EXPERIMENT 7

COLLABORATIVE EFFORTS TOWARD OPTIMIZATION OF A GREEN OXIDATION OF VARIOUS ALCOHOLS

Introduction to Green Chemistry

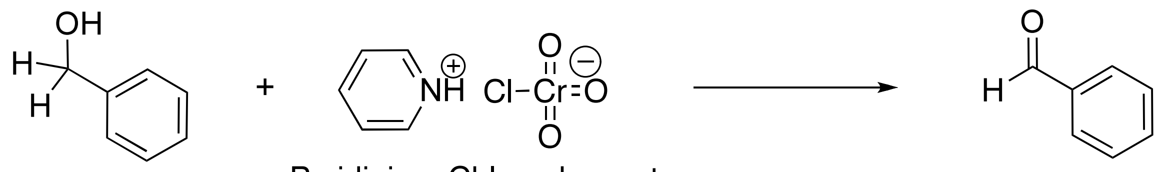
Green Chemistry is often defined as the design of chemical products and procedures that reduce or eliminate the use and generation of environmentally hazardous substances. Green Chemistry is viewed as a proactive approach to replacing toxic byproducts generated during the course of a chemical reaction with environmentally benign counterparts. Twelve guidelines for the development of “green” processes are detailed in “Green Chemistry: Theory and Practice” by Paul Anastas and John Warner. These guidelines include:

1) Prevent waste
2) Design safer chemicals and products
3) Design less hazardous chemical syntheses
4) Use renewable feedstocks
5) Use catalysts, not stoichiometric reagents
6) Avoid chemical derivatives
7) Maximize atom economy
8) Use safer solvents and reaction conditions
9) Increase energy efficiency
10) Design chemicals and products to degrade after use
11) Analyze in real time to prevent pollution
12) Minimize the potential for accidents

The overreaching goal of these twelve steps is to reduce waste through elimination of hazardous materials or solvents, degradation of unwanted chemicals to innocuous substances following the reactions, reduction of reagent consumption by employing catalytic transformations, and increasing the overall atom economy of the chemical synthesis through the minimization of protecting group usage.

In the experiments that are required for this final project, you will develop and optimize the “green” oxidation of various benzylic alcohols.

Oxidation Chemistry



The oxidation of alcohols to form aldehydes or ketones is a common transformation in organic chemistry and many reagents have been developed for this purpose. Pyridinium chlorochromate (PCC) was first described by Nobel laureate E. J. Corey and J. William Suggs of Harvard University in 1975 and was rapidly accepted due to the ease of preparation, stability, and general applicability of PCC to a variety of oxidations. The initial oxidation conditions developed by Corey have been modified since its conception with particular attention being focused on the development of workup procedures to separate the desired product from the promiscuous reduced chromium byproducts generated during the course of the oxidation reaction. One particularly effective method involves carrying out the oxidation in the presence of a fine solid support, such as silica gel.

Unfortunately, PCC has come under scrutiny because of the hazards associated with hexavalent chromium, a toxic, heavy metal. In living cells, hexavalent chromium is reduced to pentavalent chromium and finally to trivalent chromium. Trivalent chromium can bind to proteins and create haptans, which stimulate a deleterious immune response. Hexavalent chromium also poses an in halation hazard as it can increase the risk of lung cancer. As an aside, an award winning movie was made about the toxic effects this compound on the human body. Can you name this movie?

Your goal for this special project is to define a set of conditions that will allow you to oxidize a given alcohol to its corresponding aldehyde or ketone product and to develop optimized conditions using the following variables: time, temperature, solvent and concentration. You will gather and analyze this data in collaboration with your classmates with the overall goal of achieving the highest yield for the desired transformation while reducing the amount and toxicity of the waste and byproducts from the reaction. Be sure to discuss the modifications you'll be making with your GSI prior to starting the reactions with the green oxidant provided.

Your initial experiments will focus on a typical oxidation of a benzylic alcohol using the environmentally destructive oxidant, PCC. Make sure to follow the progress of the reaction using TLC.

Experimental Procedure:

Dissolve 0.25 g of benzyl alcohol ($C_6H_5CH_2OH$) in dichloromethane (2 mL). Mix 2 mol equivalents of PCC and the same weight of silica gel in a mortar and grind the resulting mixture with a pestle. Suspend the orange powder in 10 mL of dichloromethane at room temperature and add the alcohol solution in one portion with stirring on a magnetic stirplate. Continue stirring the mixture at room temperature and monitor the reaction by TLC. When all of the alcohol is consumed, filter the mixture through a pad of Celite in a Buchner funnel (suction filtration). Rinse the pad with a couple of mL of ether and evaporate all of the filtrate. Determine a yield from this reaction.

Future Experiments:

In the subsequent weeks, you will use this PCC oxidation as the benchmark for comparison to a more green oxidant given to you by your GSI. You will use the product from this reaction as a TLC standard, in addition to the determination of the response factor for quantitative gas chromatography.