



### An active collaboration between faculty and Research Safety to evaluate green chemistry and safety from the bench to the institutional level



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### Is green chemistry safer chemistry?

**Green chemistry** 

=

Safer chemistry

**Greenness** 



**Performance** 

Safety









### Perspectives lead to different priorities: Green duality



#### 2. ATOM



Reduci level by i atoms f incorpora Use ato

7. USE OF RENEW



Use chen renewabl rather t origina

#### 3. LESS HAZARDOUS



Design syntheti possible, all substa react

#### 4. DESIGNING S



Minir mol and e physica environn

Choose t

auxiliary

make up

for any

total

#### 5. SAFER SOLVE



#### 8. REDUCE



Minimi derivat groups. A reaction

## The 12 Principles of Principle

Green chemistry is an approach to chemistry that aims to maximus efficiency and minimum hazardous effects on human health and the environment. While no reaction can be perfectly [preer], the overall negative impact of chemistry research and the chemical industry can be educed by implementing the 12 Phinciples of Green Chemistry wherever possible.

7. USE OF RENEWABLE FEEDSTOCKS

8. REDUCE DERIVATIVES

9. CATALYSIS

10. DESIGN FOR DEGRADATION

11. REAL-TIME POLLUTION PREVENTION

12. SAFER CHEMISTRY FOR ACCIDENT PREVENTION

Use chemicals which are made from

renewable (i.e. plant-based) sources.

rather than other, equivalent

chemicals originating from petrochemical sources.

Minimize the use of temporary

derivatives such as protecting groups. Avoid derivatives to reduce

reaction steps, resources required,

and waste created.

Use catalytic instead of

strichiometric reagents in reactions.

Choose catalysts to help increase

selectivity, minimize waste, and

reduce reaction times and energy

can be discarded easily. Ensure

that both chemicals and their

degradation products are not toxic.

bioaccumulative, or environmentally

mersistant.

Monitor chemical reactions in

real-time as they occur to prevent

the formation and release of any

potentially hazardous and polluting

autistances

#### 1. WASTE PREVENTION



Prioritize the prevention of wests, rather than cleaning up and treating waste after it has been created. Plan ahead to minimize waste at every \$550.

#### 2. ATOM ECONOMY



Reduce waste at the molecular lavel by maximizing the number of atoms from all resignents that are incorporated into the final product. Use atom occupany to evaluate reaction efficiency.

#### 3. LESS HAZARDOUS CHEMICAL SYNTHESIS



Design chemical reactions and synthetic routes to be as safe as possible. Consider the hazards of all substances handled during the reaction, including waste.

#### 4. DESIGNING SAFER CHEMICALS



Minimize toxicity descriy by malecular design. Predict, and evalvate aspects such as physical properties, toxicity, and environmental fate throughout the design process.

#### 5. SAFER SOLVENTS & AUXILIARIES



Choose the safest solvent available for any given step. Minimize the total ancount of solvents and auxiliary substances used, as these make up a large percentage of the total waste (readed).

#### 6. DESIGN FOR ENERGY EFFICIENCY



Choose the least energy-intensive chemical mute. Avoid heating and cooling, as well as pressurated and vacuum conditions (i.e. ambient emperature is pressure are optimal).

### (K)

Choose and develop chemical procedures that are safer and inherently minimize the risk of accidents. Know the possible risks and assess them beforehand.

#### 6 COMPOUND INTEREST 2015, WWW.COMPOUNDCHEM.COM Shared under a CC Attribution-NonCommercial Acidenhatives licence



#### EVENTION

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### A holistic approach to green chemistry and safety

### Safer chemistry

### **Green chemistry**

- Incorporates concepts of scale and perspective
- Incorporates safety concepts by necessity
- Provides student ownership
- Ties green and safety concepts to increased efficiency
- Unique to 'Pilot Plant Clemson'
- Dynamic











### **Green Duality: perspective and scale**



Bench



Institution



Flammable Storage







**Chemical Storage** 





Compliance







### Incorporating process green chemistry and safety

## Cradle to grave







Experiment in green fashion: triphenylmethane dye synthesis







### Crystal violet synthesis is our "product"

### **A Colorful Grignard Reaction**

Preparation of the Triarylmethane Dyes from 4-Bromo-N,N-Dimethylaniline

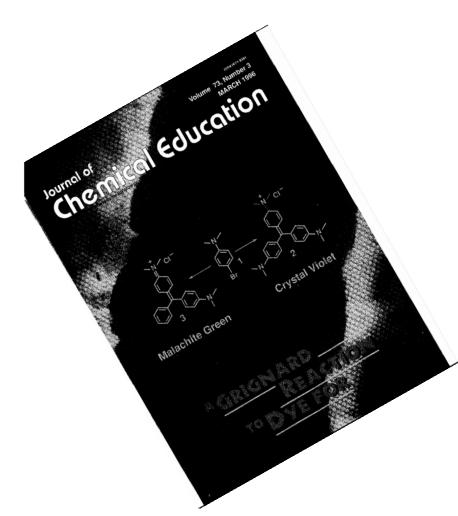
Malachite Green

Crystal Violet

Douglass F. Taber, 1 Robert P. Meagley, and Danielle Supplee

University of Delaware, Newark, DE 19716

Volume 73 Number 3 March 1996 259



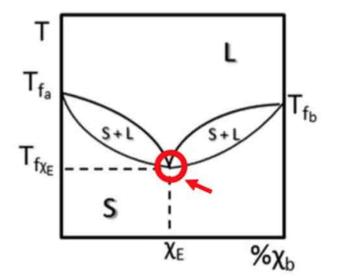




### Deep Eutectic Solvents (DES) as a greener alternative

- Cheap
- Low Toxicity
- Low Vapor Pressure
- Non flammable
- Tunable

- Derived from renewable sources
- Solvent can also act as catalyst
- Easy to Prepare wit 100% Atom Economy
- Recyclable\*



Main types of deep eutectic solvents (Smith et al., 2014).

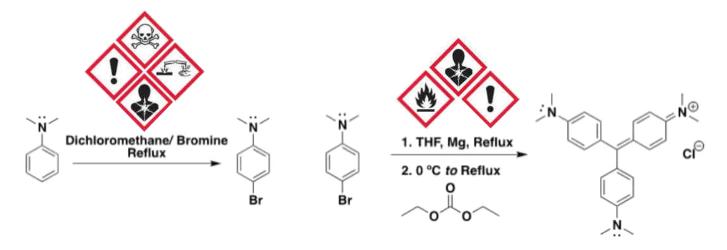
Type	Formula	Term
1	Cat <sup>+</sup> X <sup>-</sup> zMCl <sub>x</sub> <sup>-</sup>	M: Zn, Sn, Fe, Al, Ga, In
II	$Cat^{+}X^{-}zMCl_{x}\cdot yH_{2}O$	M: Cr, Co, Cu, Ni, Fe
III	$Cat^{+}X^{-}zRZ$	Z: CONH2, COOH, OH
IV	$MCl_x + RZ = MCl_{x-1}^+ \cdot RZ + MCl_{x+1}$	M: Al, Zn; Z: CONH2, OH

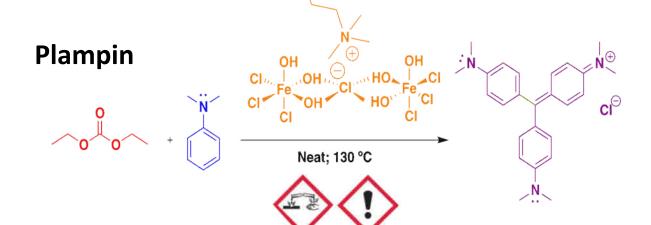




### DES based synthesis increases greenness and safety

#### **Taber**





HO







### Green metrics don't always scale simply

### **Bench level**

#### **Institutional level**

#### Reaction Yield

$$Yield = \frac{actual\ yield}{theoretical\ yield} \times 100\%$$
 ---

Avg.Yield(t)

#### Atom economy

$$A.E. = \frac{MW \ prod.}{MW \ all \ prod.} \times 100\%$$

## Inst. A. E. (t) = $\frac{\sum MW \ prod.}{\sum MW \ all \ prod.} \times 100\%$

#### Environmental factor

$$E factor = \frac{Total \ mass \ waste}{mass \ product}$$

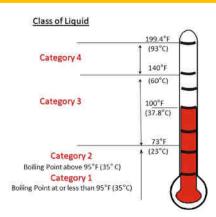
 $product \equiv waste$ 





### Safety metrics allow quantification of hazards and risk





Bench Safety Value = 
$$\frac{1}{\sum BRV}$$

### Bench Risk Value (flam)

$$BRV_{Flam} = (total\ mass)R_T$$

#### Bench Risk Rating (R)

$$R_{Haz} = \frac{1}{n_{Haz}} \qquad \qquad R_T = \sum R_{Haz}$$

 $n_{{\scriptscriptstyle Haz}}$ 



Institutional Safety Value = 
$$\frac{1}{\sum IHV}$$

#### Inst. Hazard Value (store

$$IHV_{storage} = (total\ mass)Q_{\mathrm{T}}$$

#### Inst. Hazard Facto

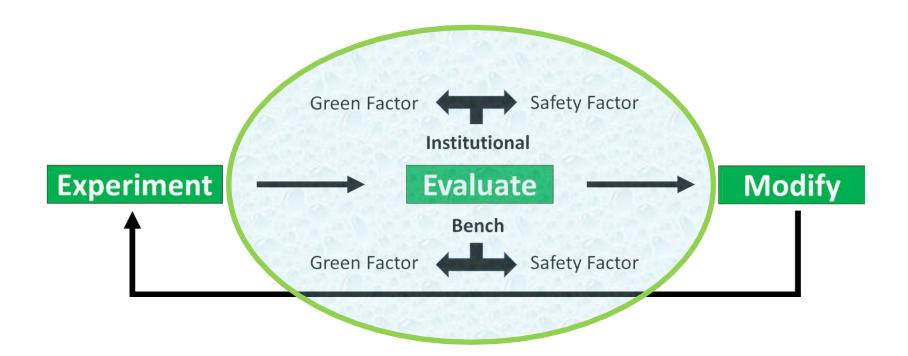
$$Q_{Haz} = rac{1}{m_{Haz}}$$
  $Q_T = \sum Q_{Haz}$ 

 $m_{{\scriptscriptstyle Haz}}$ 





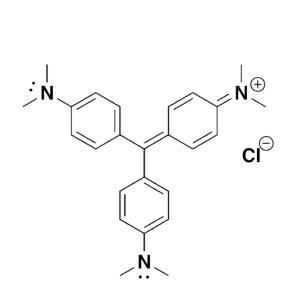
### Dynamic, iterative modification provides student ownership

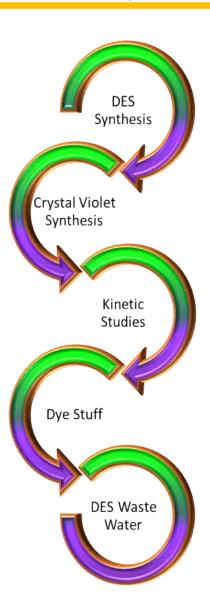






### Dealing with the atom economy and E-factor problem









#### Conclusion

- Ongoing partnership between Research Safety and faculty
- Connects green chemistry and safety as a function of scale
- Provides ownership to students through continuous iterations

Safety concepts and practices incorporated directly











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