# Green Chemistry

# Green Chemistry

Green Chemistry offers a solution to a problem

So, what is that problem?

# Green Chemistry

Here are some words that are used to describe products we buy and use:

Chemical, Green, Synthetic, Made, Home-made, Engineered, Chemical-free, Sustainable, Preservative, Recycled, Modified, Pesticide, Natural, Organic

Which do people generally like to hear about their products?

# Green Chemistry

What do people generally like to hear about products?

Natural
Organic
Green
Sustainable
Home-made
Chemical-free
Recycled

Chemical
Synthetic
Engineered
Modified
Made
Preservative
Pesticide

For many “chemical” and related terminology is negative

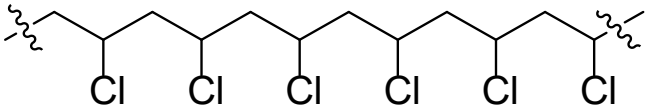
But why?

# Green Chemistry

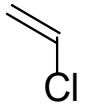
Here's a reason:

What's this stuff? PVC pipe

PVC = polyvinyl chloride




Made from vinyl chloride




To have PVC we occasionally have to deal with incidents like…..

The 2023 Ohio Train Derailment

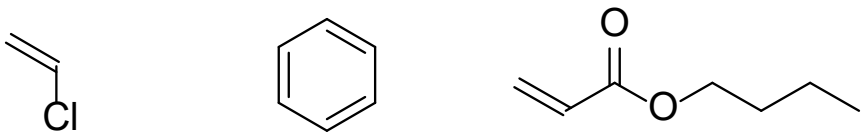
# Green Chemistry

The 2023 Ohio Train Derailment:

- East Palestine, Ohio

- 49 cars in derailment pile, which caught fire and burned for days

- 11 were tank cars, which dumped 100,000 gallons of hazardous materials, including vinyl chloride, benzene residue, and butyl acrylate.



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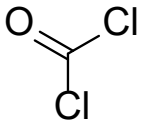
The 2023 Ohio Train Derailment:

- To reduce the explosion risk, the vinyl chloride cars were ruptured, drained into a trench, and the material set on fire.

- This produced HCl and phosgene and soot!




- All kinds of concerns about soil, water, and air contamination!

# Green Chemistry

Have you heard of all of these?

| | | |
|---|---|---|
| DDT | benzene | ozone |
| arsenic | carbon dioxide | lead |
| mercury | dioxin | BPA |
| PFAS | | |

These are some of the well-recognized chemicals causing environmental concern

# Green Chemistry

Advances in chemistry have provided us with many things.

e.g. Related to Transport, Communication, Living, etc.

Let's pick one area – Transportation
What are chemistry advances that were not available say 50 years ago?

# Green Chemistry

Advances in chemistry have provided us with many things.

- These have come at some cost, one manifestation is "pollution"

  - Aside from gradual impacts on the environment, there have been many notable "incidents"

  - Some US examples:

    - Cuyahoga river ~1870-1970 (caught fire (13 times!))
    - Love canal ~1970 (various chemicals)
    - Times beach ~1983 (dioxin contamination)

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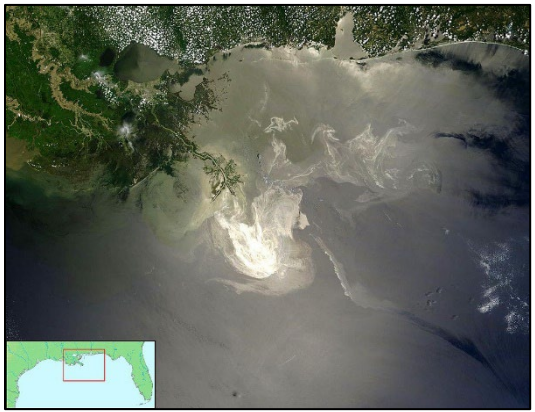
- Some More Recent Big Incidents

- Deepwater Horizon oil spill, April 2011
- 210 million gallons released



- Cement creek Colorado 2015
- 3 million gallons of mine (Gold King mine) waste into river
- Arsenic, cadmium, lead, mercury, (aluminum, copper)

# Green Chemistry

Actually - There's some kind of notable chemical incident in the US about every other day!

### Fire, Rocky Mount Recyclers — Rocky Mount, North Carolina

**(March 7, 2024)**

For more than 24 hours, a massive fire burned at the recycling facility. Smoke billowed into the neighborhood for hours. According to ABC11 "Officials say the toxic chemicals released into the air do not pose a threat to people in the area." Rocky Mount Recyclers accepts appliances, cars, batteries and "unprepared scrap", according to the company's website.

**INCIDENT TYPE:** Incident at facility not covered by RMP

**INCIDENT SECTOR(S):** Waste & Recycling

**WEATHER RELATED:** no

### Fire, VanDeMark Chemicals phosgene manufacturing facility — Lockford, New York

**(March 4, 2024)**

A fire at the chemical company caused $8,000 worth of structural damage but the value of products lost was not determined. VanDeMark manufactures phosgene and phosgene derivatives. Phosgene is made from chlorine. VanDeMark has as much as **1,140,000 pounds of chlorine and 377,000 pounds of chlorine** onsite at any moment. Chlorine and phosgene are deadly gases.

**INCIDENT TYPE:** Incident at RMP facility

**INCIDENT SECTOR(S):** Plastics & Petrochemical Manufacturing

**WEATHER RELATED:** no

**TAG(S):** phosgene

### Multiple explosions, massive fire, one death, one injury, Select Distributors — Clinton Township, Michigan

**(March 4, 2024)**

A warehouse that supplies vaping and electronic products to gas stations and discount merchants went up in a massive conflagration shortly. This followed a prolonged and loud explosion. Canisters of nitrous oxide exploded and sent debris into the community. A nineteen year old man who was observing the event was killed by falling debris and a police officer was injured when metal scrap hit his vehicle. As the event was occurring police issued a statement: "We can not stress enough the danger that is happening right now. Please, please, please stay inside and out of the vicinity. Debris is being projected into the air and coming down as far as a mile away from the explosion. As we do not know what is burning, we do not know the effects of the smoke/air right now, so please stay out of the area and stay safe."

**INCIDENT TYPE:** Incident at facility not covered by RMP

**INCIDENT SECTOR(S):** Chemical Transport, Distribution & Storage

**CONSEQUENCE(S):** injury death

**WEATHER RELATED:** no

**TAG(S):** nitrous oxide

Coalition to Prevent Chemical Disasters: https://preventchemicaldisasters.org/chemical-incident-tracker/overview

# Green Chemistry

- Each big incident leads to a public response and then a government response. As a result, the following policies have been developed:

  - Clear Air Act
  - The Resource Recovery and Conservation Act
  - The Safe Drinking Water Act
  - Superfund in the USA

- So, there has been a gradual evolution since about 1945 until now that has better regulated our dispensing of chemicals into the environment.

# Green Chemistry

- Chemists may have created problems, but they are also the ones to solve them!
- For example – gasoline powered cars

Emissions Problems Solved:

- Lead – alternative anti-knock additives have been employed
- $SO_x$ – most sulfur is now removed from gasoline before use
- $NO_x$ – catalytic converter - N leaves as $N_2$
- CO - catalytic converter - C leaves as $CO_2$
- Volatile hydrocarbons - catalytic converter

- Now just down to the inescapable problems of $\underline{CO_2}$ production and fossil fuel depletion

# Green Chemistry

How do we deal with chemical hazards?

What are some types of chemical hazards?

Explosive, lachrymator, vesicant, pyrophoric, carcinogen, teratogen, sternutator, caustic, corrosive, oxidizer, irritant, sensitizer.

**Hazards**

Poison is in everything, and no thing is without poison. The dosage makes it either a poison or a remedy.

Paracelsus – a renowned alchemist of the 16th century

Really? What about air? What about water? Are those poisons?

# Green Chemistry

## Air

Quick Q – What are the major components air?

78% nitrogen ($N_2$), 21% oxygen ($O_2$), ~1% argon (Ar), ~1% $H_2O$

Anyone been scuba diving?

- Breathing air at increased pressure causes humans to experience "nitrogen narcosis" - similar effect to alcohol.
- Oxygen becomes toxic above a certain pressure, when diving deep enough oxygen toxicity is also a problem.

# Green Chemistry

**Water**

abc NEWS August 4, 2023, 7:14 AM

## Mom of 2 dies of water intoxication, family says

A family in Indiana is mourning the loss of a 35-year-old mother-of-two who they said died after drinking 64 ounces of water in 20 minutes.

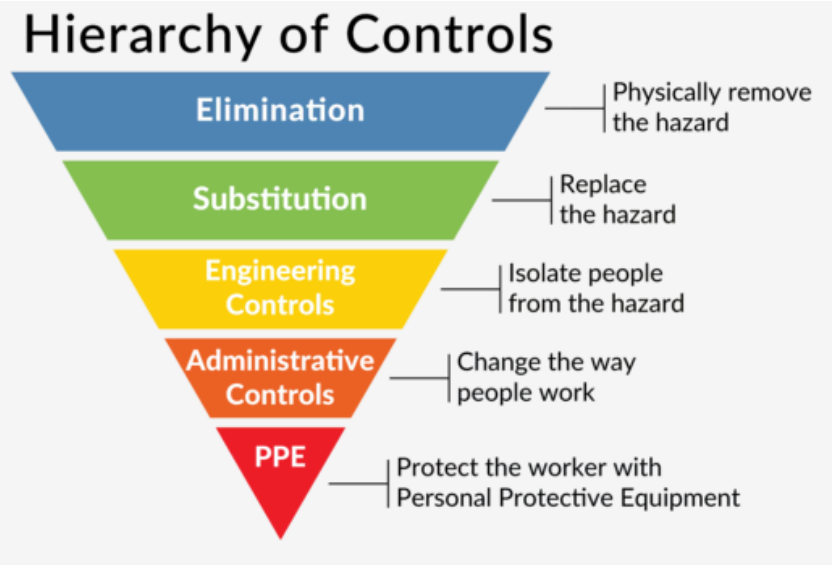
Hyponatremia (low sodium concentration in the blood)

# Green Chemistry

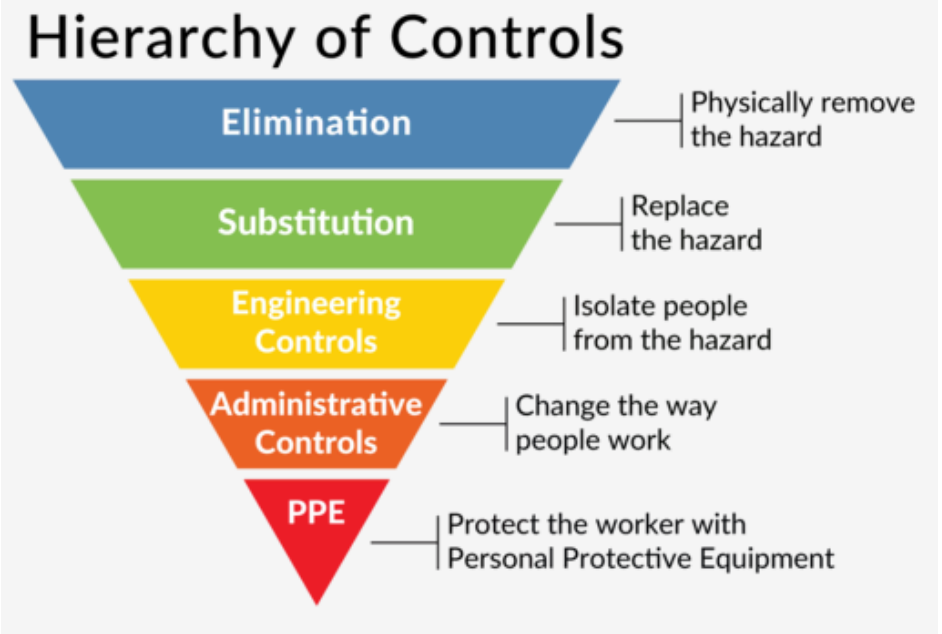
Anastas and Warner provide the following formula:

**Risk = f[hazard,exposure]**

- One strategy is that if we can reduce or eliminate exposure we can reduce or eliminate risk
- From there we can consider ideas of exposure controls



# Green Chemistry




Which control method is most effective?

https://makesafetools.com/osha-hierarchy-of-controls/

# Green Chemistry

Problems with “exposure controls” (= “end of pipe” controls)

Uncertainties exist with all of the following:

- Risks are not known for many (most?) substances
- Synergistic effects
- Chronic effects
- Bioaccumulation

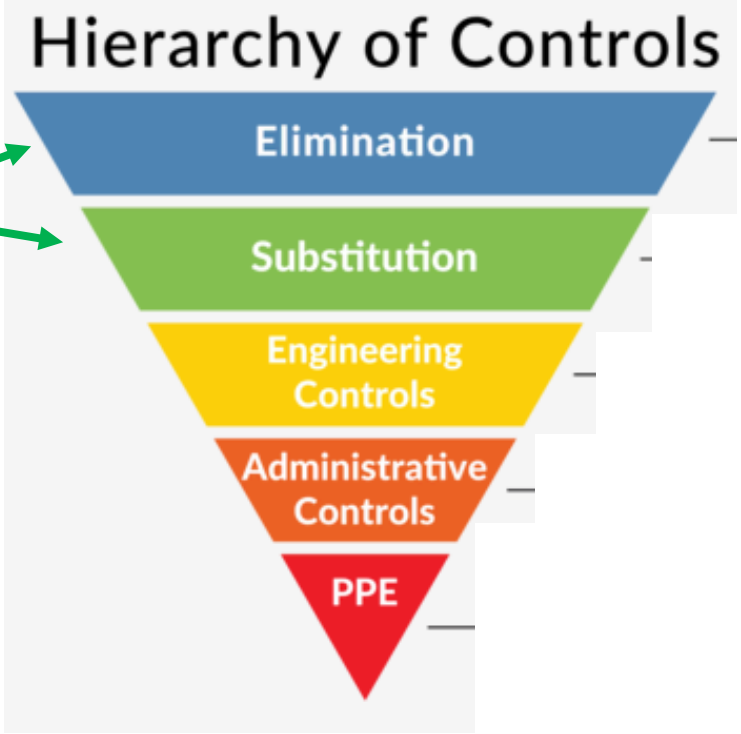
**and what if the exposure controls fail?**

# Green Chemistry

Green Chemistry aims to address chemical hazard problems here

No hazard = no risk

(**Risk = f[hazard,exposure]**)



# Green Chemistry

Exposure Controls

- Amounts to reducing risks to an acceptable level
- Acceptable to whom?

Green Chemistry minimizes hazards by not using hazardous materials or generating hazardous products in the first place!

# Green Chemistry

"Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal. Green chemistry is also known as sustainable chemistry."

- Environmental Protection Agency (EPA)

https://www.epa.gov/greenchemistry/basics-green-chemistry#definition

# Green Chemistry

Green Chemistry vs Cleaning up Pollution?

Cleaning up pollution (also called remediation) involves treating waste streams (end-of-the-pipe treatment) or cleanup of environmental spills and other releases

- **Removes hazardous materials from the environment**

Green Chemistry reduces pollution at its source by minimizing or eliminating the hazards of chemical feedstocks, reagents, solvents, and products

- **Keeps hazardous materials out of the environment in the first place**

https://www.epa.gov/greenchemistry/basics-green-chemistry#definition

# 12 Principles of Green Chemistry

1. Prevent Waste
2. Maximize Atom Economy
3. Design Less Hazardous Chemical Syntheses
4. Design Safer Chemicals and Products
5. Use Safer Solvents and Reaction Conditions
6. Increase Energy Efficiency
7. Use Renewable Feedstocks
8. Avoid Chemical Derivatives
9. Use Catalysts, not Stoichiometric Reagents
10. Design Chemicals and Products to Degrade after Use
11. Analyze in Real-time to Prevent Pollution
12. Minimize the Potential for Accidents

https://www.epa.gov/greenchemistry/basics-green-chemistry#definition

# Green Chemistry

- Using Green Chemistry has broad benefits

If, for example, a company adopts a green chemistry process they will see benefits beyond just reducing environmental impact from their process:

Lowered costs –

- Fewer hazardous shipping costs
- Reduced waste disposal costs
- Reduced infrastructure costs (more hazards = more expensive equipment to deal with them)
- Less time used managing safety/hazards
- etc.

# Green Chemistry - Examples

1996 Green Chemistry Challenge Award Winner -
Dow Chemical Company – Designing an Environmentally Safe Marine Antifoulant


We are talking about ships – e.g cargo ships

What is fouling?

Unwanted growth of plants and animals on the ships hull

What's the problem?

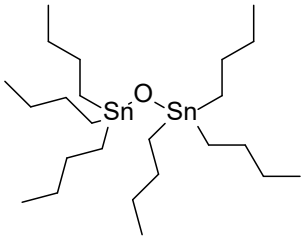
Increased drag through the water

Use a chemical agent to kill the fouling organisms

# Green Chemistry - Examples

1996 Green Chemistry Challenge Award Winner -
Dow Chemical Company – Designing an Environmentally Safe Marine Antifoulant

- TBTO was heavily used. It was incorporated in the paint on the hull.
- Slowly leached out killing the fouling organisms
- Long half-life in the environment (~6 months)
- Bioconcentrates in marine organisms (chronically toxic)

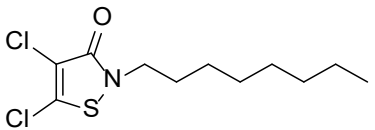



Tributyltin oxide (TBTO)

# Green Chemistry - Examples

1996 Green Chemistry Challenge Award Winner -
Dow Chemical Company – Designing an Environmentally Safe Marine Antifoulant

- Dow developed “Sea-Nine 211”
- Low water solubility
- No bioaccumulation in the food chain
- Not persistent (half-life <1 h)
- Competitive price/performance




4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI)

- TBTO banned worldwide by the International Marine Organization, phased out by 2008

# Green Chemistry - Examples

The Green Chemistry Challenge Awards promote the environmental and economic benefits of developing and using novel green chemistry.

Sponsored

by the Environmental Protection Agency (EPA)

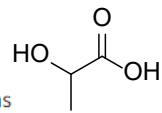
Partners

American Chemical Society (ACS) Green Chemistry Institute
Industrial
Trade Associations
Academic Institutions
other Government Agencies

# Green Chemistry Challenge

## 2023 Award Winners

- **Academic Category: University of Michigan, Ann Arbor, Michigan**, for developing new ways to refine common agricultural waste such as rice hulls into materials that can be used in lithium-ion batteries and other products which are important for the transition to green energy. The new processes can replace the energy and carbon intensive methods currently used to obtain silicon metals.
- **Design of Greener Chemicals: The Clorox Company, Oakland, California**, for designing Clorox EcoClean™ Disinfecting Cleaner, a Design for the Environment-certified disinfecting cleaner that can be used without personal protective equipment, is formulated without alcohol and can be used safely on most surfaces without bleaching. The product disinfects 99.999% of illness-causing germs in two minutes or less when used as directed.
- **Greener Synthetic Pathways: Solugen, Houston, Texas,** for developing the Bioforge™, a chemical manufacturing platform that converts plant-derived substances into a range of materials that have historically been made from fossil fuels — without resulting emissions or waste. Materials made in the Bioforge™ include those used for water treatment and detergents.
- **Greener Reaction Conditions: Captis Aire LLC, East Point, Georgia**, for the patent pending CAIRE Technology that captures more than 90% of terpenes, a waste product from the wood manufacturing process, and converts it into valuable chemicals including those used in products such as biofuels, flavors and fragrances. Currently these terpenes can be an air pollutant, an irritant to eyes, lungs and skin, and are commonly burned as waste which releases greenhouse gases.
- **Small Business Award: Modern Meadow, Nutley, New Jersey**, for developing a more efficient textile dyeing process called Bio-FREED™ Powered by Bio-Alloy™ which uses a bio-based protein foam to dye any type of fiber. Compared to traditional dyeing methods, Bio-FREED™ conserves 95% of water, reduces energy consumption by 75%, and utilizes 80% fewer dyes and chemicals. Bio-FREED also does not require a separate step to fix the dye and requires one or even no washes at the end of the dyeing process, compared to 4-7 washes for traditional dyeing.
- **Specific Environmental Benefit – Climate Change: Air Company, Brooklyn, New York**, for developing a technology that mimics photosynthesis to transform the greenhouse gas carbon dioxide into other organic chemicals, producing oxygen as the only byproduct. The technology both removes carbon dioxidefrom the air by using it as a chemical reactant and reduces the need for fossil fuels by transforming it into fuels, including aviation fuels.

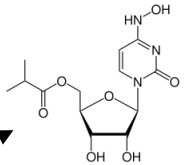


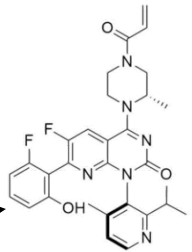
lactic acid

https://www.epa.gov/greenchemistry/green-chemistry-challenge-winners

# Green Chemistry Challenge

## 2022 Award Winners





- **For Greener Synthetic Pathways**

  Merck & Co., Inc.

  Developing a greener way to make LAGEVRIO™ (molnupiravir), an antiviral treatment for COVID-19 (summary)

- **For Greener Reaction Conditions**

  Amgen

  An improved manufacturing process for LUMAKRAS™ (sotorasib), a novel drug for the treatment of certain non-small cell lung cancers (summary)

- **For Small Business**

  Provivi

  Creating Provivi FAW™, a biological pheromone-based product that controls the fall armyworm, a destructive pest of corn (summary)

- **For Academic**

  Professor Song Lin of Cornell University

  Developing a new, more efficient process using electrochemistry to create large and complicated molecules that are widely used in the pharmaceutical industry (summary)

- **For Specific Environmental Benefit—Climate Change**

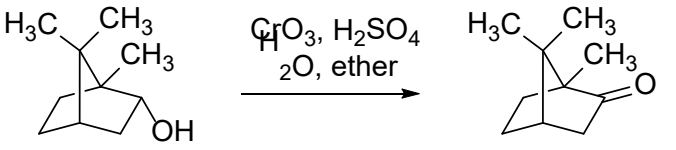
  University of California Davis

  A technology that reduces greenhouse gas emissions by producing chemicals for making plastic from biomass rather than petroleum (summary)

https://www.epa.gov/greenchemistry/green-chemistry-challenge-winners

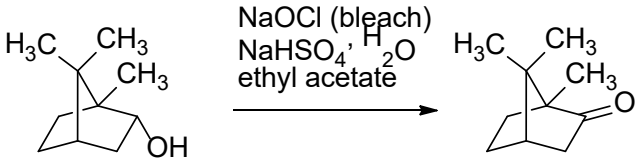
# Example - Greener Oxidation Procedure – U of A

## Old Procedure:




borneol camphor

## Current Procedure:



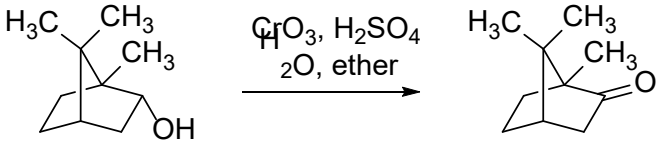

borneol camphor

What makes the newer procedure greener?

1. Reactant/reagent/solvent safety?
   - for people doing the experiment
   - to the environment
2. Waste
   - what is the waste?
   - how does it need to be disposed of?

# Greener Oxidation Procedure – U of A

## Old Procedure:




borneol camphor

Other products:

Unreacted Cr(VI) – highly toxic, carcinogenic, major environmental hazard

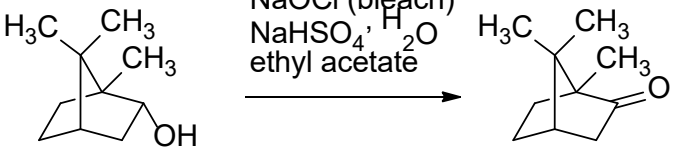
Cr(III) - environmental hazard

$H_2SO_4$ - highly corrosive

Ether - volatile, flammable

Water

## New Procedure:

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Other products (after $NaHSO_3$ addition):

$Na^+$

$K^+$

$HSO_4^-$

$SO_4^{2-}$

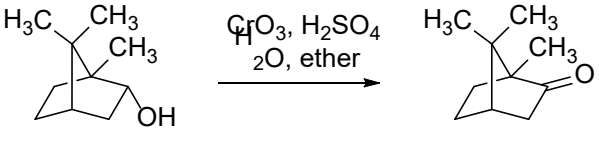
$Cl^-$

Ethyl acetate - flammable

Water

# Greener Oxidation Procedure – U of A

## Old Procedure:

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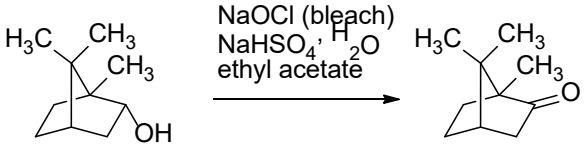


borneol camphor

Which of the 12 principles of green chemistry are incorporated in this example?

1. Prevent Waste
2. Maximize Atom Economy
3. Design Less Hazardous Chemical Syntheses
4. Design Safer Chemicals and Products
5. Use Safer Solvents and Reaction Conditions
6. Increase Energy Efficiency
7. Use Renewable Feedstocks
8. Avoid Chemical Derivatives
9. Use Catalysts, not Stoichiometric Reagents
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# Greener Oxidation Procedure – U of A

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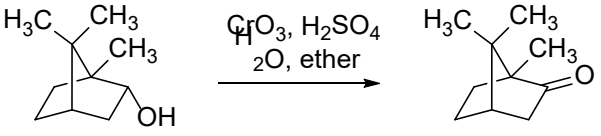


borneol → camphor

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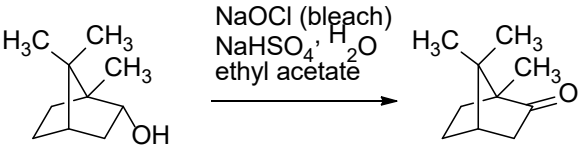


borneol → camphor

Is the new procedure perfectly green? If not, what types of changes would be needed to make it even greener?

# Green Chemistry

- Importantly, in practice very few processes are entirely green
- Realistically, while that is the goal, a more typical sub-goal is to make processes “greener”
- Metrics have been developed to assess the “greenness” of processes e.g. Atom economy, Effective mass efficiency, E factor, EcoScale

# Greener Oxidation Procedure – U of A

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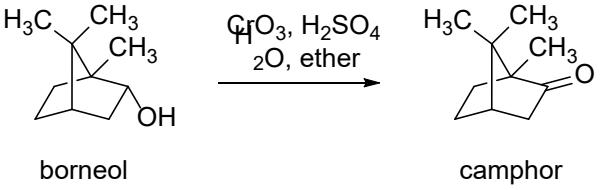


borneol camphor

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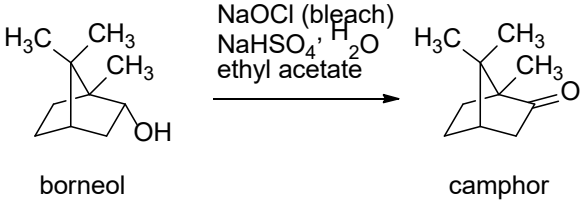


borneol camphor

- In this oxidation lab experiment example ideally, there would be no solvent (or water as solvent?), oxygen from the air would be used (maybe with a catalyst) as the oxidizing agent, etc.

# Green Chemistry

This Page (EPA) contains link to many resources for further information about Green Chemistry

https://www.epa.gov/greenchemistry/green-chemistry-resources#education