Oxidation of $t$-Butylcyclohexanol with Pyridinium Chlorochromate on a Silica Gel Substrate

Adapted by Morgan Mihok from a macroscale experiment in J. Chem. Ed. entitled A Facile Oxidation of Alcohols Using Pyridinium Chlorochromate/Silica Gel

The procedure is based on an experiment by Frederick Luzzio, et al. J. Chem. Ed. 1999, 76, 974.1

Introduction

Oxidation reactions of alcohols greatly increase the synthetic usefulness of these compounds. Only primary and secondary alcohols can be easily oxidized, with the former converted to aldehydes or carboxylic acids and the latter to the corresponding ketones. While the strength and selectivity of oxidizing agents varies widely, the use of oxochromium(VI)—amine reagents is fundamental for a number of organic oxidative transformations. Pyridinium chlorochromate is the most commonly used of these reagents, due in part to its availability, stability, and versatility as a reagent. Generally, oxidation with PCC proceeds through a simple, one step reaction:

$$\text{PCC} + \text{RCH}_2\text{OH} \rightarrow \text{RCH}_2\text{O} + \text{CrO}_3\text{Cl}$$

The silica substrate used in this particular reaction acts to absorb the reduced chromium tars produced, thus simplifying the work-up and increasing yield. The main drawback to this is that the amount of PCC required is somewhat greater.2

Prelab Exercise: Suggest a mechanism for the reaction above. From your mechanism, deduce why tertiary alcohols are not easily oxidized.

Cautions: PCC is a strong oxidizing agent! Handle with care! Wear gloves during the grinding process and do it under a hood. You do not want to oxidize your skin.

Synthesis: Weigh out 0.276 g PCC and 0.276 g silica gel (230-400 mesh). Combine and grind with a mortar and pestle to form a light orange powder. Add this powder to a 25 mL roundbottom flask along with 3 mL of dichloromethane (CH$_2$Cl$_2$) and a 1/2” stirbar. While stirring, add 100 mg 4-$t$-butyl cyclohexanol. Test the reaction solution every five minutes with TLC (develop in iodine) to test the completion of the reaction (completion should be achieved in 15-25 minutes).

Isolation and Purification: Dilute the reaction solution with 5 mL ether and filter the solution through a pipet containing with a cotton plug, 1 cm Celite, and 2.5 - 3 cm 35-70 mesh silica gel. Concentrate the filtrate by blowing on it with N$_2$ until it is a yellow oil, the dilute with 2 mL ether and transfer to a reaction tube. Do pipet liquid/liquid extraction with 2 x 2.5 mL of H$_2$O and saturated NaCl solution. Transfer the organic layer to a 10 mL flask, dry over anhyd NaSO$_4$, and transfer the solution to a tared 10 mL flask and allow the solvent to evaporate overnight.
Cleaning up: Any residue containing unreacted PCC or reduced chromium from this experiment must be disposed of in the heavy metals container. The H₂O and saturated NaCl washings can be poured down the drain.

Analysis: Weigh the flask (it should be yellow crystals) and characterize the product by IR, NMR, and melting point analyses. Make sure to include the structure and identifying characteristics of the compounds on your spectra.

Final Report: Analyze and annotate all spectra. Give percent yield and possible reasons for it.

1) Would the final product have been any different if you had used a stronger oxidizing agent such as chromic acid? What would your products have been if you had been oxidizing the following compound?

(2) Given that pyridinium chlorochromate is only sparingly soluble in CH₂Cl₂ while 4-t-butylcyclohexanol is relatively soluble in CH₂Cl₂, suggest a reason for the importance of grinding the PCC and silica gel to form a fine powder. (Hint: What basic physical property is changed by this?)