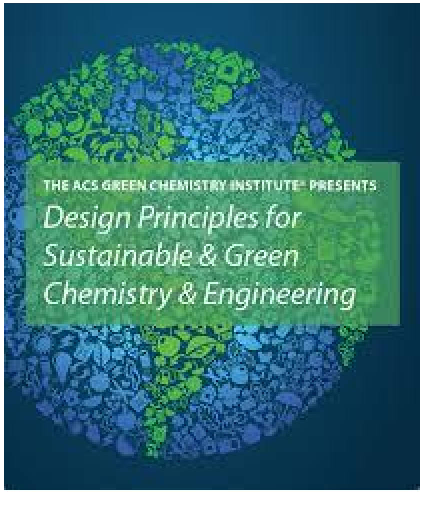
CHEM 406/511

CHEM Special Topic

Sustainable and Green Chemistry



Modified By Dr. Cheng-Yu Lai

Learning Goals

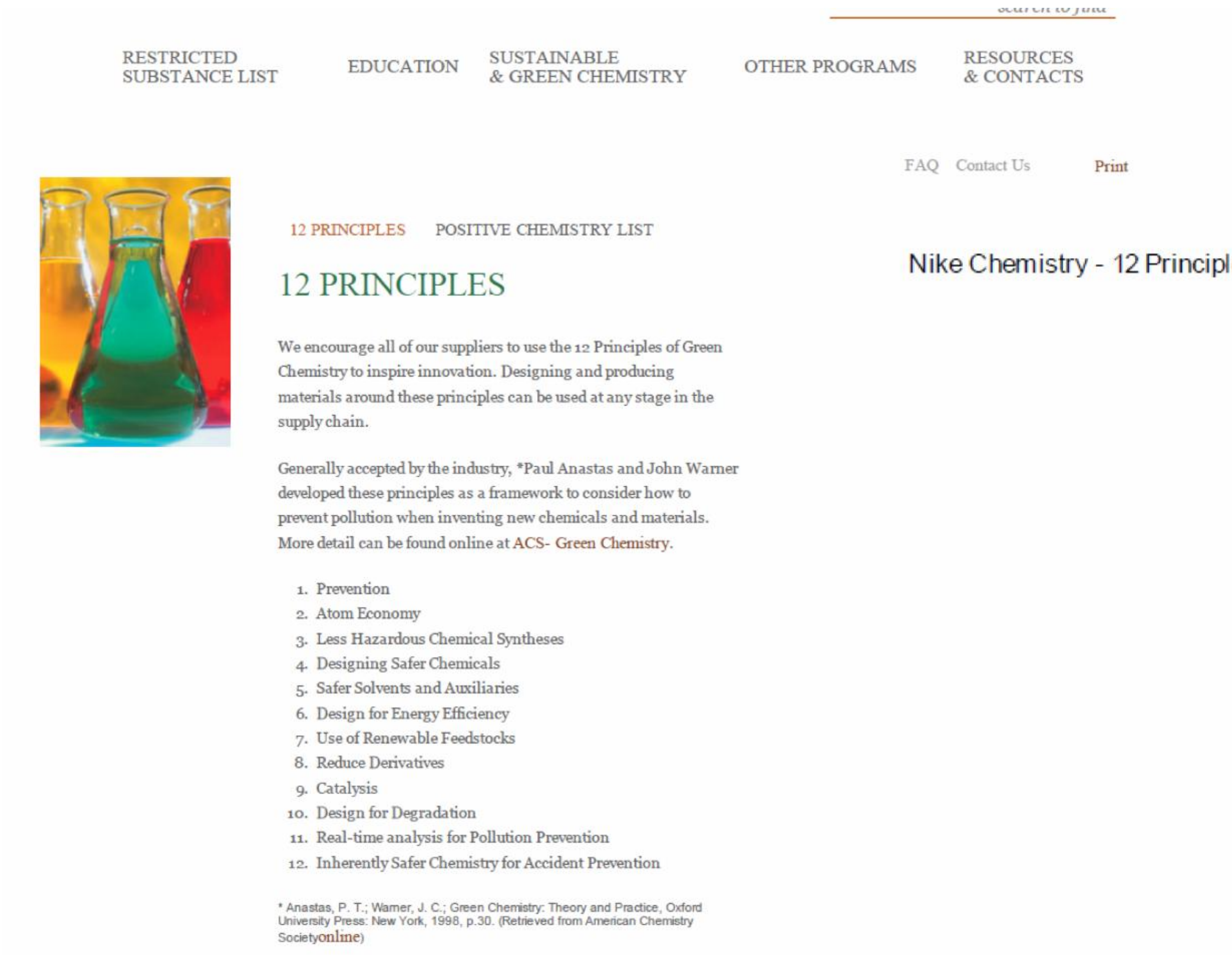
1. Learn to work and communicate across disciplines
2. Understand what makes a chemicals safe/unsafe
3. Evaluate the "greeness" of a chemical process
4. Understand the role of law and economics in shaping industrial activity
5. Be familiar with current and emerging chemical regulation
6. Be able to trace impacts of chemicals from "cradle to grave"
7. Make a business case for and against green chemistry
8. Understand the use of alternatives assessments that combine chemical, environmental health, regulatory, and business considerations to develop safer products.

Why do we need Green Chemistry ?

- Chemistry is undeniably a very prominent part of our daily lives.
- Chemical developments also bring new environmental problems and harmful unexpected side effects, which result in the need for ‘greener’ chemical products.
- A famous example is the pesticide DDT.

- **Green chemistry** looks at pollution prevention on the molecular scale and is an extremely important area of Chemistry due to the importance of Chemistry in our world today and the implications it can show on our environment.
- The **Green Chemistry** program supports the invention of more environmentally friendly chemical processes which reduce or even eliminate the generation of hazardous substances.
- This program works very closely with the twelve principles of **Green Chemistry.**

Nike Chemistry - 12 Principles



12 PRINCIPLES

We encourage all of our suppliers to use the 12 Principles of Green Chemistry to inspire innovation. Designing and producing materials around these principles can be used at any stage in the supply chain.

Generally accepted by the industry, *Paul Anastas and John Warner developed these principles as a framework to consider how to prevent pollution when inventing new chemicals and materials. More detail can be found online at ACS- Green Chemistry.

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

* Anastas, P. T.; Warner, J. C.; Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30. (Retrieved from American Chemistry Societyonline)

http://www.nikeincchemistry.com/sustainable-and-green-chemistry/12-green-principles

12 Principles of Green Chemistry

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

2. **Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.**

Environmental Disasters

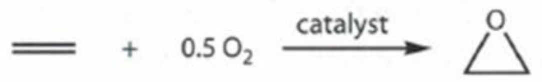
- Love Canal
  - in Niagara Falls, NY a chemical and plastics company had used an old canal bed as a chemical dump from 1930s to 1950s. The land was then used for a new school and housing track. The chemicals leaked through a clay cap that sealed the dump. It was contaminated with at least 82 chemicals (benzene, chlorinated hydrocarbons, dioxin). Health effects of the people living there included: high birth defect incidence and siezure-inducing nervous disease among the children.

http://ublib.buffalo.edu/libraries/projects/lovecanal/

Atom Economy

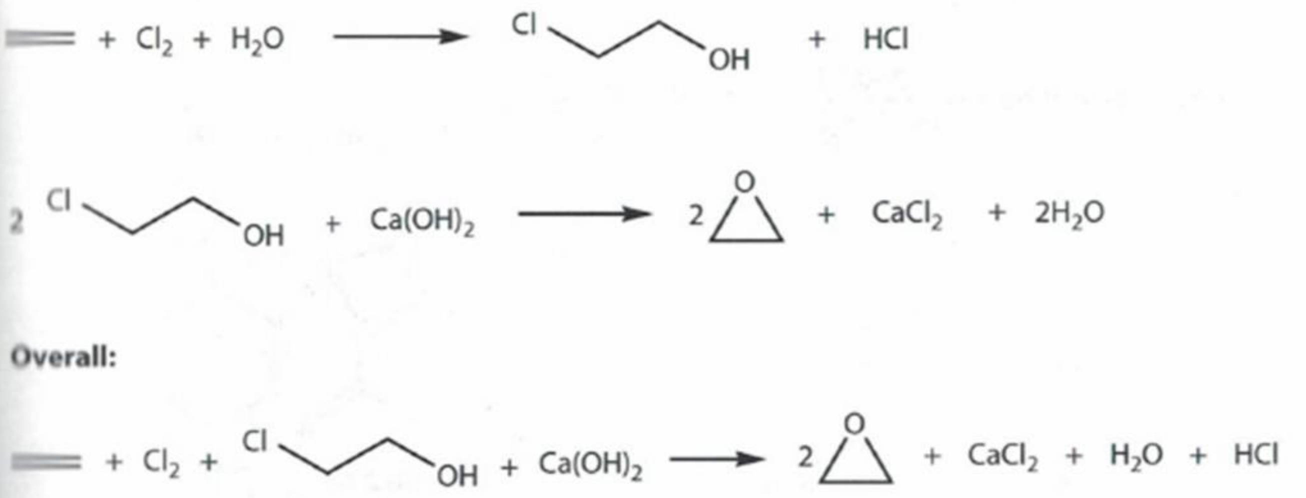
$$\% \text{ Yield} = \frac{\text{experimental quantity of desired product}}{\text{theoretical maximum quantity of desired product}} \times 100$$

$$\underset{\text{(intrinsic)}}{\% \text{ Atom Economy}} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$



Molar mass (g/mol):	28.05	0.5 × 32.00	44.05

$$\textbf{\% Atom Economy} = \frac{44.05}{44.05} \times 100 = 100\%$$



Overall:

28.05	70.91	80.51	74.09	2 × 44.05	110.98	18.02	36.46

$$\textbf{\% Atom Economy} = \frac{88.1}{253.56} \times 100 = 34.7\%$$

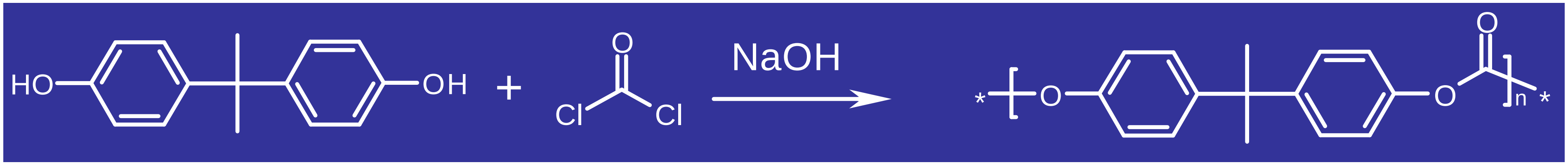
12 Principles of Green Chemistry

3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

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

Less Hazardous Chemical Synthesis

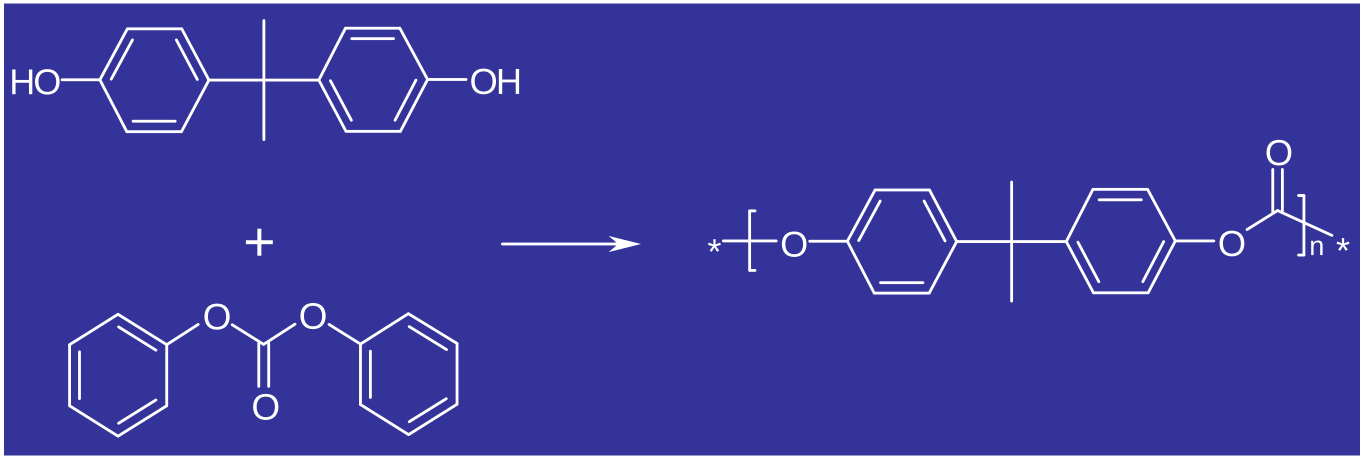
Polycarbonate Synthesis: Phosgene Process



- Disadvantages
  - phosgene is highly toxic, corrosive
  - requires large amount of CH_2Cl_2
  - polycarbonate contaminated with Cl impurities

Less Hazardous Chemical Synthesis

Polycarbonate Synthesis: Solid-State Process



- Advantages
  - diphenylcarbonate synthesized without phosgene
  - eliminates use of CH_2Cl_2
  - higher-quality polycarbonates

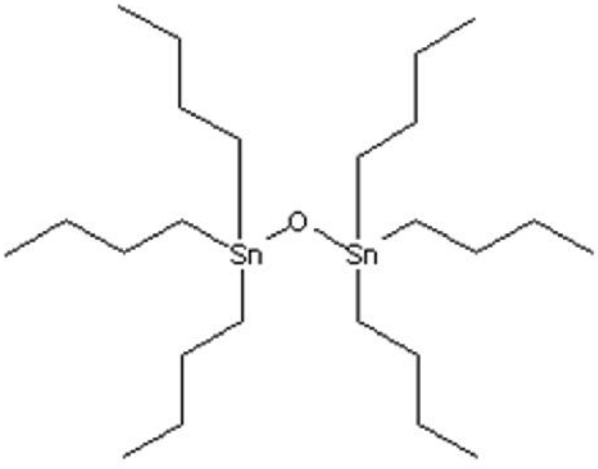
Komiya *et al.*, Asahi Chemical Industry Co.

Designing Safer Chemicals
Case Study: Antifoulants

http://academic.scranton.edu/faculty/CANNM1/environmentalmodule.html

Designing Safer Chemicals: Case Study: Antifoulants

Antifoulants are generally dispersed in the paint as it is applied to the hull. Organotin compounds have traditionally been used, particularly tributyltin oxide (TBTO). TBTO works by gradually leaching from the hull killing the fouling organisms in the surrounding area



Tributyltin Oxide

TBTO and other organotin antifoulants have long half-lives in the environment (half-life of TBTO in seawater is > 6 months). They also bioconcentrate in marine organisms (the concentration of TBTO in marine organisms to be 104 times greater than in the surrounding water).

Organotin compounds are chronically toxic to marine life and can enter food chain. They are bioaccumulative.

http://academic.scranton.edu/faculty/CANNM1/environmentalmodule.html

Designing Safer Chemicals: Case Study: Antifoulants

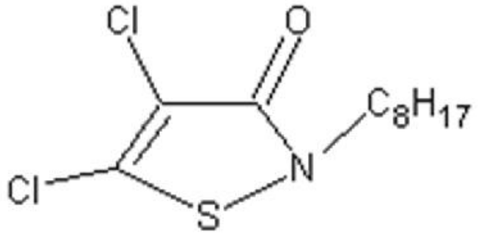
Sea-Nine® 211

http://www.rohmhaas.com/seanine/index.html

Rohm and Haas

Presidential Green Chemistry Challenge Award, 1996

The active ingredient in Sea-Nine® 211, 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOI), is a member of the isothiazolone family of antifoulants.



4,5-dichloro-2-n-octyl-4-isothiazolin-3-one

DCOI

http://academic.scranton.edu/faculty/CANNM1/environmentalmodule.html

12 Principles of Green Chemistry

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

6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

Safer Solvents

- Solvent Substitution
- Water as a solvent
- New solvents
  - Ionic liquids
  - Supercritical fluids

Solvent Selection

Preferred	**Useable**	**Undesirable**
Water	**Cyclohexane**	**Pentane**
Acetone	**Heptane**	**Hexane(s)**
Ethanol	**Toluene**	**Di-isopropyl ether**
2-Propanol	**Methylcyclohexane**	**Diethyl ether**
1-Propanol	**Methyl t-butyl ether**	**Dichloromethane**
Ethyl acetate	**Isooctane**	**Dichloroethane**
Isopropyl acetate	**Acetonitrile**	**Chloroform**
Methanol	**2-MethylTHF**	**Dimethyl formamide**
Methyl ethyl ketone	**Tetrahydrofuran**	**N-Methylpyrrolidinone**
1-Butanol	**Xylenes**	**Pyridine**
***t*-Butanol**	**Dimethyl sulfoxide**	**Dimethyl acetate**
	Acetic acid	**Dioxane**
	Ethylene glycol	**Dimethoxyethane**
		Benzene
		Carbon tetrachloride

“Green chemistry tools to influence a medicinal chemistry and research chemistry based organization”
Dunn and Perry, et. al., Green Chem., 2008, 10, 31-36

Red Solvent	**Flash point (° C)**	**Reason**
Pentane	-49	Very low flash point, good alternative available.
Hexane(s)	-23	More toxic than the alternative heptane, classified as a HAP in the US.
Di-isopropyl ether	-12	Very powerful peroxide former, good alternative ethers available.
Diethyl ether	-40	Very low flash point, good alternative ethers available.
Dichloromethane	n/a	High volume use, regulated by EU solvent directive, classified as HAP in US.
Dichloroethane	15	Carcinogen, classified as a HAP in the US.
Chloroform	n/a	Carcinogen, classified as a HAP in the US.
Dimethyl formamide	57	Toxicity, strongly regulated by EU Solvent Directive, classified as HAP in the US.
N-Methylpyrrolidinone	86	Toxicity, strongly regulated by EU Solvent Directive.
Pyridine	20	Carcinogenic/mutagenic/reprotoxic (CMR) category 3 carcinogen, toxicity, very low threshold limit value (TLV) for worker exposures.
Dimethyl acetate	70	Toxicity, strongly regulated by EU Solvent Directive.
Dioxane	12	CMR category 3 carcinogen, classified as HAP in US.
Dimethoxyethane	0	CMR category 2 carcinogen, toxicity.
Benzene	-11	Avoid use: CMR category 1 carcinogen, toxic to humans and environment, very low TLV (0.5 ppm), strongly regulated in EU and the US (HAP).
Carbon tetrachloride	n/a	Avoid use: CMR category 3 carcinogen, toxic, ozone depletor, banned under the Montreal protocol, not available for large-scale use, strongly regulated in the EU and the US (HAP).

“Green chemistry tools to influence a medicinal chemistry and research chemistry based organization”
Dunn and Perry, et. al., Green Chem., 2008, 10, 31-36

Solvent replacement table

Undesirable Solvent	**Alternative**
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or diethyl ether	2-MeTHF or *tert*-butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or *tert*-butyl methyl ether
Chloroform, dichloroethane or carbon tetrachloride	Dichloromethane
Dimethyl formamide, dimethyl acetamide or N-methylpyrrolidinone	Acetonitrile
Pyridine	Et_3N (if pyridine is used as a base)
Dichloromethane (extractions)	EtOAc, MTBE, toluene, 2-MeTHF
Dichloromethane (chromatography)	EtOAc/heptane
Benzene	Toluene

“Green chemistry tools to influence a medicinal chemistry and research chemistry based organization”
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Energy in a chemical process

- Thermal (electric)
- Cooling (water condensers, water circulators)
- Distillation
- Equipment (lab hood)
- Photo
- Microwave

Source of energy:

- Power plant – coal, oil, natural gas

12 Principles of Green Chemistry

7. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.
   - Lai Group Research

8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

7. Use of Renewable Feedstocks

Biomaterials [Carbohydrates, Proteins, Lipids]
Highly Functionalized Molecules

Or Petroleum Products [Hydrocarbons]

Monomer

Singly Functionalized Compounds [Olefins, Alkylchlorides]

Highly Functionalized Molecules

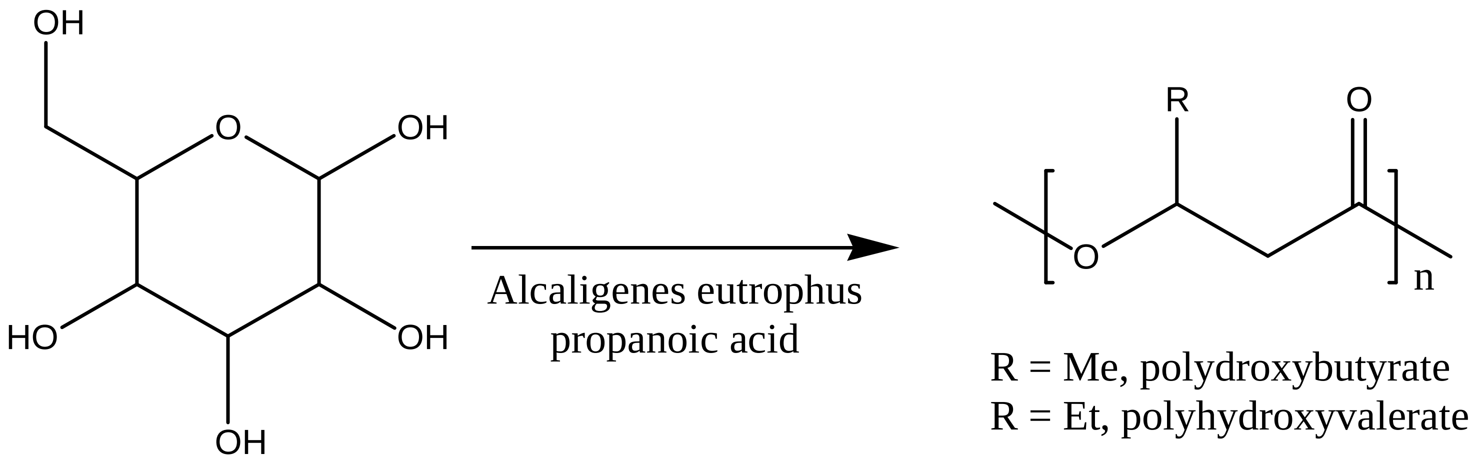
“A raw material of feedstock should be renewable rather than depleting wherever technically and economically practical”

Non-renewable

Renewable

Polymers from Renewable Resources: Polyhydroxyalkanoates (PHAs)

- Fermentation of glucose in the presence of bacteria and propanoic acid (product contains 5-20% polyhydroxyvalerate)
- Similar to polypropene and polyethene
- Biodegradable



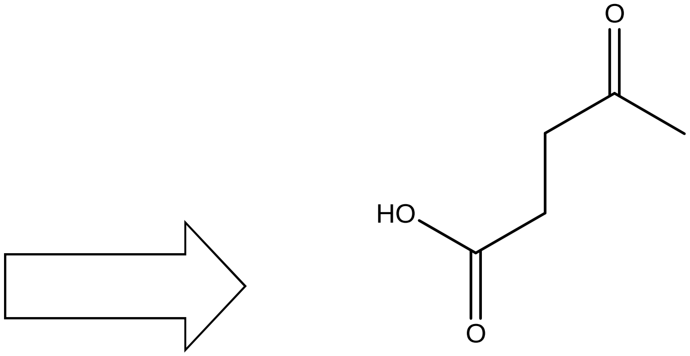
R = Me, polydroxybutyrate
R = Et, polyhydroxyvalerate

Raw Materials from Renewable Resources: The BioFine Process

Paper mill
sludge

Agricultural
residues,
Waste wood

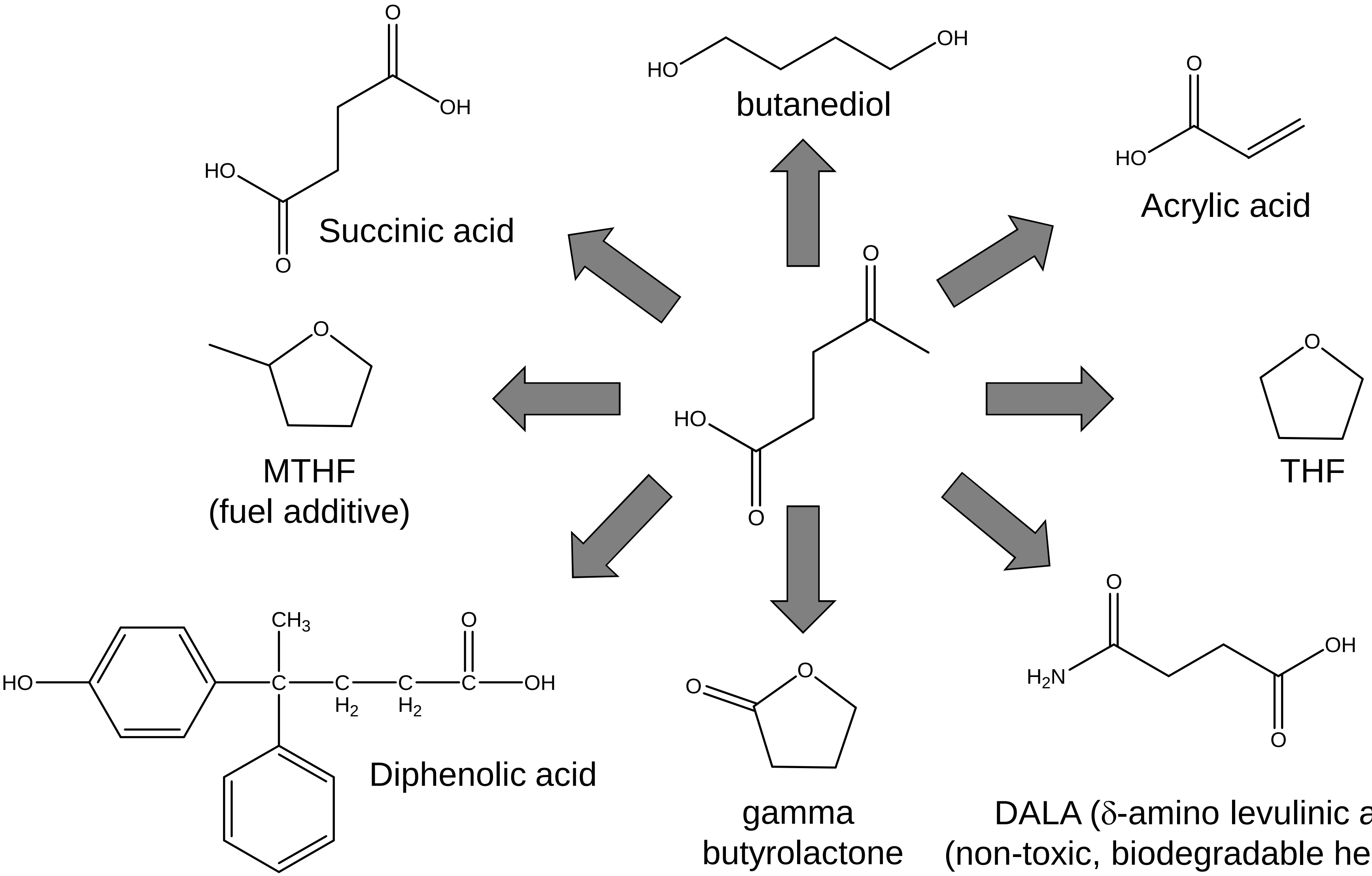
Municipal solid waste
and waste paper



Levulinic acid

Green Chemistry Challenge Award
1999 Small Business Award

Levulinic acid as a platform chemical



Succinic acid

butanediol

Acrylic acid

MTHF
(fuel additive)

THF

Diphenolic acid

gamma
butyrolactone

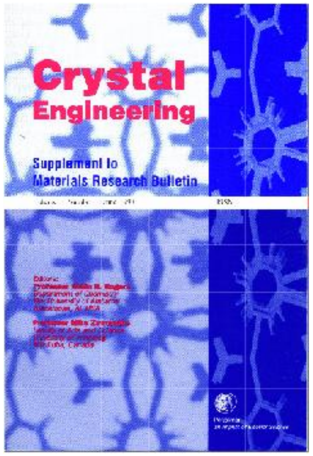
DALA (δ-amino levulinic acid)
(non-toxic, biodegradable herbicide)

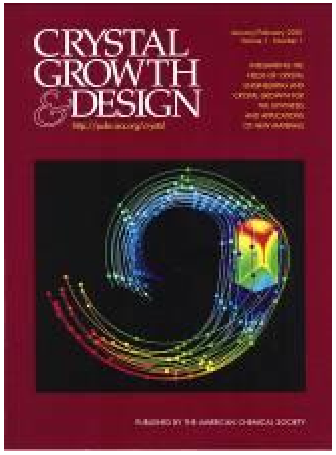
2 synthetic steps are added each time one is used

Overall yield and atom economy will decrease

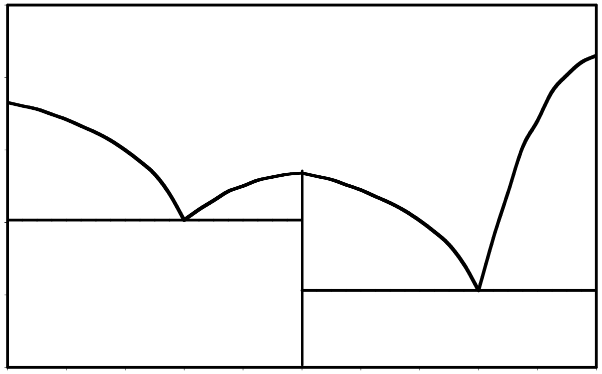
“Protecting groups are used because there is no direct way to solve the problem without them.”

NonCovalent Derivatization





Entropic Control in Materials Design



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"Aromatic-Aromatic Interactions in Molecular Recognition: A Family of Artificial Receptors for Thymine that Shows Both Face-To-Face and Edge-To-Face Orientations." Muehldorf, A. V.; Van Engen, D.; Warner, J. C.; Hamilton, A. D., *J. Am. Chem. Soc.*, **1988**, *110*, 6561.

12 Principles of Green Chemistry

9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Chemical products would be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

Catalysis

Heterogeneous vs Homogenous

• Distinct solid phase	• Same phase as rxn medium
• Readily separated	• Difficult to separate
• Readily regenerated & recycled	• Expensive and/or difficult to separate
• Rates not as fast	• Very high rates
• Diffusion limited	• Not diffusion controlled
• Sensitive to poisons	• Robust to poisons
• Lower selectivity	• High selectivity
• Long service life	• Short service life
• High energy process	• Mild conditions
• Poor mechanistic understanding	• Mechanisms well understood

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Heterogeneous vs Homogenous

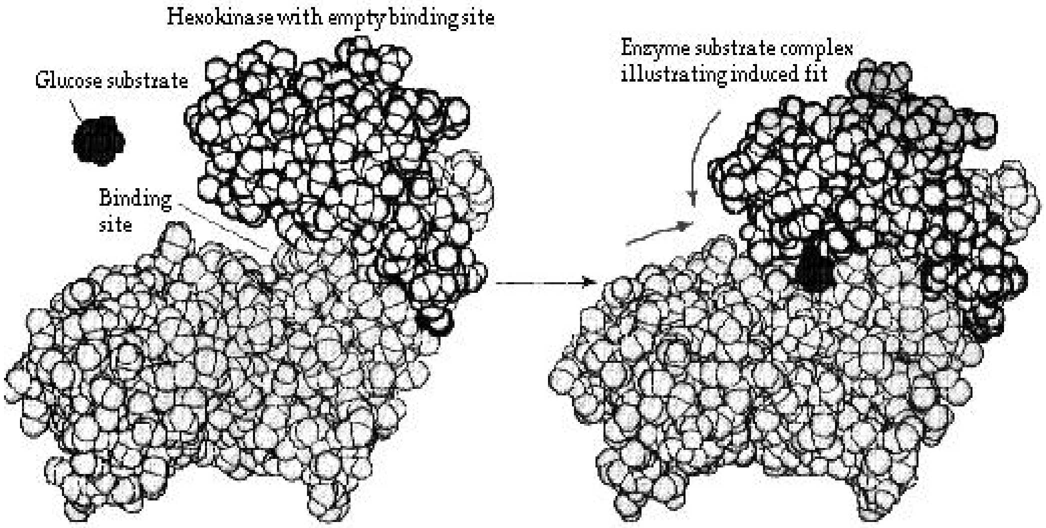
- Distinct solid phase
- **Readily separated**
- **Readily regenerated & recycled**
- Rates not as fast
- Diffusion limited
- Sensitive to poisons
- Lower selectivity
- **Long service life**
- High energy process
- Poor mechanistic understanding

Green catalyst

- Same phase as rxn medium
- Difficult to separate
- Expensive and/or difficult to separate
- **Very high rates**
- Not diffusion controlled
- **Robust to poisons**
- **High selectivity**
- Short service life
- **Mild conditions**
- Mechanisms well understood

Biocatalysis

- Enzymes or whole-cell microorganisms
- Benefits
  - Fast rxns due to correct orientations
  - Orientation of site gives high stereospecificity
  - Substrate specificity
  - Water soluble
  - Naturally occurring
  - Moderate conditions
  - Possibility for tandem rxns (one-pot)



Design for Degradation

Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

- Persistence examples
- Sulfonated detergents
  - Alkylbenzene sulfonates – 1950’s & 60’s
  - Foam in sewage plants, rivers and streams
  - Persistence was due to long alkyl chain
  - Introduction of alkene group into the chain increased degradation
- Chlorofluorocarbons (CFCs)
  - Do not break down, persist in atmosphere and contribute to destruction of ozone layer
- DDT
  - Bioaccumulate and cause thinning of egg shells

12 Principles of Green Chemistry

11. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Real-time Analysis for Pollution Prevention

Real time analysis for a chemist is the process of "checking the progress of chemical reactions as it happens."

Knowing when your product is "done" can save a lot of waste, time and energy!

Safer Chemistry for Accident Prevention

Thank you