

12 Principles of Green Chemistry

(It's Not Easy Being Green)



Dr .Vijaykumar S. Marakatti
National Post-Doctoral Fellow,
JNCASR ,Bangalore



OUTLINE

- 1) History
- 2) 12 principles in detail
- 3) Important Green Process

HISTORY

U.S. Environmental Protection Agency -1970

Protecting human health and the environment - use of DDT and other chemical pesticides, Safe Drinking Water Act in 1974

Love Canal Tragedy, NW

Canal to connect Niagara river to the falls to generate electricity.

Hooker_Chemical_Company - 82 different compounds, 11 of them suspected carcinogens -22, 000 tons

100 homes and a public school built

Trees and gardens were turning black and dying

entire swimming pool had been had been popped up from its foundation

birth defects, increase of white cells – leukaemia



Bhopal disaster, India

1984, methyl isocyanate – Nearly 25,000 death



Photo - Courtesy : Pablo Bartholomew
Copyright © 1995 All Right Reserved - Pablo Bartholomew / Nelphotograph.com



Chloracne

Seveso disaster, Italy (1976)

Icmesa chemical Company
2,3,7,8-tetrachlorodibenzo-*p*-dioxin

Schweizerhalle (Switzerland)



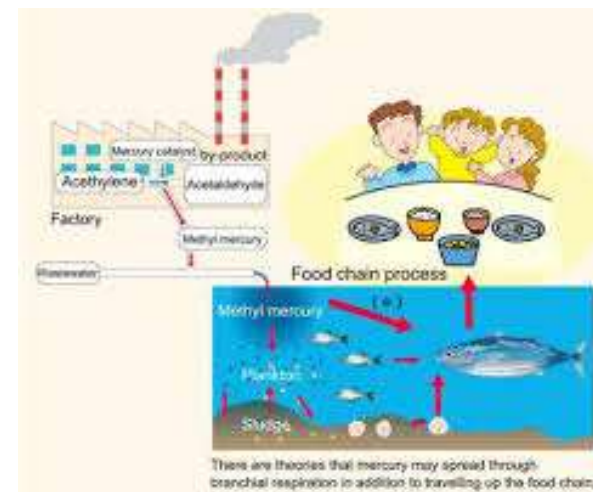
12 tons - Mercury ethoxyethyl-hydroxyde- Fungicide

Several tones of fishes were dead in Rhine river

Minamata, Japan

Methyl mercury,- Fish – People.

1000 people died



Organization for Economic Co-operation and Development (OECD)- 1980

30 industrialized countries- Environmental protection

1990

Staff of the EPA Office of Pollution Prevention and Toxins, coined the phrase "*Green Chemistry*" and showed the seeds of productive collaboration between government, industry, and academia.

Presidential Green Chemistry Challenge Awards – Bill Clinton

1997

The University of Massachusetts at Boston established the field's first Green Chemistry Ph.D. program

Green Chemistry Institute (GCI)

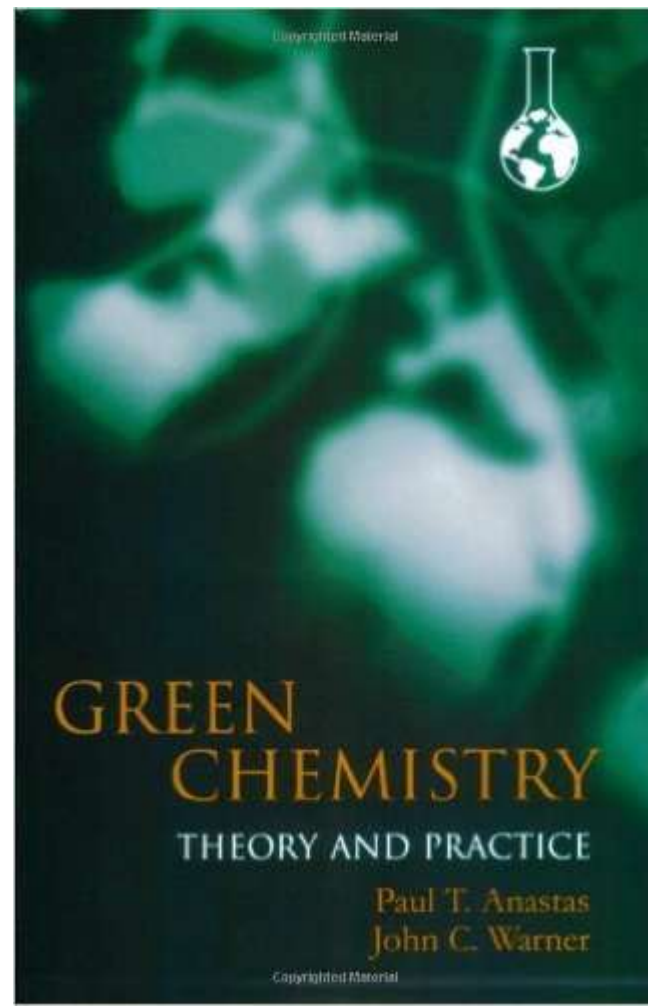
Chemist, Dennis Hjeresen and Dr. Joe Breen



ACS
Green Chemistry
Institute®

BOOK

*The 12 Principles of Green Chemistry outlined within this work declared a **philosophy that motivated academic and industrial scientists at the time and continues to guide the green chemistry movement.***



Definition of Green Chemistry

“The design of chemical products and processes that are more environmentally benign and reduce negative impacts to human health and the environment.”

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

1 . Principle

Prevent Waste

It is better to prevent waste than to treat or clean up waste after it has been created

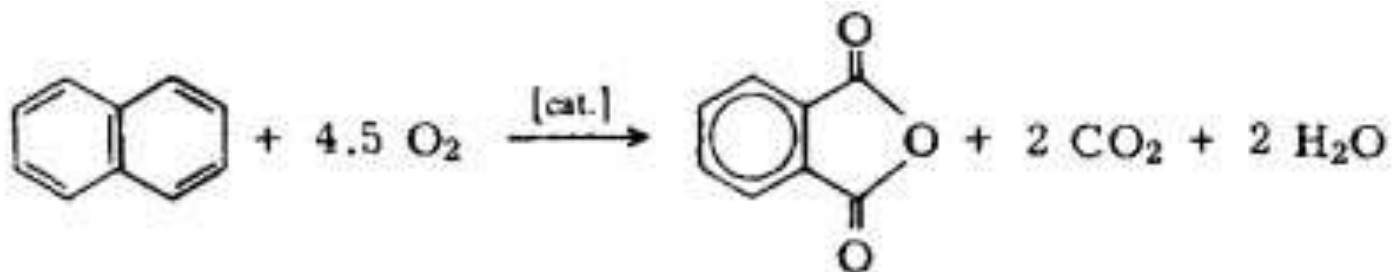
- 1. Identify byproducts; quantify if possible***
- 2. Report conversions, selectivity, and productivities***
- 3. Establish a full mass balance for the process***
- 4. Quantify catalyst and solvent losses***

2. Principle

Atom Economy

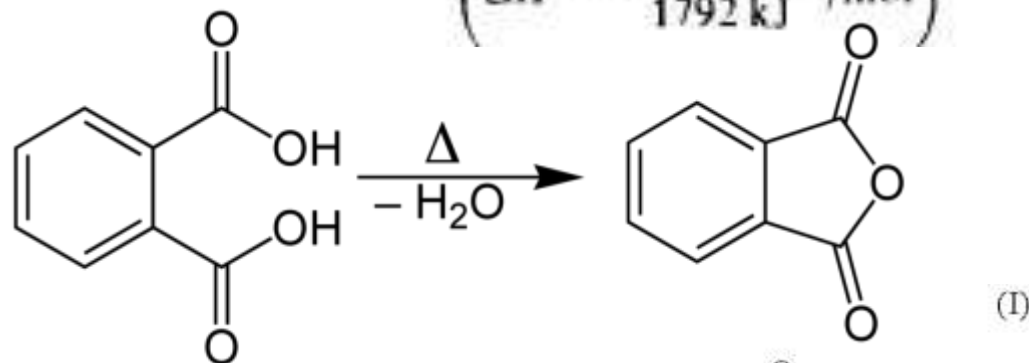
Synthetic methods should be designed to **maximize the incorporation of all materials used in the process into the final product**

X

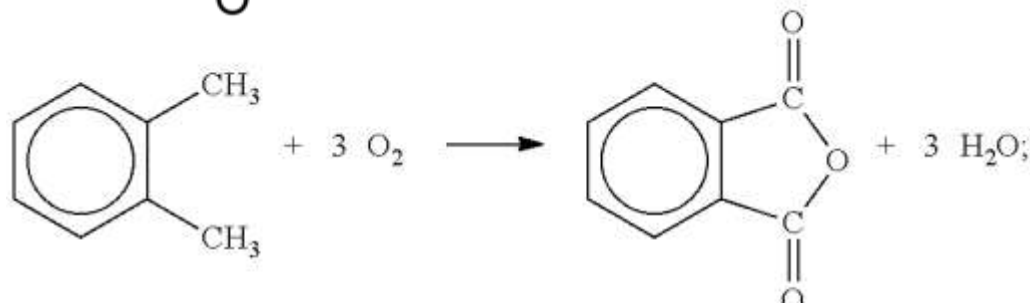


$$\left(\Delta H = -428 \text{ kcal/mol} \right. \quad \left. -1792 \text{ kJ/mol} \right) \quad (1)$$

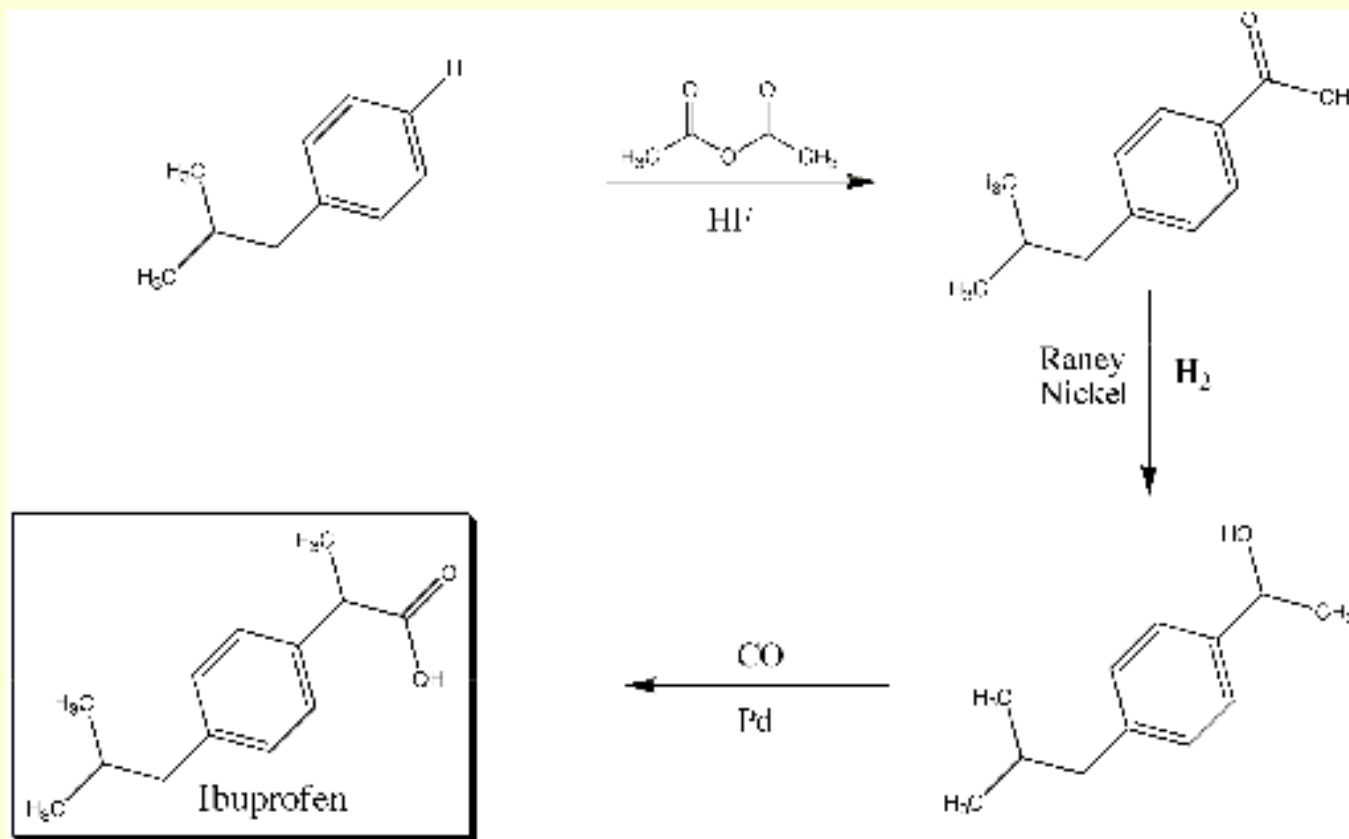
✓



✓



The BHC synthesis of Ibuprofen

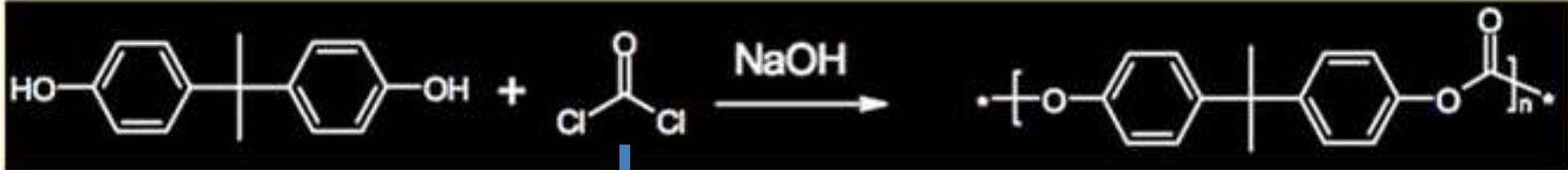


3 bottles of ibuprofen generate less than 1 bottle of waste!

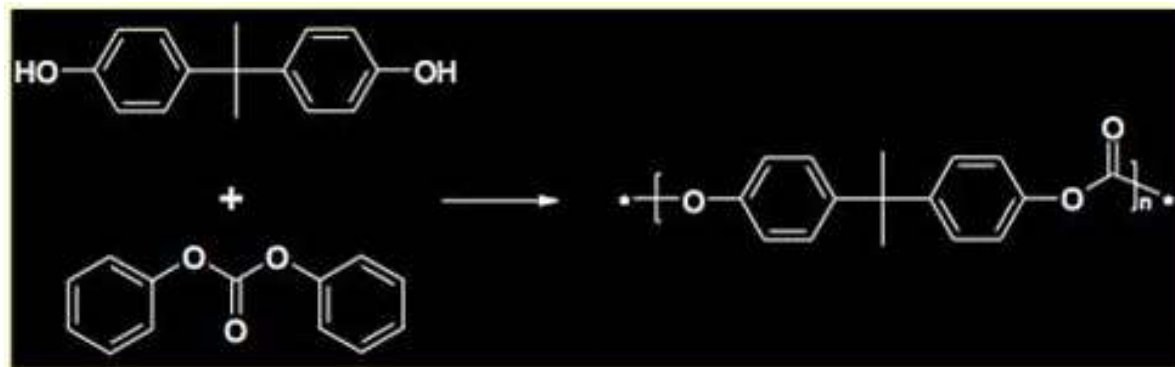
3. Principle

Use and production of Less Hazardous Chemical

Polycarbonate Synthesis : Phosgene Process



Phosgene -toxic corrosive , large CH₂Cl₂ required, contaminated with Cl impurities.



No Phosgene, CH₂Cl₂, high quality polymer

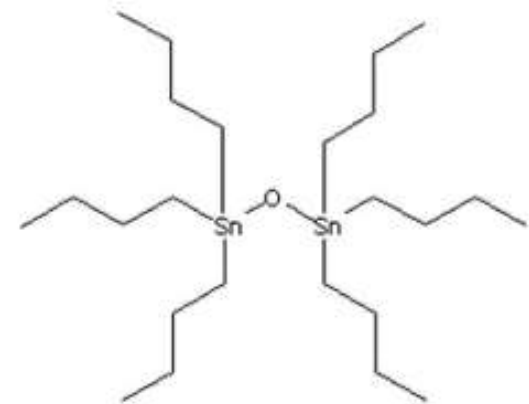
4. Principle Designing safer chemicals

Chemical Product should be designed to preserve the efficiency of the function with less toxicity

Antifoulants



TBTO

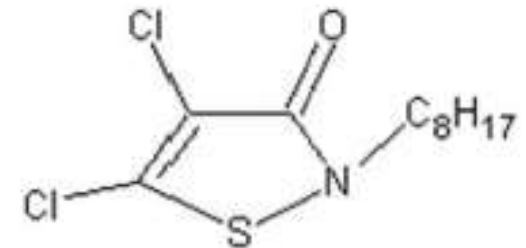


Tributyltin Oxide

Chronically toxic, to marine life , enter food chain and are bioaccumulative

SeaNine®


Reduces Fuel Consumption, high acute toxicity then chronic toxicity



5. Principle

Minimize the use of solvents and auxiliaries

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

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).

Solvent Replaceable Table

Undesirable Solvent	Alternative
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or diethyl ether	2-MeTHF or <i>tert</i> -butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or <i>tert</i> -butyl methyl ether
Chloroform, dichloroethane or carbon tetrachloride	Dichloromethane
Dimethyl formamide, dimethyl acetamide or N-methylpyrrolidinone	Acetonitrile
Pyridine	Et ₃ N (if pyridine is used as a base)
Dichloromethane (extractions)	EtOAc, MTBE, toluene, 2-MeTHF
Dichloromethane (chromatography)	EtOAc/heptane
Benzene	Toluene

6. Principle

Design for Energy Efficiency

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

Source of energy:

- Power plant – coal, oil, natural gas

Use of renewable Energy Sources

7. Principle

Use of renewable Feed stock

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.



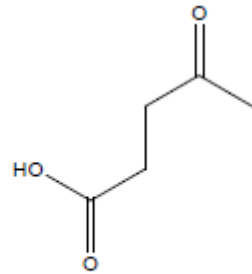
Paper mill sludge



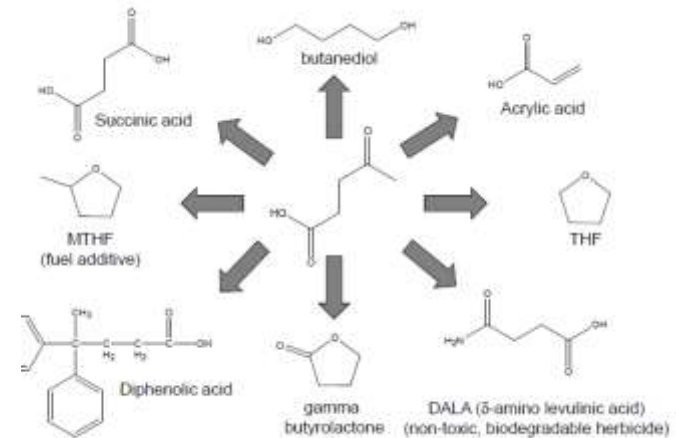
Agricultural residues,
Waste wood



Municipal solid waste
and waste paper



Levulinic acid



8. Principle

Reduce Derivatives

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

9. Principle

Catalytic reagents are superior to stoichiometric reagents.

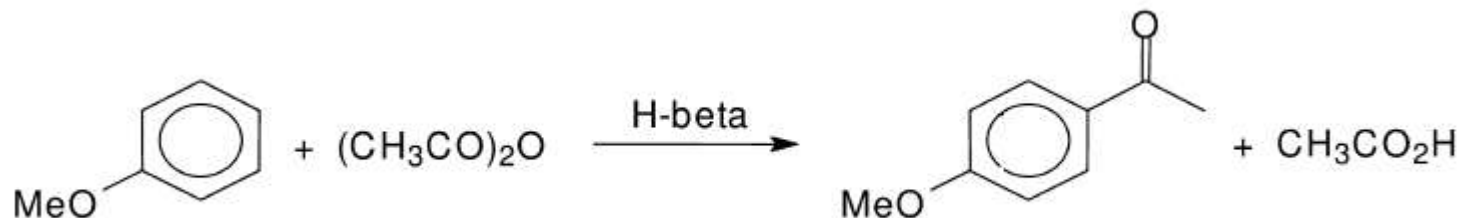
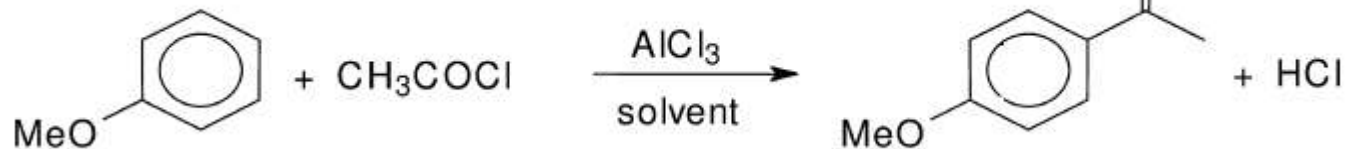
- **Reduces energy**
- **Increases efficiency**
- **Reduces by-product formation**

10. Principle

Design for Degradation

can we recycle everything?

design it so that it breaks down at the end of its useful lifetime.



Homogeneous

$\text{AlCl}_3 > 1$ equivalent

Solvent

Hydrolysis of products

Phase separation

Distillation organic phase

Solvent recycle

85-95% yield

4.5 kg aqueous effluent per kg

12 unit operations

Heterogeneous

H-beta, catalytic & regenerable

No solvent

No water necessary

-

Distillation organic phase

-

> 95% yield, higher purity

0.035 kg aqueous effluent per kg

3 unit operations

Nylon synthesis by green route

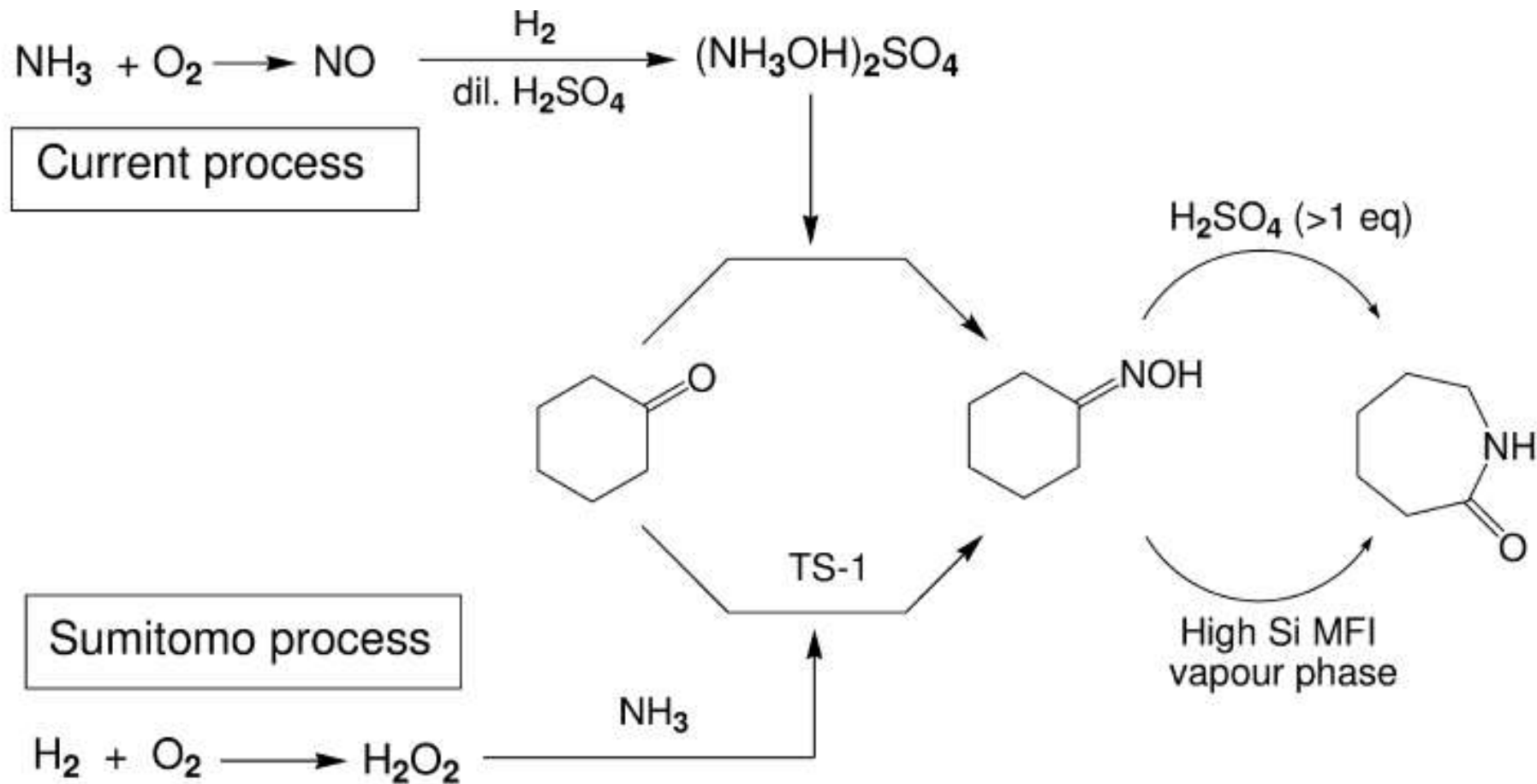


Fig. 1.9 Sumitomo vs. conventional process for caprolactam manufacture.

11. Principle

Real-time analysis for Pollution Prevention

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. Principle

Inherently Safer Chemistry for Accident Prevention

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.

Chemists try to avoid things that explode, light on fire, are air-sensitive, etc.

In the “real world” when these things happen, lives are lost.²



Safer Chemistry for Accident Prevention



Cornered

by Mike Baldwin

© 2006 Mike Baldwin. Out by Universal Press Syndicate. www.cornered.com
cornered@comcast.com

3/22/06



Noble Prizes in Green Chemistry



Development of the metathesis method in organic synthesis

Chauvin , Grubbs and Schrock-2005

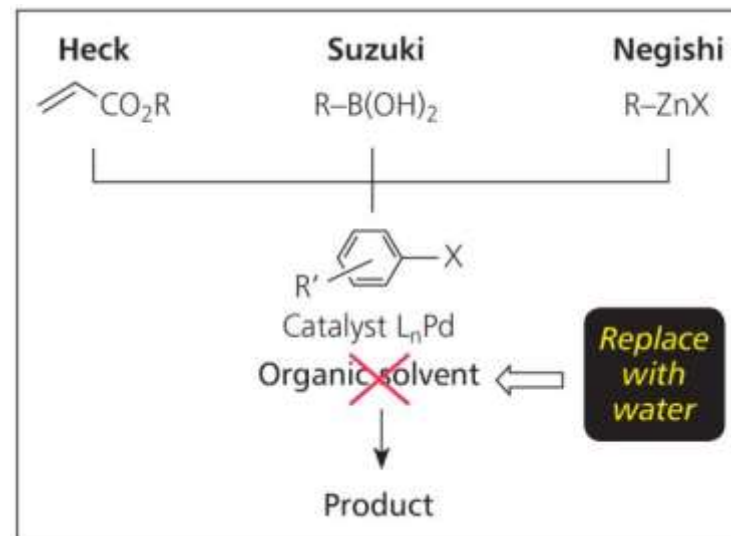
Ru based catalyst – Highly active , less steps for synthesis and all varieties of olefin can be used .

Green Solvents, normal T and P, less hazardous waste , Less energy

Palladium-catalysed cross-couplings Reactions

Heck, Suzuki-Miyaura and Negishi-2001

Water is used as a solvent replacing the organic solvents



US EPA and the ACS Green Chemistry Institute

Presidential Green Chemistry Challenge Award.

Computer Chips

Los Alamos National Laboratory

Water purification and consumption is an additional heavy burden. A typical plant processing **40,000 silicon wafers** per month consumes several **million gallons of water** per day. $-SC CO_2$



Feather based Computer chips

Prof . Richard Wool

Affordable Composites from Renewable Sources

8 billion-plus broilers, 3 billions pound waste.



FUEL FROM CHICKEN FEATHERS

Professor Manoranjan

University of Nevada, Reno's Renewable Energy Centre

153 million gallons of biodiesel annually in the U.S. and 593 million gallons worldwide.



Green synthesis of sitagliptin

Merck and Codexis Company

*Sitagliptin active ingredient in Januvia™, a treatment for type 2 diabetes
Rh based catalyst , high pressure hydrogenation etc*



Bio catalysis - transaminase enzymes

Green synthesis of Zocor

Professor Yi Tang, of the University of California,

Medicine for treating high cholesterol



Micro-organisms convert cornstarch into a resin

As strong as Rigid petroleum-based plastic

Ingeo biopolymer



 **NatureWorks**
Ingeo: naturally advanced materials

Bio-degradable and Compostable Packaging solutions with *ecoflex*

- ✓ Compostable polyester film that called "*Ecoflex*"
- ✓ Biodegradable bags, "*Ecovio*®," made of this film along with cassava starch and calcium carbonate
- ✓ bags completely disintegrate into water, CO₂, and biomass in industrial composting systems



Paint

- ✓ Oil-based "alkyd" paints give off large amounts of volatile organic compounds (VOCs)
- ✓ *Sefose*® technology from P&G is prepared from natural, renewable feedstocks in a patented, solventless process.



- ✓ Sherwin-Williams developed water-based acrylic alkyd paints with low VOCs that can be made from recycled soda bottle plastic (PET), acrylics, and soybean oil.

Chemists Must Place a Major Focus on the Environmental Consequences of Chemical Products and the Processes by which these Products are Made.

We must consider our chemical ecological footprint.



GREEN CHEMISTRY

PREVENTING POLLUTION

SUSTAINING THE EARTH

