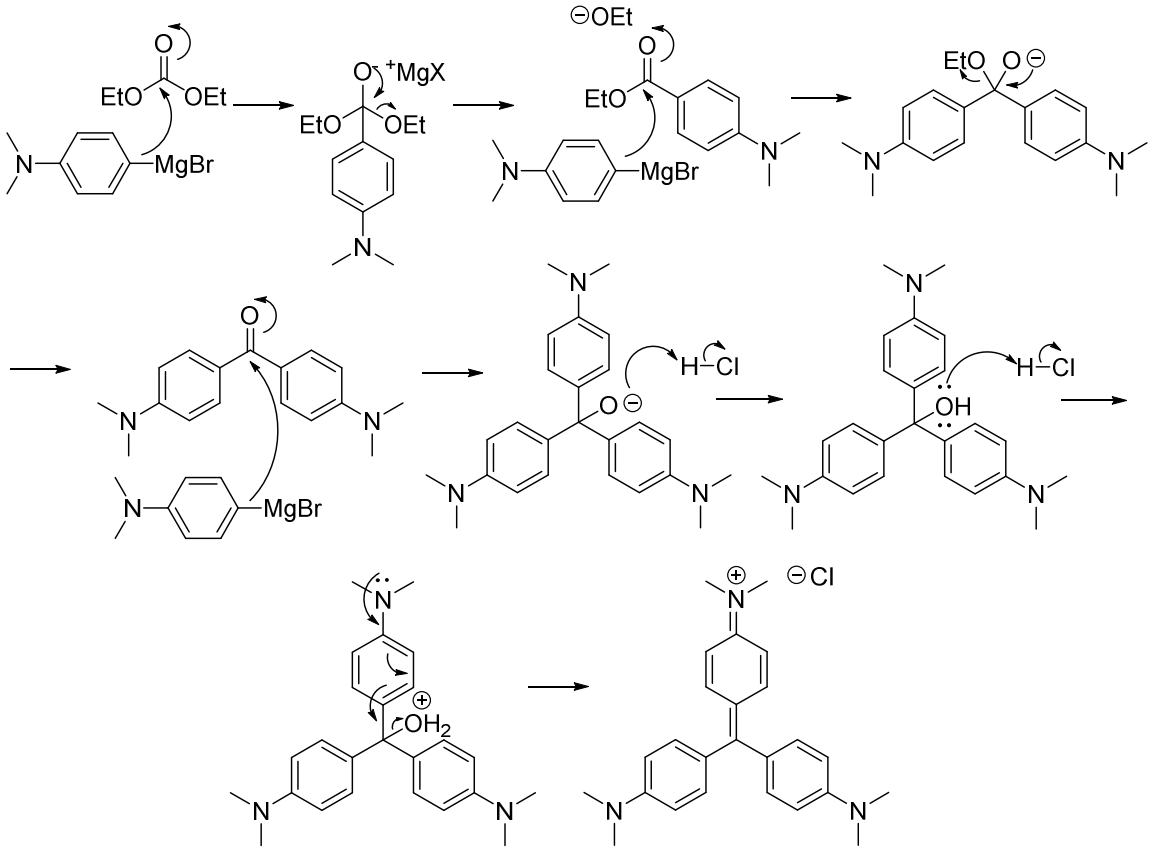
Bromobenzene 0.02 moles | Magnesium turnings 0.02 moles | Phenylmagnesium bromide

a) What is the structure of the white solid? **Answer:** MgBrOH.

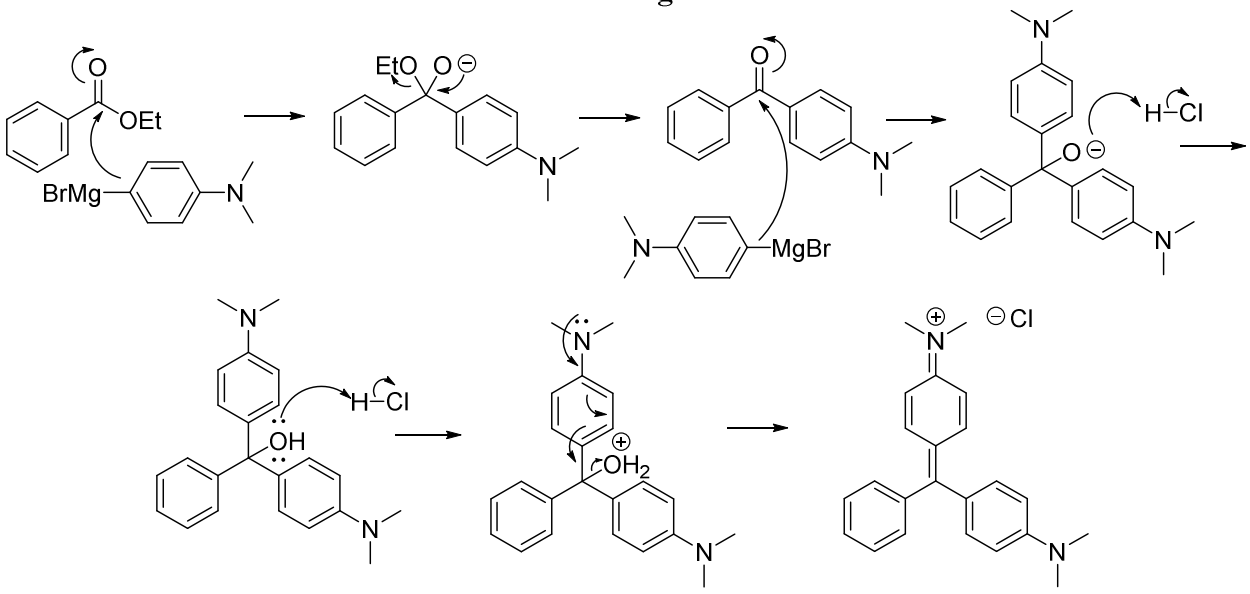
b) How many moles of the white solid will be formed? What effect will this have on the success of the Grignard reaction? **Answer:** There will be 0.02 moles of C_6H_5MgBr reacting with 0.028 moles of water. Therefore, all of the C_6H_5MgBr will react with the water, forming 0.02 moles of HOMgBr, and leaving no C_6H_5MgBr to react with the benzophenone.

2) Choose one of the two dyes from this lab and write out the complete mechanism for its formation, assuming the Grignard reagent has already been formed.

Crystal violet

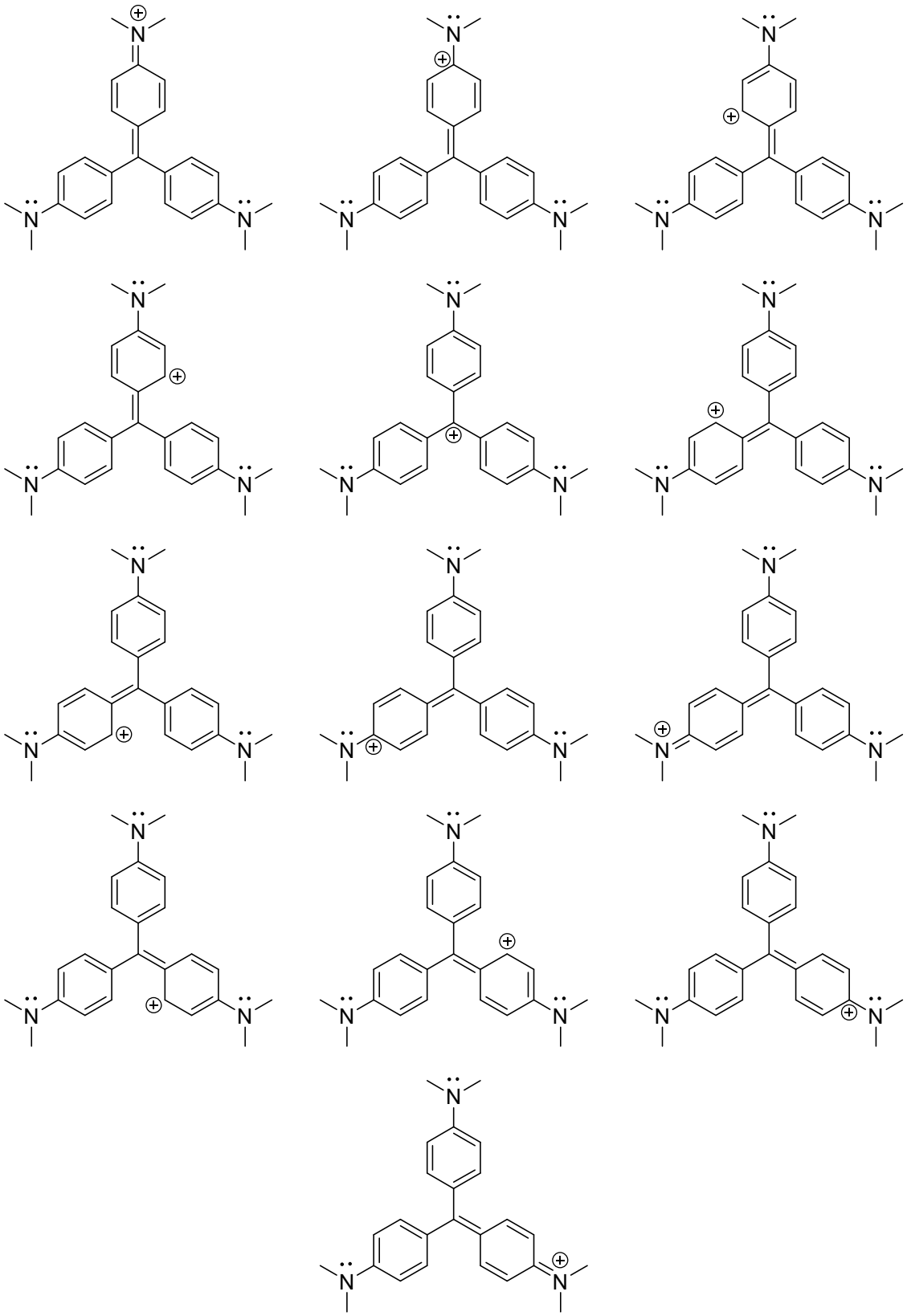


Malachite green



3) Choose one of the two dyes from this lab and show all of its resonance forms.

Crystal violet resonance states



Answer: Crystal violet has thirteen resonance states. Malachite green has one fewer, because it has no nitrogen on the lower-left ring to put the positive charge onto.

4) Does crystal violet or malachite green absorb light at a longer wavelength? **Answer:** Crystal violet appears violet, so it must absorb yellow-green light at 560-590 nm. Malachite green appears green, so it must absorb red light at 605-700 nm. Therefore, malachite green absorbs light at a longer wavelength. (The actual literature values for the λ_{max} of these dyes in water are 590 nm for crystal violet and 617 nm for malachite green. These are taken from http://omlc.org/spectra/PhotochemCAD.)

5) What would happen to the color of your dye if you added sodium hydroxide until the solution's pH was 10? Why? Show a mechanism for this reaction. **Answer:** The dye would go back to being colorless. This would be almost the reverse of the step where HCl was added. The colorless product of this reaction is called the "leuco" form of the dye, from the Greek word for white. Another example of a dye with a leuco form is phenolphthalein, which is used as a pH indicator; above a certain pH, phenolphthalein is converted from its leuco form to bright pink.