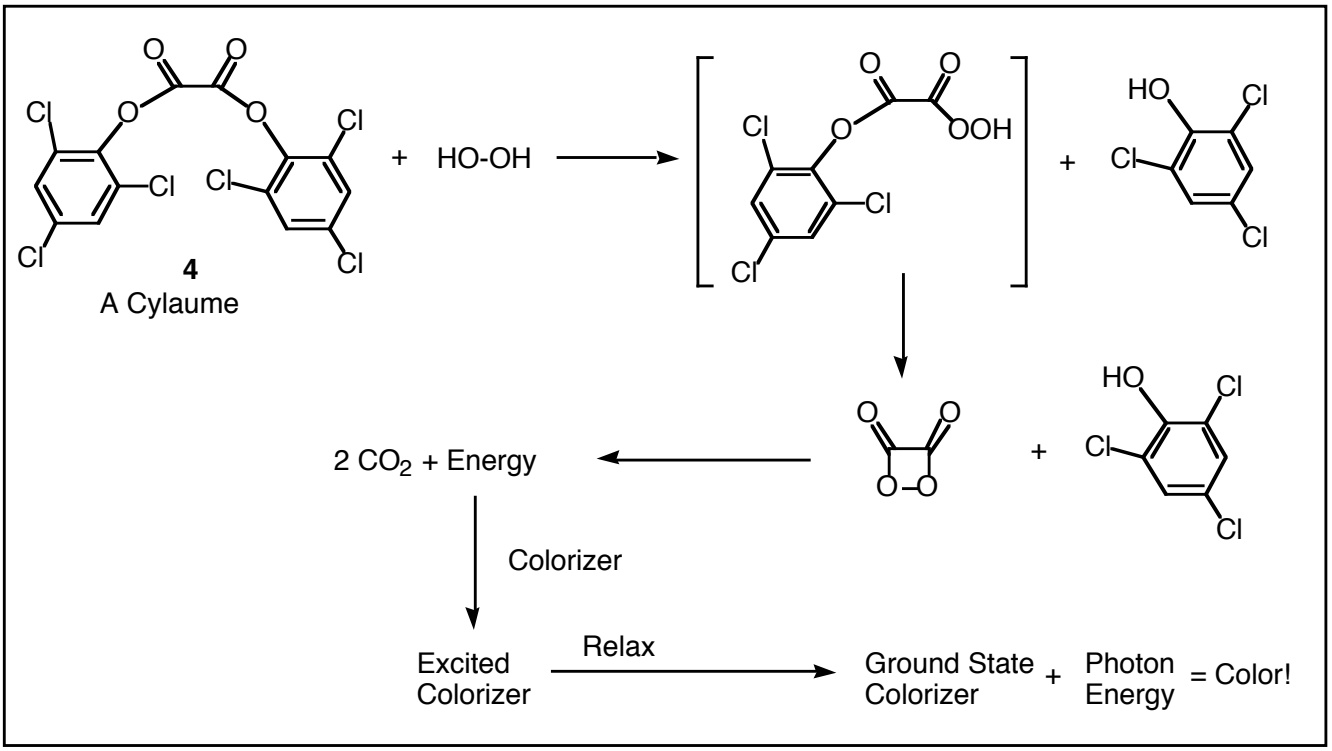
Chemiluminescence: Synthesis of Cyalume and Making it Glow

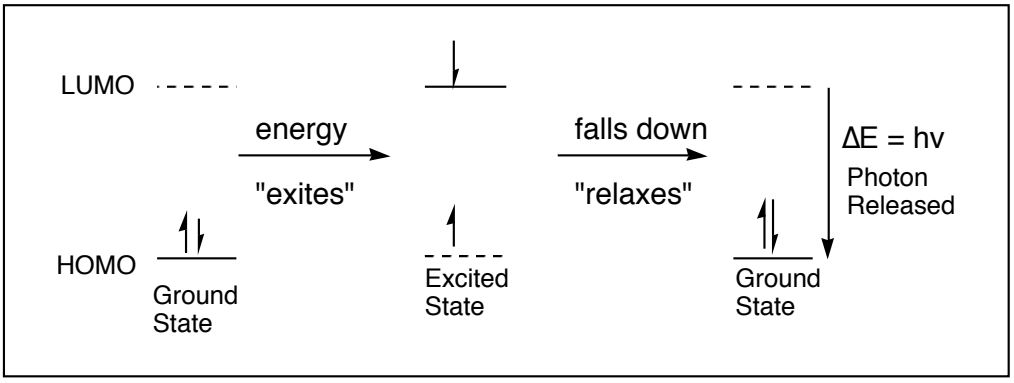
Intro *Chemiluminescence* is the process whereby light is produced by a chemical reaction. The flashes of the male firefly in quest of a mate is an example of natural chemiluminescence. In this experiment we will make Cyalume, the chemical used in "light sticks." A light stick contains a solution of cyalume containing a trace catalytic amount of a colorizing agent (catalyst). Inside is a sealed vial of aqueous hydrogen peroxide. When you bend the light stick, the hydrogen peroxide vial breaks, the hydrogen peroxide reacts with the cyalume (those are the two stoichiometric reactants), and energy is released. This energy is absorbed/released by the catalytic colorizing agent, resulting in the bright glow of varying color; the same stoichiometric reactants can be used, but when different colorizing catalysts are included, different colors result. Cyalume is an invention of the American Cyanamide Company. In today's experiment, we will make some cyalume, then make up two glow solutions: one will use a commercial colorizer, and the other will use a home-made colorizer that you will synthesize later this semester. (We'll use material that students from previous year made.)

Nature of the Energy Release and Glow Formation

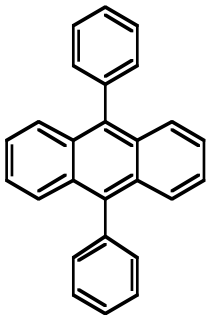
The chemistry that forms the color glow in a light stick is shown below. A cyalume is a symmetric diester, such as **4**. It reacts with hydrogen peroxide (red oxygens) by oxygen exchange. Trichlorophenol (green) is released as each of the two red oxygens of hydrogen peroxide connect to the two blue carbonyl groups. The 4-memeberd ring "squarate" diester, including the two carbonyls from the original cyalume and the two oxygens from hydrogen peroxide, is unstable due to ring-strain, and fragments to give two molecules of carbon dioxide and energy.



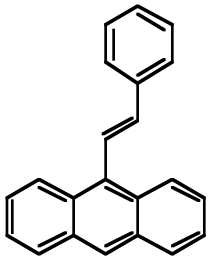
The energy released during the fragmentation "excites" a colorizing molecule that must be present. In other words, an electron in the colorizer gets "excited" from its ground state to an excited state. When it subsequently relaxes back to the ground state, a photon of energy is released. If the energy gap ΔE between the excited state and the ground state is in the visible region of the electromagnetic spectrum, then visible photons of distinctive color are released. This is what causes the bright colors. Since different colorizers have different ΔE, they release photons of different colors.



Several things to note about the exitation/relatation process: 1) The energy gap between the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) determines the photon frequency and the color of the photon released. 2) For most organics, the HOMO-LUMO gap is not in the visible frequency. 3) To have a HOMO-LUMO gap that's in the visible spectrum, extensive conjugation is required. The examples shown below, which are the colorizers we will use, are representative. 4) Only a catalytic amount of colorizer is required. Excitation and relaxation regenerates the original molecule in its ground state, ready to repeat the process.



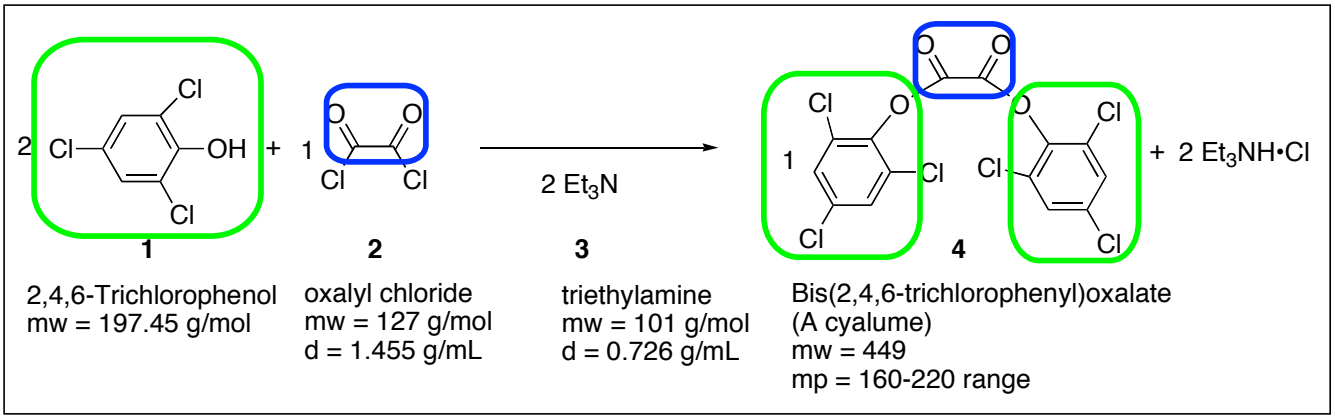
commercial
colorizer
(purple glow)



homemade
colorizer
(yellow/green flow)

Cyalume Synthesis Overview

The synthetic reaction is shown below. Oxalyl chloride **2** (the blue reactant) is a symmetric acid chloride that is highly electrophilic and is very reactive because of the chloride leaving group. One oxalyl chloride reacts with two molecules of phenol **1** (green chemical) to give the diester **4**, which is a cyalume. (Not all cyalumes have the same 2,4,6-trichloro substitution pattern on the arene rings.) Triethylamine is an amine base which serves to absorb the two HCl's that get produced during formation of the diester.



1
2,4,6-Trichlorophenol
mw = 197.45 g/mol

2
oxalyl chloride
mw = 127 g/mol
d = 1.455 g/mL

3
triethylamine
mw = 101 g/mol
d = 0.726 g/mL

4
Bis(2,4,6-trichlorophenyl)oxalate
(A cyalume)
mw = 449
mp = 160-220 range

Part I: Cyalume Synthesis Procedure

1. Work with partner
2. Use a 25-mL round-bottomed flask containing a medium-sized stir bar (not the really small "flea" stir-bars, use the next larger one…)
3. Add about 0.790 g of trichlorophenol. (Record to three significant figures.)
4. Add 6 mL of toluene (solvent, bp = 111ºC). (This is solvent, so need not measure precisely.) (Record observations).
5. Add 0.56 mL of triethylamine by syringe, and swirl. (Bring the solution to the dispensing hood, with both partners to watch. Record observations).
6. Bring to other hood where instructor will inject 0.200 mL of oxalyl chloride. Swirl. The oxalyl chloride is a smelly lachrymator (makes you cry), and needs to be measured with a special syringe in the hood. (Both partners come. Record observations.)
7. After swirling your mixture, attach a reflux condenser, and reflux the mixture gently while stirring for 15 minutes on a hot plate/stir plate to complete the reaction. Note: With no heat, the reaction is too slow. But with excess heat, decomposition can occur. You'd like to have it hot enough so that your toluene can barely boil, but you don't want to go to extremes and have it boiling super-crazy.
   - Set the hot plate heat setting to 6.
   - Since the hot plate doesn't make very good contact with the flask, that's why the hot plate needs to be set that high. Make sure it's actually contacting the flask.
   - During the fifteen minutes of heating, you could calculate your moles of each of the three reactants, identify which is limiting, and calculate your theoretical yield. You can also write up much of your report.
8. Cool the mixture well, eventually in ice, and collect the solid (both cyalume and triethylamine hydrochloride salt) with a small Buchner funnel and vacuum.
   - Use a bent/curved spatula to try to help drag/scrape as much as possible of your solid material out of the round-bottomed flask.
9. Use about 5 mL of hexane to rinse the flask and rinse the solids in the Buchner funnel. Pour the liquid into the organic waste bottle.
10. Make sure the solid is pretty dry before the next step.
11. Transfer the solid into a beaker, and add 10-12 mL of water. Stir the solution well with a spatula, trying to break up the solid chunks if necessary.
    - Purpose: The triethylamine hydrochloride, being ionic, should dissolve into the water. The cyalume, being organic, should remain insoluble.
12. Filter using a small Buchner funnel.
13. Rinse with an additional 5-10 mL of water.
14. Transfer the cyalume solid into your smallest beaker. Add 2 mL of toluene.
15. Heat on a hot-plate until the toluene achieves a gentle boil. (Hot-plate setting of maybe 4?) Maintain a gentle boil for 2-4 minutes (record observations, for example whether there are brown particles left, or whether it all dissolves….), then remove from the heat and let the solution cool, eventually to ice-cold.
    - Heating a solid that doesn't dissolve completely is called "**digestion**". So long as the crystal has some solubility in the solvent, digestion still allows back-and-forth between solid phase and solution, and can frequently still allow impurities to be released to the solvent. In the current case, if you use more toluene in order to get a true recrystallization, sometimes it's hard to initiate crystal growth, and the loss of product to solvent is frequently very severe.
16. Filter on a Hirsch funnel (smallest ceramic filtration unit). (You'll need to "mold" your 42.5mm filter paper.)
17. Rinse with 2-4 mL of hexane (one or two pipets worth..).
18. Vacuum thoroughly. (10 minutes should be good.)
19. Take mass. (Do this today, don't need to wait.)
20. Take out sample for melting point. (Can wait if you wish, but you can do this today if you want.)

Part II: The Chemiluminescent Reaction

1. The instructor will distributed two vials to each pair of students. Each will have about 3 mg of colorizer, one with the commercial colorizer and the other with the home-made colorizer.
2. Add 0.1g (or more) of cylaume to each vial.
    - 0.1 grams should be enough to get a good glow
    - Excess can be donated to Dr. Jasperse's cyalume jar in the acetone/waste hood
    - I can use your student-prepared cyalume for school demonstrations
    - If you have a good yield, you could also put in >0.1g of cyalume into each of your vials. Probably the reaction will glow longer if you put in more cyalume fuel.
3. Add 5 mL of diethyl phthalate (organic solvent, bp > 298ºC) into each of the two vials.
4. Warm the vials on a hot plate. (The heating is not essential. But the initial glow will be more dramatic if the temperature is hot, resulting in faster reaction.) Don't heat too much; you need to be able to carry the vials. Suggestion: hot-plate setting of 3.5, for five minutes.
5. Bring your vials, with their caps, to the dark room. (Room across the hall.) Both partners come.
6. The instructor will then inject 0.35 mL of 30% hydrogen peroxide/water.
7. Screw the covers back on, shake, and observe the pretty lights!
8. Each partner can take one of the vials home. Show them off to your roommates to show that chemistry is fun! (Woo hoo.) Watch to see how long you can still see them glow. Some students have glow for 2 days or even longer..
9. Eventually it's best to bring the vials back and pour the material out in the waste bottle in the hood. However, if you do drain the liquid in the sink or toilet, that's acceptable also.

Lab Report

- Write up a standard synthesis lab report for Part I. (Review to make sure you know what the standard synthesis style lab report should look like. Ask instructor if in doubt.)
    - Hand-written work should be OK.
    - Make sure your first page shows the reaction; lists the chemicals used (actual measured amounts); shows the mole calculations for the trichlorophenol, the oxalyl chloride, and the triethylamine; shows the work unit conversions involved in the mole calculations; identifies which reactant is limiting; and shows the theoretical yield in grams.
    - Normally the procedure can start on a second page.
    - The data/results should come following the procedure, and should include mp, mass yield, and percent yield.
    - No assigned post-lab questions.
- You don't need to write anything up for Part II. That's just for fun!
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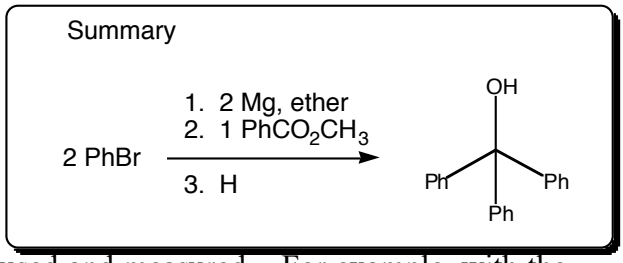
Standard Synthesis Laboratory Report Format (example): The following layout is standard for a "synthesis reaction" report. Provide the parts and information in the sequence specified.

1. Title = Reaction Summary
For an organic reaction, there is no point in having a Worded Title: The chemical reaction is the best title summary of what you did!



2. Listing of all Chemicals Used
- This should include all chemicals used, including solvents.
- For each chemical, you should include the actual quantity used and measured. For example, with the methyl benzoate you measured a volume by syringe, rather than by weighing on a balance. So you should list the volume you actually used rather than just the weight.
- For reactants that might possibly be limiting reactants and might possibly factor into calculation of the theoretical yield, you must include more than just the quantity of chemical used. You should also include a conversion from what you measured into the number of moles used.
- In some cases, there may be considerable roundoff (you needn't keep precise record of the quantity of solvent that was used, for example, or of sodium sulfate drying agent…)
- If a person was later to repeat your experiment, they should be able to look at this list and know all the chemicals they'd need to have on hand and in what quantities, in order to complete the experiment.

3. Calculation of Theoretical Yield
- Specify which chemical is the limiting reactant
- Given moles of limiting reactant, calculate theoretical moles of product
- Given moles of product, calculate theoretical grams of product.
- Note: Why do this so early in report?
    - First, because it fits in near your mole calculations above.
    - Second, if calculated in advance. as with most research, you know which chemical is limiting and thus must be measured most carefully, but you also know which are in excess and thus need not be measured with equal precision.
    - Third, it's nice to know approximately how much material is expected, so you can recognize whether your actual results are reasonable or problematic.

4. Writeup of Actual Procedure.
- For this particular experiment, the "procedure" section will be by far the biggest portion of your report.
- This should be a concise but detailed description of things, including:
    - What you actually did (even if not recommended or not from recipe)
    - All observations should be included. These include all observed changes, such as:
        - Changes in **color**
        - Changes in **solubility** (formation of precipitate or cloudiness…)
        - Changes in **temperature** (like, reaction became hot…)
        - Formation of **bubbles**
    - Time and temperature details:
        - Whenever you heat something or cool something, the procedure should specify
        - Specify times. Whether you boiled for 5 minutes or 5 hours matters!
- Writing details: As a record of what actually happened, the report must be written in **past tense**, not **command tense**. (Rather than "Add this", should read "I added this", or "I dropped that…")
    - Use of personal pronouns is accepted in this class. You may use "I" or "we" to simplify writing.

5. Product Analysis
- Any GC, NMR, mp, bp, or TLC information. For this report, mp information must be included. What's required depends on the actual experiment and what data was obtained.
- Final yield and percent yield information.

6. Discussion/Summary. Need not be long, but any conclusions or excuses would go here…
7. Answers to any assigned Questions