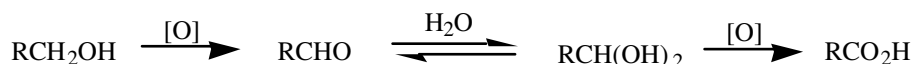


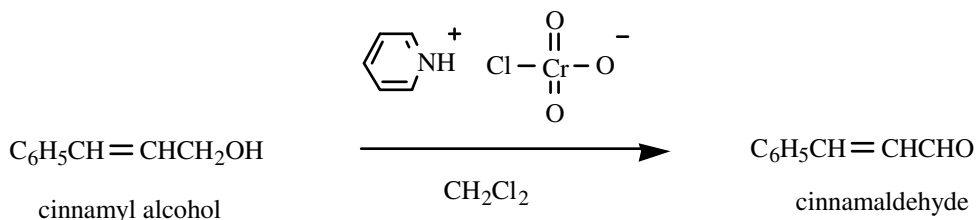
## SELECTIVE OXIDATION OF ALCOHOLS WITH PYRIDINIUM CHLOROCHROMATE (PCC) (12/12/2004)

Organic chemists must often choose from hundreds of oxidizing agents and reaction conditions to perform a desired oxidation without affecting other functional groups present or causing side reactions. Oxidations of primary alcohols to aldehydes without further oxidation to carboxylic acids is difficult to accomplish with oxidizing agents in aqueous solution because small amounts of aldehyde hydrates, which are in equilibrium with the aldehyde, are readily oxidized to the corresponding carboxylic acids.

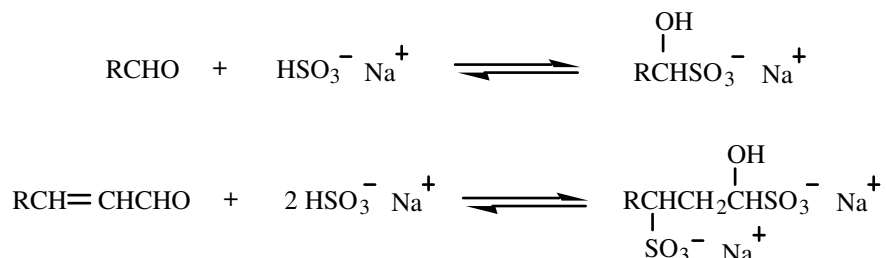


However, selective oxidation of primary alcohols to aldehydes can be easily accomplished by using chromium (VI) reagents that are soluble in organic solvents under anhydrous conditions which avoids hydrate formation. The two most convenient reagents for this conversion are chromium trioxide dipyridine complex ( $\text{CrO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ ), known as Collins reagent, and pyridinium chlorochromate ( $\text{C}_5\text{H}_5\text{NH}^+ \text{CrO}_3\text{Cl}^-$ ), which is often abbreviated as PCC and also known as Corey-Suggs reagent. Both of these reagents are soluble in dry methylene chloride, which is the solvent of choice when using either reagent for oxidations of alcohols.

In this experiment we will use PCC in methylene chloride to oxidize cinnamyl alcohol to cinnamaldehyde.



To facilitate isolation and handling of the aldehyde product advantage can be taken of the fact that aldehydes (and a small number of ketones such as methyl ketones, cyclohexanone, and cyclopentanone) form solid adducts when treated with a saturated aqueous solution of sodium bisulfite. Saturated aldehydes form 1:1 adducts, but  $\alpha,\beta$ -unsaturated aldehydes form 2:1 adducts.



These bisulfite adducts can be filtered and washed free of other organic compounds. The pure aldehydes can be regenerated from the adducts, if desired, by treatment with either dilute hydrochloric acid or aqueous sodium carbonate solutions.

## Experimental Section

### *Procedure*

Dissolve 15 mmol of cinnamyl alcohol in 15 mL of methylene chloride and place in an addition funnel. Place 15 mmol of PCC in a 100 mL round-bottomed flask and add 20 mL of methylene chloride. Add a magnetic stir bar to the flask and set the apparatus over a thermowell that is assembled on the magnetic stir plate. This will allow stirring of the reaction mixture while reflux. Equip the round bottom flask with a condenser and the addition funnel containing the cinnamyl alcohol using a Claisen (Y shaped) adapter. Add the alcohol solution dropwise to the PCC suspension with gentle stirring using the magnetic stir bar. Once the addition is complete, heat the reaction mixture at reflux for 20 minutes with a thermowell. Decant the solvent layer from the tarry black residue, and rinse the residue twice with about 5 mL of methylene chloride. Evaporate the combined methylene chloride solutions on a rotary evaporator. Dilute the residual material with 50 mL of diethyl ether and filter through cotton plug to remove the insoluble chromium salts. Wash the ether layer with 15 mL of 1M NaOH, followed by 15 mL of saturated salt solution, then dry the ether/product solution with anhydrous Na<sub>2</sub>SO<sub>4</sub>.

Next, spot a TLC plate with the ether/product solution. It is a good idea to spot it at least 3 times. Run a TLC of the oxidation product versus the supplied reference standard of cinnamyl alcohol. If the TLC shows the presence of cinnamyl alcohol, how will this affect your calculated percent yield of cinnamaldehyde (include your answer in the postlab exercise)?

Decant the ether/product solution from the drying agent and then evaporate the ether on a rotary evaporator. Store the flask in the drawer until next week.

### *Part II (2<sup>nd</sup> Week of Experiment)*

Weigh the residual liquid to calculate the percent yield assuming the liquid to be pure cinnamaldehyde. Save five drops of your product in a product vial for an IR spectrum. Reweigh the remaining product. The remaining product will be used to prepare the bisulfite adduct. Add 3 mL of absolute ethanol to 10 mL of 40% aqueous NaHSO<sub>3</sub> solution, and then add this solution to the remaining product, stopper and shake. The bisulfite adduct will precipitate. Collect the precipitate by vacuum filtration and wash the precipitate with about 5 mL of absolute ethanol followed by a similar amount of diethyl ether. Weigh the bisulfite adduct and calculate a percent yield.

Dissolve some of your product (cinnamaldehyde) in chloroform as directed by your instructor. Fill an IR solution cell with this solution and obtain an IR spectrum.

- 🔔 Avoid contact with Pyridinium Chlorochromate (PCC)! Chromium compounds in the +6 oxidation state are suspected carcinogens.
- 🔔 Clean up all spills on the balance and balance bench immediately! PCC waste should be handled carefully and discarded in the tub for hazardous waste (located in the waste hood).
- 🔔 Monitor reflux carefully.
- 🔔 **FLASK CLEANING TIPS:** To remove the tarry black residue from the reaction flask, add some acetone and swirl. Then add 2-3 milliliters of concentrated HCl (available in reagent hood) and swirl again. Allow the solution to stand in the rbf for as long as possible (do not leave overnight in lab drawer!). Use a glass stir rod to help break up the tarry residue if necessary. Dissolve solid completely and discard in sink with plenty of running water. **CAUTION:** the cleaning solution generates heat!

Name: \_\_\_\_\_ Section: \_\_\_\_\_ Date: \_\_\_\_\_

**POSTLAB EXERCISE:**  
SELECTIVE OXIDATION OF ALCOHOLS  
WITH PYRIDINIUM CHLOROCHROMATE (PCC) (12/12/2004)

➤ Due 1 week after completion of the experimental portion of the notebook (30pts TOTAL). Please answer questions on this form. Attach sample calculations and copies of any TLC plates, GC traces, and/or spectra which you interpret (*on the spectra, please!*). Points for % yield would be assigned by the lab supervisor.

**A. PRODUCT INFORMATION (14pts)**

% Yield of Cinnamaldehyde (5pts):	
%Yield of Bisulfite Adduct (0pts)	
<b>ACTUAL Cinnamaldehyde %Yield (5pts)</b>	
<b>Appearance Description (Bisulfite Adduct) (2pts):</b>	

(2pts) Indicate the appearance of your TLC plate and attach original to this form. Be sure to identify the components.



## B. SUMMARY QUESTIONS (16pts)

1. (6pts) Show your calculations on the reverse side for percent yield of a) cinnamaldehyde; b) the bisulfite adduct and; c) the actual percent yield of cinnamaldehyde:
2. (2pts) Compare the IR spectrum of cinnamaldehyde with the IR spectrum of cinnamyl alcohol (<http://www.chemistry.mtu.edu/%7Ekmsmith/Organic/Manuals/2421/Oxidation/Oxspectra.htm>). What are the major differences between the two spectra?
3. (2pts) Identify the major functional groups of each of the two compounds *on the spectra*. Be sure to attach both spectra.
4. a) (2pts) How many impurities does the TLC analysis indicate are present in the product and what is the identity of at least one of the impurities?  
  
b) (1pt) How did the impurities affect your percent yield of the bisulfite adduct?
5. (3pts) Interpret the  $^1\text{H}$  NMR spectrum of cinnamaldehyde (<http://www.chemistry.mtu.edu/%7Ekmsmith/Organic/Manuals/2421/Oxidation/Oxspectra.htm>) by making specific proton assignments. Please make the proton assignments *on the  $^1\text{H}$  NMR spectrum and attach*.