The Green Chemistry Commitment's

*Green Chemistry Education Webinar Series*

# A Guide to Green Chemistry Experiments for Undergraduate Organic Chemistry Labs

Erika Daley
My Green Lab
Program Manager

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Program Manager

The Green Chemistry Commitment's

*Green Chemistry Education Webinar Series*

# Welcome to the Green Chemistry Commitment Green Chemistry Education Webinar Series

- Submit questions at any time during the webinar!
- Recording and supporting documents will be available: http://www.beyondbenign.org/he-webinars/

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*Green Chemistry Education Webinar Series*

## Join the conversation!

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#greenchemistry

https://www.facebook.com/beyond.benign.green.chemistry.education/

**Thanks for joining!**

The Green Chemistry Commitment's

*Green Chemistry Education Webinar Series*

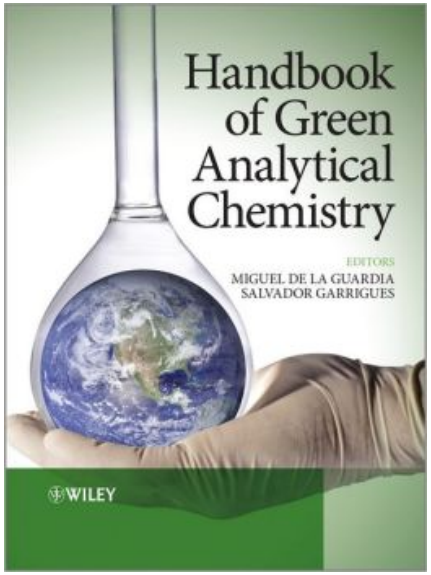
# What is the Green Chemistry Commitment?

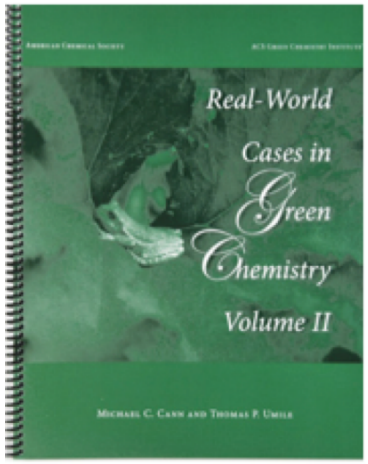
- A consortium program aimed at uniting the green chemistry community to:
  - expand the community of green chemists
  - grow departmental resources
  - improve connections to industry and job opportunities in green chemistry
  - affect systemic and lasting change in chemistry education
- Voluntary, *flexible* program for adopting green chemistry student learning objectives
- A program for recognizing the work that your institution is currently doing in green chemistry

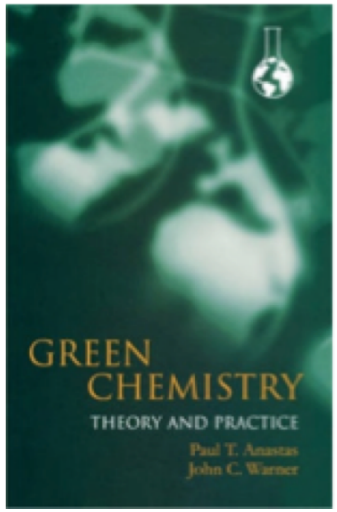
**http://www.beyondbenign.org/he-green-chemistry-commitment/**

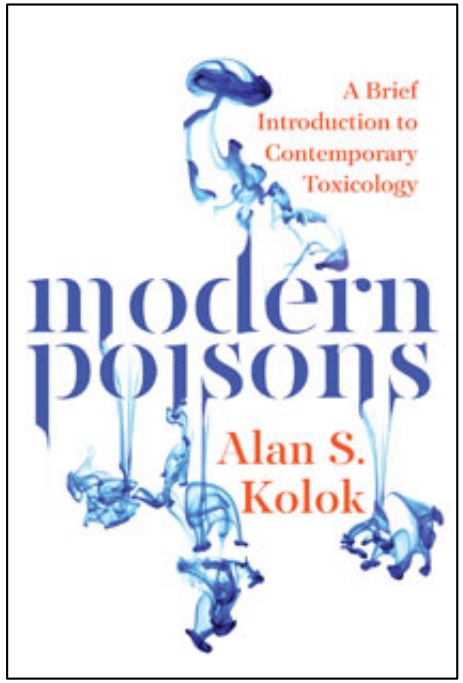
**Derrick_Ward@beyondbenign.org**

# Green Chemistry Textbooks



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# A Guide to Green Chemistry Experiments for Undergraduate Organic Chemistry Labs

Derrick Ward & Erika Daley

March 6th, 2018

# About Us

beyondbenign
green chemistry education

- Massachusetts-based 501-c3 non-profit
- Dedicated to green chemistry education
  - K-12 & Higher Ed.
- Develop curriculum resources centered around the principles and practices of green chemistry
- Green Chemistry Commitment

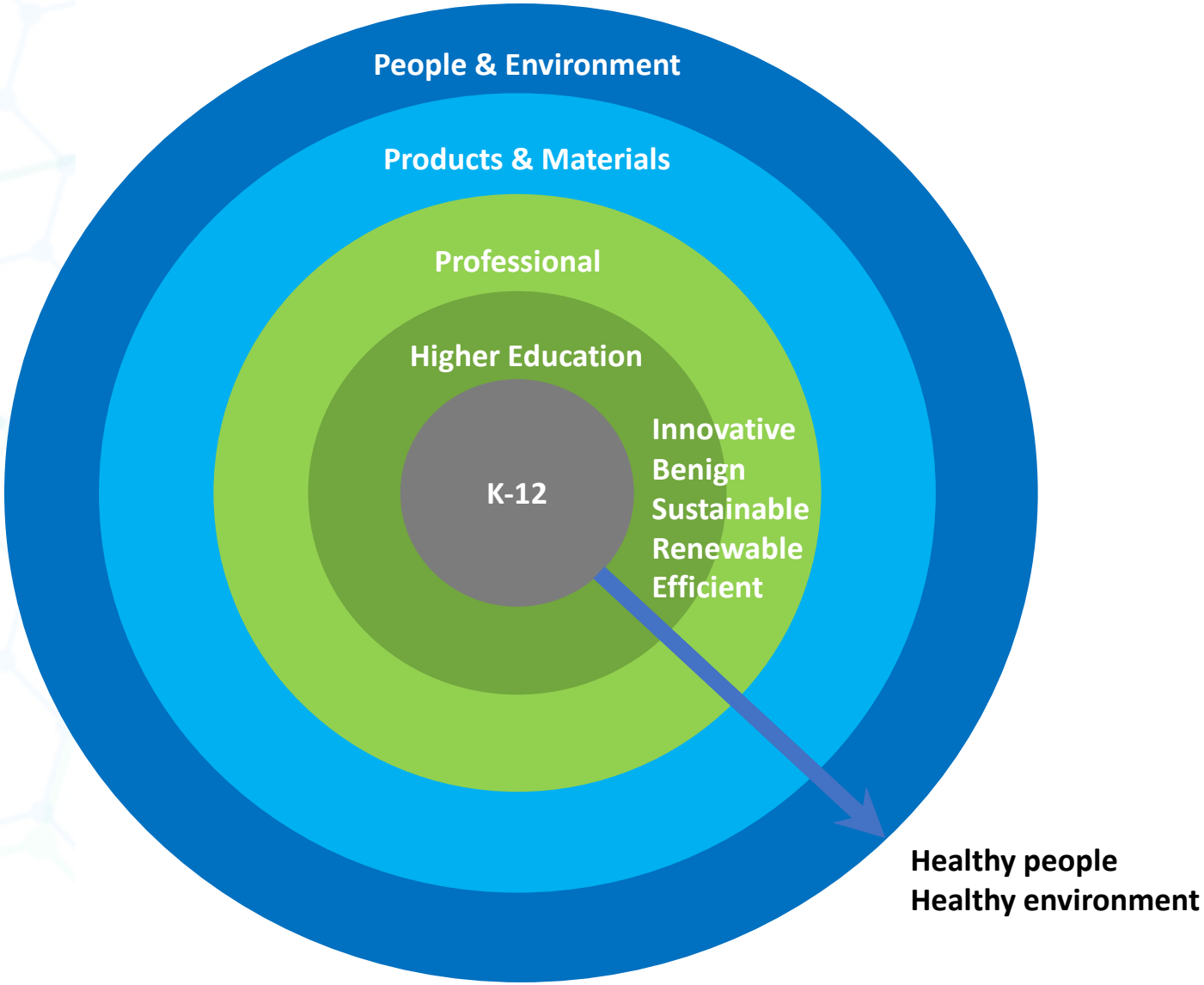
my green lab.

- California-based 501-c3 non-profit
- Build a culture of sustainability through science
- Green Lab Certification
- ACT Label
- Center for Energy Efficient Laboratories (CEEL)

# What Brought Us Together?

- The need for green chemistry in higher education
- Gap in available resources for simple, customizable green chemistry alternatives for teaching labs
- Collaboration to complement each others expertise

# Reimaging Chemistry Education



# Lets Take a Poll

What teaching lab experiment would you most like to see an alternative for?

# A Guide to Green Chemistry Experiments for Undergraduate Organic Chemistry Labs

Brought to you by Beyond Benign and My Green Lab through the generous support of MilliporeSigma

# Contents Of The New Guide

**Introduction & Green Chemistry Resources**

- EH&S Assessments
- Solvent Substitution Guides
- Reagent and Reaction Selection Resources
- Greener Laboratory Techniques
- Introduction to Green Chemistry for TA's
- 12 Principles of Green Chemistry

# Contents Of The New Guide

**10 Customizable Experiment Packages**

- Introduction
- Greener alternative demonstration(s)
- Traditional demonstration
- EH&S metrics for each demonstration
- Comparative analysis
- TA guide
- Sample quiz questions

# EH&S Metrics for Experiment Assessments

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# Qualitative Assessment

**Less Hazardous Chemical Synthesis**

**Renewable Feedstocks**

**Energy Efficiency**

**Catalysis**

**Safe Solvents**

**Accident Prevention**

# Quantitative Assessment

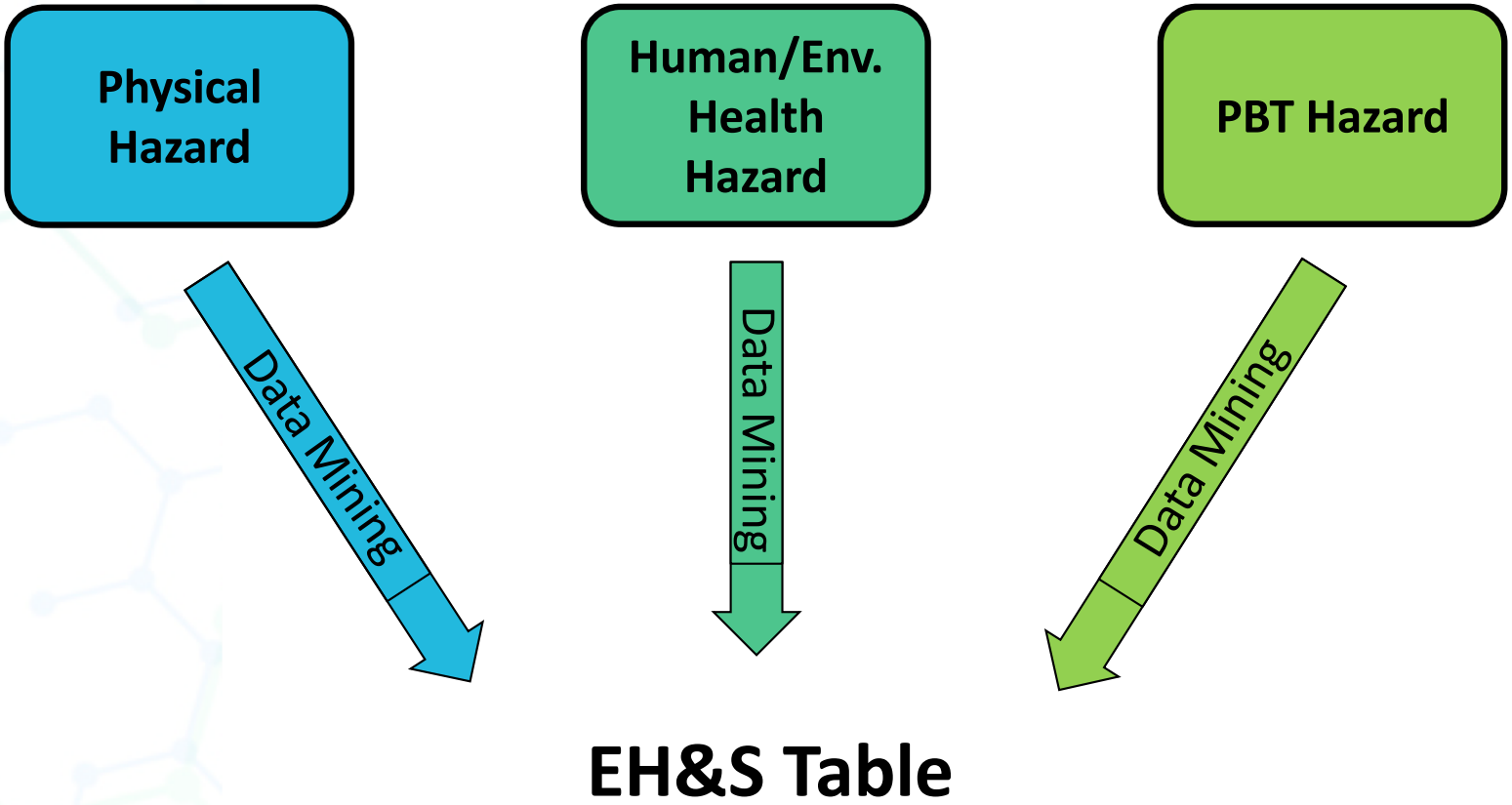
1. Volume of Waste
2. Environmental, Health, and Safety (EH&S)
   - Physical Hazards
   - Human Health Hazards
   - Persistence, Bioaccumulation, Toxicity (PBT)

# Volume of Waste

- This analysis is based on the assumption that all solvents, reagents and products will be transformed to waste products

**In our assessment, we are assuming that the product will be minimal in relation to the waste created and that the products are eventually discarded as waste**

# Quantitative Hazard Analysis



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# EH&S Table

| Chemical Name<br>Aldrich Catalog # | Amount per 100 students (g or mL) | EH&S |
|---|---|---|
| Cyclohexane | (varies) | |
| Toluene<br>244511 | (varies) | |
| Ethanol<br>459836 | (varies) | |
| Acetone<br>650501 | (varies) | |
| Water<br>n/a | (varies) | |

EHS Key:

- Physical hazard
- Toxicity/Health hazard
- Persistent Bioaccumulative Toxic (PBT) Chemicals

- * Very high hazard
- High hazard
- Moderate hazard
- Low hazard
- No data

→ **Physical Hazard**
→ **Health Hazard**
→ **PBT Criteria**

# EH&S Table

| Chemical Name<br>Aldrich Catalog # | Amount per 100 students (g or mL) | EH&S |
|---|---|---|
| Cyclohexane | (varies) | |
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| Ethanol<br>459836 | (varies) | |
| Acetone<br>650501 | (varies) | |
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- * Very high hazard
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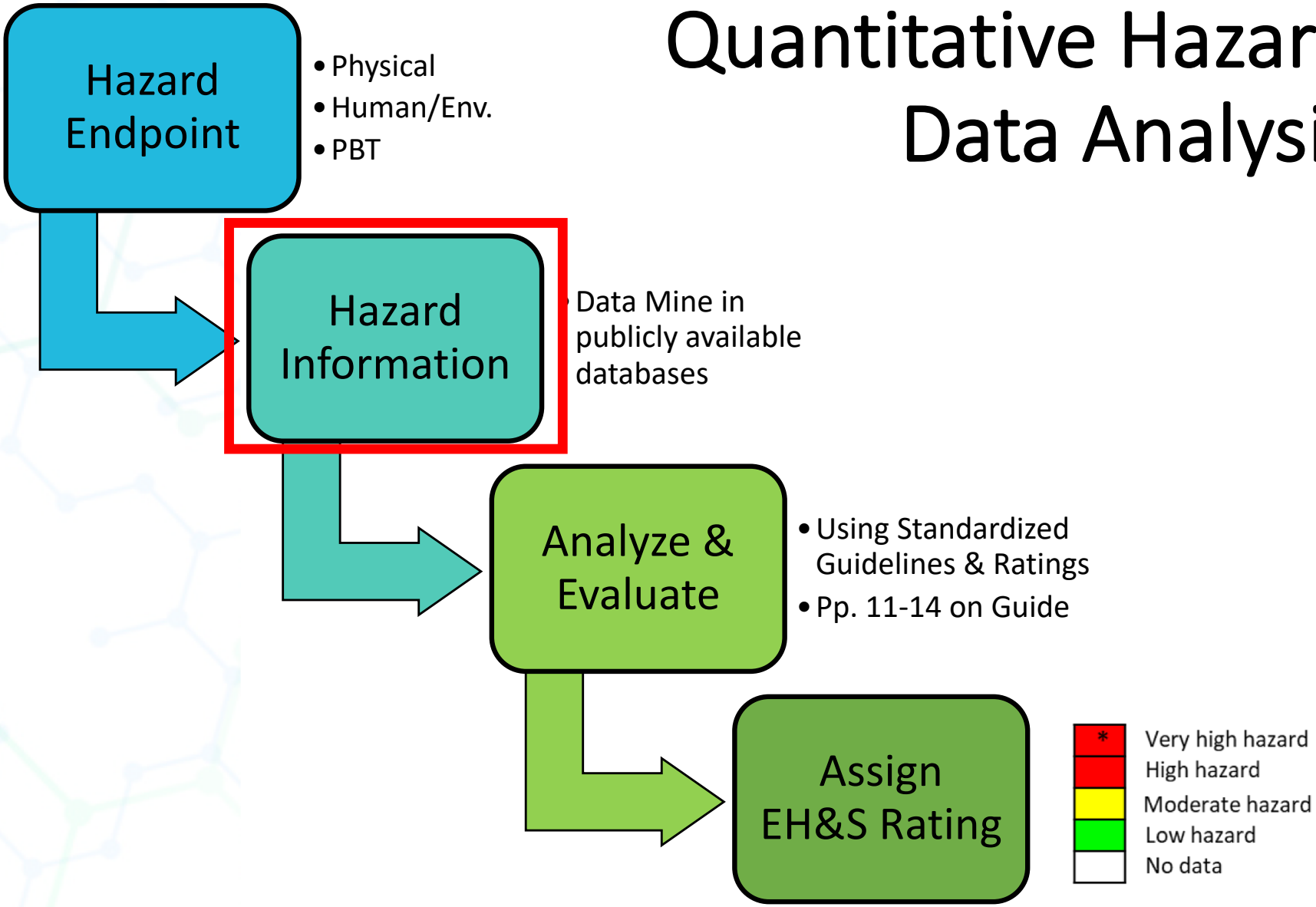
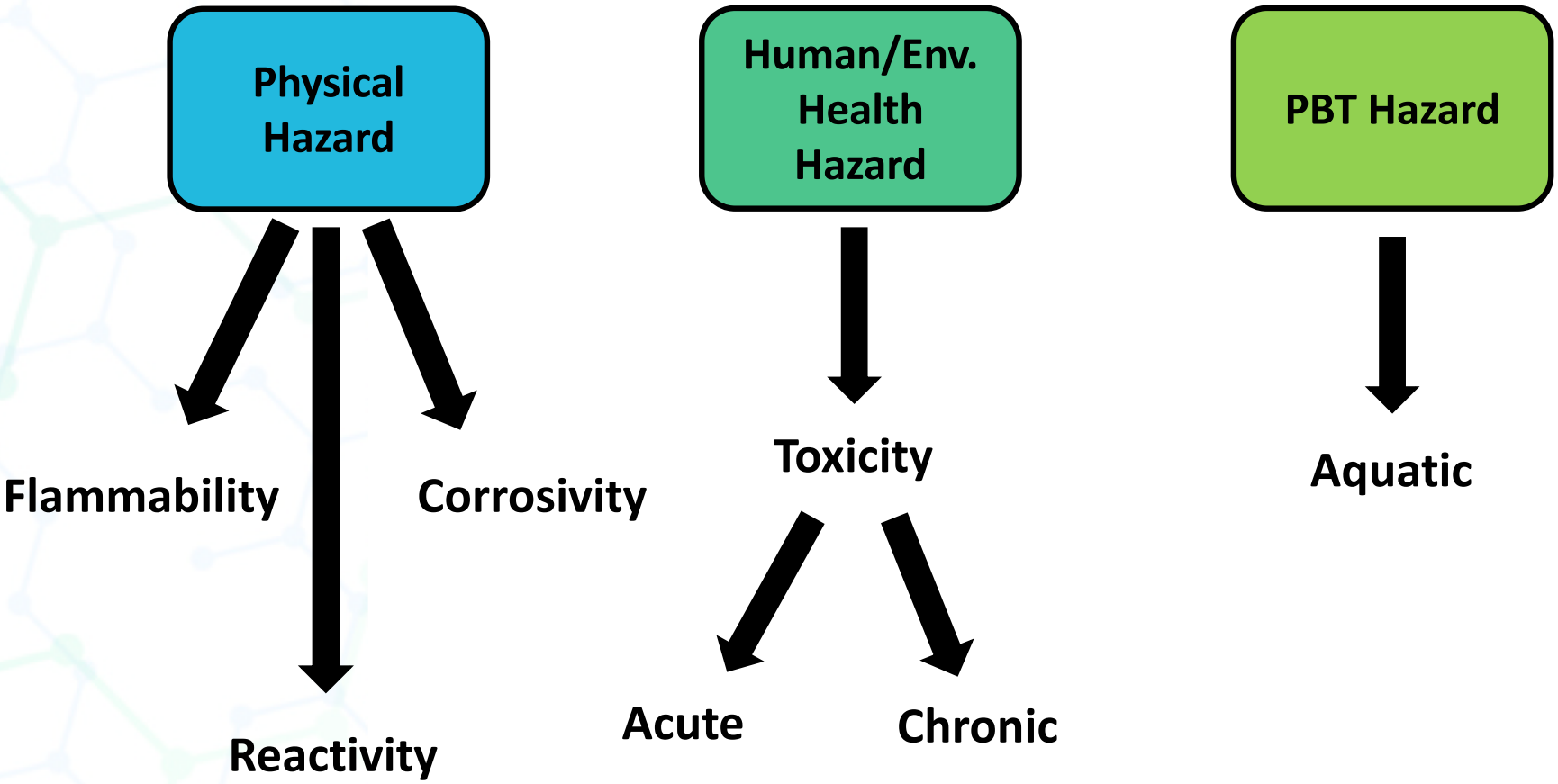
- Moderate hazard
- Low hazard
- No data

How did you get these EH&S ratings?

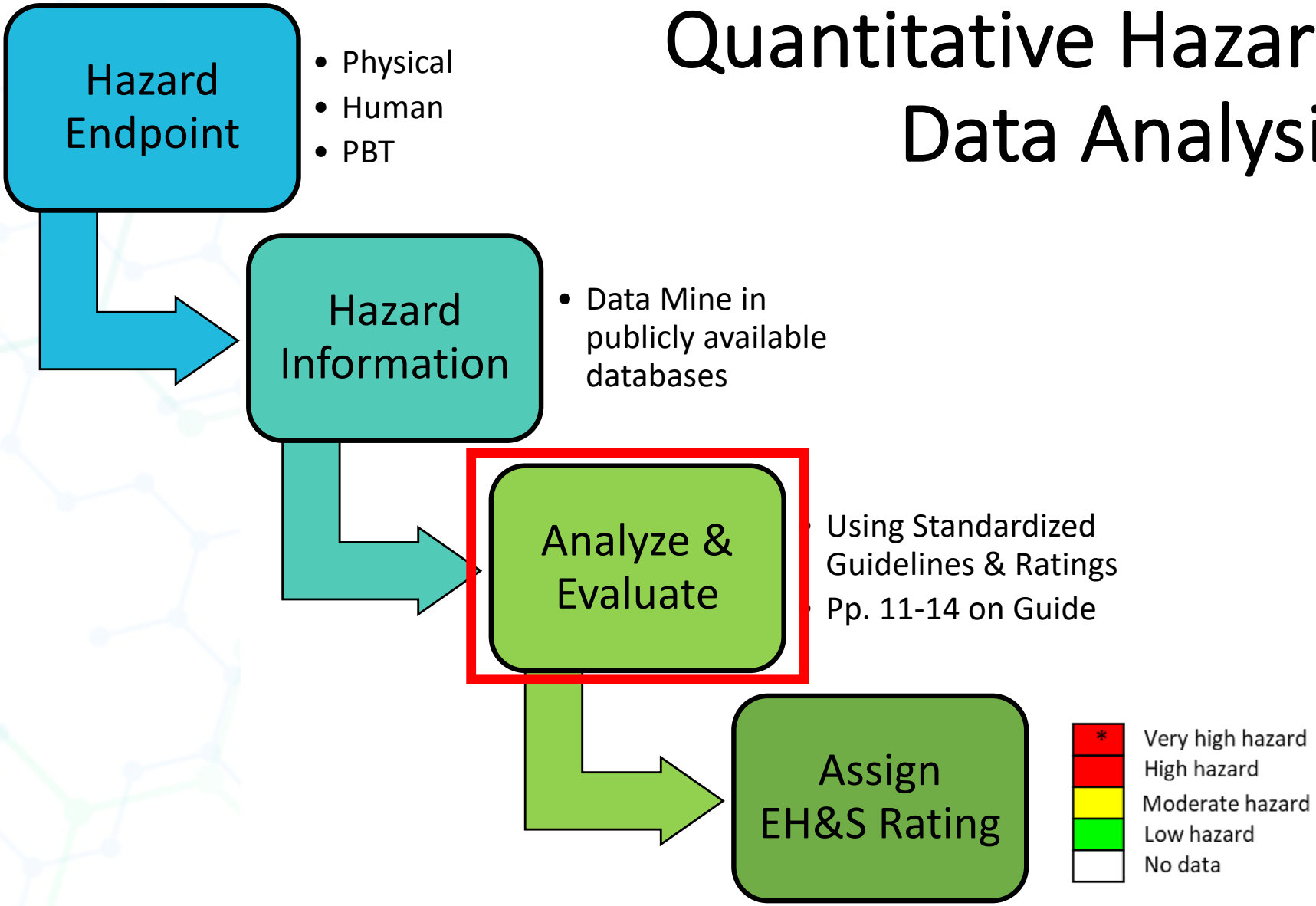
# Quantitative Hazard Data Analysis



# Quantitative Hazard Analysis



# Quantitative Hazard Data Analysis

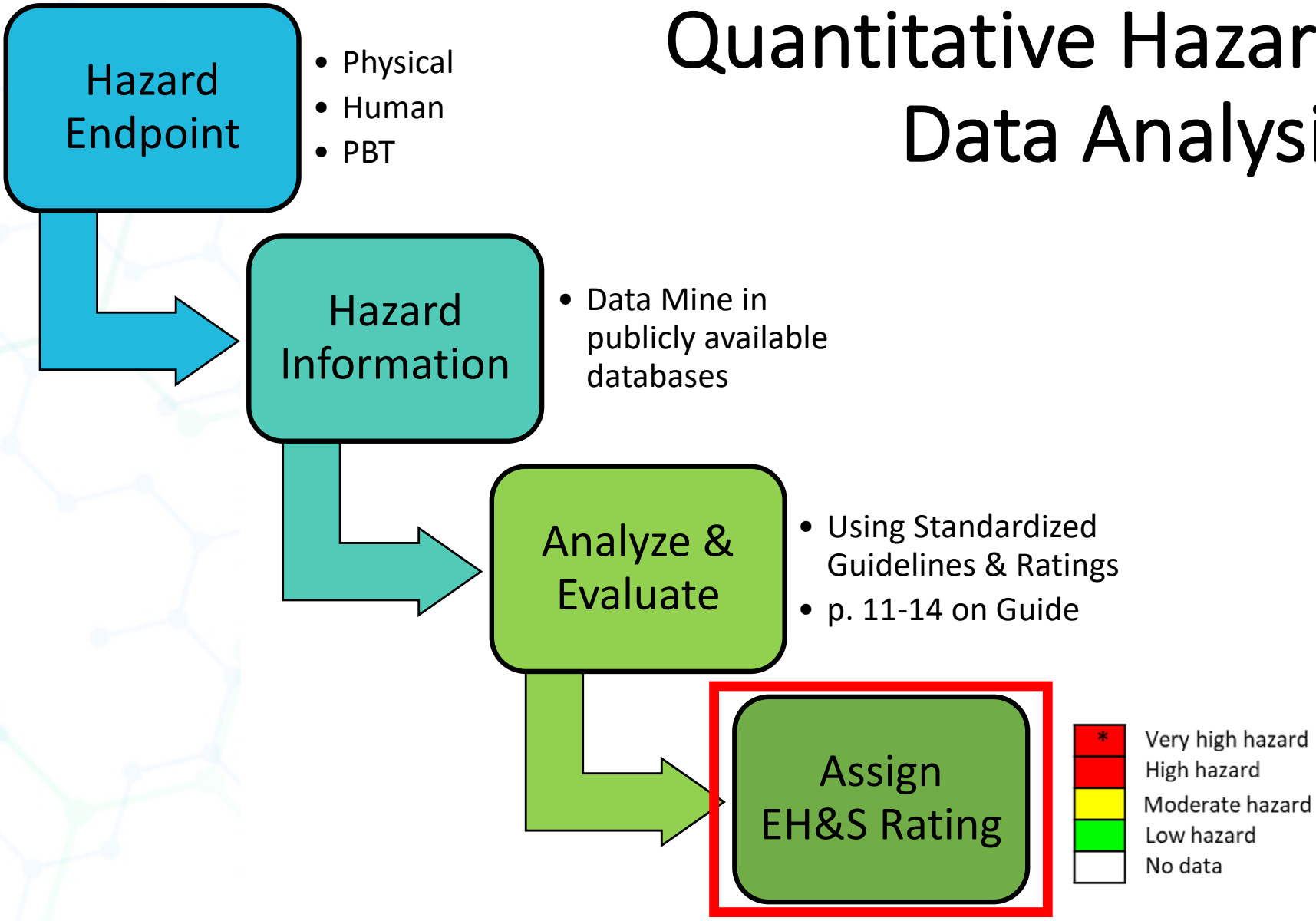


# Hazard Information

- National Fire Protection Association (NFPA)
- Global Harmonized System (GHS)
- Safety Data Sheet (SDS)
  - Chemical Suppliers
- Toxic Effects of Chemical Substances Databases
  - ToxPlanet
  - Pharos
  - GreenScreen for Safer Chemicals

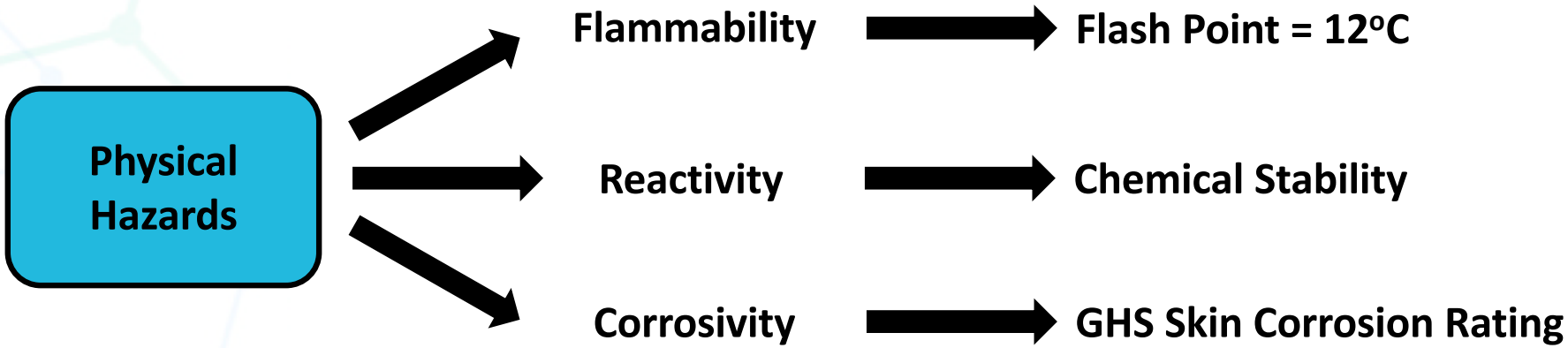
*Refer to Pg. 11-14 in the Guide for more technical criteria to analyze and evaluate hazards*

# Quantitative Hazard Data Analysis



# EH&S Evaluation of Ethanol

## Step 1: Identify and Obtain All Hazard Information



# EH&S Evaluation of Ethanol

## Step 1: Identify and Obtain All Hazard Information

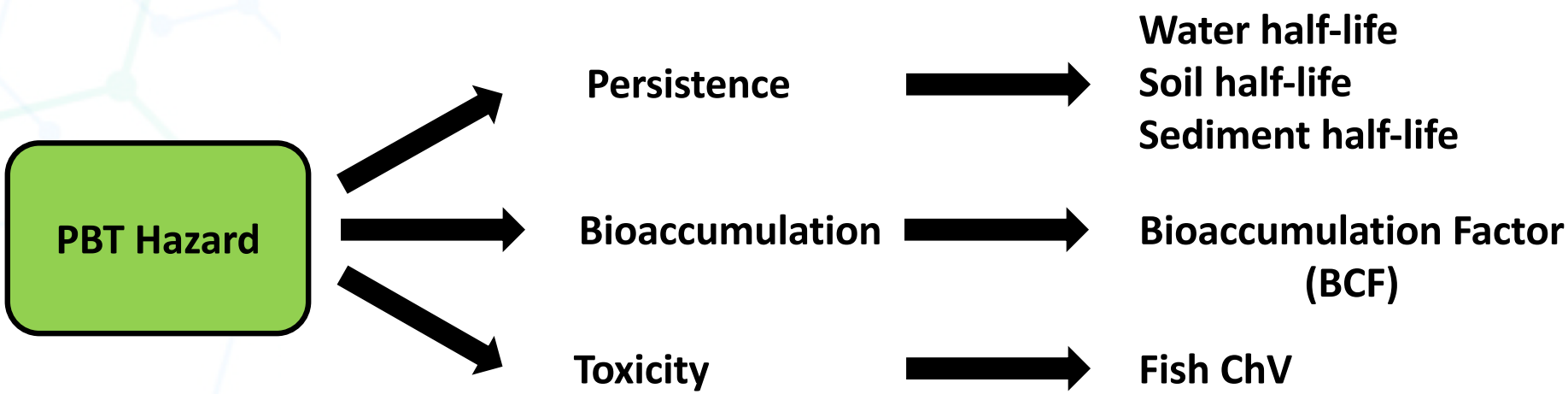
**Human Health Hazard**

**Acute Toxicity** →
- **Oral $LD_{50}$**
- **Dermal $LD_{50}$**
- **$LC_{50}$**

**Chronic Toxicity** →
- **Carcinogenicity**
- **Mutagenicity**
- **Neurotoxicity**
- **Sensitization**
- **Reproductive Toxicity**
- **Developmental Toxicity**
- **Endocrine Activity**

# EH&S Evaluation of Ethanol

## Step 1: Identify and Obtain All Hazard Information



# EH&S Evaluation of Ethanol

## Step 2: Evaluate Hazard Information

**Physical Hazard**

**Flammability:**
- NFPA Rating = 3

**Reactivity:**
- NFPA Rating = 0

**Corrosivity:**
- GHS Category 1B

**Human Health Hazard**

- All hazards were due to oral exposure

**PBT Hazard**

- Fish ChV 250mg/l
- BCF = 3.2

# EH&S Evaluation of Ethanol

## Step 3: Assign Worst-Case Hazard Rating

**Physical Hazard**

**Flammability:**
- NFPA Rating = 3

**Reactivity:**
- NFPA Rating = 0

**Corrosivity:**
- GHS Category 1B

**Human Health Hazard**

- All hazards were due to oral exposure

↓

**Moderate Hazard**

**PBT Hazard**

- Fish ChV 250mg/l
- BCF = 3.2

↓

**Low Hazard**

# Putting the Pieces Together

| Chemical Name<br>Aldrich Catalog # | Amount per 100 students (g or mL) | EH&S |
|---|---|---|
| Cyclohexane | (varies) | |
| Toluene<br>244511 | (varies) | |
| Ethanol<br>459836 | (varies) | |
| Acetone<br>650501 | (varies) | |
| Water<br>n/a | (varies) | |

EHS Key:

- Physical hazard
- Toxicity/Health hazard
- Persistent Bioaccumulative Toxic (PBT) Chemicals

- * Very high hazard
- High hazard
- Moderate hazard
- Low hazard
- No data

This is how you get these EH&S ratings!

# Contents Of The New Guide

**Introduction & Green Chemistry Resources**

- EH&S Assessments
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- Greener Laboratory Techniques
- Introduction to Green Chemistry for TA's
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# Solvent Substitution Resources

- Pfizer Solvent Selection Tool
- GlaxoSmithKline Solvent Selection Guide
- ACS Green Chemistry Institute Pharmaceutical Roundtable Solvent Selection Guide
- Overview and compilation of multiple guides
  - CHEM21 Solvent Selection Guide
  - Prat, D.; Hayler, J.; Wells, A. Green Chem., 2014, 16, 4546.

# Additional Resources

**Reagent and Reaction Selection**

- Key publications
- ACS GCI Reagents Guide
- The Greener Organic Chemistry Reaction Index in *Green Organic Chemistry in Lecture and Laboratory*

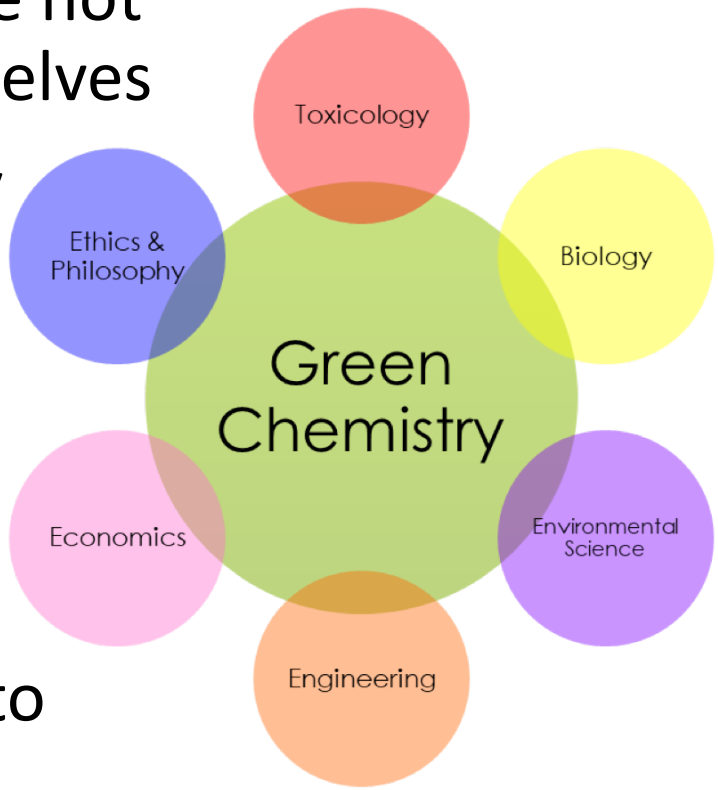
**Laboratory Techniques**

- Greener recommendations to common synthetic techniques

# Additional Resources

**Introduction to Green Chemistry for TA's**

- 'Green Chemistry 101'
- Intended to provide basics for those not educated in green chemistry themselves
- For anyone new to green chemistry

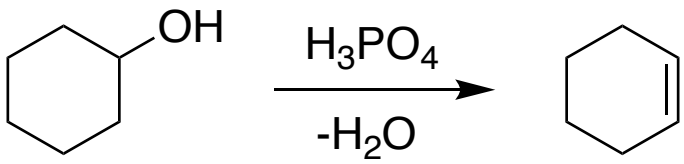



**12 Principles of Green Chemistry**

- Describes each principle
- Thank you to the Green Chemistry Initiative at the University of Toronto

# Example Experiment Packages From the Guide

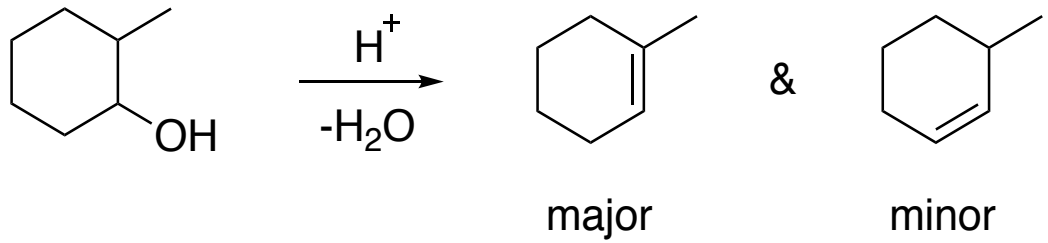
# Alcohol Dehydration




**Traditional Approach**

- Preparation of an alkene through dehydration of an alcohol
- Employs concentrated phosphoric acid as a catalyst

# Alcohol Dehydration




**Greener Alternative**

- Eliminates use of concentrated acid by using Montmorillonite KSF clay as the catalyst
- Less Hazardous Chemical Synthesis
- Safer Solvents & Auxiliaries
- Use of Renewable Feedstocks
- Catalysis
- Real-Time Pollution Prevention
- Safer Chemistry for Accident Prevention
- Waste Prevention

# Comparative Analysis

## Health and Safety Evaluation

### Greener Alternative

| Chemical Name<br>Aldrich Catalog # | Amount per 100 students (g or mL) | EH&S |
|---|---|---|
| 2-methylcyclohexanol<br>153087 | 100 mL | |
| Montmorillonite KSF*<br>281530 | 12.5 g | |
| Poly(ethylene glycol), avg. $M_n$ 400 (PEG 400)<br>202398 | 150 mL | |
| Sodium sulfate<br>798592 | 100 g | |

EHS Key:

- Physical hazard
- Toxicity/Health hazard
- Persistent Bioaccumulative Toxic (PBT) Chemicals

- * Very high hazard
- High hazard
- Moderate hazard
- Low hazard
- No data

### Traditional Approach

| Chemical Name<br>Aldrich Catalog # | Amount per 100 students (g or mL) | EH&S |
|---|---|---|
| Cyclohexanol<br>105899 | 100 mL | |
| Phosphoric acid, conc.<br>W290017 | 25 mL | |
| Toluene<br>179418 | 150 mL | |
| Sodium chloride<br>793566 | 42 g | |
| Calcium chloride<br>C1016 | 25 g | |
| Ethanol<br>E7023 | 250 mL | |
| Acetone<br>34850 | 250 mL | |
| Water<br>N/A | 250 mL | |

# Comparative Analysis

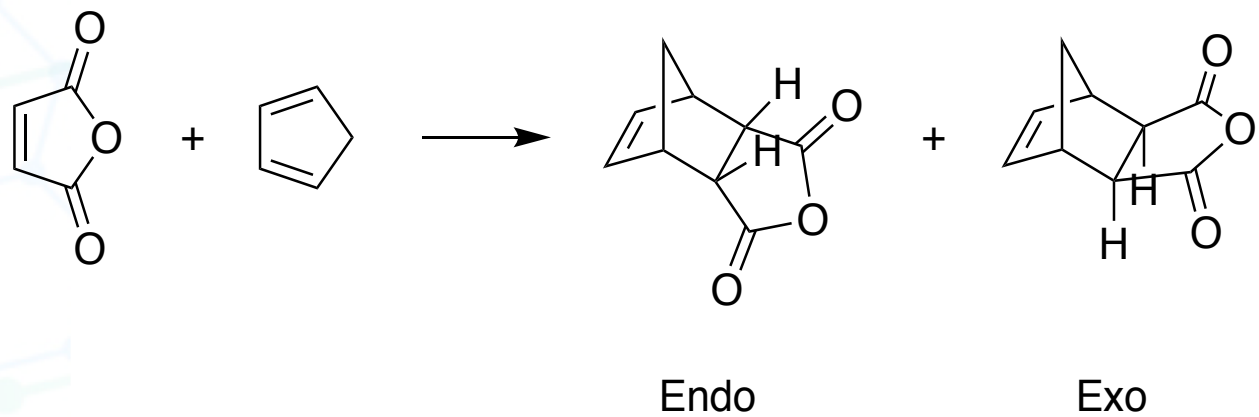
The greener method offers the following improvements:

- Eliminates the use of toluene and acetone as solvents, and the conc. phosphoric acid catalyst
- Reduced waste and employs reusable catalyst
- Cost decrease - reagents per 100 students is approx. $47 for the greener method vs. $76 for the traditional method*

*Actual cost will vary.

| Synthesis | Waste reduction (per 100 students) | "Greener" benefits |
|---|---|---|
| **Greener method** | 375 mL | |
| **Traditional method** | 1100 mL | |

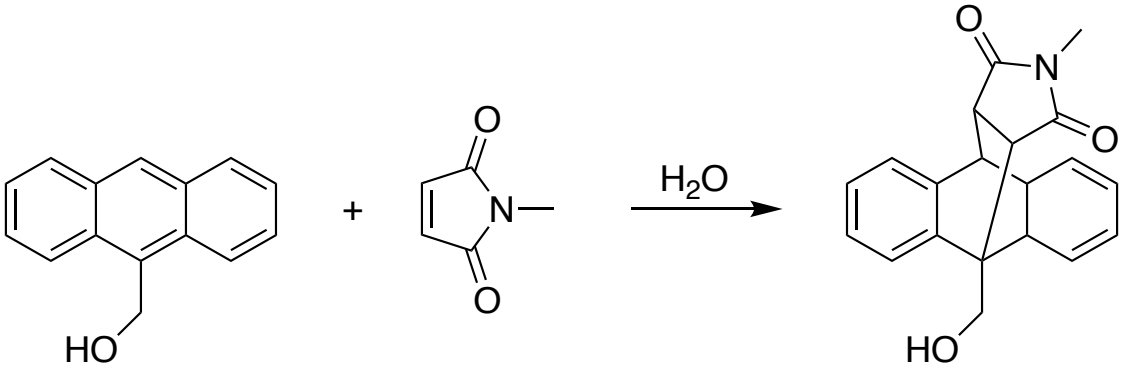
# Diels-Alder




**Traditional Approach**

- Uses ethyl acetate and petroleum ether
- Reagents and solvents have high hazard EH&S profiles

# Diels-Alder




**Greener Alternative**

- Less Hazardous Chemical Synthesis
- Safer Solvents and Auxiliaries
- Design for Energy Efficiency
- Real-Time Pollution Prevention
- Safer Chemistry for Accident Prevention
- Waste Prevention
- Atom Economy

# Comparative Analysis

## Health and Safety Evaluation

### Greener Alternative

| Chemical Name<br>Aldrich Catalog # | Amount per 100 students (g or mL) | EH&S |
|---|---|---|
| 9-Anthracenemethanol<br>187240 | 3.25 g | |
| N-methylmaleimide<br>389412 | 5.2 g | |
| Water<br>n/a | 2500 mL | |

### Traditional Approach

| Chemical Name<br>Aldrich Catalog # | Amount per 100 students (g or mL) | EH&S |
|---|---|---|
| Dicyclopentadiene<br>454338 | 345 g | |
| Maleic anhydride<br>M188 | 5 g | |
| Ethyl acetate<br>270989 | 20 mL | |
| Petroleum ether<br>320447 | 20 mL | *F |
| Calcium chloride, anhyd.<br>793639 | 25 g | |

EHS Key:

- Physical hazard
- Toxicity/Health hazard
- Persistent Bioaccumulative Toxic (PBT) Chemicals
- * Very high hazard
- High hazard
- Moderate hazard
- Low hazard
- No data

# Comparative Analysis

- Greener method uses water as a solvent thus eliminating the need for hazardous organic solvents
- Greener method has overall lower EH&S hazard profile
- Cost increase - reagents per 100 students is approx. $54 for the greener method vs. $37 for the traditional method*

*Actual cost will vary.

| Synthesis | Waste reduction (per 100 students) | "Greener" benefits |
|---|---|---|
| **Greener method** | 2500 mL aqueous waste | |
| **Traditional method** | 390 mL liquid waste<br>25 g solid waste | |

# Download Your Copy of the Guide

1. Go to https://www.mygreenlab.org/gccg-form.html
2. Complete registration form
   - This information will be kept confidential
   - Provides metrics on use and impact of the guide for the purposes of the creators only
   - The form needs to be completed for every download
     - Multiple downloads are permitted
3. Download your **free** copy
4. We would love to hear from you!
   - Implemented teaching experiments, used as a resource in your research lab, questions, or comments?
   - Contact Us or email info@mygreenlab.org

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# Thank you!

Recordings, supporting documents and upcoming webinars (with registration links):

http://www.beyondbenign.org/he-webinars/

Sign-up for Beyond Benign's quarterly newsletter and webinar announcements on our homepage:
www.beyondbenign.org

Sign-up for My Green Lab's monthly newsletter to stay up to date on all things lab-sustainability related at:
https://www.mygreenlab.org/newsletter.html

# Supplemental Hazard Assessment Guideline Tables

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# Qualitative Assessment

| Qualitative endpoint | Icon | Criteria |
|---|---|---|
| Less Hazardous Chemical Synthesis | | Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment. |
| Renewable feedstocks | | The chemical can be derived from a renewable feedstock. For example: ethanol can be derived from bio-based feedstocks |
| Energy efficiency | | The reaction avoids the use of energy when compared to the traditional version. For example: the grinding of two reagents at room temperature using a mortar and pestle versus reflux conditions |
| Catalysis | | The use of catalytic reagents as opposed to stoichiometric reagents. |
| Safer Solvents and Auxiliaries | | The use of safer solvents as compared to traditional alternatives (see Safer Solvent section). |
| Accident Prevention | | The avoidance of the use of substances that have potential for chemical accidents, including releases, explosions and fires. For example: avoiding the use of a pyrophoric reagent |

# Physical Hazards

## Flammability Assessment Guidelines

| Human Health Rating | NFPA Rating | Degree of Flammability |
|---|---|---|
| **Low** | 0 | Materials that will not burn (materials that will not burn in air when exposed to a temperature of 820 °C for a period of 5 minutes) |
| **Low** | 1 | Materials that must be preheated before they will ignite (flash point at or above 93.3 °C) |
| **Moderate** | 2 | Materials that must be moderately heated or exposed to relatively high ambient temperatures before they will ignite (flash point between 37.8 and 93.3 °C) |
| **High** | 3 | Liquids and solids that can ignite under almost all temperature conditions (Liquids having a flash point below 22.8 °C and having a boiling point at or above 37.8 °C or having a flash point between 22.8 and 37.8 °C) |
| **Very High** | 4 | Materials which will rapidly vaporize at atmospheric pressure and normal temperatures, or are readily dispersed in air and which burn readily (includes pyrophoric substances. Flash point below room temperature at 22.8 °C) |

# Physical Hazards

## Reactivity Assessment Guidelines

| Human health rating | NFPA Rating | Degree of Reactivity |
|---|---|---|
| **Low** | 0 | Materials that are stable even under exposure to fire. |
| **Low** | 1 | Materials that are normally stable, but become explosive at elevated temperatures and pressure. |
| **Moderate** | 2 | Materials that easily undergo a violent reaction, but do not explosively decompose |
| **High** | 3 | Materials that are easily capable of explosive decomposition, but require an ignition source or will react explosively with water. |
| **Very High** | 4 | Materials that are easily capable of explosive decomposition at normal temperatures and pressure. |

# Physical Hazards

## Corrosivity Assessment Guidelines

| Human health rating | GHS Rating | Degree of Corrosivity |
|---|---|---|
| **Low** | N/A | No listing or phrases |
| **Moderate** | Category 1C | > 1 hour and ≤ 4 hours exposures and ≤ 14 days observations; pH extremes of ≤2 and ≥ 11.5 including acid/alkali reserve capacity. |
| **High** | Category 1B | >3 minutes ≤ 1 hour exposure and ≤ 14 days observations; pH extremes of ≤2 and ≥ 11.5 including acid/alkali reserve capacity. |
| **Very High** | Category 1A | ≤ 3 minutes exposure and ≤ 1 hour observation;<br>pH extremes of ≤2 and ≥ 11.5 including acid/alkali reserve capacity.<br>Hazard Phrase: H314 |

# Human Health Hazards

## Acute Mammalian Toxicity

| Hazard Level | Acute Mammalian Toxicity Criteria: |
|---|---|
| **Very High** | GHS Category 1 or 2; Risk Phrases R26, R27, R28; Hazard Phrases H300, H310, H330; Technical Criteria: Oral LD50 ≤ 50 mg/kg; Dermal LD50 ≤ 200 mg/kg; Inhalation (g) LC50 ≤ 500 ppm; Inhalation (v) LC50 ≤ 2 mg/l; Inhalation (dust, mist) LC50 ≤ 0.5 mg/l; NFPA Health 4 |
| **High** | GHS Category 3; Risk Phrases R23, R24, R25; Hazard Phrases H301, H311, H331; Technical Criteria: Oral LD50 > 50 but ≤ 300 mg/kg; Dermal LD50 > 200 but ≤ 1,000 mg/kg; Inhalation (g) LC50 > 500 but ≤ 2,500 ppm; Inhalation (v) LC50 > 2.0 but ≤ 10.0 mg/l; Inhalation (dust, mist) LC50 > 0.5 but ≤ 1.0 mg/l; NFPA Health 3 |
| **Moderate** | GHS Category 4; Risk Phrases R20, R21, R22; Hazard Phrases H302, H312, H332; Tech. Criteria: Oral LD50 > 300 but ≤ 2,000 mg/kg; Dermal LD50 > 1,000 but ≤ 2,000 mg/kg; Inh. (g) LC50 > 2,500 but ≤ 20,000 ppm; Inh. (v) LC50 > 10.0 but ≤ 20.0 mg/l; Inh. (dust, mist) LC50 > 1.0 but ≤ 5.0 mg/l; NFPA |
| **Low** | GHS Category 5; Hazard Phrases H303, H313, H333; Technical Criteria: Oral LD50 > 2,000 mg/kg; Dermal LD50 > 2,000 mg/kg; Inh. (g) LC50 > 20,000 ppm; Inh. (v) LC50 > 20.0 mg/l; Inh. (dust, mist) LC50 > 5.0 mg/l |

# Human Health Hazards

## Chronic Toxicity

| Hazard Level | Chronic Toxicity Criteria: |
|---|---|
| **High** | Carcinogenicity: Risk Phrases - R45 or R49; Hazard Phrases - H350 or H350i; Mutagenicity/Genotoxicity: GHS Category 1A or 1B; Risk Phrases - R46; Hazard Phrases - H340; Reproductive Toxicity: GHS Category 1A or 1B; Risk Phrases - R60; Hazard Phrases - H360F, H360FD, H360Fd; Developmental Toxicity: GHS Category 1A or 1B; Risk Phrases - R61 or R64; Hazard Phrases - H360D, H360FD, HD360Df, H362; Sensitization, Respiration: GHS Category 1A and 1B; Hazard Phrase- H334; Sensitization, Skin Category 1A; Hazard Phrases – H317; Neurotoxicity (Repeated exposure)- GHS CNS Category 1 or 2; 90-day rat inhalation (vapor) study < 0.2 (mg/L/6h/day); Endocrine- Substances listed on the EU – SVHC Authorization List for Endocrine Activity |
| **Moderate** | Carcinogenicity: Risk Phrases - R40; Hazard Phrases - H351; Mutagenicity/Genotoxicity: GHS Category 2; Risk Phrases - R68; Hazard Phrases - H341; Reproductive Toxicity: GHS Category 2; Risk Phrases - R62; Hazard Phrases - H360, H361f, H361fd; Developmental Toxicity: GHS Category 2; Risk Phrases R63; Hazard Phrases H360Fd, H361d, H361fd; Sensitization, Respiration: Risk Phrases – R42; Sensitization, Skin Category 1B Risk Phrases- R43; Neurotoxicity (Repeated exposure)- GHS CNS Category 3, 90-day rat inhalation (vapor) study 0.2—1.0 (mg/L/6h/day); Risk Phrase R67; Hazard Phrase – H336; Endocrine - indication of Endocrine Activity in the scientific literature; Substitute It Now (SIN) List or TEDX Potential List |
| **Low** | Carcinogenicity: no risk or hazard phrases; Mutagenicity/Genotoxicity: No listings or phrases; Reproductive Toxicity: No listings or phrases; Developmental Toxicity: No listings or phrases; Sensitization, Respiration: No listings or phrases; Sensitization, Skin: No listings or phrases; Neurotoxicity – No listings or phrases; 90-day rat inhalation (vapor) study > 1.0 (mg/L/6h/day); Endocrine Activity- no listing. |

# Human Health Hazards

## Aquatic Toxicity

| Hazard Level | Acute Aquatic Toxicity Criteria: |
|---|---|
| **Very High** | GHS Category 1; Risk Phrases R50, Hazard Phrases H400; Technical Criteria: 96 hr LC50 (fish) ≤ 1 mg/l, 48 hr EC50 (crustacea) ≤ 1 mg/l, 72 or 96 ErC50 (algae) ≤ 1 mg/l |
| **High** | GHS Category 2; Risk Phrases R51, Hazard Phrases H401; Technical Criteria: 96 hr LC50 (fish) > 1 but ≤ 10 mg/l, 48 hr EC50 (crustacea) > 1 but ≤ 10 mg/l, 72 or 96 ErC50 (algae)> 1 but ≤ 10 mg/l |
| **Moderate** | GHS Category 3; Risk Phrases R52, Hazard Phrases H402; Technical Criteria: 96 hr LC50 (fish) > 10 but ≤ 100 mg/l, 48 hr EC50 (crustacea) > 10 but ≤ 100 mg/l, 72 or 96 ErC50 (algae ) > 1 but ≤ 100 mg/l |
| **Low** | Technical Criteria: 96 hr LC50 (fish) > 100 mg/l, 48 hr EC50 (crustacea) > 100 mg/l, 72 or 96 ErC50 (algae )> 100 mg/l |

# PBT Assessment Guidelines

## Persistence, Bioaccumulation, and Toxicity (PBT) Criteria

| Hazard Level | PBT Criteria: |
|---|---|
| **Very High** | EPA Standards Persistence: Water, Soil, and sediment Half-life > 6 months (> 180 days); Bioaccumulation: BCF > 5,000; Fish ChV <0.1 mg/l |
| **High** | EPA Standards Persistence: Water, Soil, and sediment Half-life >= 2 months (>= 60 days); Half-life in Air >2 days; Bioaccumulation: BCF > = 1,000; Fish ChV <0.1mg/l |
| **Moderate** | Suspected PB (modeling); Fish ChV 0.1-10 mg/l |
| **Low** | Listed as not persistent or bioaccumulative; Fish ChV >10 mg/l |