A Greener Alcohol Dehydration

A case study prepared by Beyond Benign as part of the Green Chemistry in Higher Education program: A workshop for EPA Region 2 Colleges and Universities

A Greener Alcohol Dehydration

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Summary:
The dehydration reaction of alcohols to generate alkenes are commonly performed reactions in the Organic Chemistry laboratory. The reaction generally proceeds by heating the alcohols in the presence of a strong acid, such as sulfuric or phosphoric acid, at high temperatures. Both acids can cause serious burns to the skin and eyes. A greener alcohol dehydration reaction is outlined in this case study, which uses a reusable catalyst.

Reduction in waste and purchasing costs:

For every semester this reaction is implemented with 100 students, there is an estimated ***cost savings of $116.00*** in purchasing and waste disposal costs and a ***elimination in the use of 527 mL cyclohexanol, 100 mL concentrated phosphoric acid, and 1.25L toluene***. The greener version of the Alcohol Dehydration also ***results in a reduction of waste by 0.56 gallons***, all of which have human health and aquatic hazards.

Background:
This case study is a result of an EPA Region 2 Source Reduction grant[1] titled *Green Chemistry in Higher Education: A Workshop for Region 2 Colleges and Universities*. The Green Chemistry in Higher Education workshop was carried out at Siena College on July 18-21, 2013. 29 faculty members participated from 20 different institutions in New York and New Jersey. The workshop consisted of three main focus areas: green chemistry case studies for lecture and course work, green chemistry laboratory exercises, and toxicology and environmental impact.

During the workshop participants were able to test a variety of greener laboratory exercises for introductory and organic chemistry courses. One of the labs was a greener method for preparing alcohols from alkenes for the organic chemistry laboratory course. The lab was developed by Professor Irv Levy from Gordon College, an instructor at the Siena College Green Chemistry in Higher Education workshop. Two faculty members reported including this experiment in their organic course: Darren Smith, Rochester Institute for Technology and Andrea Stadler, St. Joseph's College.

[1] **Disclaimer: Although the information in this document has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement X9-96296312 to Beyond Benign, it has not gone through the Agency's publications review process and, therefore, may not necessarily reflect the views of the Agency and no official endorsement should be inferred.**

Additional Resources for Green Chemistry in General Chemistry and Beyond:

Greener Educational Materials (GEMs) Database (University of Oregon)

- Website: http://greenchem.uoregon.edu/gems.html
- Description: Searchable database with Green Chemistry educational materials uploaded by faculty members and educators world-wide
- Most curriculum is available for download (free-of-charge) or with primary literature information
- Google map of Green Chemistry educators

American Chemical Society's Green Chemistry Institute

- Website: www.acs.org/greenchemistry
- Description: Green Chemistry Resources for educators and students
- Experiments and Curriculum available for download
- List of ACS books on Green Chemistry

Green Chemistry Commitment

- Website: www.greenchemistrycommitment.org
- Description: A program of Beyond Benign to adopt Green Chemistry Learning Objectives in higher education.
- Case studies are available, university highlights, and curriculum resources

Beyond Benign

- Website: www.beyondbenign.org
- Description: Green Chemistry Curriculum available on-line (free-of-charge)
- Regional Outreach and Community Educational Events

GCEdNet - Green Chemistry Education Network

- Website: http://cmetim.ning.com/
- Description: A place where Green Chemistry educators share resources
- Blogs, discussions and chat rooms

University of Scranton Greening Across The Chemistry Curriculum

- Website: http://www.scranton.edu/faculty/cannm/green-chemistry/english/drefusmodules.shtml
- Description: Green Chemistry modules available for download
- Power point presentations, hand-outs available

Carnegie Mellon University Institute for Green Science

- Website: http://igs.chem.cmu.edu/
- Description: Green Chemistry modules available for download
- Power point presentations, hand-outs available

Traditional Experiment:

Most undergraduate organic chemistry labs study the preparation of alkenes via the dehydration reaction of alcohols. Traditionally, concentrated sulfuric or phosphoric acid is used as a catalyst for this reaction.[2] These concentrated acids are corrosive and cause unnecessary waste that can be harmful to human health and the environment.

Alcohol Dehydration

Traditional Experiment

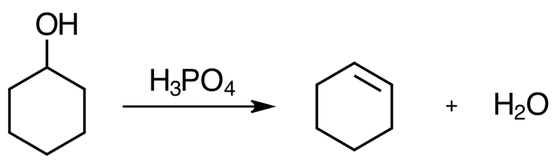
Chemicals avoided per class of 100 students:

527.4 mL cyclohexanol

100 mL conc. phosphoric acid

1.25 L toluene

Traditional dehydration of cyclohexanol to cyclohexene:



The chemicals that are typically used in this experiment are listed below, along with a list of the hazards. The amounts are estimated based on common procedures.[2,3]

Table 1. Chemicals used and health and safety information for traditional experiment:

Chemical:	**Amount per group of 2 students:**	**Flammability:**[4]	**Human health toxicity:**[5]	**Aquatic toxicity:**[5]
Cyclohexanol (0.948 g/mL)	10 g	Combustible Liquid NFPA Code: 2 Flash Point: 67°C	Moderate Toxicity LD50 (oral, rat) 1,400 mg/kg; LD50 (rabbit, dermal) 1,000 mg/kg	Moderate Toxicity LC50 (fish, 96 hr) 705 mg/l; EC50 (daphnia, 48 hr) 500 mg/l; EC50 (algae, 72 hr) 29.2 mg/l
Phosphoric acid, 85% (1.685 g/mL)	2 mL	n/a	Causes severe skin burns and eye damage.	
Toluene	25 mL	Flammable NFPA Code: 3, Flash Point: 6 C	*Suspected reproductive and developmental hazard*	High Toxicity, LC50 (fish, 96 hr) 7.63 mg/l; EC50 (daphnia, 24 hr) 8.00 mg/l; EC50 (algae, 24 hr) 10 mg/l
Sodium chloride, saturated solution (solubility: 359 g/L)	10 mL (3.59 g/10 mL)	n/a	*Low Toxicity*	*Low Toxicity*
Calcium chloride	5 g	n/a	*Low Toxicity*	*Low Toxicity*

[2] Dehydration of 2-methylcyclohexanol. *J. Chem. Educ*. **1967** *44* (10), 620.
[3] Williamson, K. L., Maters, K. M., Macroscale and Microscale Organic Experiments, Sixth Edition, 2011, Cengage Learning, Inc.
[4] NFPA codes can be found here: http://en.wikipedia.org/wiki/NFPA_704#Red
[5] Human health and aquatic toxicity data was gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

Traditional Experiment, Continued:

The purchasing and waste disposal costs associated with this procedure are estimated in the following table. Purchasing costs were estimated based on prices available from Sigma-Aldrich:[5]

Total amounts of chemicals used and disposed of per class of 100 students:

- ***527.4 mL cyclohexanol (0.14 gal)***
- ***100 mL conc. Phosphoric acid (0.03 gal)***
- ***1.25 L (0.33 gal) toluene***
- ***0.63 gallons of liquid and 0.55 lbs solid waste***

Alcohol Dehydration
Traditional Experiment

Volume of waste and purchasing and waste disposal costs per class of 100 students:
0.63 gallons of liquid and 0.55 lbs solid waste
$195.32 in purchasing and disposal costs

Table 2. Purchasing and waste disposal costs:

Chemical:	Amount per 100 students:	Waste disposal cost[6]	Purchasing cost:[6]	Purchasing cost per 100 students:	Waste disposal cost per 100 students:	Total cost (per 100 students)
Cyclohexanol (0.948 g/mL)	500 g (527.4 mL, 0.14 gal)	$11.27/gal	$43.10, 1 L	$22.73	$1.58	$24.31
Phosphoric acid, 85% (1.685 g/mL)	100 mL (0.17 kg) (0.026 gal)	$11.27/gal	$61.00, 1 kg	$10.37	$0.29	$10.66
Toluene	1,250 mL (0.33 gal)	$11.27/gal	$85.20, 2.5 L	$42.60	$3.72	$46.32
Sodium chloride, saturated solution (solubility: 359 g/L)	500 mL (179.5 g/500 mL) (0.13 gal)	$11.27/gal	$39.90, 500 g	$14.32	$1.47	$15.79
Calcium chloride	250 g (0.55 lb)	$1.35/lb	$195.00, 500 g	$97.50	$0.74	$98.24
TOTAL	**0.63 gal and 0.55 lb**			**$187.52**	**$7.80**	**$195.32**

Total purchasing and waste disposal costs per class of 100 students:

- ***$187.52 in purchasing costs***
- ***$7.80 in waste disposal costs***
- ***$195.32 total cost***

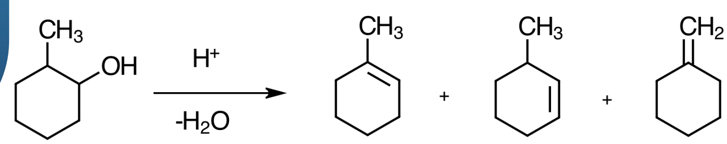
[6] Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html, Accessed July 18, 2014].
[7] Waste disposal costs are based on the EPA Cost Calculator Tool [http://www.epa.gov/p2/pubs/resources/measurement.html#calc, accessed December 2014].

Greener Alcohol Dehydration
A Greener Approach

Volume of waste and purchasing and waste disposal costs per class of 100 students:
0.07 gallons of liquid waste
$79.32 in purchasing and disposal costs

A Greener Approach:

Professor Irv Levy at Gordon College developed a greener approach to the traditional alcohol dehydration reaction that eliminates the use of strong acids. The new approach uses a Montmorillonite KSF clay catalyst that can be reused. We present a summary of this new approach, along with a comparison of the hazards and costs associated with the greener approach versus the traditional approach. The procedure can be found in Appendix A of this case study.



Overview of the greener reaction:
An alternative greener method is proposed, using Montmorillonite KSF clay, a non-toxic and reusable catalyst.[2] The clay catalyzes the dehydration reaction of 2-methylcyclohexanol to give an isomeric mixture of alkenes. The major product of this reaction is 1-methylcyclohexene, which comprises approximately 67% of the product when formed via the traditional acid-catalyzed method. The minor products of this reaction are 3-methylcyclohexene and a small amount of methylenecyclohexane, as shown above.

Chemicals used and hazards:
The chemicals that are used in the greener experiment are listed in Table 3, along with a list of the hazards. The amounts are estimated based on Professor Levy's procedure in Appendix A.

Table 3. Chemicals used and health and safety information for greener approach:

Chemical:	**Amount per group of 2 students:**	**Flammability:**[4]	**Human health toxicity:**[5]	**Aquatic toxicity:**[5]
2-methylcyclo-hexanol	5 mL	Combustible Liquid, NFPA Code: 2, Flash Point: 62°C	*Moderate Toxicity:* LD50 (oral, rat) 1,125 mg/kg), causes serious eye irritation	*Low Aquatic Toxicity*
Montmorillo-nite KSF clay	0.25 g	n/a	*Inhalation hazard:* Silicon dioxide can cause cancer at certain particle sizes	*Low Aquatic Toxicity*
Poly(ethylene glycol) (PEG - 400)	3 mL	n/a	*Low Toxicity:* LD50 (oral, rat) 5,000 mg/kg, LD50 (dermal, rabbit) 5,000 mg/kg	*Low Aquatic Toxicity*
Sodium sulfate	2 g	n/a	*Low toxicity* LD50 (oral, mouse) – 5,989 mg/kg	*Moderate aquatic toxicity* LC50 (fish, 96 hr) - 120 mg/l; LC50 (fish, 96 hr) – 4,380 mg/l

[4] NFPA codes can be found here: http://en.wikipedia.org/wiki/NFPA_704#Red
[5] Human health and aquatic toxicity data was gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

Greener Alcohol Dehydration

A Greener Approach

Volume of waste and purchasing and waste disposal costs per class of 100 students:

0.07 gallons of liquid waste

$79.32 in purchasing and disposal costs

A Greener Approach, Continued:

The purchasing and waste disposal costs associated with this procedure are estimated in the following table. Purchasing costs were estimated based on prices available from Sigma-Aldrich:[6]

Total amounts of chemicals used and disposed of per class of 100 students:

- ***250 mL 2-methylcyclohexanol***
- ***12.5 grams Montmorillonite KSF clay (can be reused)***
- ***150 mL Poly(ethylene glycol) solvent***
- ***0.07 gallons liquid waste***

Table 4. Purchasing and waste disposal costs:

Chemical:	**Amount per 100 students:**	**Waste disposal cost**[7]	**Purchasing cost:**[6]	**Purchasing cost per 100 students:**	**Waste disposal cost per 100 students:**	**Total cost (per 100 students)**
2-methylcyclohexanol	250 mL (0.066 gal)	$11.27/gal	$37.50, 250 mL	$37.50	$0.74	$38.24
Montmorillonite KSF clay	12.5 g	$1.35/lb	$27.10, 100g	$3.39	$0.00	$3.39
Poly(ethylene glycol) (PEG - 400)	150 mL (169.2 g) (0.04 gal)	$11.27/gal	$40.50, 250 g	$27.41	$0.45	$27.86
Sodium sulfate	100 g (0.0022 lb)	$1.35/lb	500 g - $49.10	$9.82	$0.00	$9.82
TOTAL	**0.07 gal**			**$78.12**	**$1.19**	**$79.32**

Total purchasing and waste disposal costs per class of 100 students:

- ***$78.12 in purchasing costs***
- ***$1.19 in waste disposal costs***
- ***$79.32 total cost***

[6] Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html, Accessed July 18, 2014].

[7] Waste disposal costs are based on the EPA Cost Calculator Tool

Greener Alcohol Dehydration
Summary

Waste avoided:
Reduction in 0.56 gallons liquid waste
Avoids use of concentrated phosphoric acid
Cost comparison:
Reduction in purchasing and disposal costs of $116.00

Traditional Experiment Summary:

Total amounts of chemicals used and disposed of per class of 100 students:

- ***527.4 mL cyclohexanol (0.14 gal)***
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- ***1.25 L (0.33 gal) toluene***
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Total purchasing and waste disposal costs per class of 100 students:

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A Greener Approach Summary:

Total amounts of chemicals used and disposed of per class of 100 students:

- ***250 mL 2-methylcyclohexanol***
- ***12.5 grams Montmorillonite KSF clay (can be reused)***
- ***150 mL Poly(ethylene glycol) solvent***
- ***0.07 gallons liquid waste***

Total purchasing and waste disposal costs per class of 100 students:

- ***$78.12 in purchasing costs***
- ***$1.19 in waste disposal costs***
- ***$79.32 total cost***

Conclusions:

The greener procedure uses some chemicals that pose some hazards, such as 2-methylcyclohexanol, which is flammable and has moderate human toxicity. However, the greener version avoids the use of strong acids. It also should be noted that the Montmorillonite KSF clay catalyst can also pose some human health hazards due to the particle size of the silicon dioxide particles. Larger particle sizes for the catalyst should be used to avoid the inhalation hazards associated with these particles.

Another benefit to the solid catalyst is that is can be reused and therefore reduce waste and purchasing costs. It should also be noted that this procedure can be performed as a microwave experiment, allowing for the introduction of alternative energy methodologies.

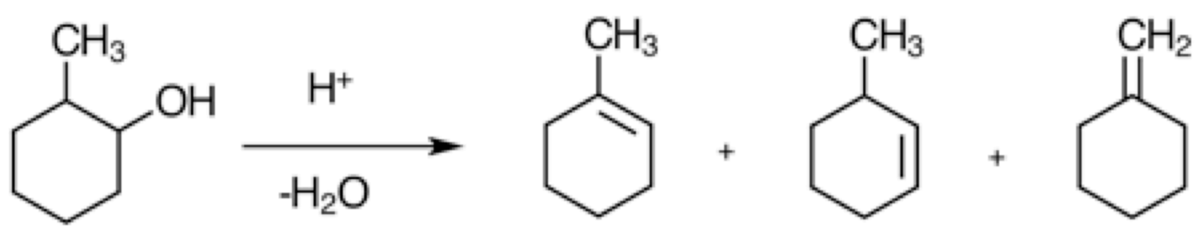
APPENDIX A: Alternative Greener Method for Preparation of Alkenes from Alcohol

Rachael Albury[*], Justin Andrews[*], Emmanuel Asonganyie[‡], Shirley Coll[‡], Maureen Githui[‡], Irvin Levy[*‡] & Lindsey Warnock[‡]; Gordon College[*] and Salem State University[‡]

Background:

Most undergraduate organic chemistry labs study the preparation of alkenes via the dehydration reaction of alcohols. Traditionally, concentrated sulfuric or phosphoric acid is used as a catalyst for this reaction.[1] These concentrated acids are corrosive and cause unnecessary waste that can be harmful to human health and the environment. An alternative greener method is proposed, using Montmorillonite KSF clay, a non-toxic and reusable catalyst.[2]

The clay catalyzes the dehydration reaction of 2-methylcyclohexanol to give an isomeric mixture of alkenes. The major product of this reaction is 1-methylcyclohexene, which comprises approximately 67% of the product when formed via the traditional acid-catalyzed method. The minor products of this reaction are 3-methylcyclohexene and a small amount of methylenecyclohexane, as shown below:



Experimental Procedure:

Into a 25 mL round bottom flask, add 5 mL of 2-methylcyclohexanol and 0.25 g of Montmorillonite KSF clay, along with a magnetic stirring bar. Attach a condenser and reflux the solution with stirring for 90 min. After this time, allow the flask to cool briefly, add about 3 mL of PEG-400 (or another suitable high boiling solvent) and reassemble the apparatus for a simple distillation to allow isolation of the product from the unreacted alcohol and the catalyst. Collect about 2 mL of product, dry over sodium sulfate, and analyze via gas chromatography to determine the percentages of different isomers in the product mixture.

Microwave method. This procedure also works very well in a laboratory microwave reactor. Typical method: 2 mL alcohol, 100 mg catalyst, stir bar, in 10 mL capped reaction tube. 165 °C, 10 mins. Cool, dry over sodium sulfate, filter through cotton plug in glass pipet. GC analysis shows percentages of products and percentage yield of product (wait for alcohol peak to emerge from GC). Warning! Because of the volatile flammable products formed, this method is not suitable for use in a domestic microwave oven.

References:

1. Dehydration of 2-methylcyclohexanol. *J. Chem. Educ.* **1967** *44* (10), 620.
2. Alkene preparation via the principles of green chemistry. *Educación Química* **2010**, *21*(2), 183-189.

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