

MODULE 2: STANDARD & “GREENER” APPROACHES to NYLON SYNTHESIS (Feb 14 – Mar 4)

For an interesting account on the historical development and significance of polymers, please read the accompanying section on “Exploding Billiard Balls and Other Polymers” from The Substance of Civilization: Materials and Human History from the Stone Age to the Age of Silicon, by Stephen L. Sass (Arcade, NY) 1998, p. 215-237.

Introduction

Polymers are ubiquitous. From the Greek meaning "many parts," polymers are high molecular weight molecules made up of repeating units of smaller molecules. Most polymers consist of long chains held together by hydrogen bonds, van der Waals forces and the tangling of the long chains. Most are amorphous, linear macromolecules that are thermoplastic and soften at high temperature. When heated, the covalent bonds of some thermoplastic polymers do not break, but the chains slide over one another to adopt new shapes. These shapes can be films, sheets, extrusions, or molded parts in a myriad of forms. Other polymers crosslink to form a three-dimensional network of a dark, insoluble, infusible substance, and are said to be thermosetting. Synthetic organic polymers, or plastics, are now among our most common structural materials. In the United States we make and use more synthetic polymers than we do steel, aluminum, and copper combined-at present 60 billion pounds worth \$25 billion.¹

Polymers can be classified in a few different ways. There are the two broad categories formed by the polymerization reaction itself - (a) addition polymers, in which a double bond of a monomer is transformed into a single bond between monomers (e.g. polystyrene), and (b) condensation polymers, in which a small molecule, such as water, alcohol or HCl, is split out as the polymerization reaction occurs. Nylon $[\text{CO}(\text{CH}_2)_4\text{CONH}(\text{CH}_2)_6\text{NH}]_n$, one of the most important condensation polymers, was developed by Wallace Carothers at DuPont. It was introduced commercially in 1938 as the first totally synthetic fiber.

The strength of commercial nylon is due to the fact that the polymer chains are stretched out straight (or close to straight) and lined up next to each other, all along the same axis. When they are aligned in parallel, intermolecular hydrogen bonds and other secondary interactions (e.g. van der Waals, dipole-dipole) between the individual chains work to hold the chains together very tightly (Figure 1). These non-covalent intermolecular interactions between macromolecules are so strong that it is energetically costly for individual chains to slide past one another. When nylon is arranged in fibers, it can be spun into threads and used as textiles. The clothes you're wearing are made out of polymeric fibers. So is carpet. So is rope. So is thread. Notice that when you pull on a nylon rope, it doesn't stretch very much.

Nylon is a polyamide that is formed on an industrial scale by the condensation of hexamethylene diamine and a dicarboxylic acid. Depending on the carbon chain length of the diacid, different types of nylon can be made. Nylon of different types can have distinctly different physical properties, which gives it a broad range of commercial application. For example, nylon 6.6 (made from adipic acid, a 6C chain) is used to make textiles, while nylon 6.10 (made from sebacic acid, a 10C chain), is used for bristles and high-impact sports equipment.

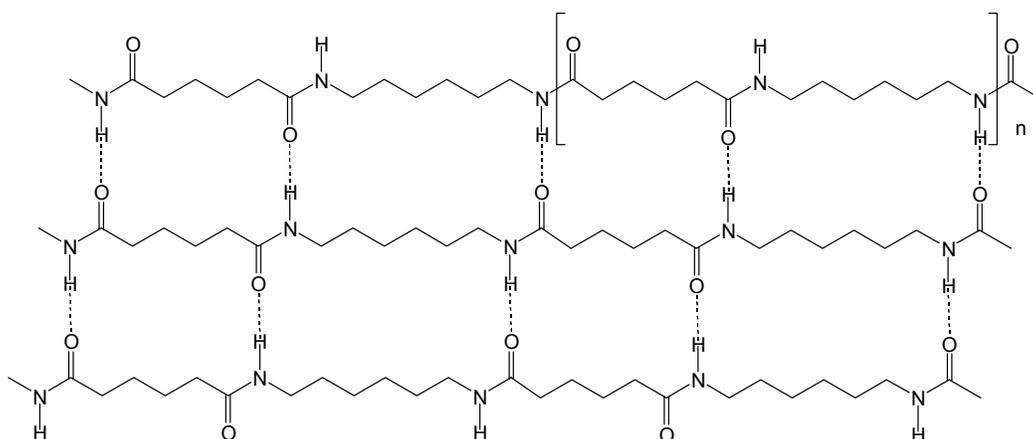


Figure 1. Intermolecular hydrogen bonding in nylon 6.6.

The traditional industrial synthesis of nylon 6.6 involves mixing adipic acid with hexamethylene diamine to form a salt that melts at 180°C (Figure 2). This is converted into the polyamide by heating to 280°C under pressure, which eliminates water. The adipic acid used in this polymerization is usually obtained by the oxidative cleavage of cyclohexene with nitric acid, a very strong oxidizing acid. There are a number of less than desirable features of this reaction protocol if one considers the magnitude of nylon production world-wide. Nitric acid reacts quite vigorously with a variety of organic compounds, a factor that presents some obvious chemical safety hazards. It also poses some environmental risks – it results in the emission of nitrous oxide (N₂O), a suspected greenhouse gas, and the industrial scale production of adipic acid is also believed to generate ~10% of all non-natural nitrogen oxide (“NO_x”) emissions. High pressures required for polymerization may also pose safety issues if reactors are not properly built and maintained.

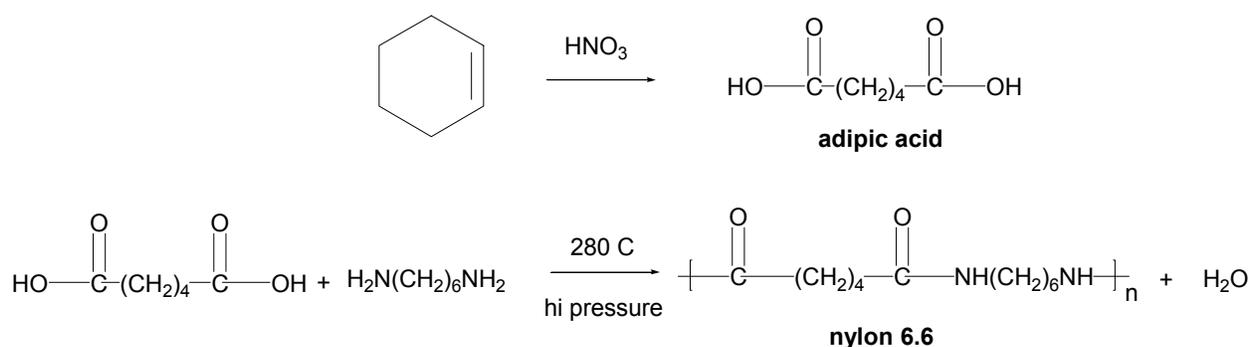


Figure 2. Industrial synthesis of adipic acid and nylon 6.6.

Over the next three weeks, you will synthesize adipic acid and nylon 6.6 via markedly different methods. First two weeks, you will explore two different adipic acid (a.k.a. 1,6-hexane dicarboxylic acid) syntheses starting with cyclohexene. The first reaction is a very common and

effective laboratory-scale procedure that appears in numerous organic chemistry lab textbooks. The second week's reaction conditions are a modification of a more environmentally friendly procedure first reported in the journal *Science* (K. Sato, M. Aoki, R. Noyori, 281, 1646-1647, 1998), a copy of which appears in the back of the handout. Ryoji Noyori, the author of this paper, is the recipient of the 2001 Nobel Prize in Chemistry (shared with K. B. Sharpless and W.S. Knowles) for the development of chiral hydrogenation and oxidation reactions. In the last week, you will pool these adipic acid samples together, convert it to the diacyl chloride, and make nylon 6.6. via room temperature interfacial polymerization.

Part A: Permanganate Oxidation of Cyclohexene to Adipic Acid²

The first laboratory-scale adipic acid synthesis will be accomplished by oxidative cleavage of cyclohexene by potassium permanganate. In general, there are a wide variety of agents capable of oxidizing alkenes. Under mild conditions (e.g. cold, dilute solutions of permanganate), cis-1,2-diols can be formed. Stronger oxidation conditions, such as hot concentrated permanganate, ozone or dichromate, can result in oxidative cleavage where the carbon-carbon double bond is broken. In these cases, if the alkene is not tetrasubstituted, the intermediate aldehyde will be immediately oxidized further to the corresponding carboxylic acid. In this experiment, cyclohexene will be treated with basic potassium permanganate, and adipic acid will be formed via ring opening (Figure 3). The produce will be precipitated with hydrochloric acid. Manganese dioxide (MnO_2) will be removed by means of a filter acid (Celite), and decolorizing carbon may be used to remove any colored impurities before the final acidification step. This is a very common and effective laboratory-scale procedure that appears in numerous organic chemistry lab textbooks. This synthesis is more environmentally friendly than the industrial nitric acid route, though it still involves a potent oxidizer and generates significant quantities of MnO_2 waste.

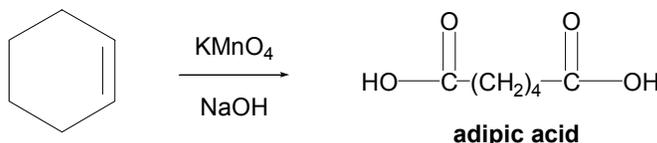


Figure 3. Synthesis of adipic acid by permanganate oxidation of cyclohexene.

Procedure

1. To a solution of 15g of potassium permanganate in 125 mL of water in a 250-mL conical flask, add 5.2mL of cyclohexene followed by 1 mL of 3M sodium hydroxide. The contents of the flask have to be swirled continuously to allow proper mixing.
2. Allow the temperature to rise to no higher than 45°C. (Use an ice bath.) When the temperature no longer rises above 45°C outside of the ice bath, allow the solution to stand for about 5 minutes at room temperature, then heat the mixture to boiling on the hot plate for about 10 minutes.
4. Test for the presence of unreacted permanganate by placing a drop of the reaction mixture on a piece of filter paper. Any unreacted permanganate will appear as a

- purple ring around the spot of brown MnO_2 . If permanganate remains, add small portions of a saturated aqueous sodium thiosulfate to the mixture until the spot test is negative.
- Mix 2.0 g of a filter aid (Celite) and 8-10 mL of water in a small beaker. Swirl the beaker and pour the suspension into a Büchner funnel fitted with a piece of filter paper and then turn the vacuum on *slowly* (otherwise the filter cake may crack).
 - When the entire solution has been filtered, the filtrate can be discarded in the sink. The quarter-inch filter cake layer on the top of the filter paper will trap fine particles of MnO_2 .
 - Vacuum filter the product suspension through the Celite pad and wash thoroughly with about 40mL of water.
 - Concentrate the solution to a volume of about 35mL by heating it on a hot plate. If the concentrate is colored, add a pinch of decolorizing carbon, reheat, and gravity filter while it is still hot.
 - In the hood, carefully add concentrated HCl to the filtrate until the solution tests acidic to litmus paper (pH = 4) and then add an additional 5 mL of the acid.
 - Allow the solution to cool, and isolate the precipitated adipic acid by vacuum filtration.
 - The product can be recrystallized from ~15-20 mL hot water. Determine percent yield, mp, and the IR.* You should save all of the adipic acid synthesized for future weeks. This can be stored in your drawer in a vial or a test tube covered with parafilm. Next week the TA will demonstrate how to prepare an NMR sample and how to take spectra of your sample. (*Depending on time available, the IR and/or mp may alternatively be taken the following week.)

SAFETY INFO:

Work with all chemicals in the hood. Concentrated HCl is extremely corrosive. KMnO_4 is a strong oxidant.

CLEANUP:

Celite pads go in the solid heavy metal waste. Any acidic or basic aqueous solutions should be neutralized before putting them down the drain.

PRE-LAB QUESTIONS:

- Why it is important to initially do this reaction in an ice bath?
- Why should one try to avoid cracks in the Celite?
- Why is the gravity filtering in step 8 done while the liquid is still hot?

Part B: "Green" Catalytic Peroxide Oxidation of Cyclohexene to Adipic Acid^{3,4}

This week, we will explore the use of an alternative oxidation procedure from the chemical literature,⁵ which uses sodium tungstate (Na_2WO_4) as a catalyst for the hydrogen peroxide oxidation of cyclohexene to adipic acid. This catalytic hydrogen peroxide procedure is "greener" than either the nitric acid or permanganate reactions. It avoids the need for a strongly basic reaction medium, and generates only water as a byproduct. Although the mechanism of this reaction has not been established, it is presumed that given its structural similarity to permanganate, tungstate acts directly as the active oxidizing agent. One of the nice features of this reaction is that the reduced tungsten intermediates are apparently also oxidized back to the original oxidation state by hydrogen peroxide. This enables the tungstate to function as a catalyst rather than as a stoichiometric reagent.

One of the challenges of this water-based catalytic oxidation reaction, is the fact that while sodium tungstate is appreciably soluble in water, cyclohexene is virtually insoluble in aqueous solution. In order to avoid the problem of immiscible solvents, we need to either increase the solubility of tungstate in cyclohexene or increase the solubility of cyclohexene in water. By adding a phase transfer agent (often an ammonium salt bearing hydrophobic groups), the miscibility of the two phases can be increased. Although ammonium salts are ionic and readily soluble in highly polar solvents such as water, they are frequently also at least modestly soluble in less polar solvents due to the greasy tail group. These salts can ion-pair with negatively charged molecules, and drag the paired species into the less-polar media, thereby making them available for reaction. Hence, since one reactant is transferred from one phase to another, it is referred to as phase-transfer agent. This experiment uses Aliquat 336, a commercial phase transfer catalyst with the chemical structure $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{NCH}_3^+\text{Cl}^-$. The aqueous layer containing the tungstate catalyst and phase transfer catalyst can in principle be recycled, though we will not attempt this in class.

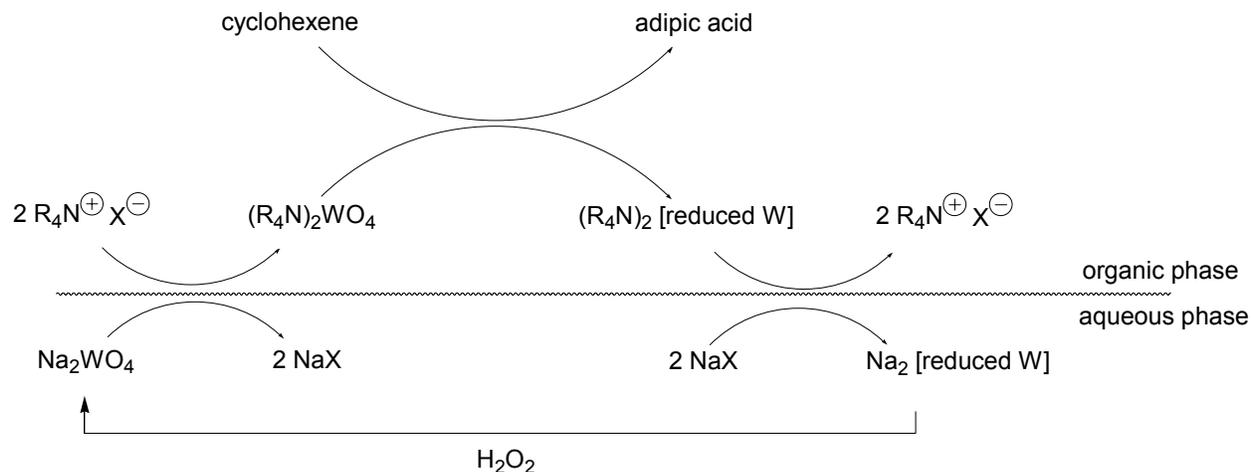


Figure 4. Synthesis of adipic acid using a sodium tungstate catalyst.

Procedure

1. (*note: the order in which reagents are added is important*) In a 50 mL round bottom flask containing a stir bar and fitted with a water-cooled condenser, place 0.50g of sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$).
2. Your TA will dispense 0.5g (or as close as possible – it does not have to be exact) of Aliquat 336 to your RBF. (It is a very viscous liquid that can be hard to transfer).
3. Next, add 12 g (density = 1 g/mL) of 30% hydrogen peroxide and 0.37g of KHSO_4 . Stir, then add 2.00g of cyclohexene.
4. Heat the mixture to reflux, and continue heating under reflux for 1.5 hours while *stirring vigorously to ensure efficient mixing*. Cover the top of the condenser with Parafilm. The reaction will not proceed if it is done below reflux. If you see liquid condensing near the top of the condenser, you need to reduce the heat as heating too strongly may result in some cyclohexene being lost through the top of the condenser. About halfway through the reflux period, rinse down any cyclohexene trapped in the condenser with a few mL of water, added via pipette. The reaction is complete when it no longer separates into two layers.

[this is a good time to do last week's NMR or IR. You and your partner should keep an eye on one another's reaction so that the spectra can be taken one at a time]

5. Transfer the hot reaction mixture to a small beaker via pipette, leaving behind any of the phase transfer catalyst that may have separated. (If the catalyst separates – and it does not always do so – it will stick to the walls of the flask or form a separate oily layer at the bottom of the flask. It is better to leave a little of the aqueous solution behind than to risk contamination of your solution with the phase transfer catalyst, otherwise the purification step becomes much more difficult.)
6. Rapidly cool the beaker containing the reaction mixture in an ice bath. A precipitate should form within 20 minutes. (If it does not readily precipitate, you may want to either introduce a seed crystal or lower the pH by adding a small amount of acid.)
7. Collect the crude product by vacuum filtration using a Büchner funnel. After the crude material has air-dried, calculate the percent yield.
8. The crude product should be recrystallized from a minimum amount of hot water, and its yield recalculated and melting point taken.

CLEANUP:

The waste containing the catalyst and phase transfer agent should go into the waste labeled “heavy metal waste.”

PRE-LAB QUESTIONS:

1. What effect (if any) does rinsing the condenser with water have on the solution composition?
2. How does introducing a seed crystal help in the crystallization of your product?

Part C: Synthesis of Adipoyl Chloride and Nylon 6.6

To avoid the high pressures required for the polymerization to occur, the adipic acid can be converted into the more reactive diacyl chloride. Nylon 6.6 can then be synthesized under normal atmospheric pressures by interfacial polymerization. An aqueous solution of hexane-1,6-diamine is carefully floated on top of a solution of the diacyl chloride dissolved in an organic solvent. At the interface where the two solutions come in contact, an S_N2 reaction occurs to form a film of polyamide. When the interface becomes blocked with polyamide, the reaction stops. However, in the case of nylon 6.6, the film is so strong that when it is picked up with a wire hook and continuously removed in the form of a rope, the polymerization will continue as the interface is replenished with new reagent monomers. This reaction works because the diamine is soluble in both water and dichloromethane, the organic solvent used. As the diamine diffuses into the organic layer, reaction occurs immediately to give the insoluble polymer. The HCl produced reacts with the sodium hydroxide in the aqueous layer. The acid chloride does not hydrolyze before reacting with the amine because it is not very soluble in water.

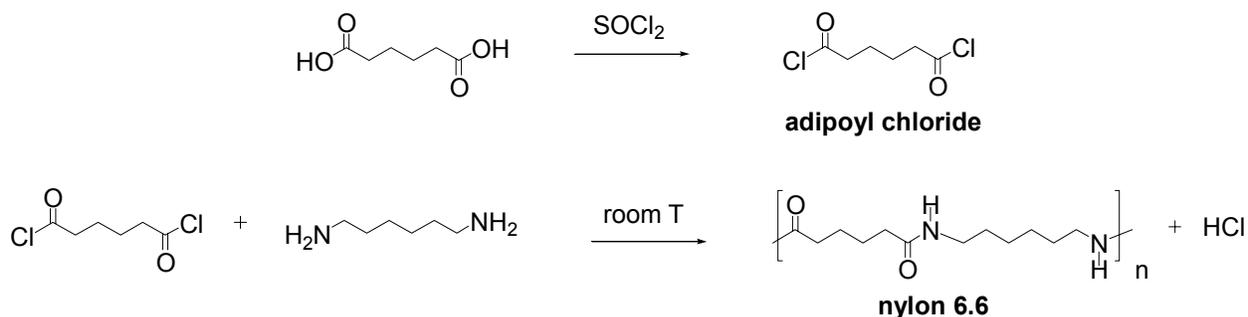


Figure 5. Synthesis of adipoyl chloride and nylon 6.6.

Procedure

Making Adipoyl Chloride

1. Assemble the glassware apparatus first (round bottom flask, condenser, vacuum adaptor with large end sealed, rubber tubing from vacuum adaptor to glass funnel in a beaker of water).
2. Place 2g of adipic acid (from the previous weeks experiments), 2mL of thionyl chloride, and 0.1mL of *N,N*-dimethylformamide in the round bottom flask. *If you have less than 2g of adipic acid, then scale all reagents accordingly and make as much nylon as you can.* {note: When transporting thionyl chloride between the dispensing hood and your hood, be sure the container is capped.} Once the *N,N*-dimethylformamide is added, the reaction begins immediately.
3. Heat to 60 - 70°C in a water bath in the hood. As the reaction proceeds, the product forms a liquid layer on the bottom. Use this liquid to wash down unreacted acid as the reaction proceeds. When the acid has all reacted and gas evolution has ceased

(about 15-20 min, but can run much longer), transfer the product, which should be a clear liquid at this point, to a 250-mL beaker using 50mL of dichloromethane.

Nylon 6.6 by Interfacial Polymerization

1. Prepare a diamine solution containing 2 g hexane-1,6-diamine, 50 mL of water and 1g of sodium hydroxide.
2. *Carefully* pour the aqueous diamine solution onto the top of the dichloromethane diacylchloride solution.
3. Pick up the polymer film at the center with a small spatula and slowly lead it over the outer surface of a bottle, beaker, or graduated cylinder as it is removed. Remove as much of the polymer as possible, wash it thoroughly in water, and press it as dry as possible. After the polymer has dried, determine its weight and calculate the yield. (Theoretical yield can be calculated in grams. To do this, you do not need to know the molecular mass of the polymer – just calculate the molecular mass of the repetitive unit and multiply this by the number of moles of limiting reagent.)
4. Try dissolving the polymer in two or three solvents (toluene, ethyl acetate, formic acid) and record any observations.

SAFETY INFO:

Thionyl chloride (and the gas evolved from its reaction with dicarboxylic acid) has a caustic smell.

CLEANUP:

Decant the water and dichloromethane. The dichloromethane should be placed in the halogenated organic solvents container. The acidic aqueous layer should be neutralized to pH ~7, diluted with water and flushed down the drain. The polymer should be *thoroughly* rinsed and squeezed as dry as possible - if you are not planning to keep it, it should be placed in the nonhazardous solid waste container.

PRE-LAB QUESTIONS:

1. Why is the end of the vacuum adaptor sealed?
2. Provide two reasons why the glass funnel is positioned in a beaker of water (step 1)?

Lab Report

Short writing assignments (typed)

1. Though the syntheses you performed these past three weeks have already been reported in the chemical literature previously, let's pretend they haven't. Write up succinct experimental procedures for the syntheses you performed, as though it were an experimental section of a journal article you plan to submit for publication. (400 words max)

2. Write a summary of the lab work you performed over the past three weeks as though it were an abstract of a journal article you plan to submit for publication. It should be succinct (250 words max), but should address all of the most important concepts and results behind the three weeks of experiments. Note: In writing this part, it may help to organize your thoughts by first making a list of what the most important findings are.
3. If there were an extra week devoted to a polymer module, what experimental question would you be most interested in asking? Briefly describe an experiment(s) that could be performed to address the question you asked. (250 words max)

Questions (handwritten or typed)

1. A new adipic acid plant is to be constructed in your hometown, and you are the CEO of the new unit. The new plant has brought many good paying jobs to the community. The plant is expected to generate a thousand tons of raw adipic acid per week. What other important factors would you want to include in your economic analysis in addition to the initial reagent costs? These can be summarized in a “top-ten” list.
2. The lab procedure for the adipic acid synthesis you performed in week 2 was modified from the one described in the original *Science* paper. List three specific differences between the two procedures and suggest how the new reaction conditions help to shorten the reaction time.
3. Do you think that polymers have a well-defined molecular weight? What strategies might you employ to attempt to control the average molecular weight of nylon 6.6?
4. What is the CAS registry number for adipic acid? What is the original literature reference for the synthesis of adipoyl chloride from adipic acid?

¹ K.L. Williamson, Macroscale and Microscale Organic Experiments 3rd Ed. (Houghton Mifflin, NY) 1999.

² P. Svoronos, E. Sarlo, R. J. Kulawiec, Organic Chemistry Laboratory Manual, 2nd Ed. (McGraw-Hill, Boston) 1997, p. 133-135.

³ K. M. Doxsee and J. E. Hutchinson, Greener Organic Chemistry: Strategies, Tools, and Laboratory Experiments, (Brooks/Cole, United States), 2004.

⁴ S. M. Reed, J. E. Hutchinson, “Green Chemistry in the Organic Teaching Laboratory: An Environmentally Benign Synthesis of Adipic Acid,” *J. Chem. Ed.*, 77, 12, 1627-1629, 2000.

⁵ K. Sato, M. Aoki, R. Nyori, “A ‘Green’ Route to Adipic Acid: Direct Oxidation of Cyclohexenes with 30 Percent Hydrogen Peroxide,” *Science*, 281, 1646-1647, 1998.