

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 ECONOMY



Reduce level by 1 atoms f incorporated. Use at

## 7. USE OF RENEWABLE



Use when renewable rather t origina

## 3. LESS HAZARDOUS



Design syntheti possible. all substa react

## 4. DESIGNING S



Minir mol and e physical environn

## 5. SAFER SOLVENT

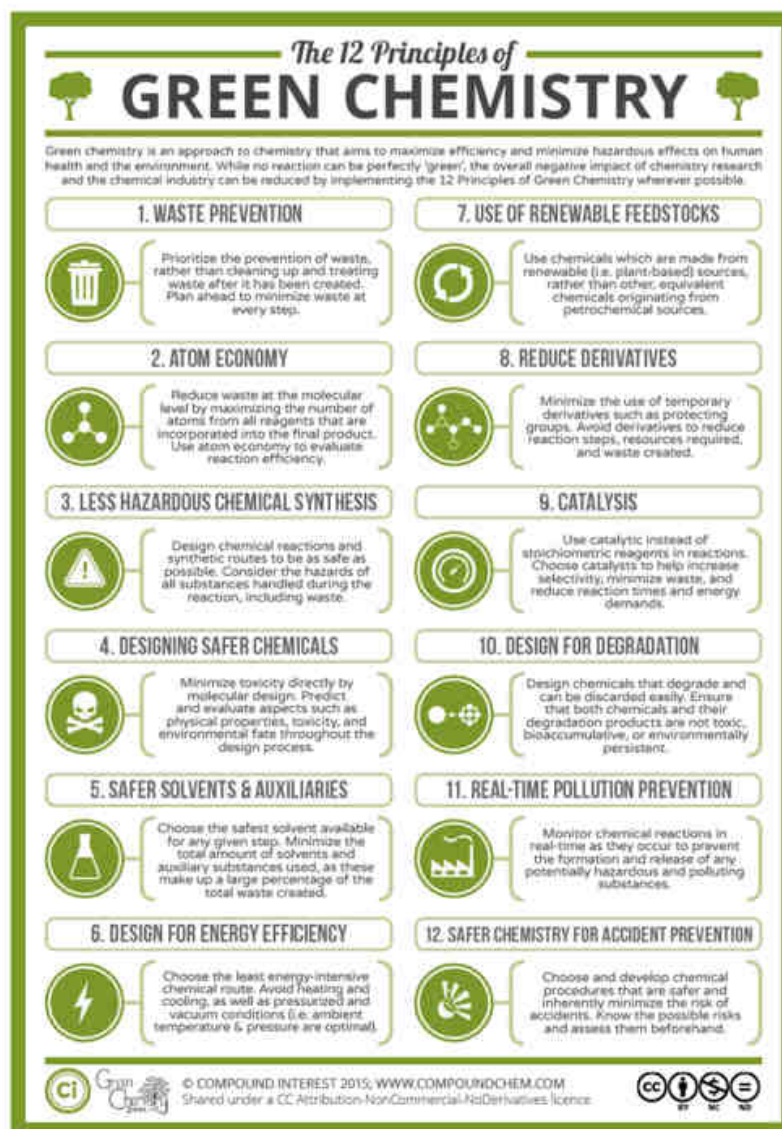


Choose 1 for any total: auxiliary make up t

## 8. REDUCE



Minimi derivat groups. A reaction: a



## EVENTION

he prevention of waste, cleaning up and treating tr it has been created. d to minimize waste at every step.

## ACCIDENT PREVENTION

and develop chemical res that are safer and ly minimize the risk of. Know the possible risks ass them beforehand.

## DEGRADATION

nicals that degrade and icarded easily. Ensure i chemicals and their i products are not toxic, tive, or environmentally persistent.

## TION PREVENTION

hemical reactions in they occur to prevent ion and release of any azardous and polluting substances.

## LYSIS

atalytic instead of ic reagents in reactions. alysts to help increas e, minimize waste, and ction times and energy demands.

## RGY EFFICIENCY

i least energy-intensive ute. Avoid heating and well as pressurized and nditions (i.e. ambient & pressure are optimal).



# 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



**Education**



**Safety**



**Environmental  
stewardship**

# 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



**TARGET AUDIENCE**



**THE CHEMICAL  
ENGINEERING  
MAJOR**



Chemistry vs Chemical Engineering


Cl\_n-C6H4-C(CH3)2-C6H4-Cl\_m



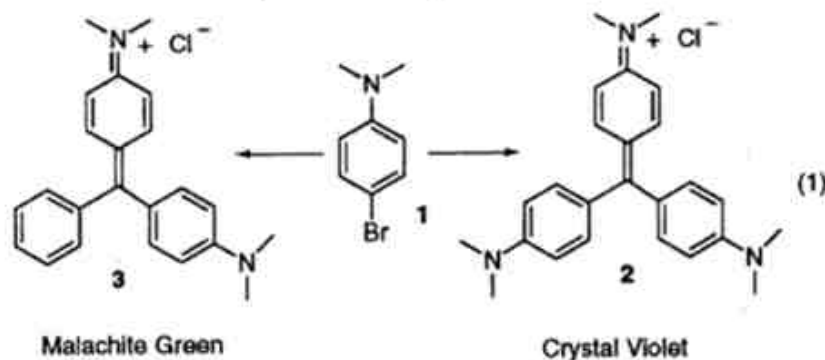


IF YOU WANT TO KNOW WHAT COLOR IS FASHIONABLE THIS SEASON  
**JUST LOOK AT THIS RIVER**  
 - A POPULAR SAYING IN THE ZHEJIANG QIANTANG RIVER AREA OF CHINA -

# Crystal violet synthesis is our “product”

## A Colorful Grignard Reaction

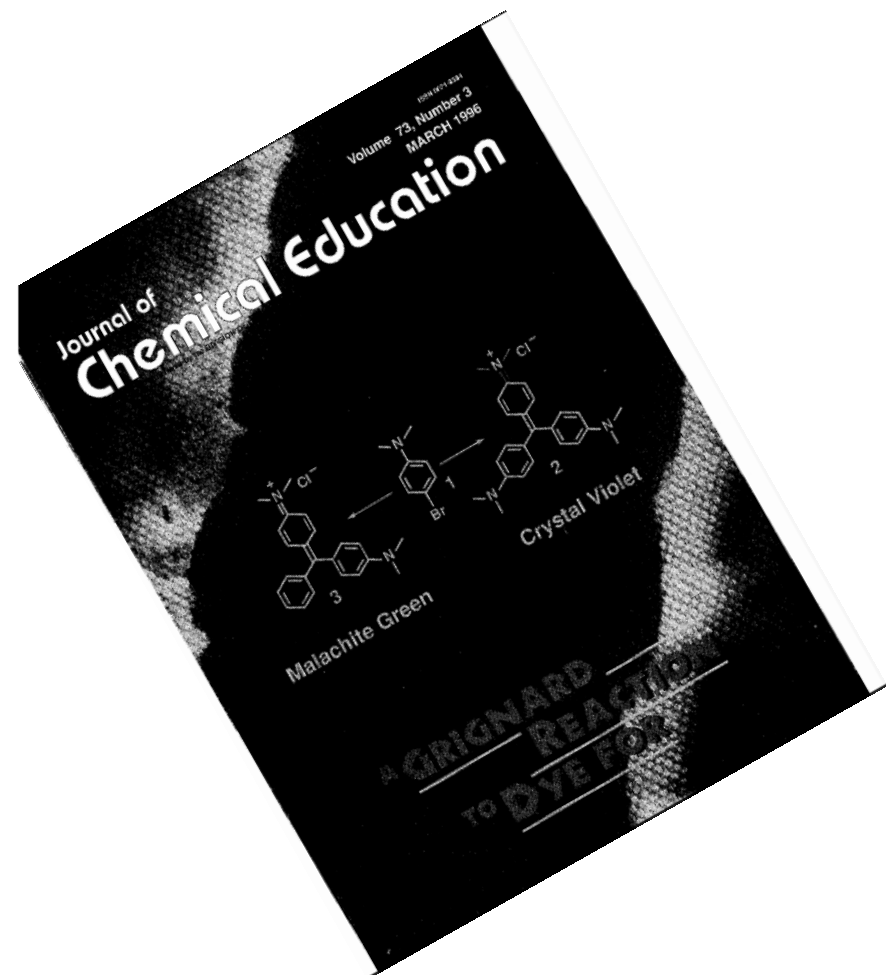
Preparation of the Triarylmethane Dyes from 4-Bromo-*N,N*-Dimethylaniline



Douglass F. Taber,<sup>1</sup> Robert P. Meagley, and Danielle Supplee

University of Delaware, Newark, DE 19716

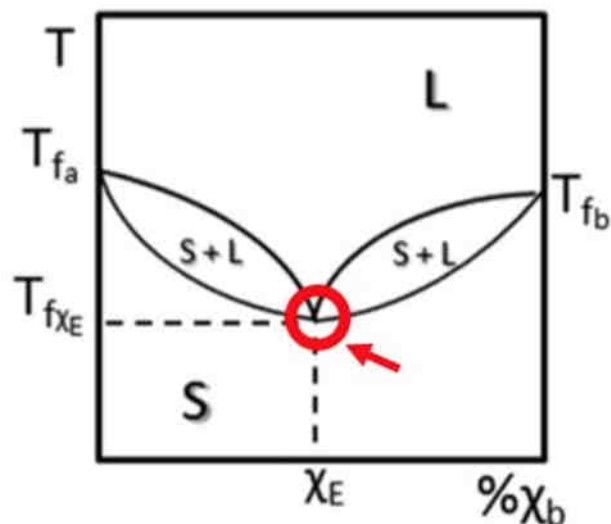
Volume 73 Number 3 March 1996 259





# 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 with 100% Atom Economy
- Recyclable\*



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

Type	Formula	Term
I	$\text{Cat}^+ \text{X}^- z \text{MCl}_x^-$	M: Zn, Sn, Fe, Al, Ga, In
II	$\text{Cat}^+ \text{X}^- z \text{MCl}_x \cdot y \text{H}_2\text{O}$	M: Cr, Co, Cu, Ni, Fe
III	$\text{Cat}^+ \text{X}^- z \text{RZ}$	Z: $\text{CONH}_2$ , $\text{COOH}$ , $\text{OH}$
IV	$\text{MCl}_x + \text{RZ} = \text{MCl}_{x-1}^+ \cdot \text{RZ} + \text{MCl}_{x+1}$	M: Al, Zn; Z: $\text{CONH}_2$ , $\text{OH}$

# Taber



# Green metrics don't always scale simply

## Bench level

### *Reaction Yield*

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

### *Atom economy*

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

### *Environmental factor*

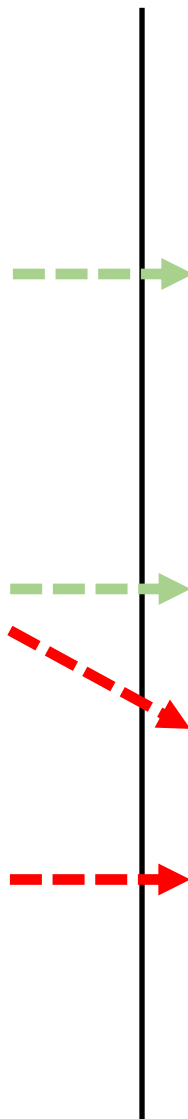
$$E \text{ factor} = \frac{\text{Total mass waste}}{\text{mass product}}$$

## Institutional level

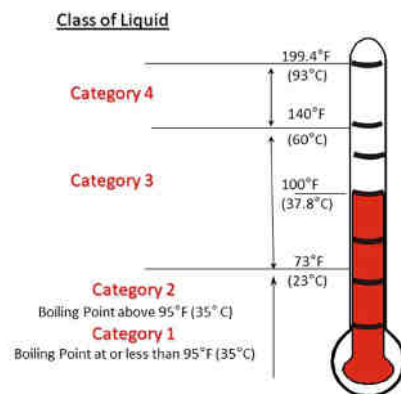
*Avg. Yield (t)*

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

*product  $\equiv$  waste*



# Safety metrics allow quantification of hazards and risk



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

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

**Bench Risk Value (flamm)**

$$R_T(\text{total mass}) = \sum_{\text{flamm}} BRV$$

**Bench Risk Rating (R)**

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

$n_{Haz}$

**Inst. Hazard Value (storage)**

$$Q_T(\text{total mass}) = \sum_{\text{storage}} VHI$$

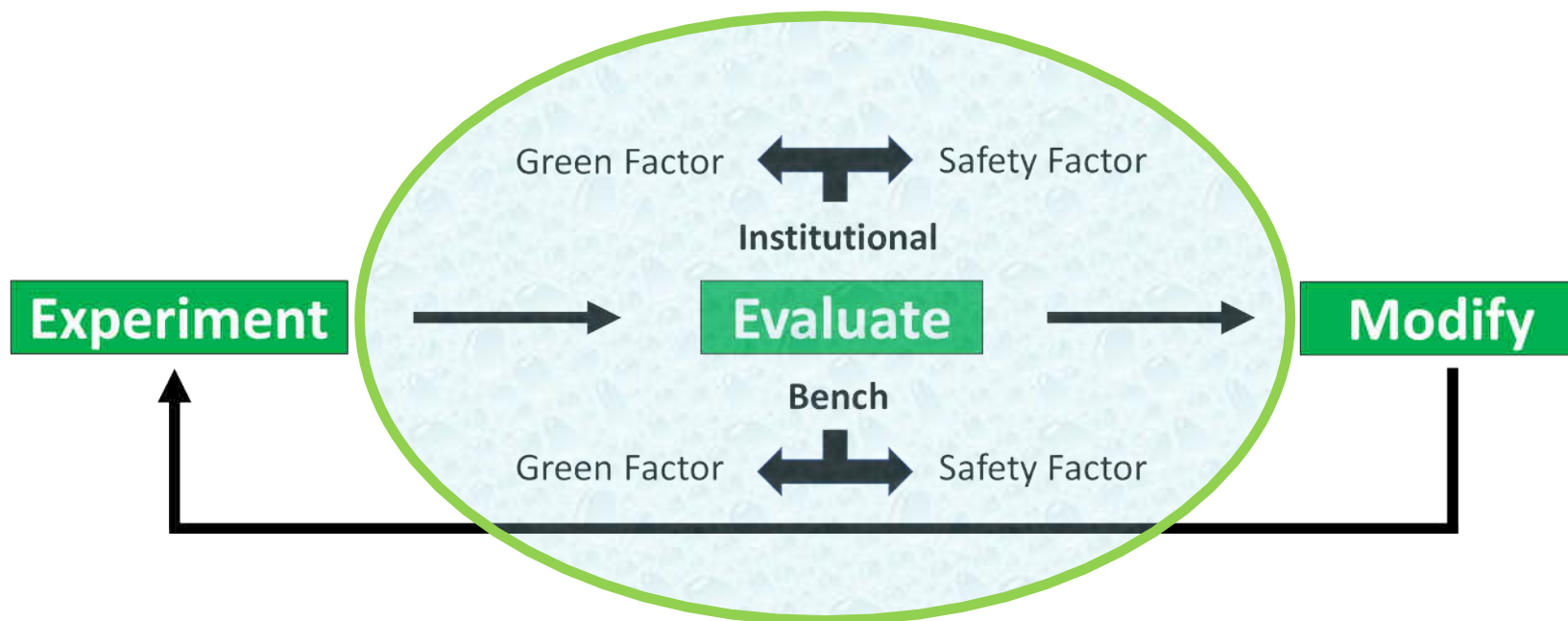
**Inst. Hazard Factor**

$$Q_{Haz} = \frac{1}{m_{Haz}} \quad Q_T = \sum Q_{Haz}$$

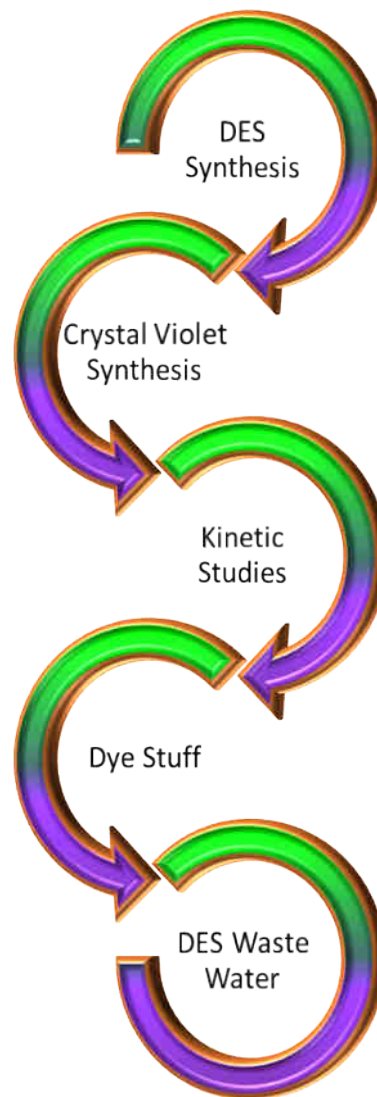
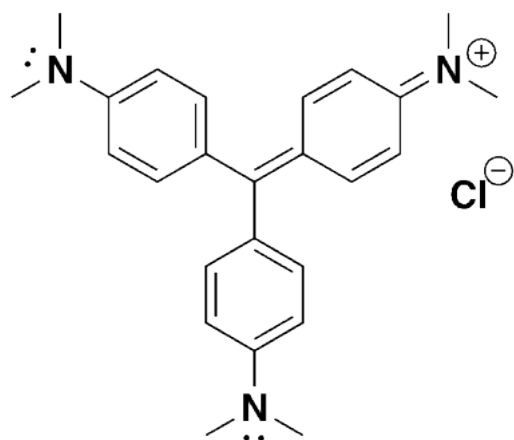
$m_{Haz}$



# 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



Education



Safety



Environmental  
stewardship

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# CLEMSON<sup>®</sup>

U N I V E R S I T Y



# SCIENCE

LOCALLY RELEVANT GLOBALLY IMPACTFUL