

The 12 Principles of Green Chemistry



IGSS'09

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Science*

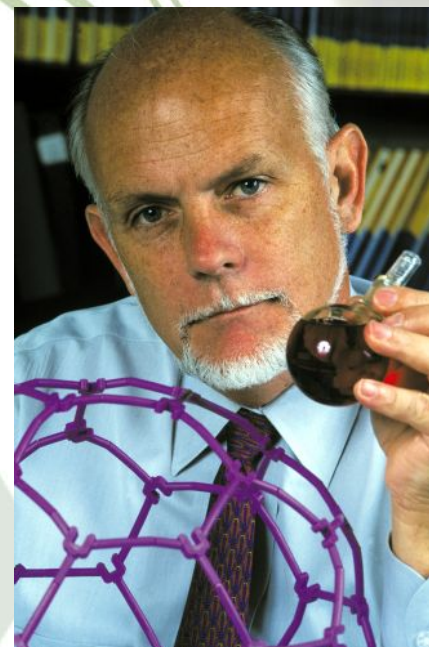
June 29th-July 31st , 2009

Smalley's Top Ten World Problems for next 50 years



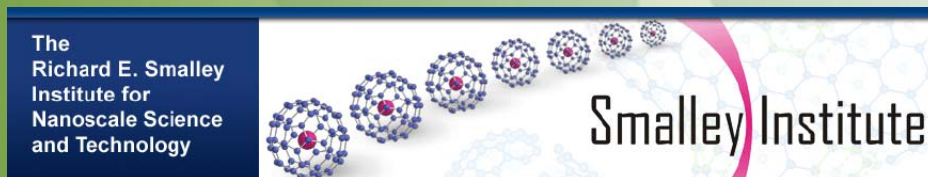
1. ENERGY
2. WATER
3. FOOD
4. ENVIRONMENT
5. POVERTY
6. TERRORISM & WAR
7. DISEASE
8. EDUCATION
9. DEMOCRACY
10. POPULATION

Bold = Green chemistry enabled



"Be a scientist, save the world."

Richard E. Smalley (1943-2005).
Rice University
Nobel Prize in Chemistry in 1996 (buckminsterfullerenes)



<http://cnst.rice.edu/content.aspx?id=246>

How do we practice "green" chemistry?



Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products

Hazard is acknowledged as another important property of matter.

- We must learn to recognize and understand hazards!
- Working knowledge of toxicology

The emphasis is on eliminating hazard rather than just preventing exposure.

- This starts with the chemical choices we make.

Green chemistry must be the best chemistry!!

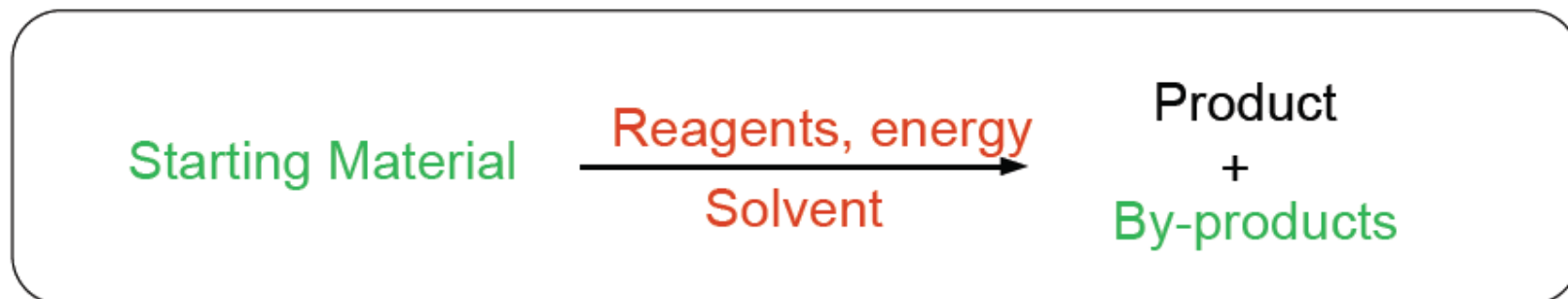
- Practical and economically-driven

Green chemistry challenges



- **Processing:** Rapid, high yield transformations at room temperature
 - catalysis or self-assembly
- **Design:** Better understanding of how molecular structure dictates desirable and undesirable properties
 - Structure-Activity Relationships (SARs)
 - Hazardless, completely recyclable products
- **Feedstock:** “Waste” or renewable resources as raw materials
- **Decision-making tools:** Metrics for comparing competing “greener” technologies w/r/t greenness, economics, etc.

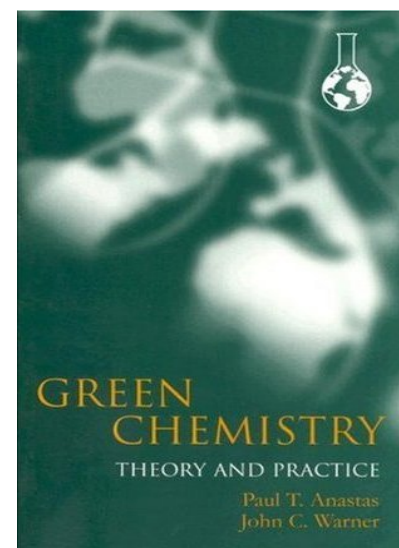
The 12 principles of green chemistry



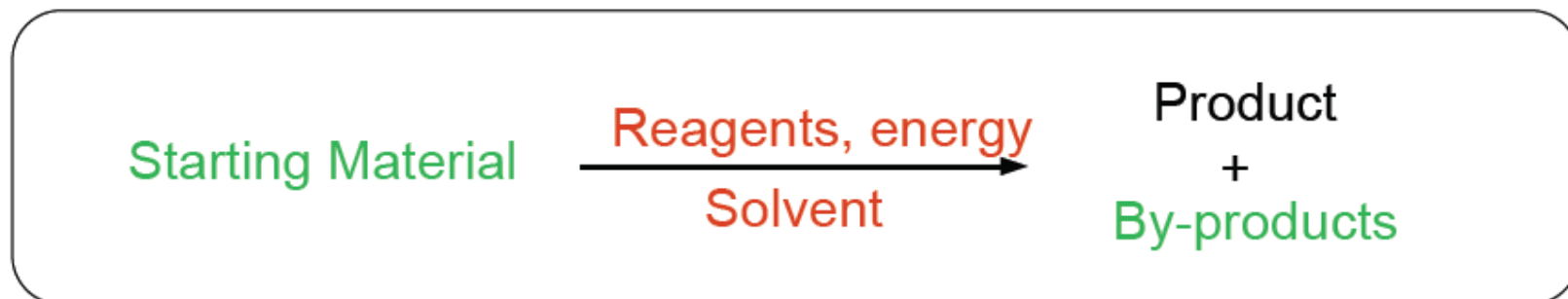
#1: Prevent, rather than treat, waste



Green Chemistry: Theory and Practice
Anastas and Warner, 1998



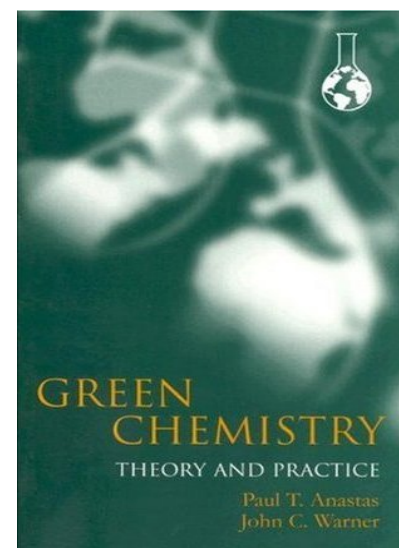
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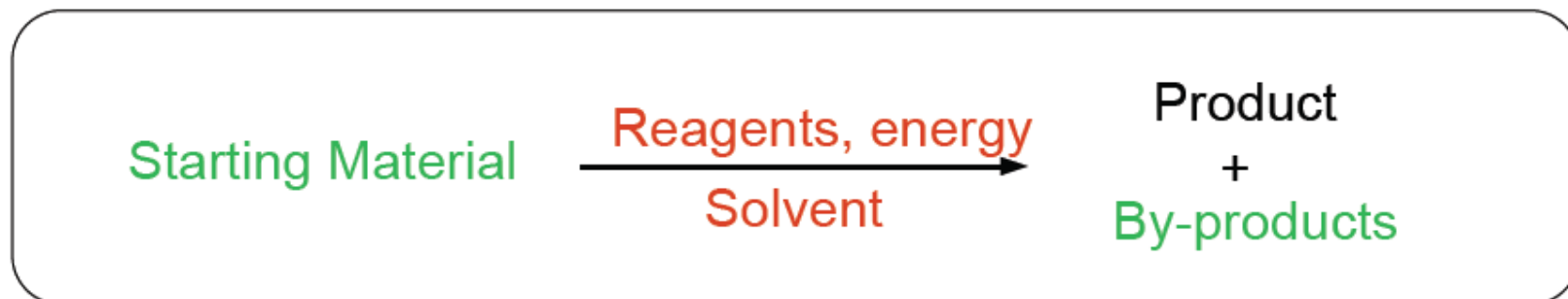
#2: Maximize use of materials – atom economy



Green Chemistry: Theory and Practice
Anastas and Warner, 1998



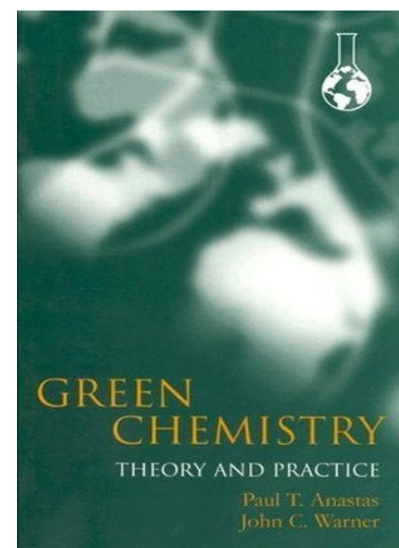
The 12 principles of green chemistry



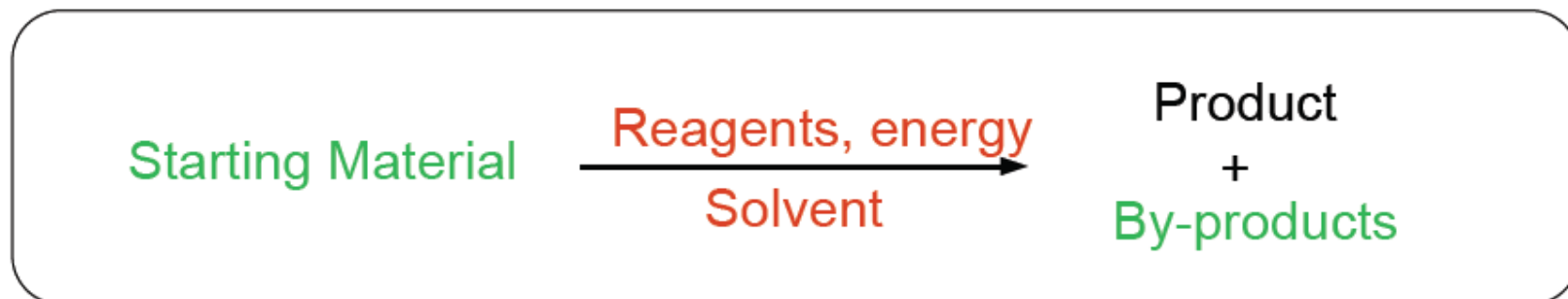
#3: Avoid hazardous materials (reagents, starting materials and solvents) and products or by-products



Green Chemistry: Theory and Practice
Anastas and Warner, 1998



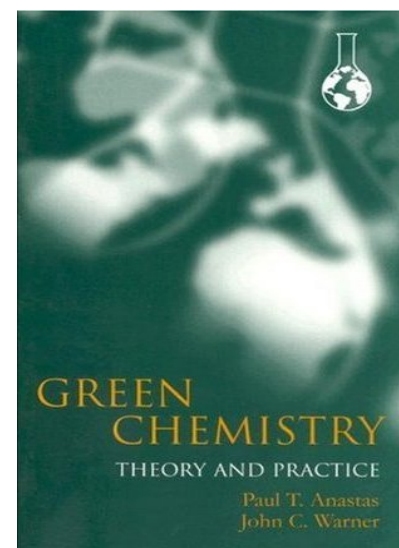
The 12 principles of green chemistry



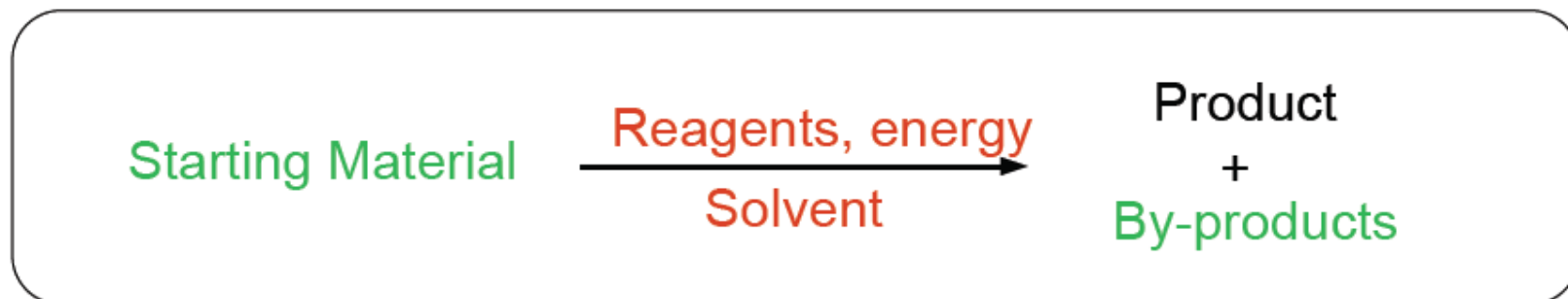
**#4: Design safer products:
design in efficacy
design out hazards**



Green Chemistry: Theory and Practice
Anastas and Warner, 1998



The 12 principles of green chemistry

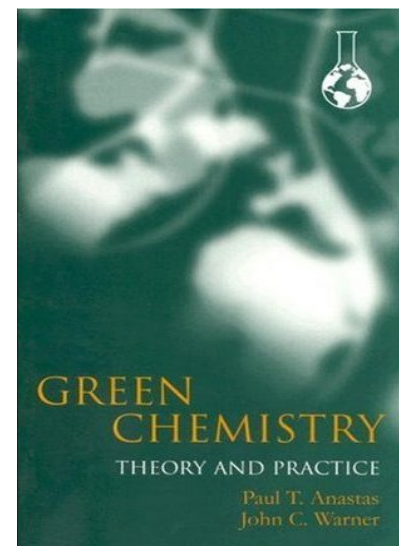


#5: Minimize the use of solvents and auxiliary substances

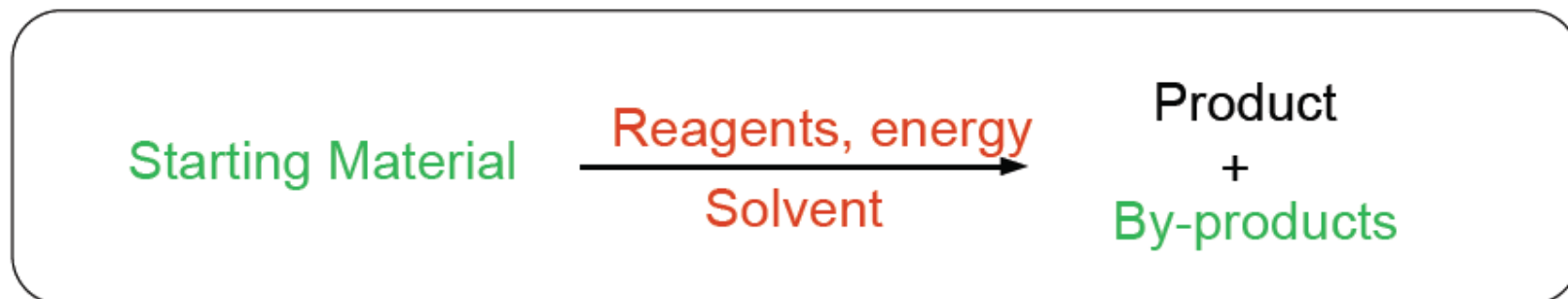
#6: Recognize energy costs and minimize them



Green Chemistry: Theory and Practice
Anastas and Warner, 1998



The 12 principles of green chemistry



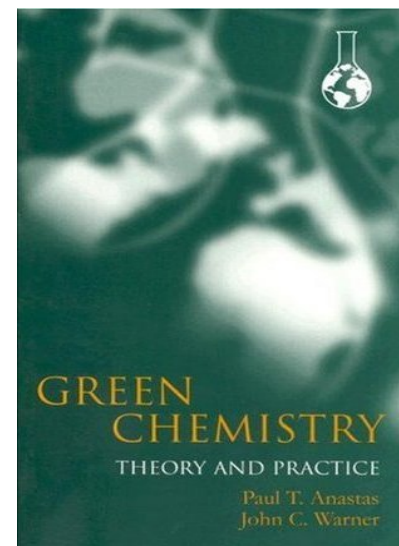
#7: Use renewable feedstock

#8: Omit needless steps - protection/deprotection, e.g.

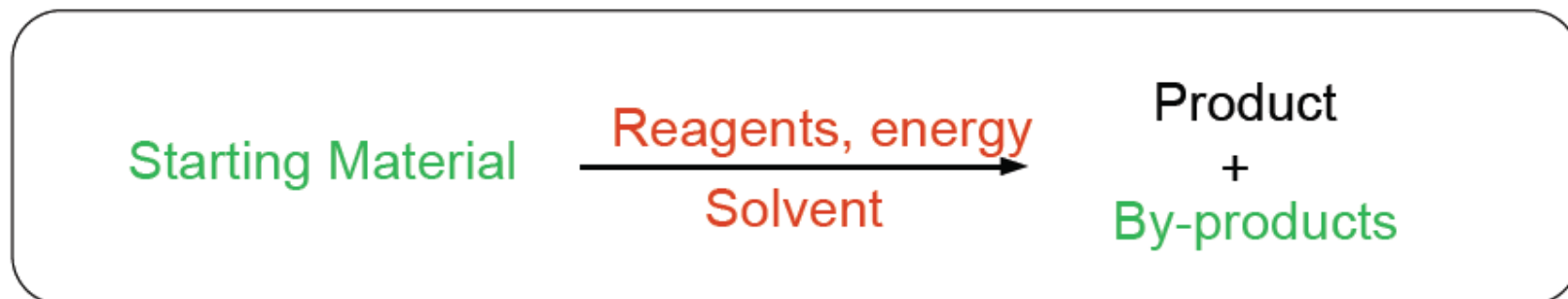
#9: Use catalysis!



Green Chemistry: Theory and Practice
Anastas and Warner, 1998



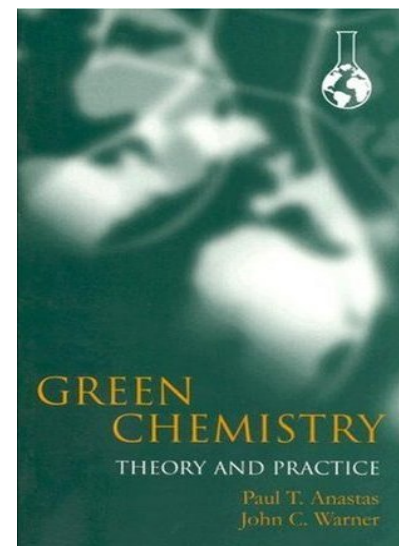
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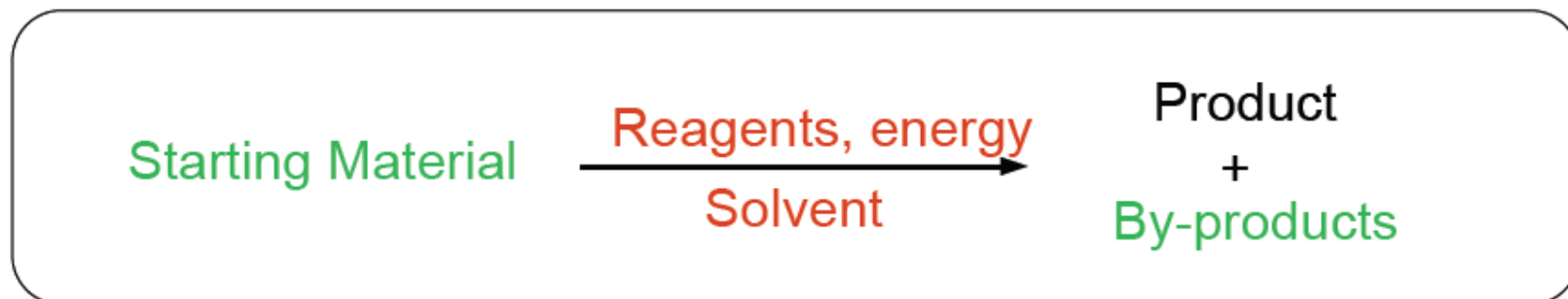
#10: Design products for end of life:
products should not be persistent in the environment, should degrade into innocuous substances



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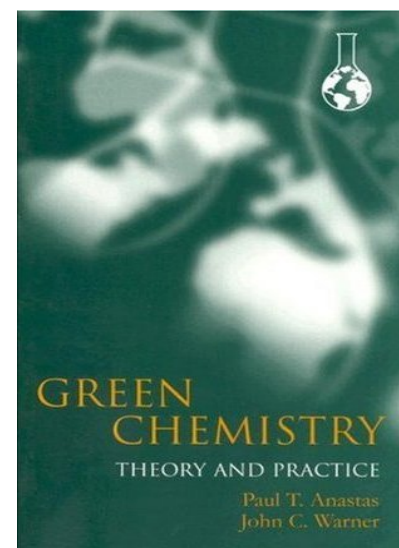
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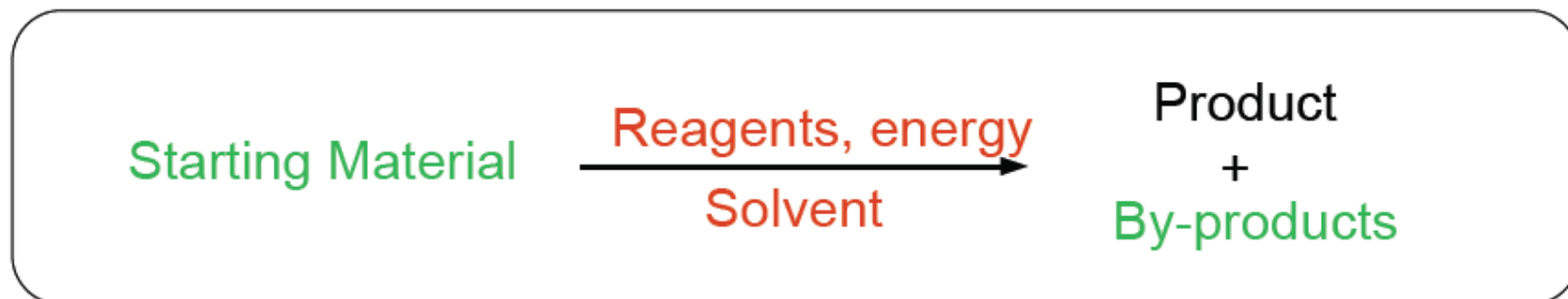
#11: Employ in-line, real-time monitoring/control to avoid generation of hazardous substances in transformations



Green Chemistry: Theory and Practice
Anastas and Warner, 1998



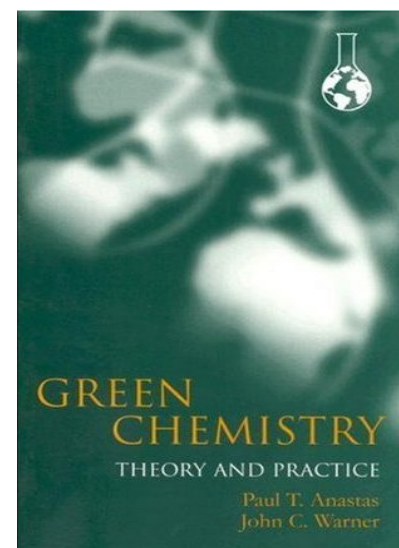
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#12: Whenever possible choose substances that minimize physical danger (explosions, fires, etc.)



Green Chemistry: Theory and Practice
Anastas and Warner, 1998





Principle 1

**It is better to prevent waste than to treat
or clean up waste after it is formed**

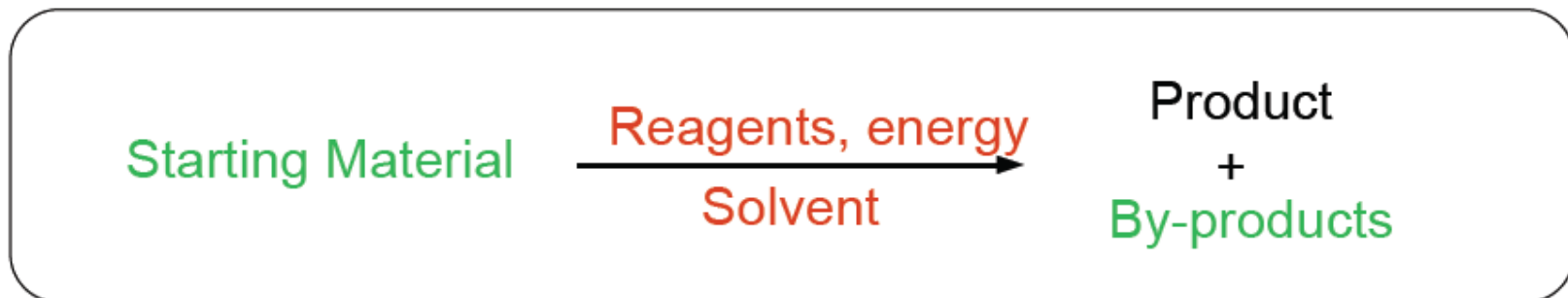






Principle 2

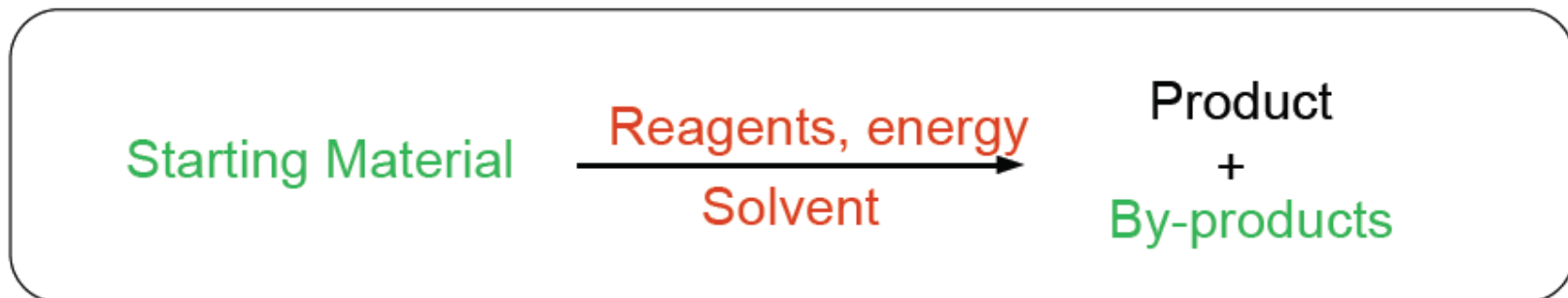
Synthetic methods should maximize the incorporation of all materials used into the final product - Atom Economy



Consider the following reaction types:

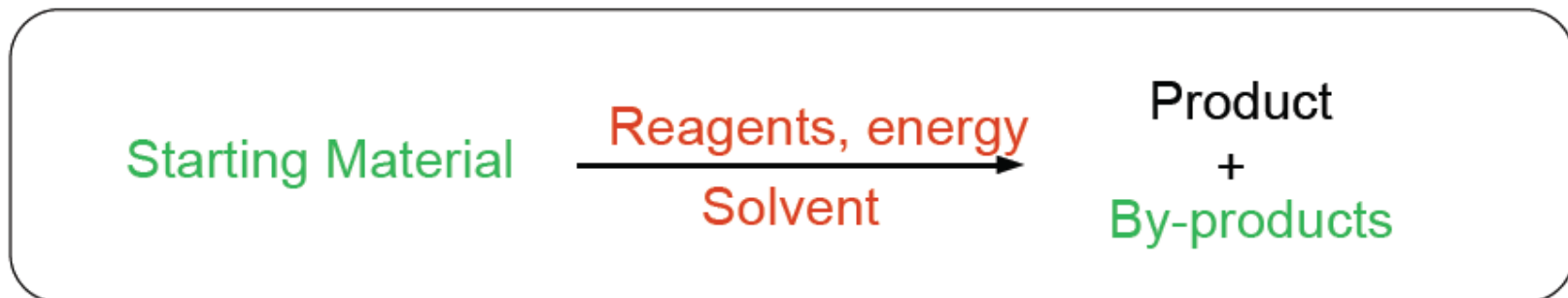
Substitution
Addition
Elimination
Rearrangements

In which reaction types do you lose atoms?



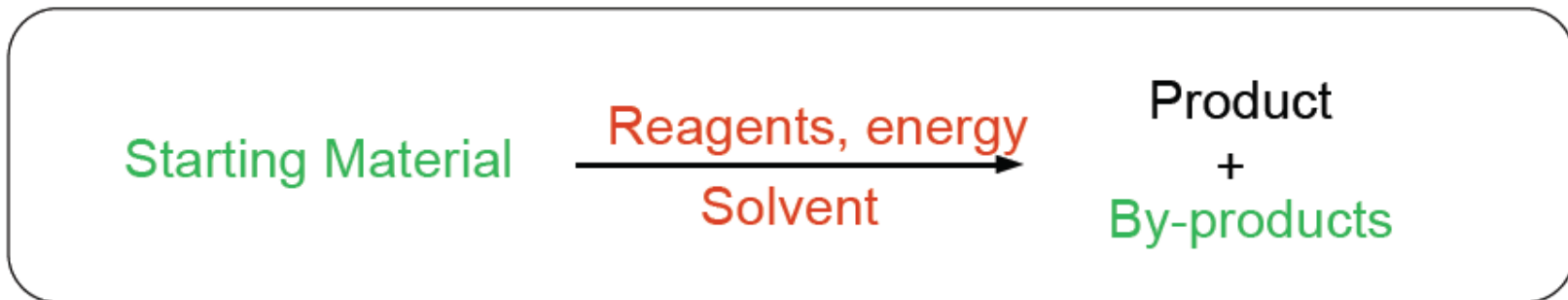
What is percent yield?

What does it measure?

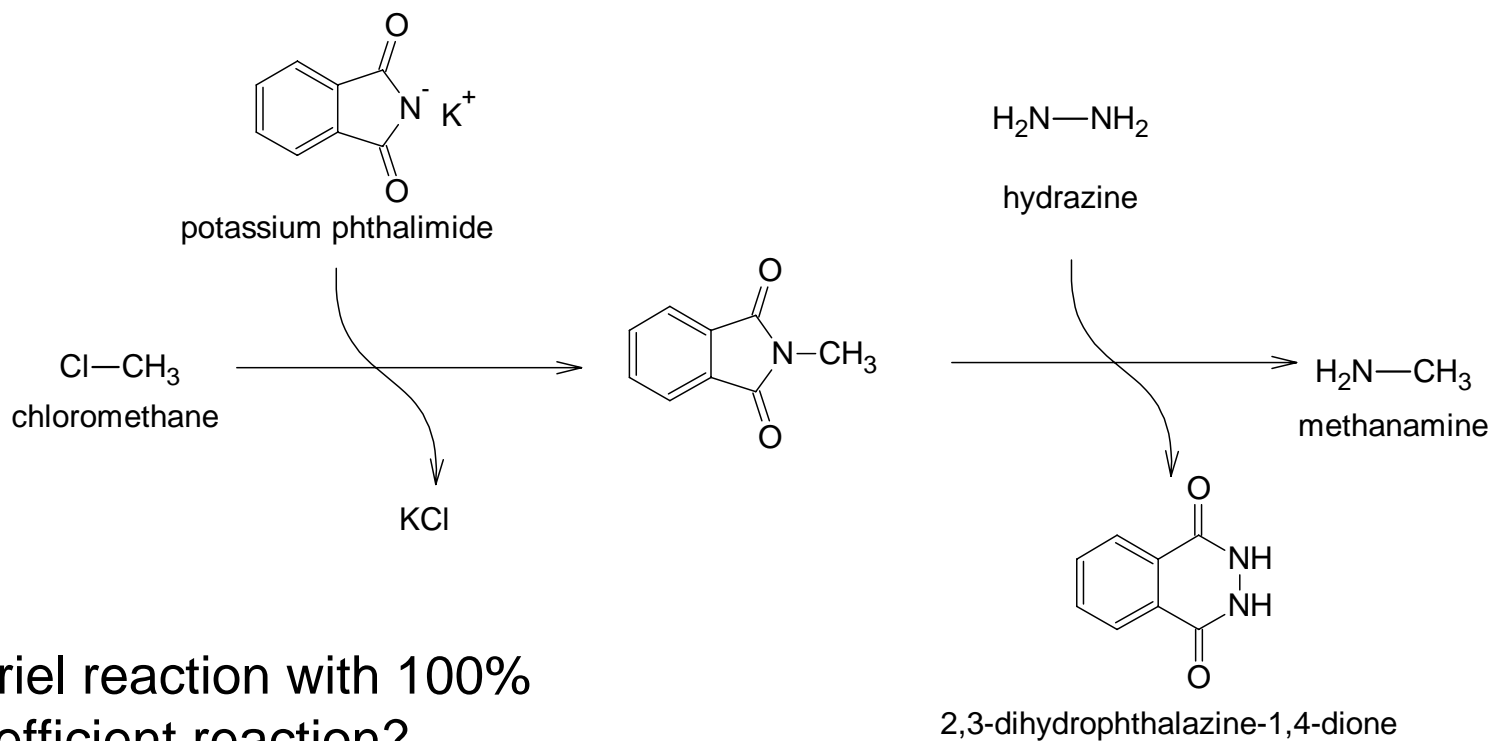


$$\text{Percent yield} = (\text{moles}_{\text{product obtained}} / \text{moles}_{\text{product possible}}) \times 100\%$$

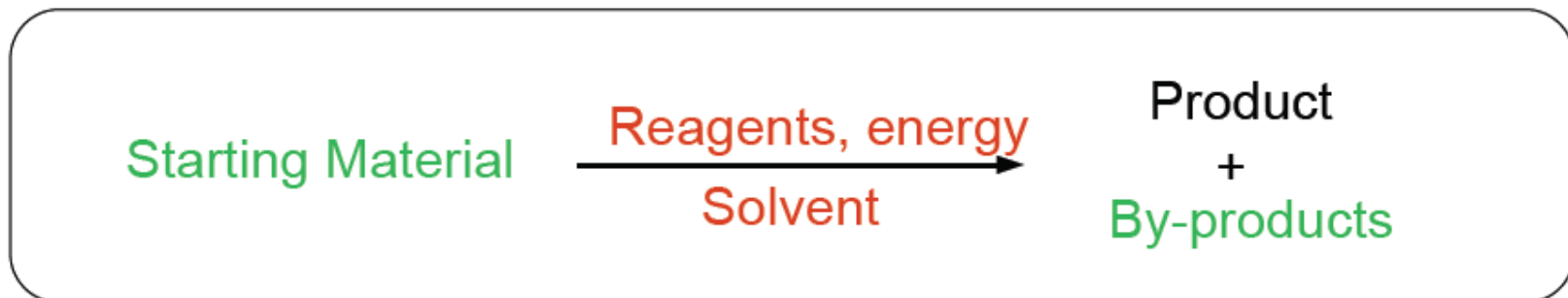
% yield is a measure of selectivity



$$\text{Percent yield} = \left(\frac{\text{moles}_{\text{product obtained}}}{\text{moles}_{\text{product possible}}} \right) \times 100\%$$

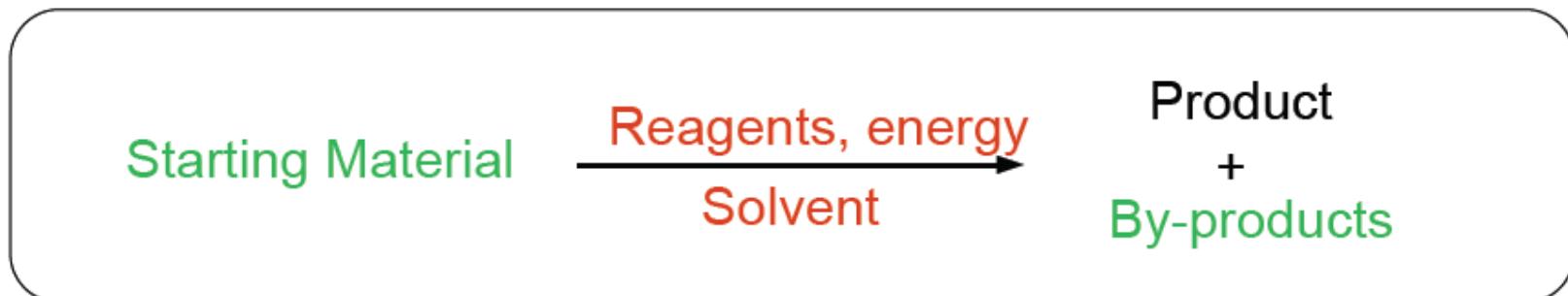


Is a Gabriel reaction with 100% yield an efficient reaction?



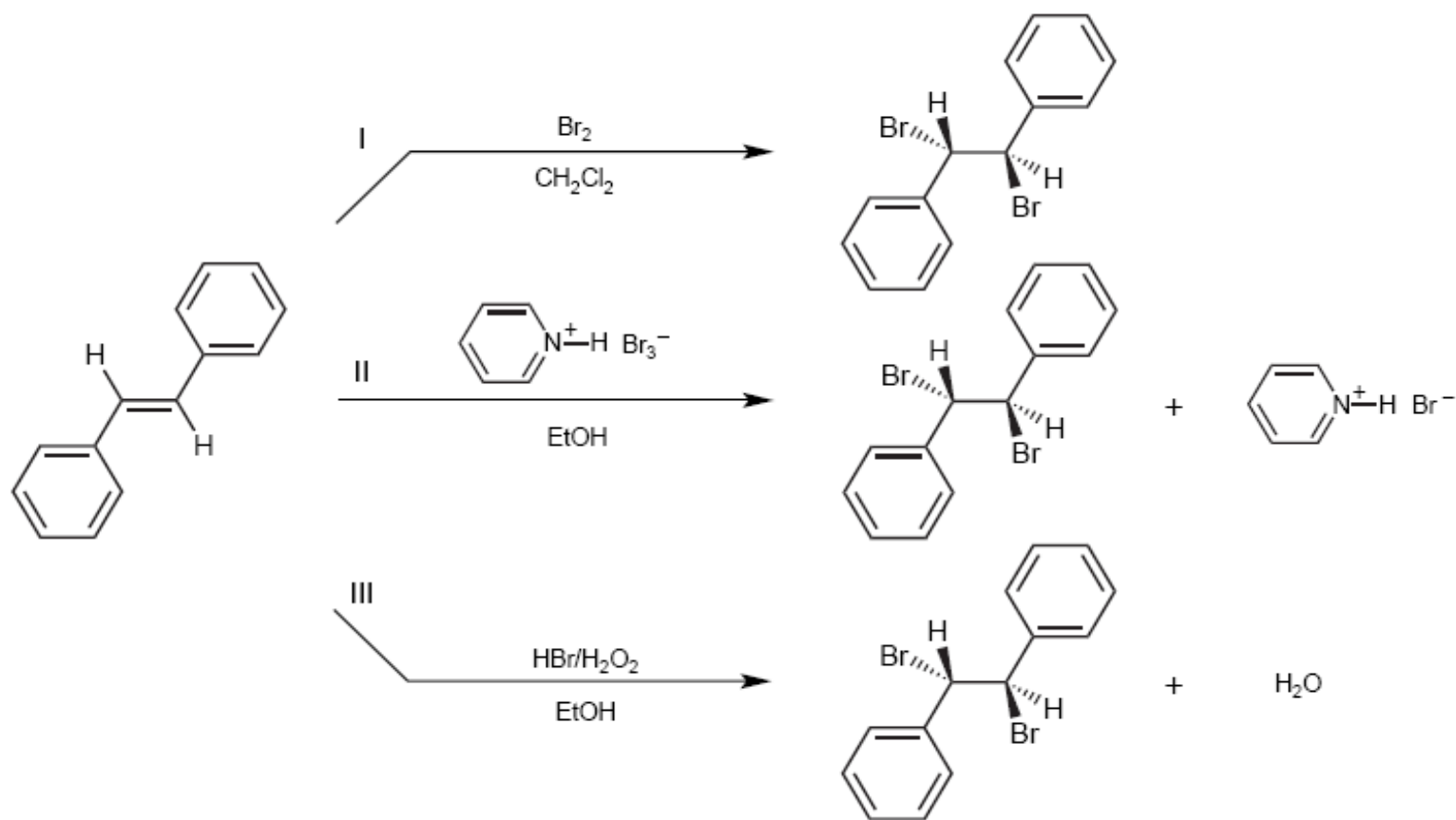
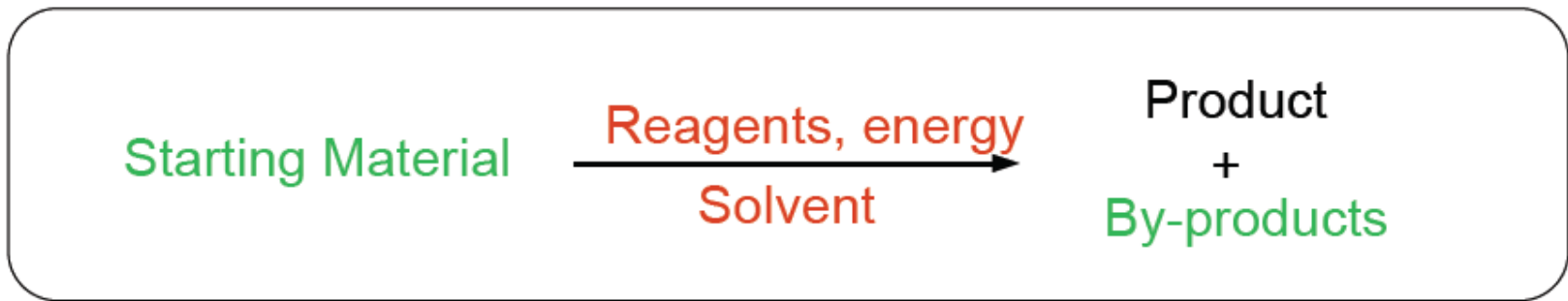
What is atom economy?

What does it measure?

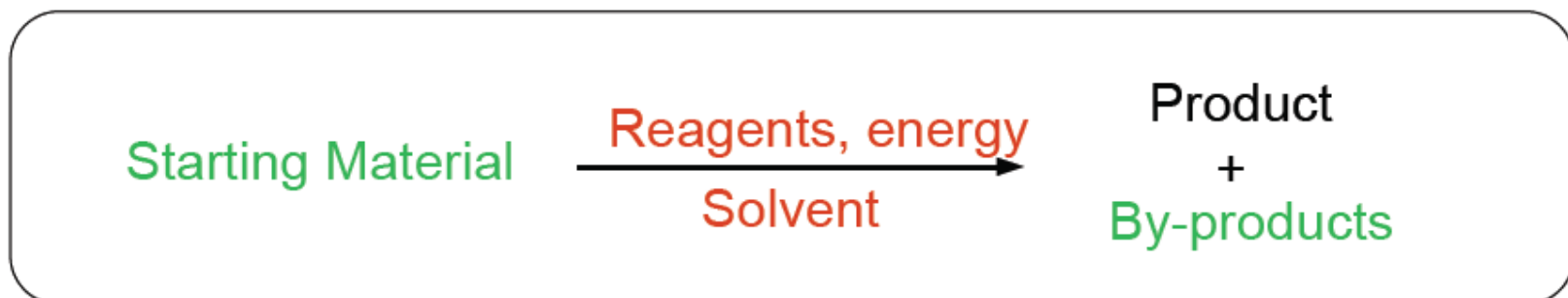


$$\text{Atom economy} = \left(\text{MW}_{\text{desired product}} / \sum \text{MW}_{\text{reagents}} \right) \times 100\%$$

a measure of intrinsic efficiency



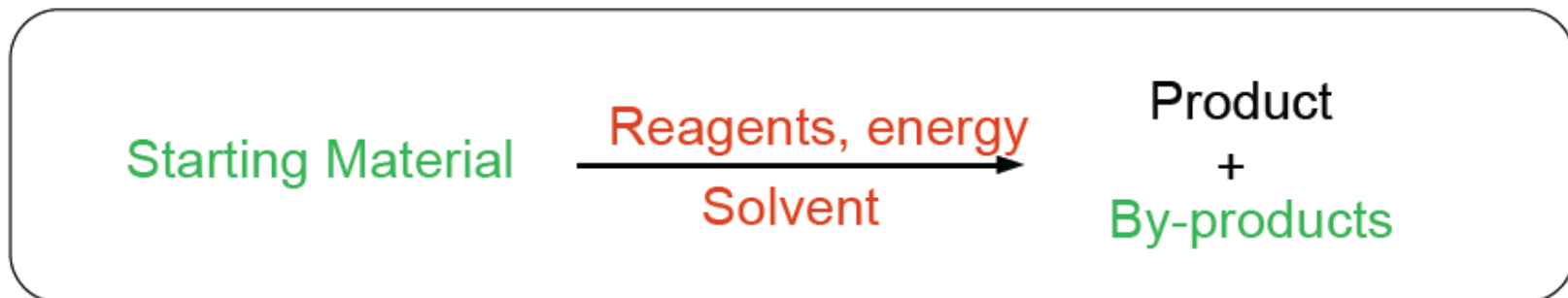
McKenzie, L. C.; Huffman, L. M.; Hutchison, J. E. The Evolution of a Green Chemistry Laboratory Experiment: Greener Brominations of Stilbene. *J. Chem. Ed.* **2005**, 82, 306-310



Do we ever deviate from ideal stoichiometry when performing a reaction?

Why?

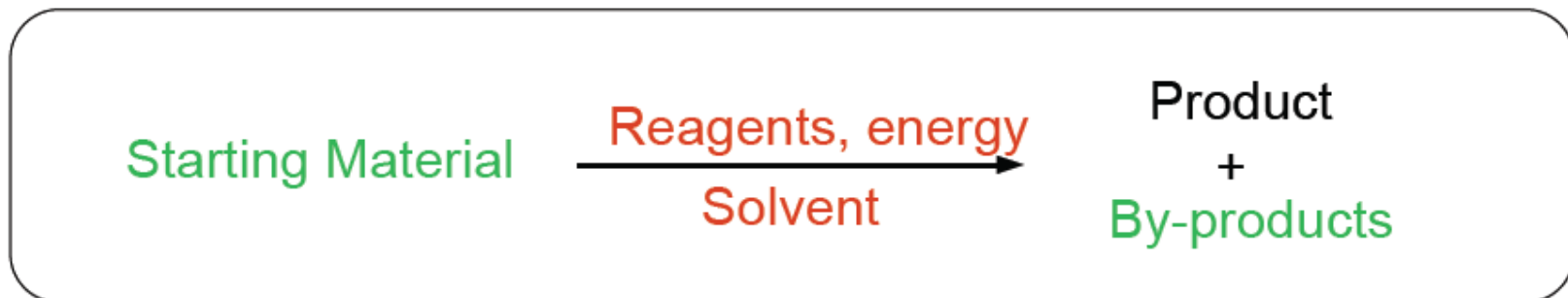
What happens to excess reagents?



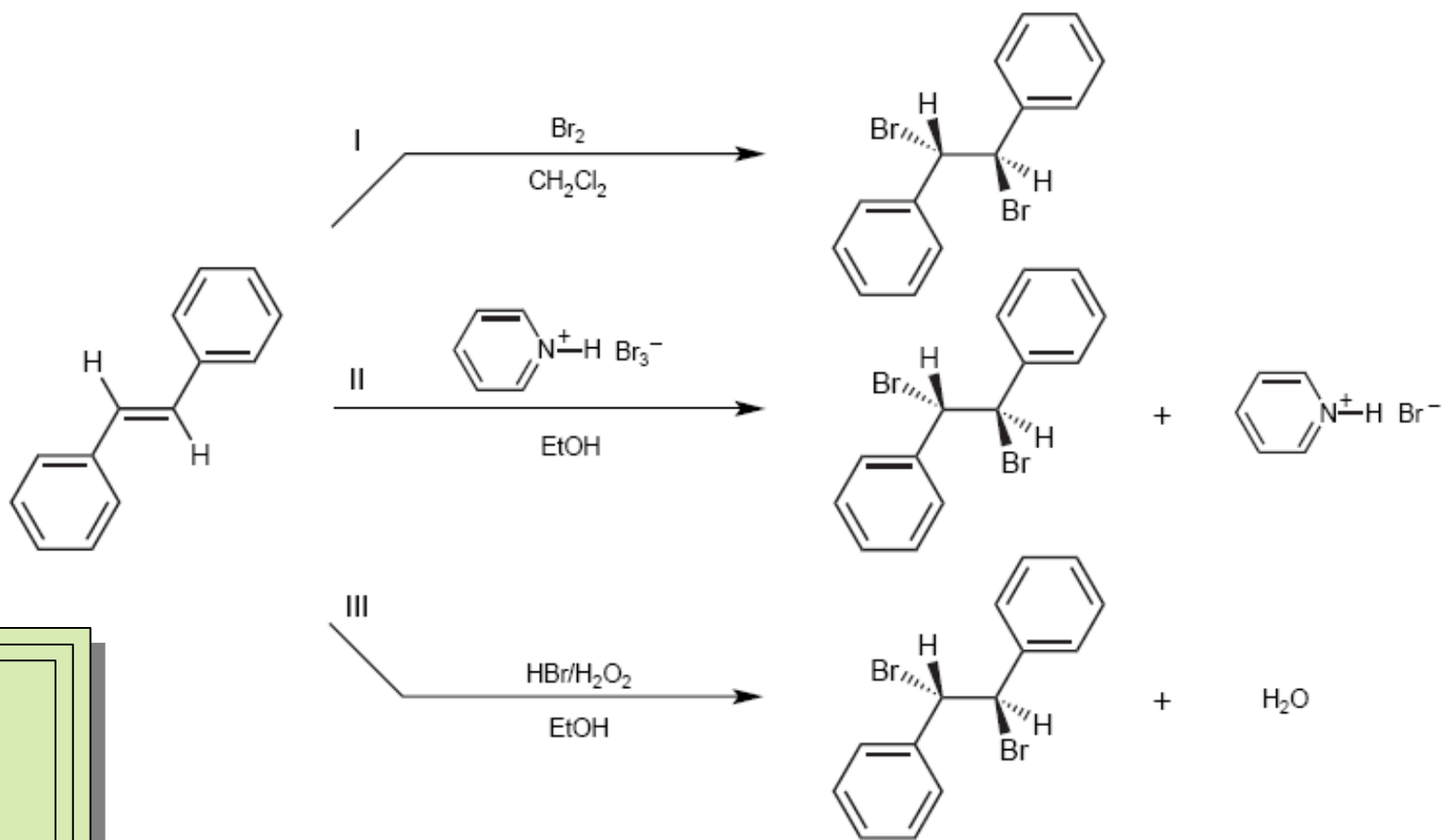
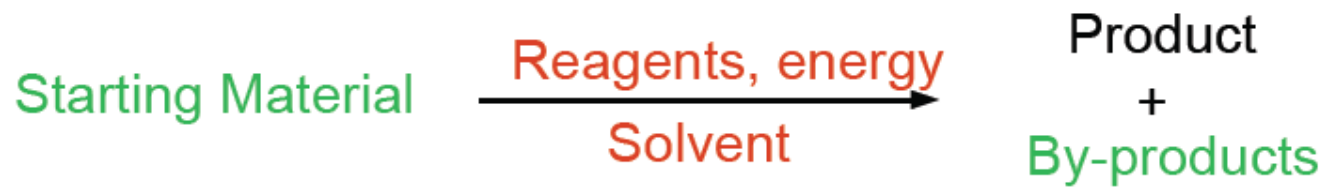
A realistic assessment of the efficiency of a reaction must address:
percent yield (a measure of selectivity)
atom economy (a measure of intrinsic efficiency)
deviations from ideal stoichiometry (a measure of the actual efficiency)

We can easily do that by comparing the mass we put into the reaction to the mass of product we obtain.

$$\text{Effective mass yield} = (\text{mass}_{\text{desired product}} / \sum \text{mass}_{\text{reagents}}) \times 100\%$$



What other aspects of a chemical reaction have we not considered?



Take
a 2nd
look

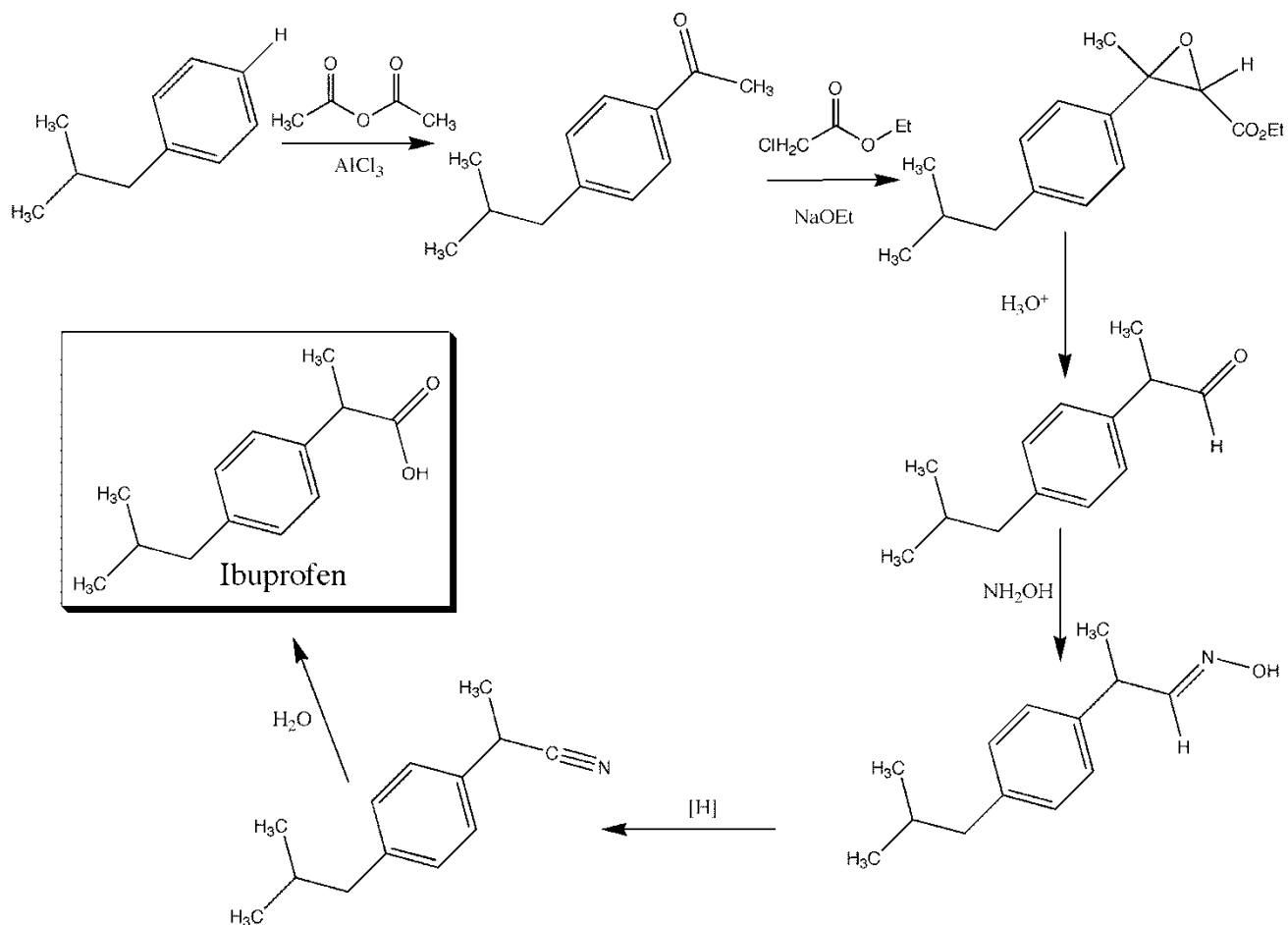


Principle 2

Synthetic methods should maximize the incorporation of all materials used into the final product - Atom Economy

One more example:

The Boots Company synthesis of Ibuprofen

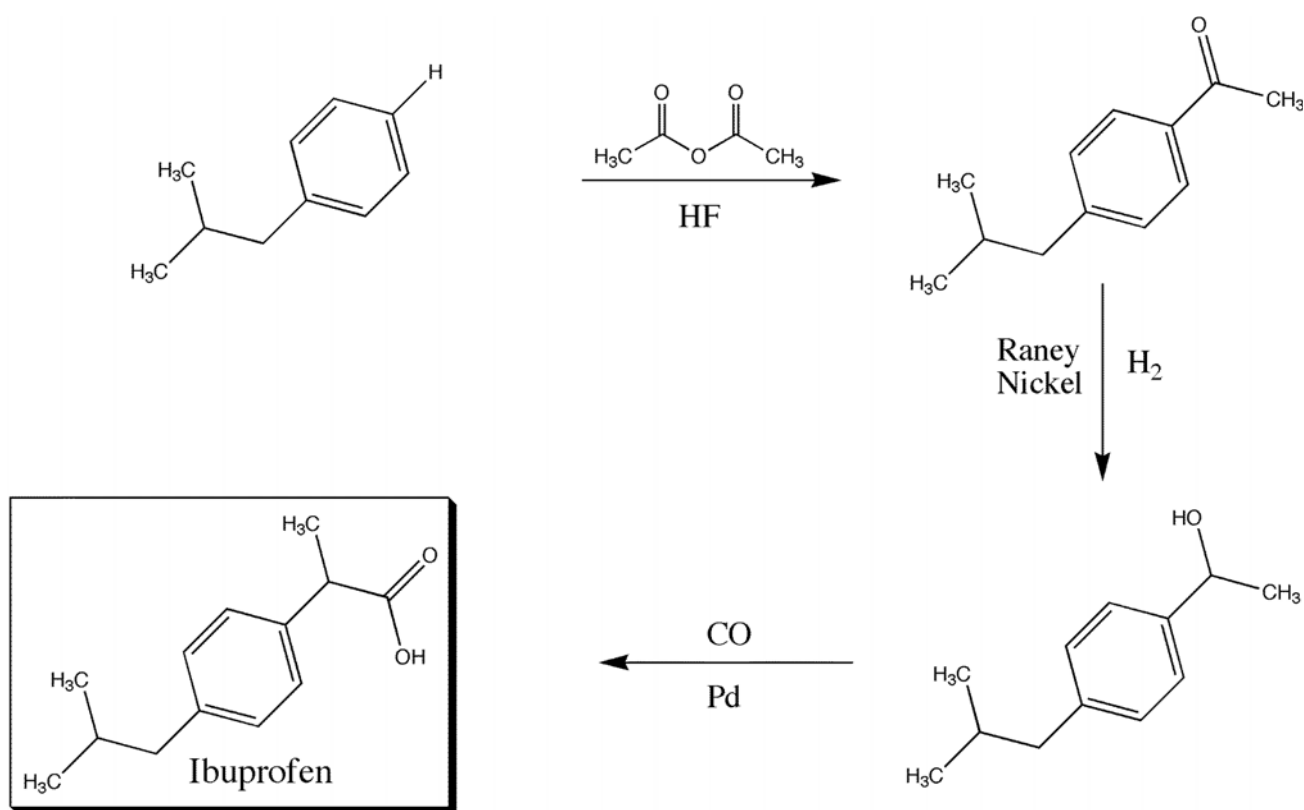


Production of 2 bottles of Ibuprofen generates 3 bottles of waste!

Principle 2: Atom economy



The BHC synthesis of Ibuprofen



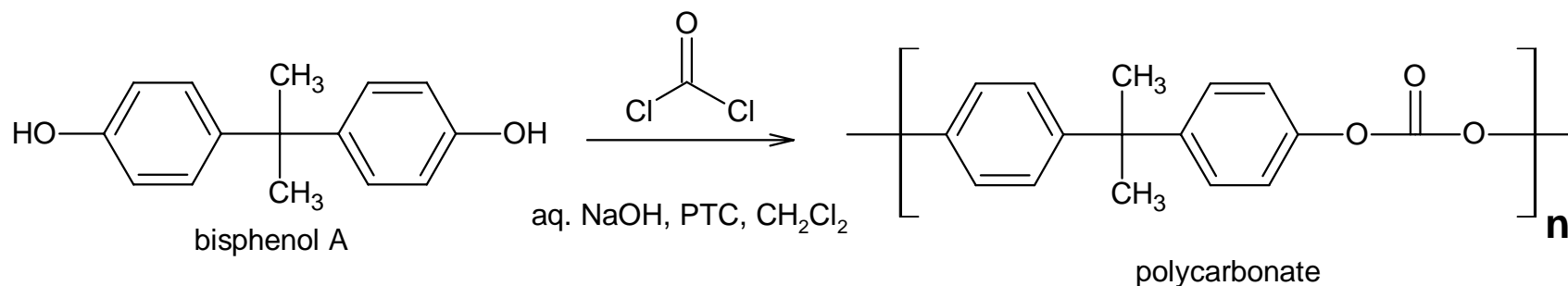
3 bottles of Ibuprofen generates less than one bottle of waste

Principle 3

Synthetic methods should use and generate substances that possess little or no toxicity to human health and the environment.

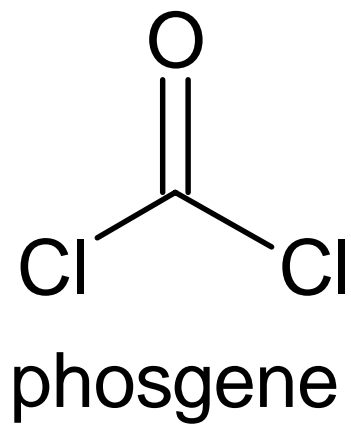


Polycarbonate synthesis: Phosgene process



Issues:

- phosgene is toxic, corrosive (classified as a WMD)
- requires large amount of CH₂Cl₂
- polycarbonate contaminated with Cl impurities

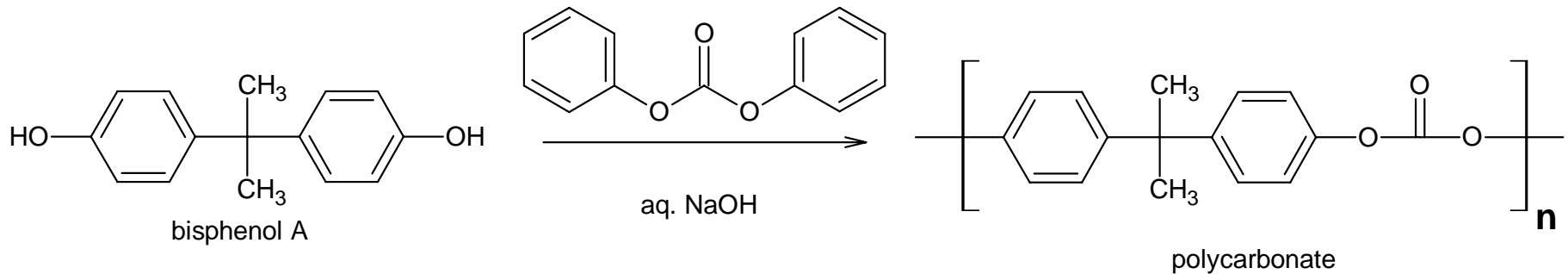


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Principle 3: Non-toxic substances

Polycarbonate synthesis: Phosgene process



1. diphenylcarbonate replaces phosgene
2. eliminates use of CH₂Cl₂
3. higher-quality polycarbonates

Note – still made from Bisphenol A...



Principle 4

Chemical products should be designed to preserve efficacy of function while reducing toxicity.





Problem: Termites!

More than 5 million homes have some type of termite problem.

About \$5 billion in termite-related property damage occurs.

Termite damage is more common than damage caused by storms, fires and earthquakes



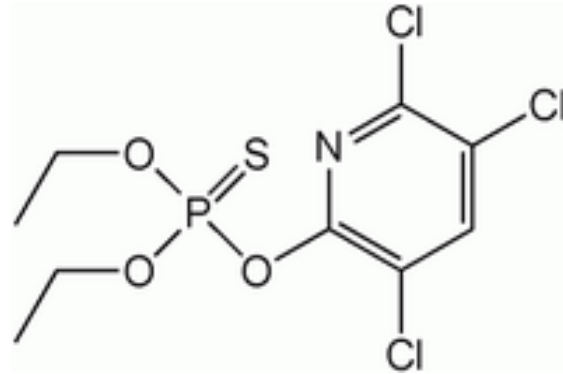
Find wood. Eat wood. Feed the colony.

HELP!!

- Liquid Chemical Treatments
 - a trench is dug around the foundation of the home
 - holes are drilled every 12 inches
 - hundreds of gallons of diluted chemical solution are injected into the soil around and under the structure
- Chlorpyrifos commonly used

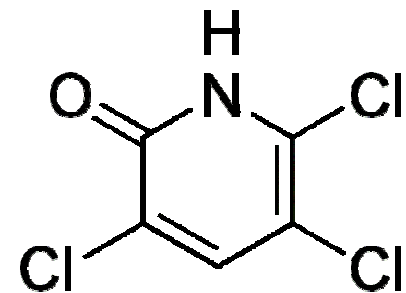
Fun fact: The termites on Earth outweigh the humans on Earth.

Chlorpyrifos



Discovered by The Dow Chemical Company in 1962

- Trade names:
 - Dursban (home and garden)
 - Lorsban (agricultural)
- A toxic crystalline organophosphate insecticide
- No longer approved for residential use in the US
- Inhibits acetylcholinesterase
- Broad use
- A CDC study found a metabolite specific to chlorpyrifos in the urine of 91% of people tested



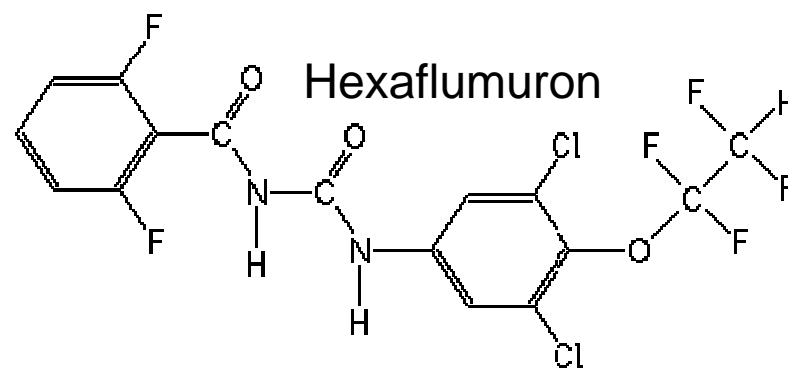
TCPy
3,5,6-trichloro-2-pyridinol

Sentricon[®] Colony Elimination System

©TMTrademark of Dow AgroSciences LLC



- A new paradigm for the elimination of subterranean termite colonies
- First introduced in 1995 as a termite baiting system
- The first major alternative to liquid termiticide soil barriers
- EPA has registered Sentricon[™] as a reduced-risk pesticide

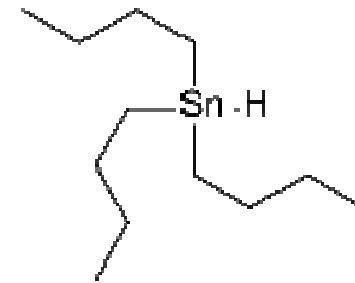


<http://www.sentricon.com/us/video/video.htm>





Problem: fouling (the growth of plants and animals on the hulls of ships) cost the shipping industry approximately \$3 billion a year in increased fuel consumption.



Dirty solution:

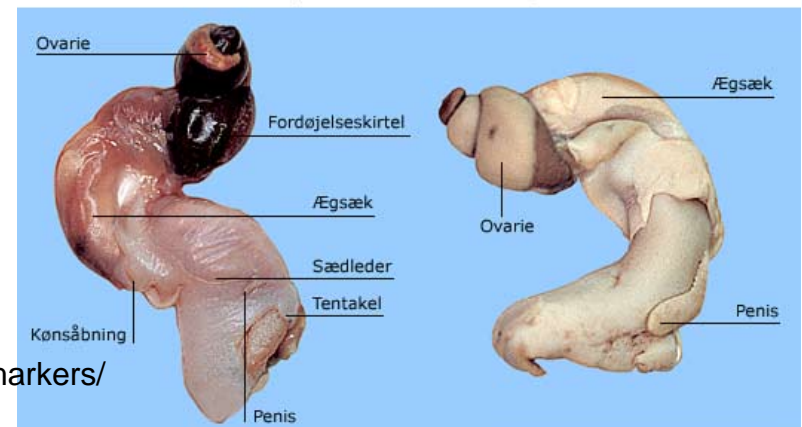
Tributyltin was used as additive for ship paint to prevent growth of marine organisms on ships.

Results:

Organotin compounds are persistent organic pollutants with a extremely high toxicity for some marine organisms. Endocrine disruption is visibly expressed in gonochoristic marine snails.

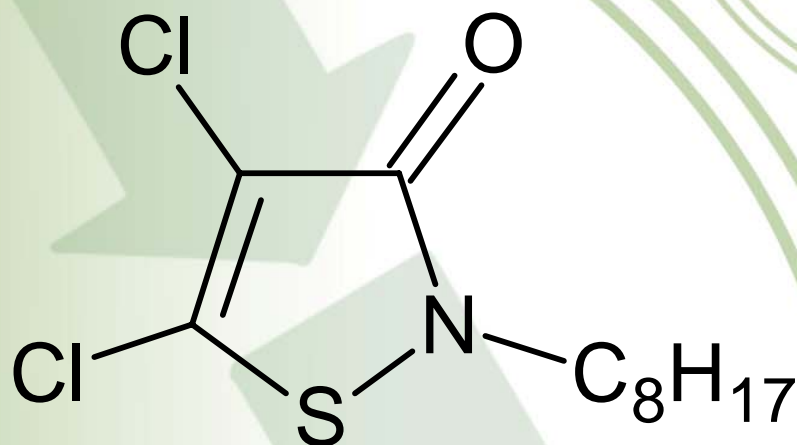
<http://www.dmu.dk/International/Water/MarineMonitoring/MADS/Biomarkers/>

Imposex hos konksnegl



Green Solution

Rohm and Haas developed Sea-Nine™, a novel antifoulant, which demonstrates high acute toxicity, no chronic toxicity



Sea-Nine™

1996 The Presidential Green Chemistry Challenge
winner for Designing Greener Chemicals Award

*The Presidential
Green Chemistry Challenge*



Sea-nine antifoulant: an environmentally acceptable alternative to organotin antifoulants, Jacobson A.H.; Willingham G.L., *The Science of the Total Environment*, Volume 258, Number 1, 21 August 2000, pp. 103-110(8)



Principle 5

The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.

Chemical Separations



- What are some common separation techniques?
- What are the challenges and green benefits associate with each?

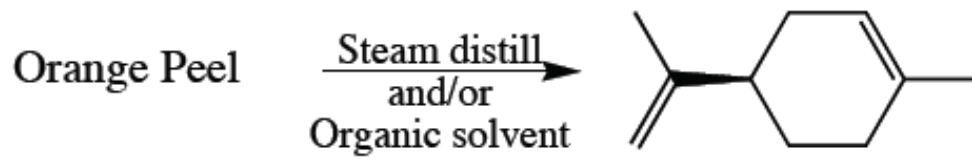
Issues with Organic Solvents



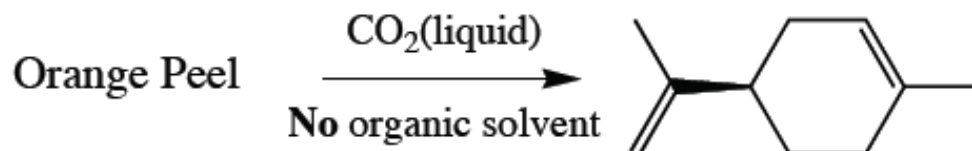
- Organic solvents are of concern to the chemical industry because of the sheer volume used in synthesis, processing, and separation.
- Organic solvents are expensive
- Organic solvents are highly regulated.
- Many organic solvents are volatile, flammable, toxic, and carcinogenic.

Liquid CO₂ as a green extraction solvent

Traditional Method



Green Method



Chemical Concepts:

Solid/liquid extraction
Natural products (terpenes)
Spectroscopy
Phase transitions

Green Lessons:

Use of safer solvents
Prevention of waste
Green materials processing

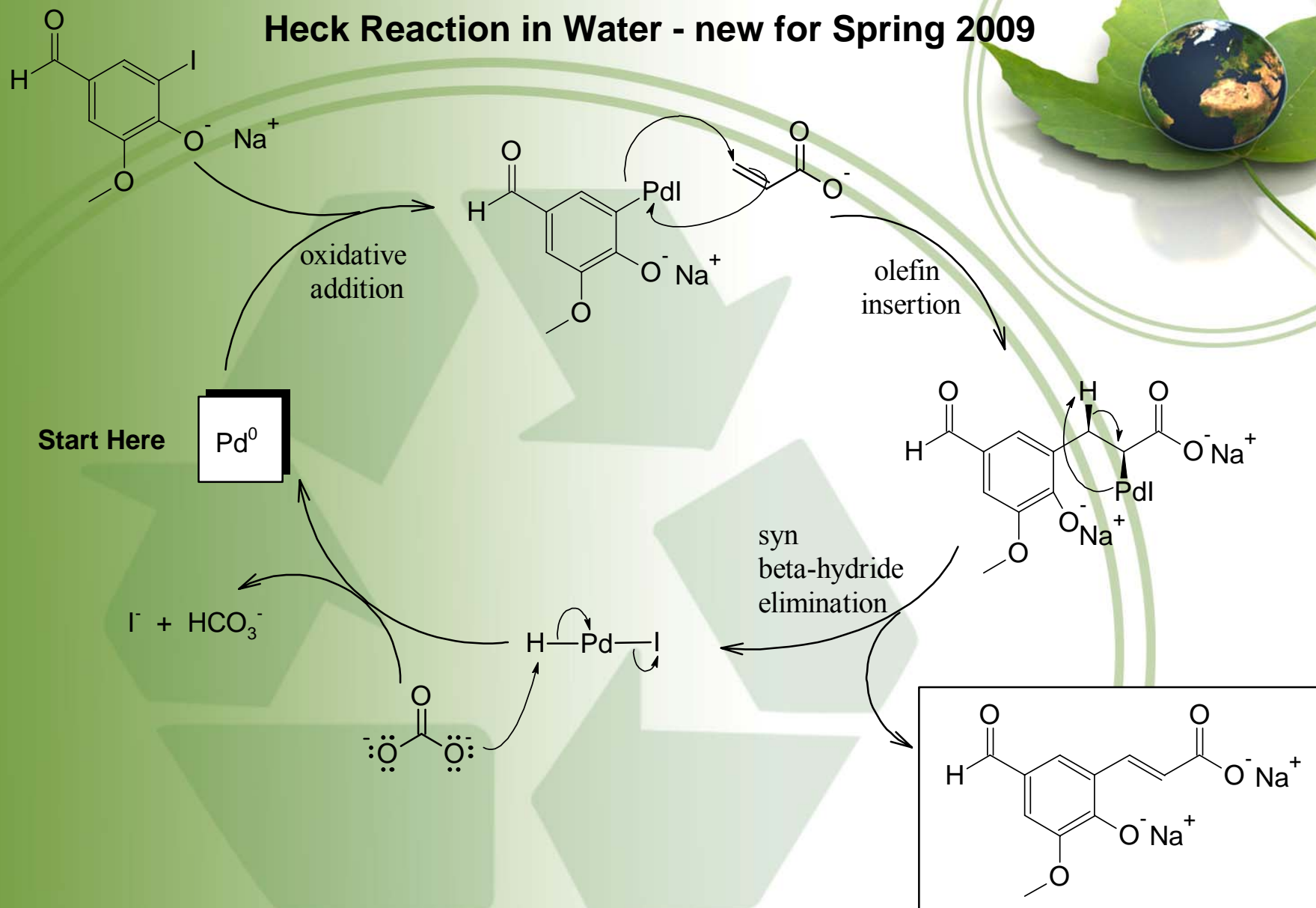
McKenzie, L. C.; Thompson, J. E.; Sullivan, R.; Hutchison, J. E. "Green chemical processing in the teaching laboratory: A convenient liquid CO₂ extraction of natural products," *Green Chem.* **2004**, 355-358.

Why Water?

- Cost - water is the world's cheapest solvent.
- Safety – doesn't get any safer than water.
- Some reactions work better in water.



Heck Reaction in Water - new for Spring 2009

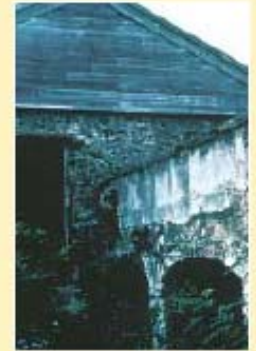




Principle 7
A raw material of feedstock should be
renewable
rather than depleting wherever
technically and
economically practicable.

Spinosad: A New Natural Product for Insect Control

- Isolated from the fermentation product of the microorganism, *Saccharopolyspora spinosa*
- Collected from soil in an abandoned rum distillery on a Caribbean Island in 1982 by an Eli Lilly scientist on vacation



Rum still where soil sample was collected



Spinosad fermentation vessels



Left and below:
Harbor Beach spinosad
fermentation facility

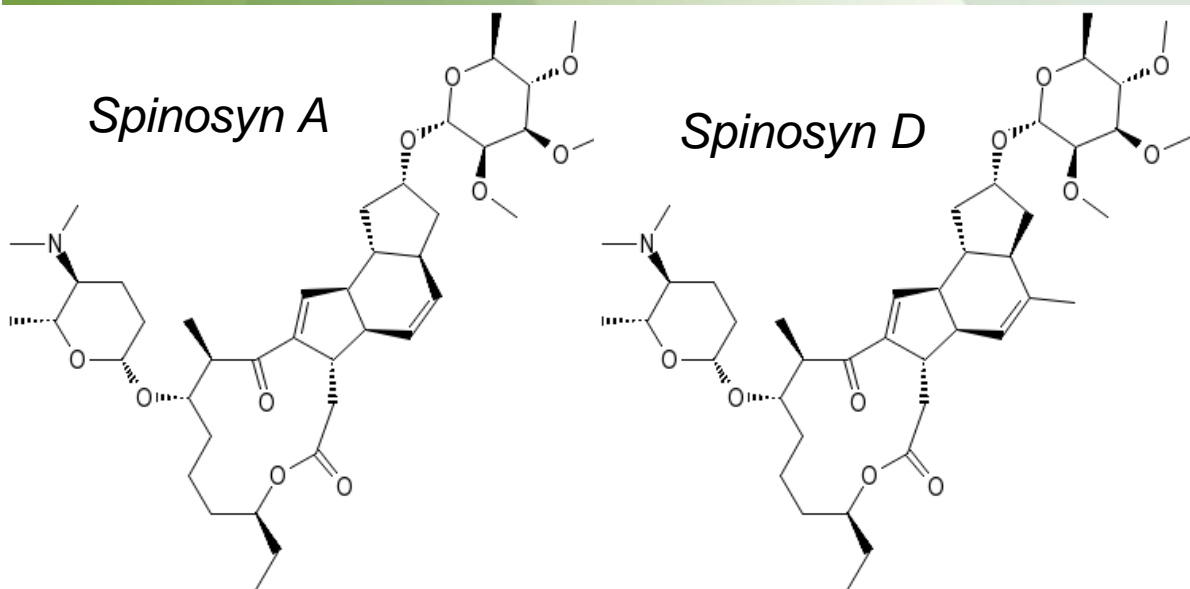


Whole broth extraction units



Spinosad: A New Natural Product for Insect Control

- Spinosad presents a favorable environmental profile:
 - It does not leach, bioaccumulate, volatilize, or persist in the environment.
 - It will degrade photochemically when exposed to light after application.
 - It does not leach through soil to groundwater.
 - It demonstrates low mammalian and avian toxicity.
 - It demonstrates high selectivity



1999 Presidential Green
Chemistry Challenge:
Designing Greener Chemicals
Award

A small, realistic globe of the Earth is positioned in the center of a large, vibrant green leaf. The globe shows the continents of North and South America in shades of brown and green, with blue oceans and white clouds. The leaf is detailed with visible veins and a natural, slightly irregular shape. The background is a soft, light green gradient with faint, stylized geometric shapes and lines, creating a clean and modern aesthetic.

APPLICATIONS

How many principles can you identify in this example?

2009 Presidential Green Chemistry Challenge:
Greener Synthetic Pathways Award

Eastman Chemical Company

A Solvent-Free Biocatalytic Process for Cosmetic and Personal Care
Ingredients

12 Principles of Green Chemistry

John Warner and Paul Anastas



1. Prevention
2. Atom Economy
3. Less Hazardous Chemical Synthesis
4. Design Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design of Energy Efficiency
7. Use Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-Time Analysis for Pollution Prevention
12. Accident Prevention

