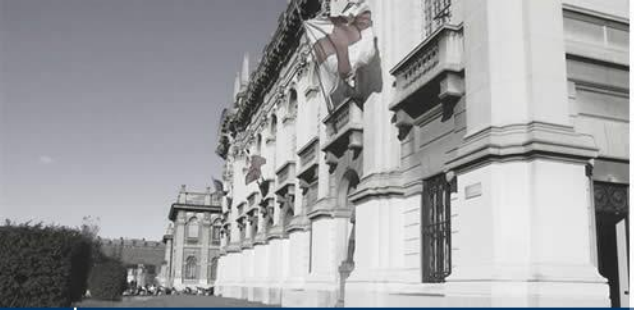


School of Industrial and Information Engineering
Course 096125 (095857)
Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

# Substitution/Reduction of Toxic Reagents.

Prof. Attilio Citterio
Dipartimento CMIC "Giulio Natta"
https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

# Product Substitution and Prevention.

**Substitution**: an ethical obligation**!**

- The substitution of dangerous substances and preparations is a general principle of prevention of chemical risk for population and for ecosystems.

**Substitution of C/M/R products as other products has its limits:**

- Does not exist always substitutes of universal use and all proposal of substitution need always of a validation study for users.
- A substitution solution will not valid unless for a limited period.

(EU view)

Flexible, non-dogmatic micro-approaches for bottom-up governance rather than global methodological risk management solutions:

- Whistle-blowers & information systems on incidents / near misses
- Tradition in several industries - and in insurance

Explicit reference to **liability** for managerial decisions expected to bring discussion back to manageable issues, including seemingly trusted tools such as insurance.

# DfE and Product Substitution.

*Goals*

- Safer Products
- Safer chemical ingredients is baseline
- Life cycle impacts are considered
- Protecting Consumers – Especially Children.

*Central Elements*

- OPPT technical tools and expertise
- Multi-stakeholder participation.

*Results*

- Industry partners reduced more than 250 million kg of chemicals of concern in recent years.

# Toxic Reagents and PIC Procedure.

PIC procedure of Rotterdam Convention apply to: (a) banned compounds or severely limited; and (b) very dangerous pesticides formulations.

Title 2 of this Convention affords the following definitions:

(a) “Chemical Compound" is a substance both as such and in mixture or preparations and both synthesized and obtained from nature, but not includes any living organism. Comprises the following categories: pesticides (included dangerous formulations) and industrial products;

(b) “banned chemical" indicates the compounds whose use within one or more categories was prohibited by definitive law provision, to protect human health or environment. They include compounds whose primary use was rejected or were withdrawn by the industry both from internal market or from other considerations during the course of internal process approval and for which exists clear evidence that this action has been taken to protect human health or environment;

(c) “severely limited chemicals" are compounds whose use within one or more categories was prohibited by final regulations to protect human health or the environment, but which for some specific uses remain permit. For these apply indications expressed to b point;

(d) "formulation of very dangerous pesticides" are chemicals formulated as pesticides producing severe effects on health or on environment observable in a short time after a single or multiple exposition, in the use conditions.

In total there are 41 chemicals currently subject to the PIC procedure. Between these 24 are pesticides, 11 industrial chemicals and 6 very dangerous pesticide formulations. (*)

# Circumstantial vs. Intrinsic. Recognize the Danger as a Flow Diagram.



## Circumstantial

- Use
- Exposition
- Treatment
- Handling
- Protection
- Recycling
- Cost.

## Intrinsic

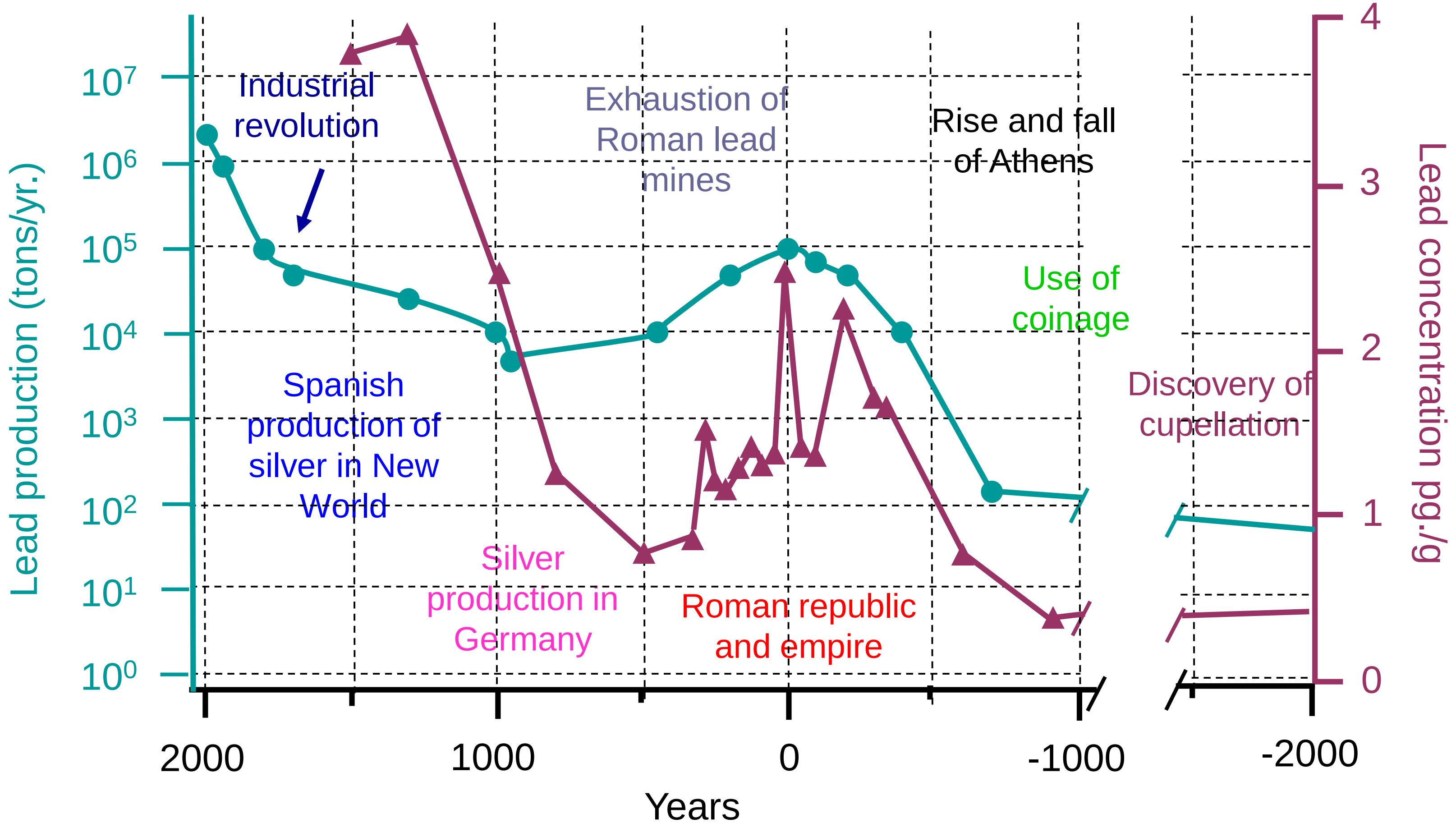
- Molecular design to reduce toxicity
- Reduced ability to manifest danger
- Intrinsic Safety towards accidents or terrorism
- Increased revenue potential.

# ID of Dangerous Materials.

| Prohibited – High Risk<br>***Substitutes already available*** | Limited – Substitutes with higher Risk<br>***to Develop*** | Ro Reduce – Lower Risk<br>***to Monitor*** |
|---|---|---|
| Arsenic & compounds | Beryllium (<2%) | Acetone |
| Asbestos | Hexavalent Chromium, | Ammonia |
| Benzene | ODS of class II | Butyl-, Sec-butyl alcohol |
| Beryllium (>2%) | Cyanides | Ethyl benzene |
| Cadmium & compounds | Dimethylformamide | n-Hexane |
| Chlorinated Solvents | HCFC-14 lb & HCFC-22 | Hydrofluoric acid – for cleaning |
| Ethyl alcohol (for hand cleaning) | Hydrazine | Isocyanates |
| Ethereal compound of ethylenglycol | Hydrofluoric acid / HF gas | N-Methyl-2-pyrrolidone |
| Formaldehyde | Lead & compounds | Isopropanol |
| Mercury & compounds | Artificial fibers, (crystobalite, fiberfrax) | Nickel coatings |
| Methanol (for hand cleaning) | MDA (4’,4’-Methylenedianiline) | Nitric acid |
| Methylene chloride | Methyl alcohol (methanol) | Petroleum distillates |
| Substances of class I $O_3$ depletors | Methyl ethyl ketone (MEK) | Phosphoric acid |
| Radioactive materials, included wastes from nickel to Thorium (TD) | Methyl iso-butyl ketone (MIBK, 4-methyl-2-pentanone) | Sulfuric acid |
| Toluene diisocyanate | Phenol, Styrene, Toluene, Xylene | 1,2,4-trimethylbenzene |

UTC PRIORITY CHEMICALS -For Elimination In New Designs by 1/2007 For Elimination In Legacy Designs/ Spares/ Services by 1/2012

# Environmental Lead is Mostly Anthropogenic.




Boutron et al. *Science*, **1994**, *265*, 1841–1843

# Prioritization Evaluated in the First Instance Trough the Dangerous Material Index (HMI).

L'HMI defines the "greenness" of products assigning values of "danger" to materials & processes

$$I_h = \sum_{n=1}^{N} \frac{T_n \cdot P_n}{D}$$

where: $I_h$ = Dangerous Material Index (P&W Wide)

N = Number of specifications in the project

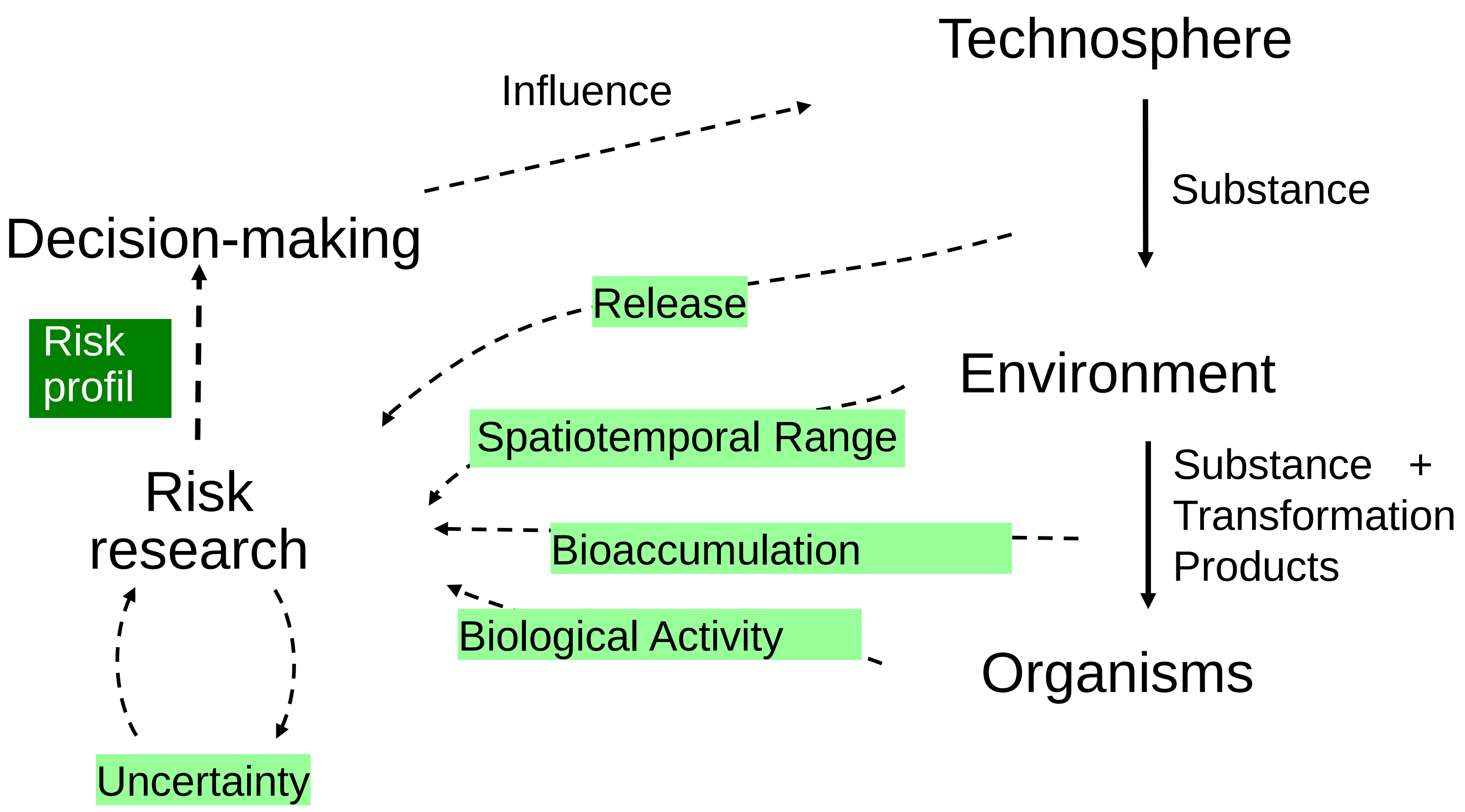
T = Toxicity value of specification*

P = Number of numbered parts requiring specifications

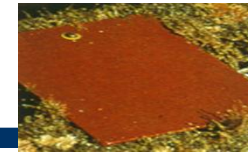
D = Total number of numbered parts in the article

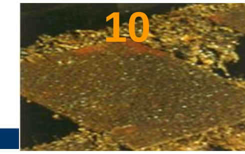
* The danger value is based on impact on aquatic ecosystem, air quality, soil and water contamination potential, stratospheric ozone depletion, and employers workplaces.

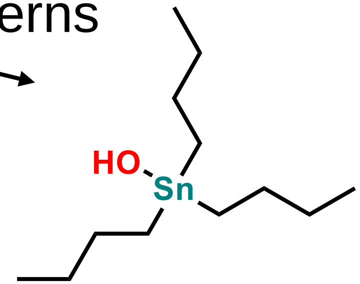
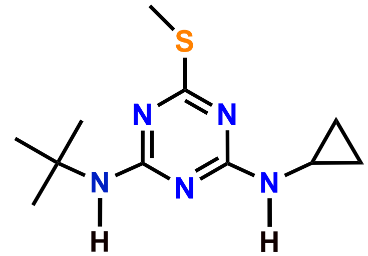
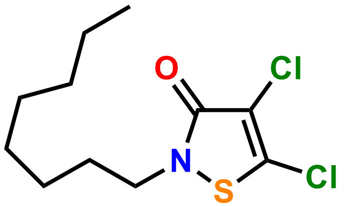
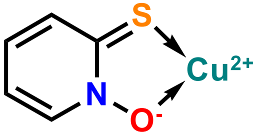
# Risk Management Cycle and Eco-toxicological Information on Chemical Products.



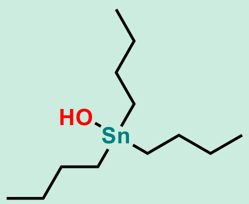
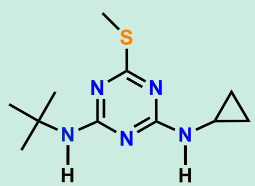
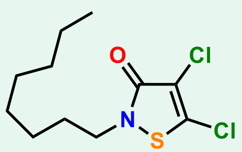
# Anti-scalant Biocides.





| | Examples of high concerns | | CAS reg. |
|---|---|---|---|
| Release | 1900 t/year |  | 1067-97-6 |
| Spatio-temporal range | 40.000 years | $Cu^{2+}$ | |
| Bioaccumulation | 200 to 30.000 L/kg |  | 28159-98-0 |
| Biological activity | 100 to 1 μg/L |  | 64359-81-5 |
| Uncertainty | $PT_2$, $CH_3Pt^+$, … |  | 4559-38-2 |

# Geometric Mean of Particle-Water Sorption Constants in Water ($K_{pw}$)*.

| Substance | | Parameter | n | Mean | $q_{0.05}$ | $q_{0.95}$ | Unit |
|---|---|---|---|---|---|---|---|
| $TBT^{+}$ |  | $K_{pw}$ | 13 | 4.7 | 0,28 | 79 | ($10^3$ L·kg$^{-1}$) |
| | | $k_w$ | 13 | .061 | .042 | .088 | (day$^{-1}$) |
| | | $k_s$ | 4 | .24 | .062 | .9 | (year$^{-1}$) |
| $Cu^{2+}$ | $Cu(H_2O)_6^{2+}$ | $K_{pw}$ | 4 | 45.7 | 10.3 | 204 | ($10^3$ L·kg$^{-1}$) |
| Irg.1051 |  | $K_{pw}$ | 1 | 3.1 | .36 | 26 | ($10^3$ L·kg$^{-1}$) |
| | | $k_w$ | 1 | .0054 | .0024 | .0012 | (day$^{-1}$) |
| | | $k_s$ | 1 | .0086 | .0038 | .19 | (year$^{-1}$) |
| DCOI |  | $K_{pw}$ | 2 | 1.1 | .13 | 9.3 | ($10^3$ L·kg$^{-1}$) |
| (sea-nine) | | $k_w$ | 5 | .44 | .007 | 2.7 | (day$^{-1}$) |
| | | $k_s$ | 1 | 6.1 | 2.7 | 14 | (year$^{-1}$) |

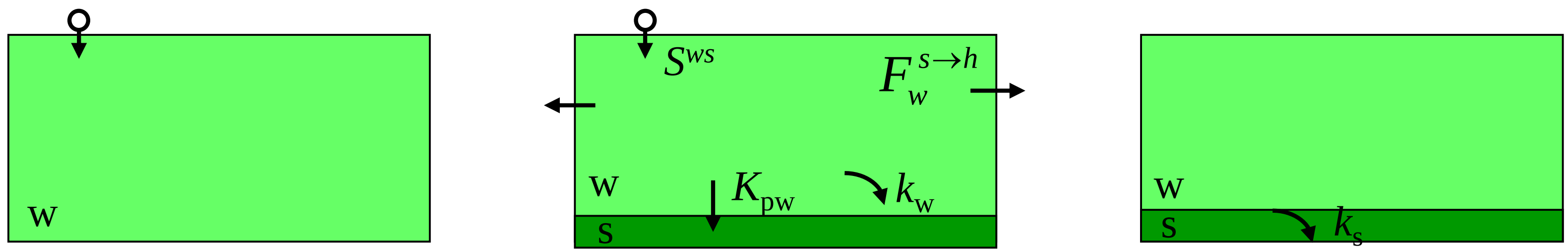
* and degradation rate constants in water ($k_w$) as well as in sediments ($k_s$), the number *n* of data points from literature used for lognormal distribution estimations and the $5_{th}$ and the $95_{th}$ percentiles ($q_{0.05}$ and $q_{0.95}$) of the estimated distributions.

# Spatiotemporal Range.

Build a fate model:

- Define environmental compartments
- Collect substance data on
  - Degradation kinetics
  - Particle water distribution
- Optional: estimate data distributions

Estimate residence times in the environment:




$S^{ws}$ = input

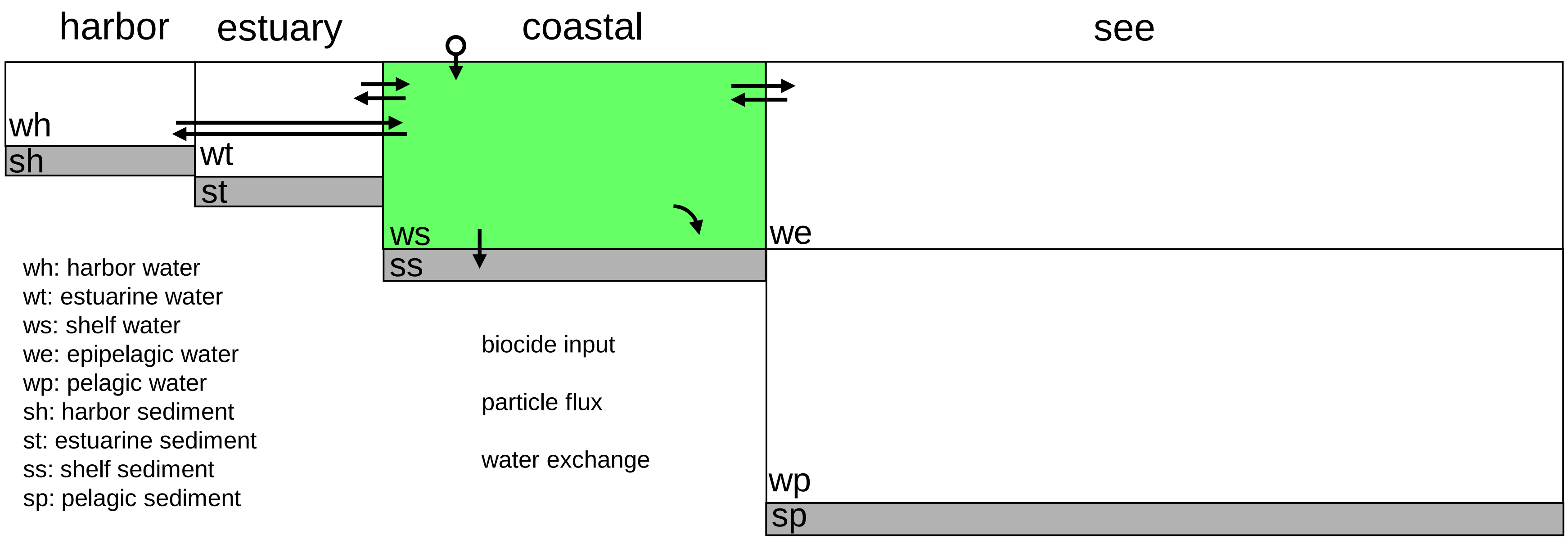
$F_w^{s \to h}$ = mass transfer

$K_{pw}$ = particle-water sorption constants in water

$k_w$ = degradation rate constants in water

$k_s$ = degradation rate constants in sediment

# Evolution Model of a Biocide in $H_2O$.

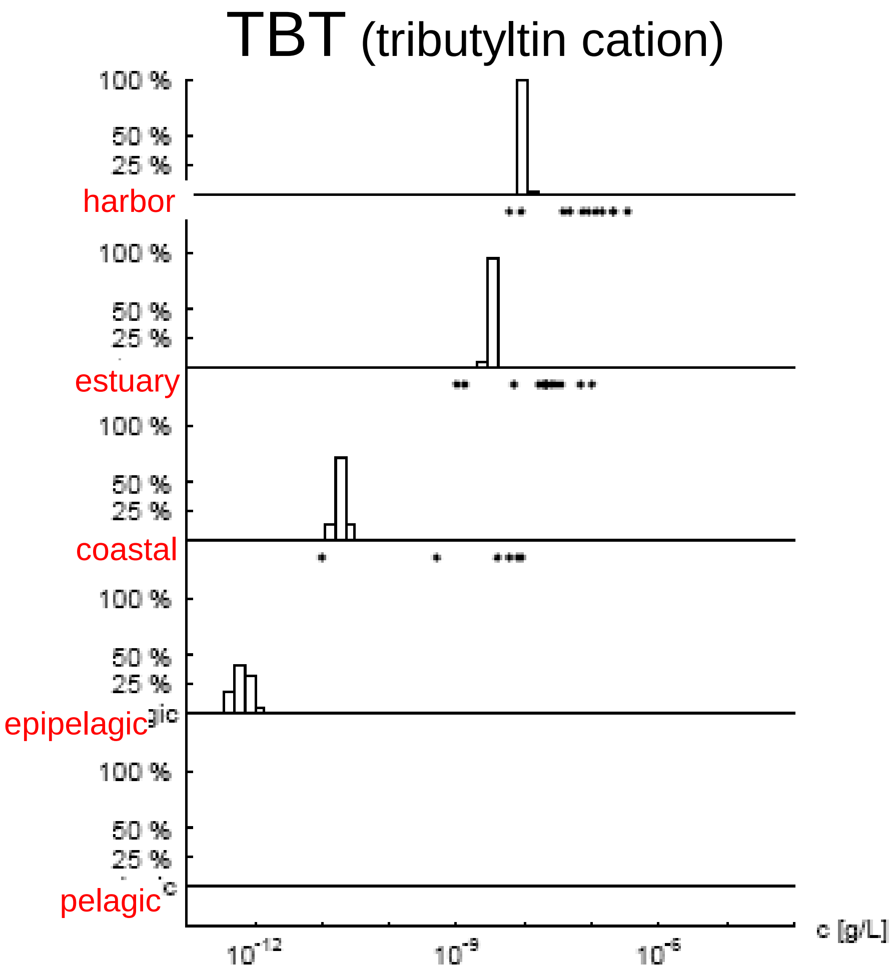


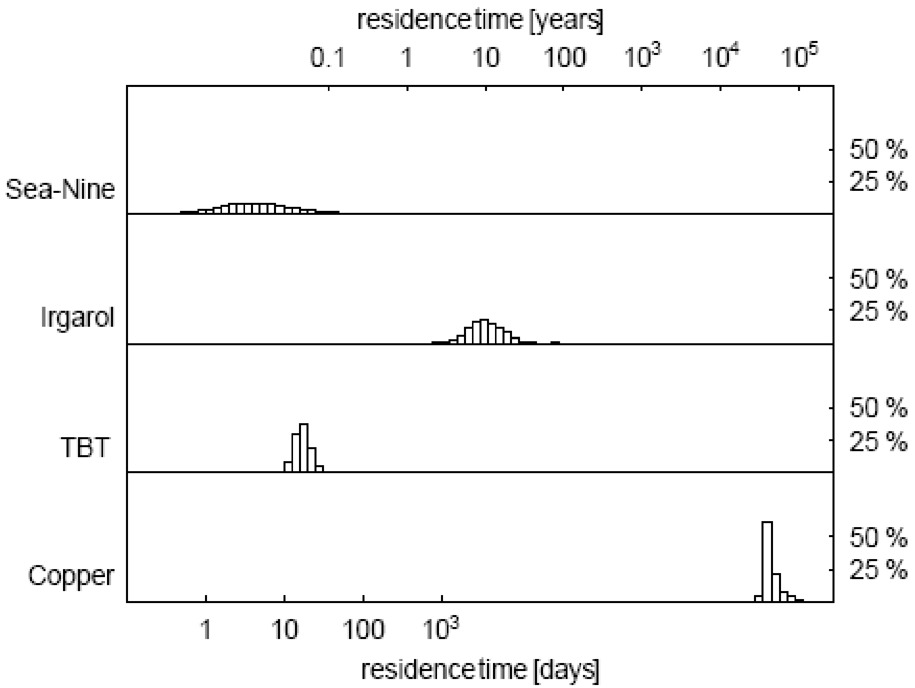

$$M^{ws} = S^{ws} - \left( \frac{F_w^{s \to h} + F_w^{s \to t} + F_w^{s \to e} + f_{diss} K_{pw} F_P^{ws \to ss}}{V^{ws}} \right) M^{ws}$$

$$M^{ws} = 0 + \frac{F_w^{h \to s}}{V^{wh}} M^{wh} + \frac{F_w^{t \to s}}{V^{wt}} M^{wt} + \frac{F_w^{e \to s}}{V^{we}} M^{we} + k_w M^{ws}$$

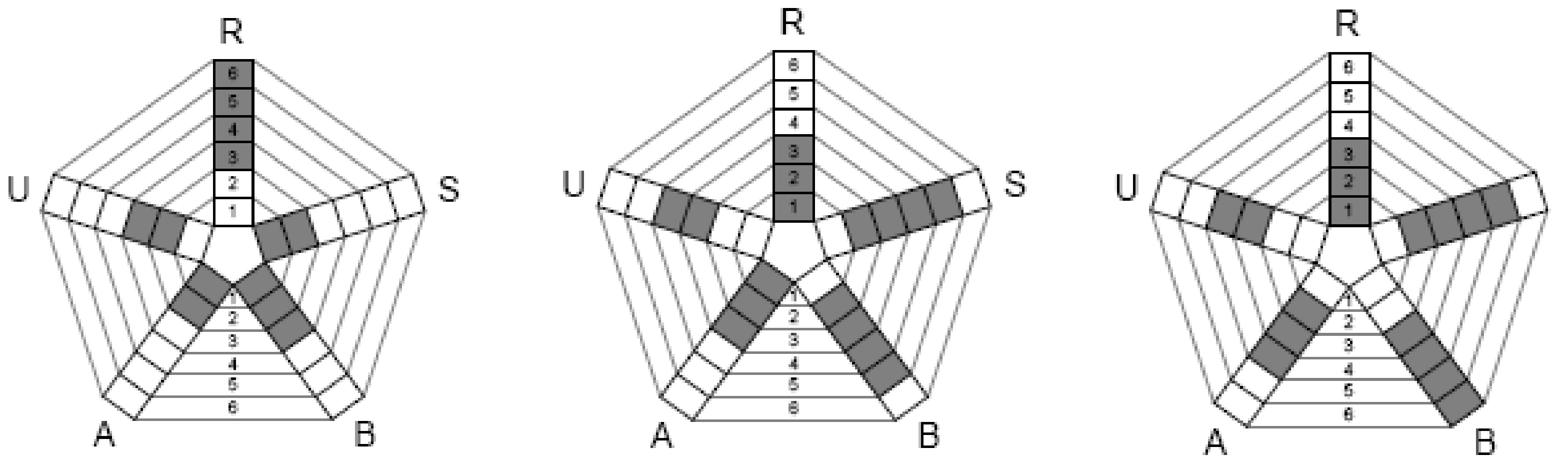
Ranke J (2002) *Environ Sci Technol* **36** 1539-1545

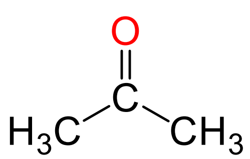
# Distribution in Different Environments and Estimation of Residence Time.

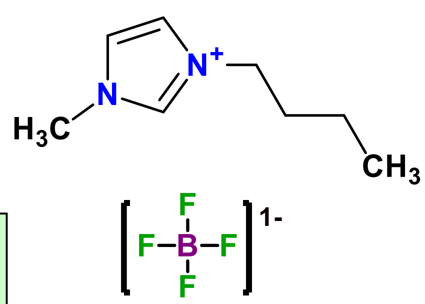


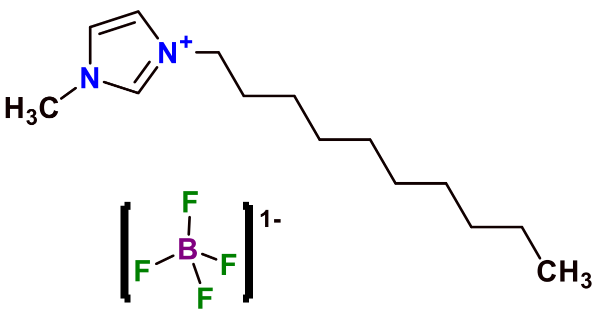



# Risk Profiles for Some "Ionic Liquids" Proposed as New non-VOC Solvents.




R = release for functional unit
S = spatio-temporal range
B = bioaccumulation
A = biological activity
U = uncertainty

*useful in the design of more environmentally-benign chemistries.*

- Structural Analysis Relationship (SAR)

SAR may be used to identify structural modifications that may improve a chemical's safety

*(if methyl-substituted analog of a substance has very high toxic, and it decreases as the substitution moves from ethyl to propyl, it is reasonable to increase the alkyl chain length to design a safer chemical!)*

# Functional Group Approaches to Green Chemistry (2).

✓ Elimination of Toxic Functional Group

- chemicals are often defined by structural features *(aldehyde, ketone, nitrile, isocyanate, etc.)*
- design safer chemical could proceed by removing the toxic functionality, which defines the class

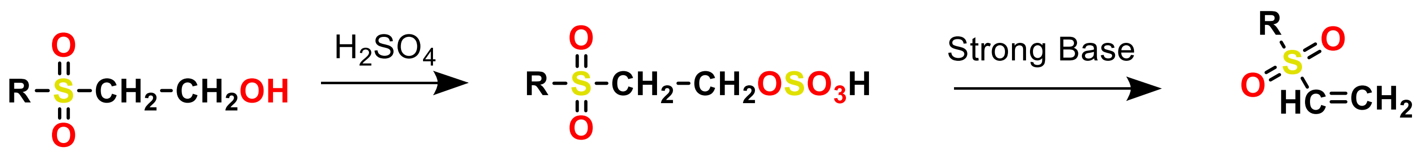
*(Example)* : masking of vinyl sulfones

*(sulfones can be made safer by masking the functional group)*

✓ Reduce Bio-Availability

if any substance is unable to reach the target substance, it is innocuous

✓ Design of Innocuous Fate




not reactive

vinyl Sulfone
highly reactive

*Previous general guidelines for improving environmental performance rely on knowledge and creativity of engineers*

- More popular method is Combinatorial Approaches *(to identify green chemistry alternatives)*
  - select a set of functional group building blocks from which a target molecule can be constructed
  - series of stoichiometric, thermodynamic, economic, and other constraints can be identified *(these serve to reduce the number of possibilities that might be considered)*
  - a set of criteria can be used to identify reaction pathways that deserve further examination

# Systematic Construction of Alternative Chemical Pathways – First Step.

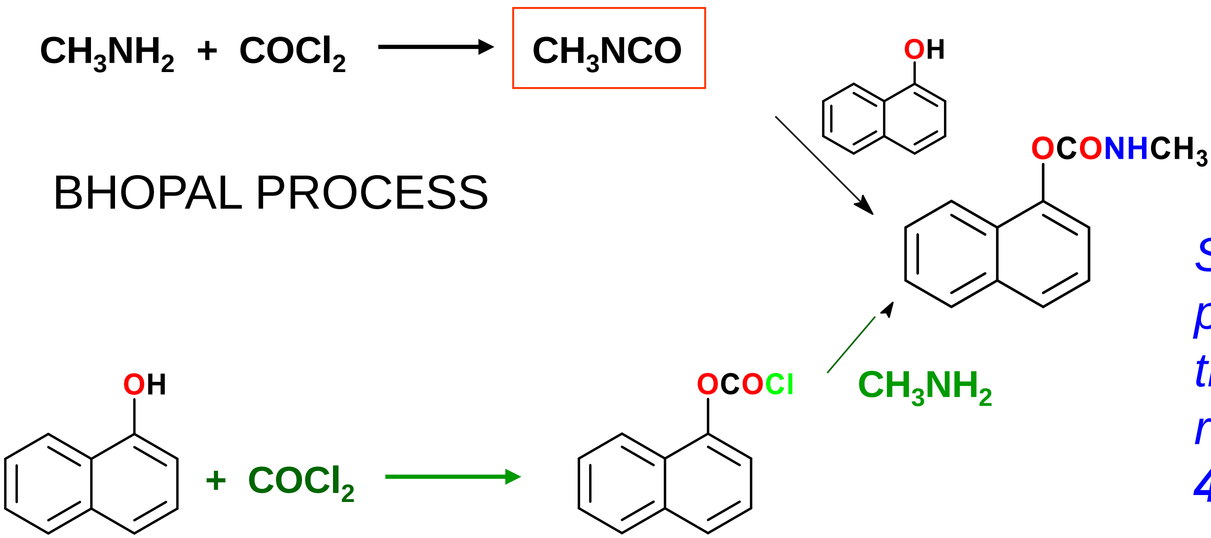
**First Step**: select a set of group building blocks

*important to identifying reaction pathways that minimize the use of hazardous materials*

- Include the groups present in the product
- Include groups present in any existing industrial raw materials, co-products or byproducts
- Include groups which provide the basic building blocks for the functionalities of the product or similar functionalities
- select sets of groups associated with the general chemical pathway employed *(cyclic, acyclic, or aromatic)*
- reject groups that violate property restrictions.

# Bhopal Chemistry - A Lesson in More Safe Intrinsic Design.

## Old Synthesis of Carbaryl (1-Naphthalenyl-methyl carbamate) thought Methylisocyanate




**ALTERNATIVE ROUTE**

*Studies have shown that process integration in the Bhopal site would reduce MIC stock* ***from 41 ton. to < 10 kg!***

**Continuous process for phosgene production!!!**

New Synthesis of Methylisocyanate

$$CH_3NH_2 + CO \xrightarrow{\text{catalyst}} CH_3NHCHO$$

$$CH_3NHCHO + O_2 \xrightarrow{\text{catalyst}} CH_3NCO$$

DuPont

# Functional Group Building Blocks.

**Synthesis of Carbaryl** : identification of alternative pathways

Product molecule contains aromatic groups

it is necessary to include a range of aromatic functionalities such as

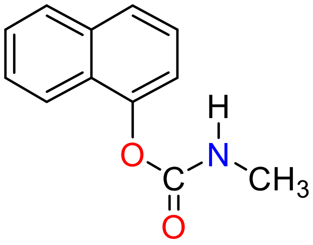
*- aromatic carbon bound to hydrogen (ACH)*

*- aromatic carbon to other aromatic carbon (AC - )*

*- aromatic carbon bound to chlorine*

*- aromatic carbon bound to a hydroxyl group (ACOH)*

*- more aromatic functionalities could be chosen, if desired*



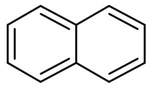

other groups appearing in the product molecule, or related to groups appearing in the product molecule are

- $CH_3$, $CH_3NH<$, $CH_3NH_2$-, - COO -, - CHO -, - $CO_2H$, - OH, - Cl

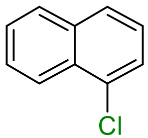
These group blocks can be used to identify a set of potential molecular reactants *(assumed only monosubstituted aromatic molecules would be used, since the product is monosubstituted. Also, assumed reactants for which carbon skeleton would need to be altered would not be used).*

# Potential Reactants on Carbaryl Synthesis Identified by Buxton.

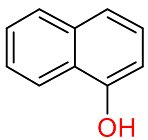




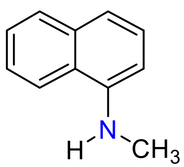
(a) Naphthalene



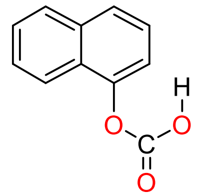

(b) 1-Chloronaphthalene



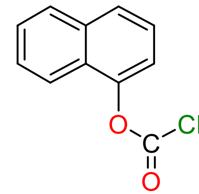

(c) 1-Naphthol



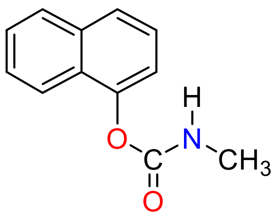

(d) N-Methyl-1-Naphthylamine




(e) 1-Naphthalenyl Hydroxyformate




(f) 1-Naphthalenyl Chloroformate




(g) Carbaryl

$Cl_2$

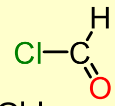
(a) Chlorine

$CH_3Cl$

(b) Chloromethane

$CH_3OH$

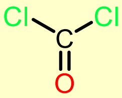
(c) Methanol



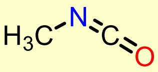

(d) Chloromethanal

$CH_3NH_2$

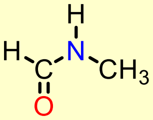
(e) Methylamine




(f) Phosgene




(g) Methyl isocyanate




(h) Methyl formamide

# Second Step: apply rules and constraints.

## Stoichiometric Constraints :

- *(Carbaryl case)* product molecule contains 7 aromatic carbons bound to hydrogen and 2 aromatic carbons bound to other aromatic carbons *(reactants must provide sufficient aromatic carbons, of various types, to generate the product molecule)*
- Similar stoichiometric constraints can be written for other types of groups in the molecule
- Some reaction pathway analysis assume that reactions, appropriately balanced for stoichiometry, *can proceed 100 % selectivity and yield*
- Other methods include thermodynamic constraints on selectivity.

# Final Step (ranked pathway).

Ranking schemes might include cost and environmental performance matrices

- economic ranking is based on the price difference between product and reactants
- environmental ranking assume a fixed % of materials used is released to the environment.

# Alternative Pathways for the Synthesis of Carbaryl.

The species numbers are listed below the Table and refer to the compounds shown in previous slide**.** The profit is the difference in value between reactants and products and environmental ranking is determined by assuming that a fixed fraction of the reactants and products are released to the environment

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | Profit | Env. Rank |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **-1** | | | | | | | | -1 | 1 | 1 | -2 | | | | | | | | 1.45 | 9 |
| | 1 | 1 | | -1 | -1 | | | | | 1 | | -1 | | | | | | | 1.03 | 7 |
| | 2 | | | -1 | -1 | | | | | 1 | -1 | | | | | | | | 1.00 | 2 |
| | 1 | | | -1 | 1 | | | | | 1 | | -1 | | | | 1 | -1 | | 1.00 | 12 |
| **-1** | | | | -1 | 1 | | | | | 1 | -1 | | | | | | | | 1.00 | 1 |
| | | 1 | | | -1 | | | -1 | | 1 | | -1 | | | | | | | 0.976 | 13 |
| | | | | | -1 | | | | | 1 | -1 | | | | | 1 | | -1 | 0.967 | 4 |
| | 1 | | | | -1 | | | -1 | | 1 | -1 | | | | | | | | 0.952 | 8 |
| | | | | | | | | -1 | | 1 | | -1 | | | | 1 | -1 | | 0.952 | 11 |
| | | 2 | | | | -1 | -1 | | -1 | 1 | | | | | | | | | 0.604 | 5 |
| | 1 | 1 | | | | -1 | | | -1 | 1 | | | | | | | | -1 | 0.543 | 6 |
| | | | | -1 | | | | | -1 | 1 | | | | | | | | | 0.503 | 3 |
| **1** | | | | | | | | -1 | -1 | 1 | | | | | | | | | 0.451 | 10 |

1 = Oxygen; 2 = Hydrogen; 3 = Hydrogen chloride; 4= Naphthol chloroformate; 5 = Methyl formamide; 6 = water; 7= Methylamine; 8 = Phosgene; 9 = Methyl isocyanate; 10 = Naphthol; 11 = Carbaryl; 12 = Naphthalene; 13 = Chloronaphthalene; 14 = methyl naphthylamine; 15 = Naphthenyl hydroxyformate; 16 = Chloride; 17 = Chloromethane; 18 = Methanol; 19 = Chloromethanal

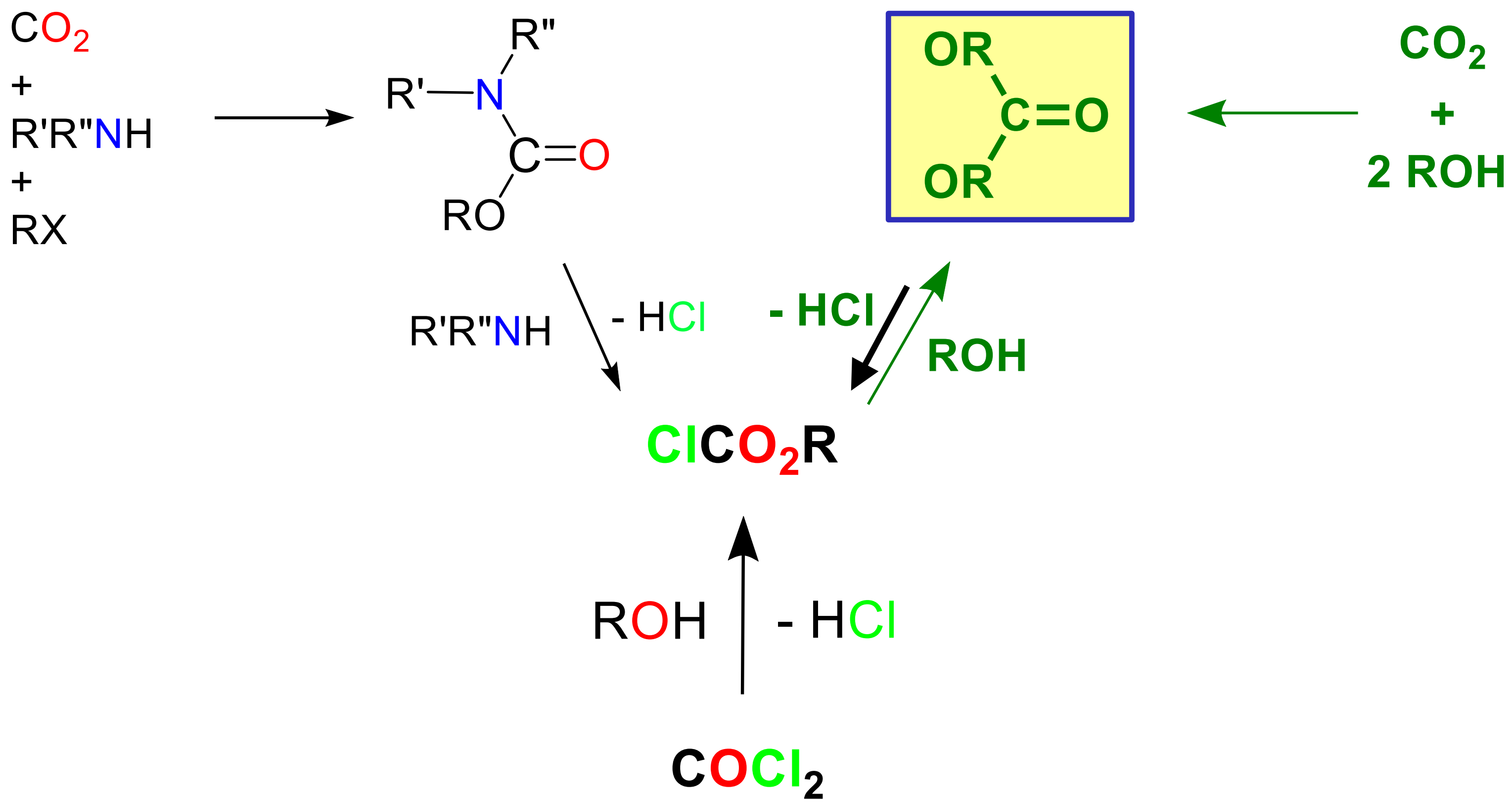
# Remarks on Carbaryl Example.

Results in the Table are intriguing (one cannot conclude that this type of analysis will yield the optimal reaction pathway)

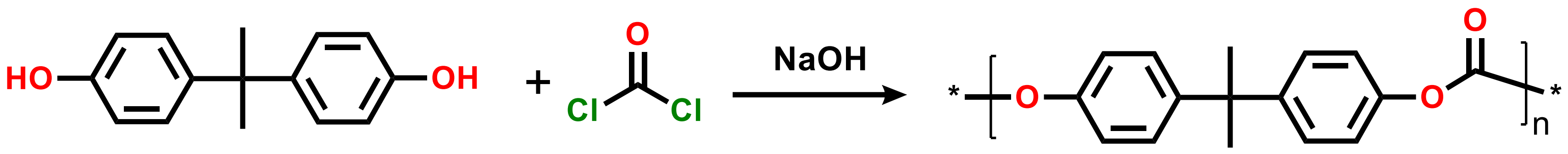
- These analysis results is to inject systematic decision rules into the search for alternative pathways.
  - sets of starting materials are identified based on the stoichiometry and chemical intuition
  - pathways can be identified and potential upper bounds for selectivity can be estimated using thermodynamics
  - alternatives can be quickly ranked using economic and environmental criteria

❖ **These systematic procedures may lead to a desirable alternative pathway, or they may merely lead to a clear definition of the constraints that should be considered in evaluating alternative pathways.**

# Potential Substitution of Phosgene with $CO_2$.



## Polycarbonate Synthesis: Phosgene Process

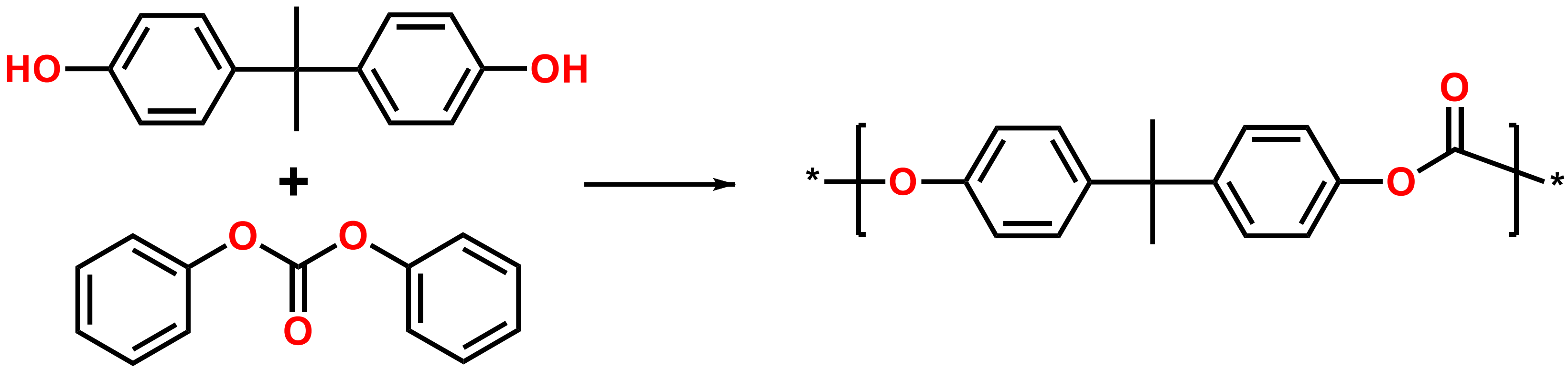



◆ Disadvantages

- Phosgene is toxic, corrosive
- The process use a large amount of $CH_2Cl_2$
- The polycarbonate is contaminated by chlorinated impurities.

# Principle 3: Substitution with Non-toxic Substances (2).

## Polycarbonate Synthesis: Solid State Process

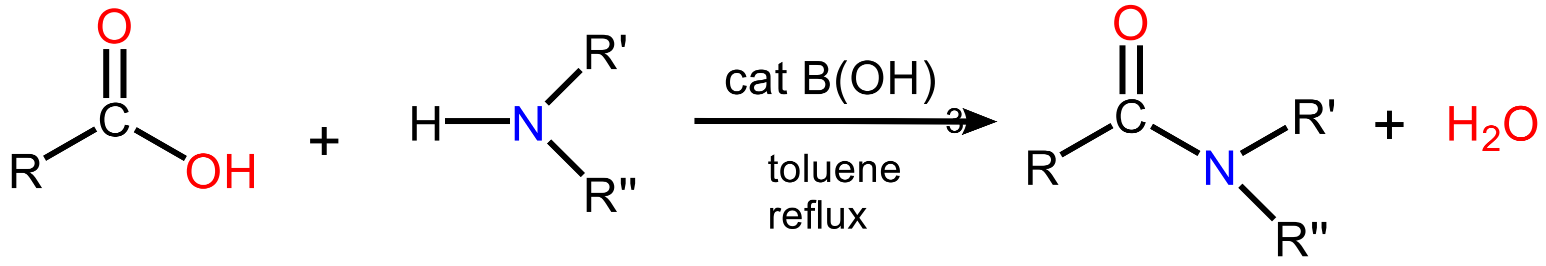



- Benefits
  - The carbonate is synthesized without phosgene
  - the use of $CH_2Cl_2$ is prevented
  - The polycarbonate has a better quality
    - Komiya *et al.*, Asahi Chemical Industry Co.

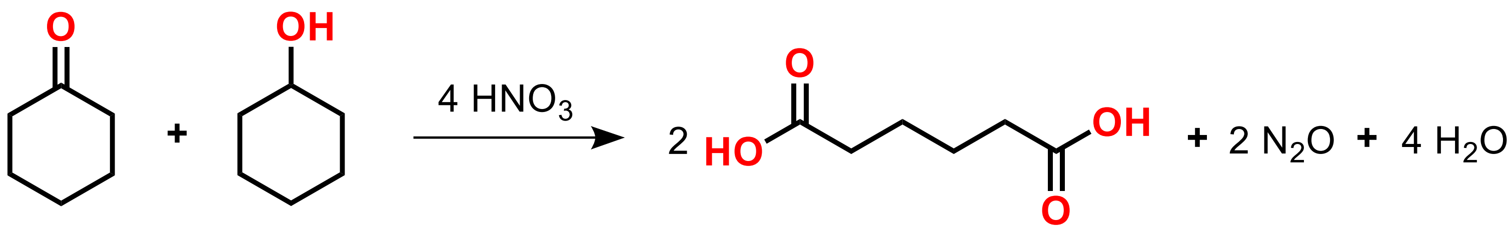
# Boric Acid Mediated Amidations.

Direct amidation of carboxylic acids with amines

- Boric Acid: non toxic, safe, inexpensive
- Does not use $SOCl_2$, $PCl_3$, phosgene
- Widely applicable
  - Hemisphere Technologies, Inc.



# Nitrous Oxide and Adipic Acid.




- $N_2O$ is a greenhouse gas 200 times more powerful than $CO_2$
- It is also involved in the ozone layer reduction
- The actual atmospheric concentration is 310 ppb with a 6% increase p.a.
- Before 1998, 10% of $N_2O$ was originated from the adipic acid production.

## Abatement Options

$$CH_4 + 4N_2O \rightarrow 4N_2 + CO_2 + 2H_2O$$

$$N_2O + 0.5O_2 \rightarrow N_2 + O_2$$

$$N_2O + 0.5O_2 \rightarrow 2NO \text{ (to nitric acid)}$$

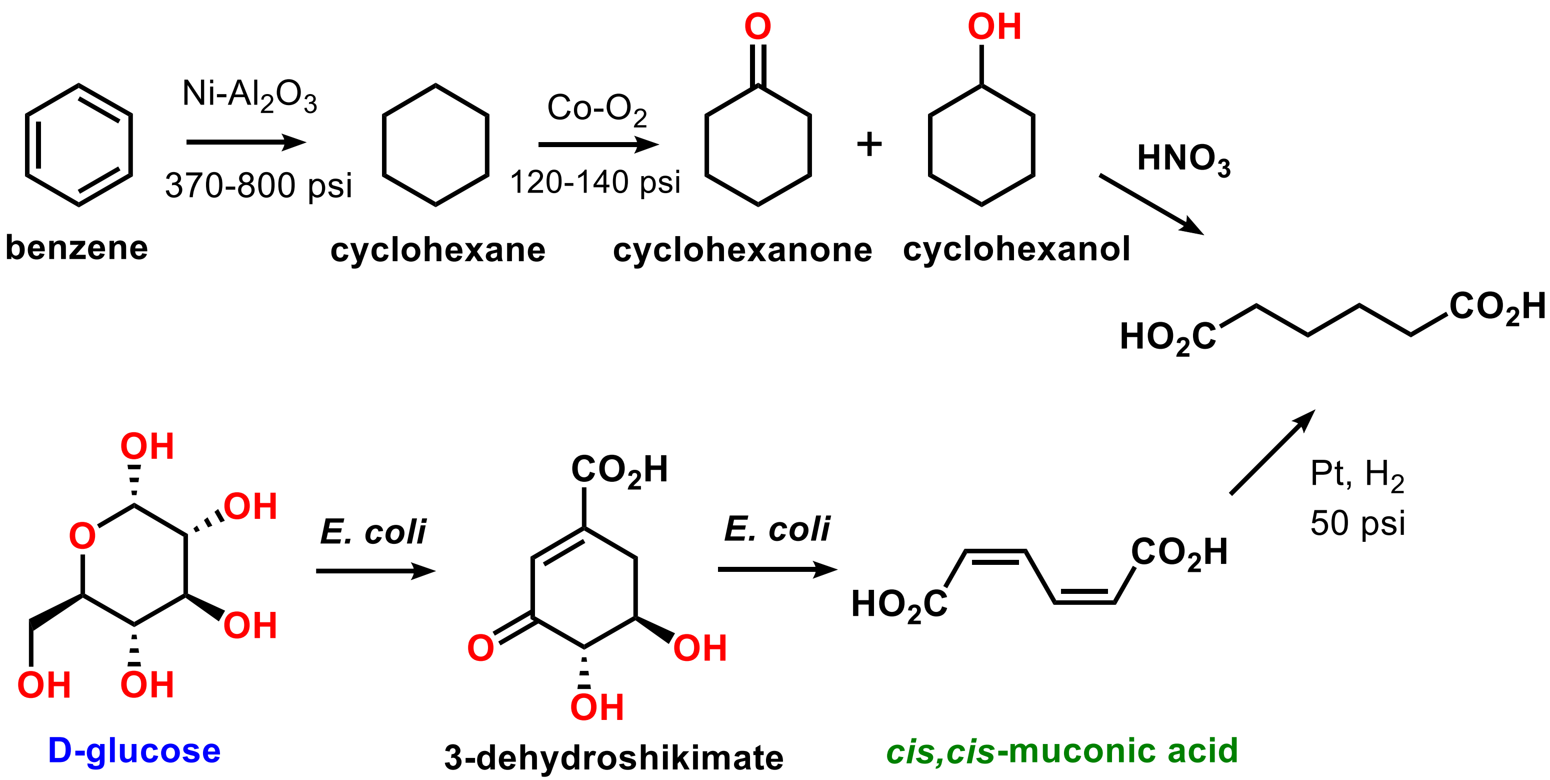
**Long term option (SM/Process Subst.)**

$$\text{glucose} \xrightarrow[\text{enzyme}]{} HO_2CCH{=}CHCH{=}CHCO_2H$$

$$\xrightarrow{H_2\ Pt} \text{Adipic Acid}$$

J W Frost & K M Draths, Chem. Br. 1995, 31 206

# Adipic Acid: Draths-Frost Biotechnological Synthesis.

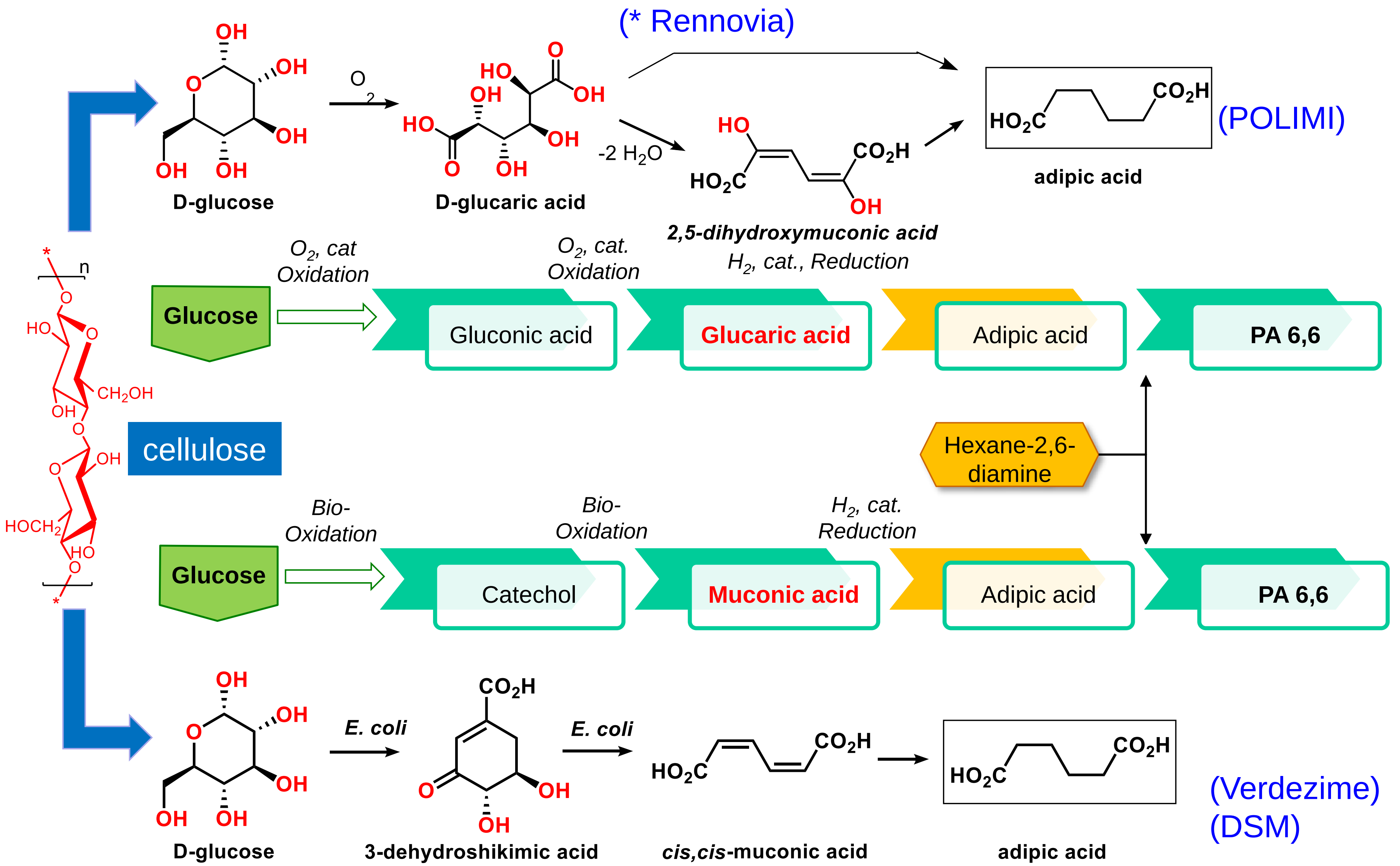



**Typical feed solution (bioreactor):**

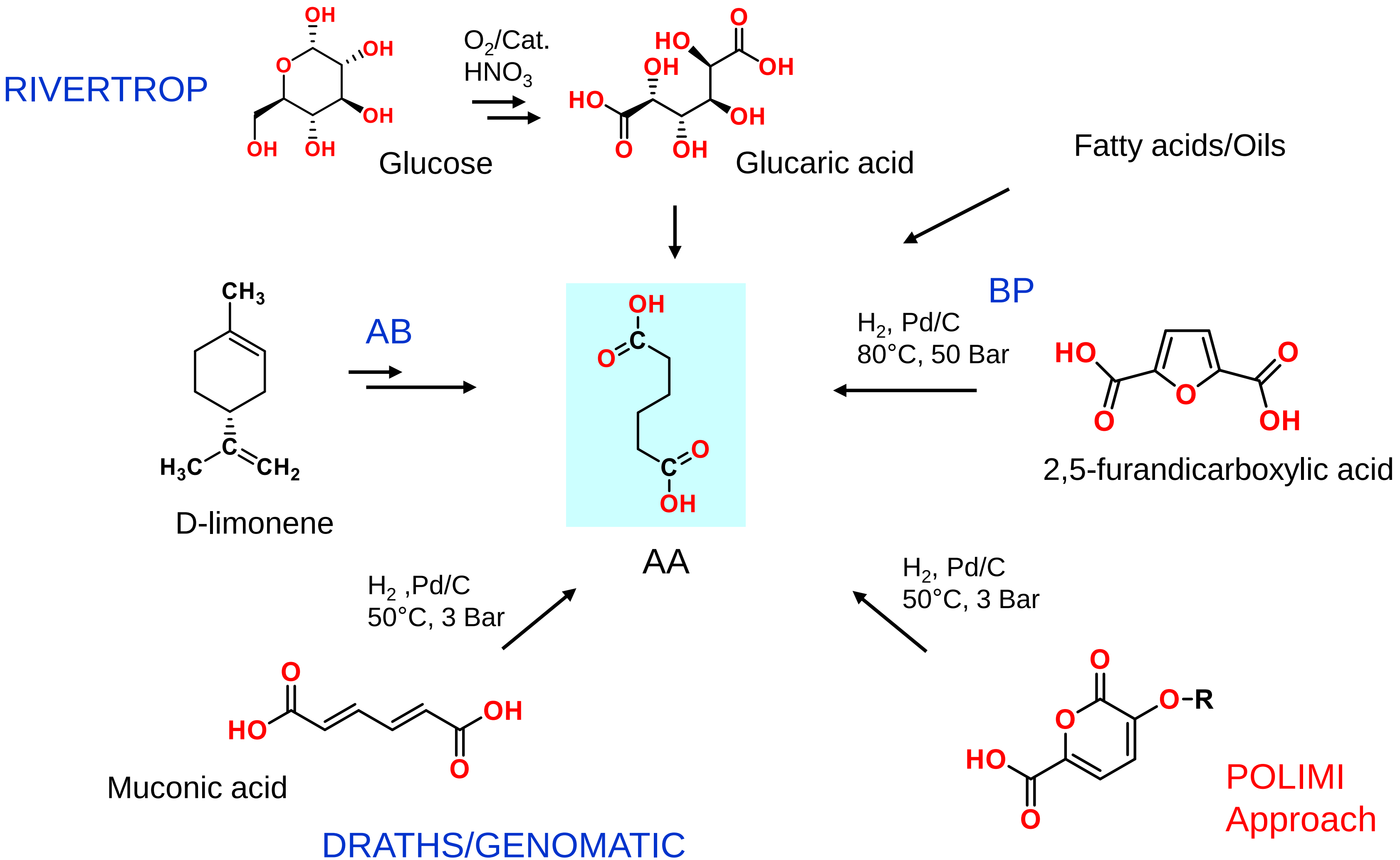
| | | | |
|---|---|---|---|
| In 1 Litre of water | 6 g $Na_2HPO_4$ | 0.12 g $MgSO_4$ | **Yield = 20.4 mmol** |
| 10 g bacto triptone | 3 g $KH_2PO_4$ | 1 mg thiamine | **% Yield = 33 %** |
| 5 g bacto yeast | 1 g $NH_4Cl$ | | |
| 10.5 g NaCl | 10 g glucose (62 mmol) | | |

# Approaches to Adipic acid: Biochemical/Chemical Conversion from Glucose.





# Bio-based Approaches to Adipic acid (from sugars, oils, and terpenes).




review MIP - Journal of Separation Science 36, 2013, 609–628

POLITECNICO DI MILANO

School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

# Examples of Substitution of Chemicals.

Prof. Attilio Citterio

Dipartimento CMIC “Giulio Natta”

https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

# Caprolactam.

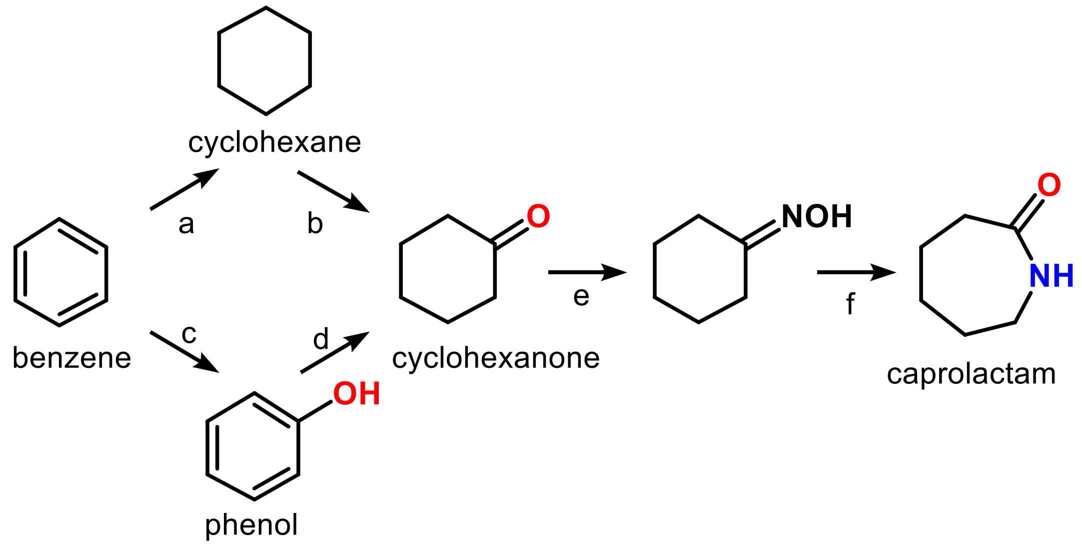
| Caprolactam, $8.8B Market |
|---|
| Volume: 4M mt<br><br>Price: ~$2.20 / kilogram<br><br>Primary Applications<br>Nylon-6 textile, resin, film, filament<br><br>Primary Manufacturers<br>BASF<br>DSM<br>Honeywell<br>China Petrochemical Development<br>Ube Industries<br>Sumitomo Chemical<br>Bayer<br>Others<br><br>Buyers: Various |

| Problems |
|---|
| Costs driven up by benzene prices<br><br>Large volumes of ammonium sulfate waste |

| Solutions |
|---|
| Chemical synthesis of caprolactam from glucose-derived lysine<br><br>Enables "renewable" structural material |

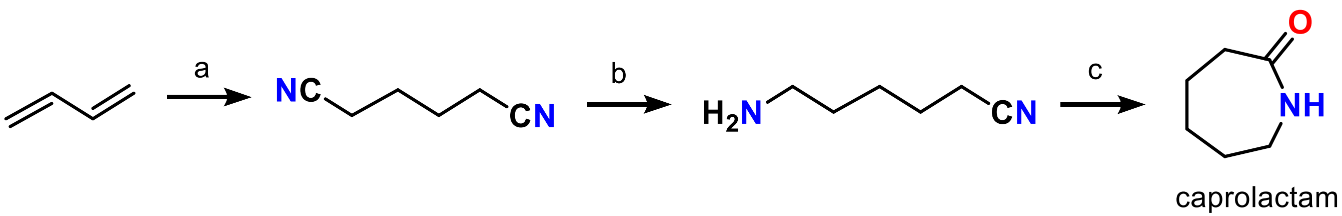
Reduction of salt waste streams

# Caprolactam Manufacture.




- **Benzene toxicity**
- **Oil Cost**
- **Waste streams**

(a) $H_2$, Pt; (b) i) $O_2$, Co, ii) Cu/Zn; (c) i) propylene, $H_{n+2}P_nO_{3n+1}$, 200 atm., 200 °C; ii) $O_2$; 90-120 °C; (d) $H_2$, Pd; (e) i) $(NH_2OH)_2H_2SO_4$, ii) $NH_3$; (f) i) $H_2SO_4$•$SO_3$, ii) $NH_3$.

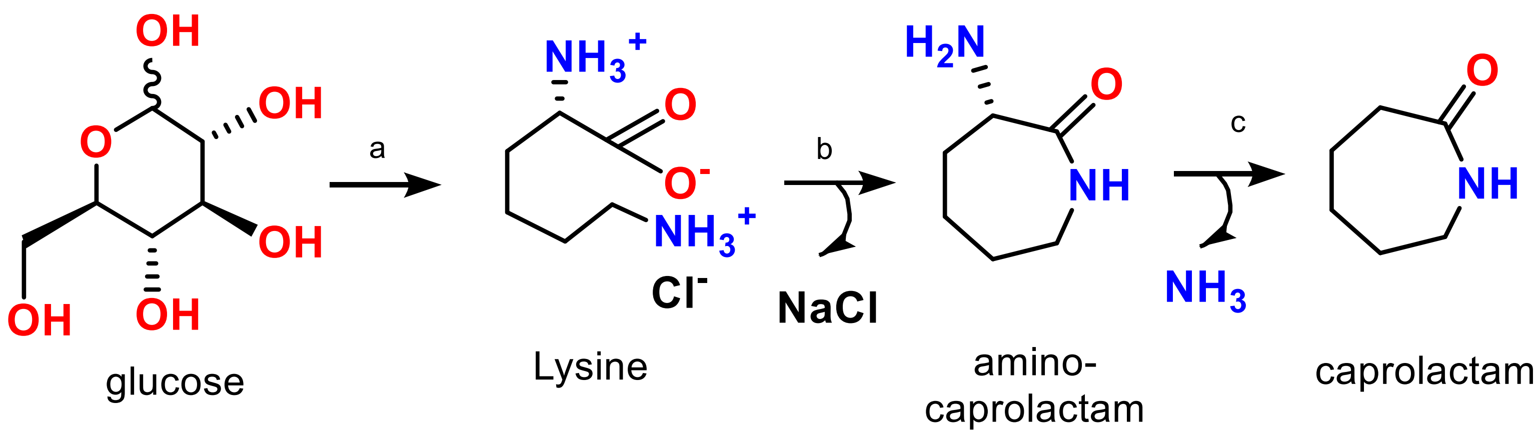



- **HCN toxicity**
- **Oil Cost**

(a) HCN, Ni; (b) $H_2$, Raney Ni/$NH_3$; c) $H_2O/NH_3$, 300-360°C, $TiO_2$ or $Al_2O_3$

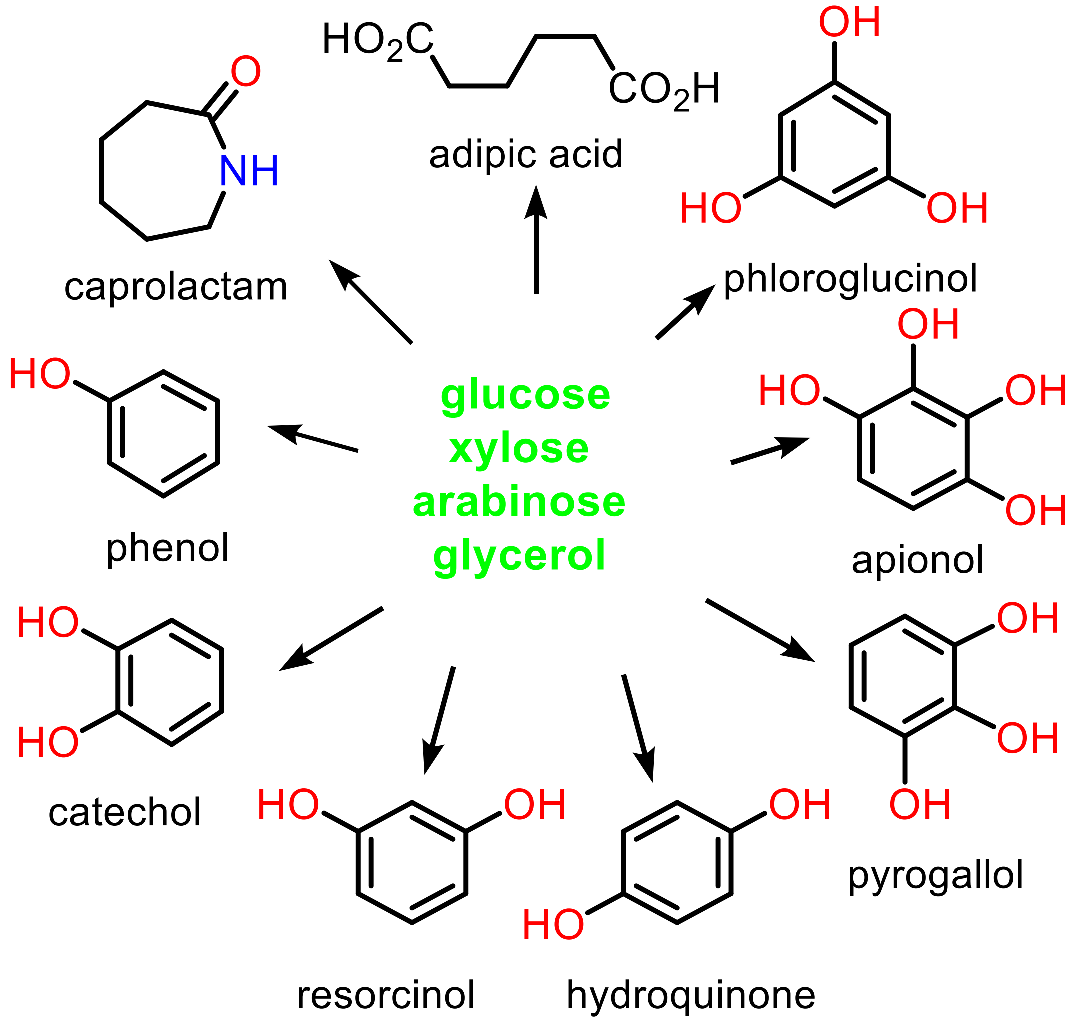
# Synthesis of Caprolactam from Renewable.

- Shielded from benzene price fluctuation
- Significant reduction in waste
- Enables “renewable” fiber



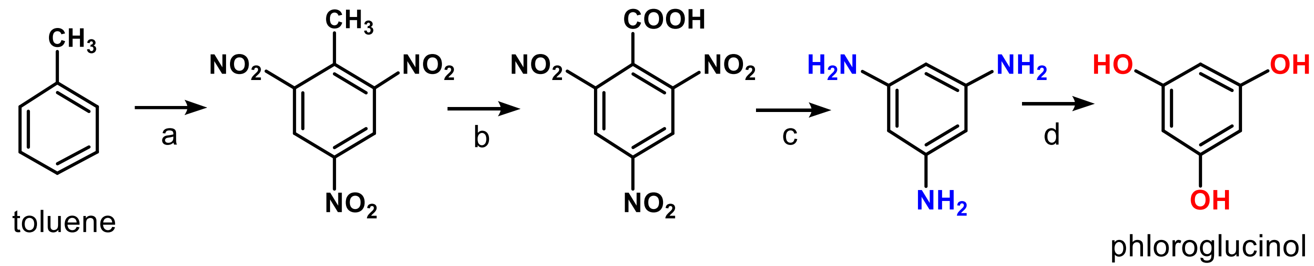

(a) microbial synthesis; (b) cyclization; (c) catalytic hydrodenitrogenation

# Aromatics from Renewables.



# Phloroglucinol.

## Existing Route to Phloroglucinol




Problems
- explosion risk
- toxic waste
  - "red water"
  - chromium salts
- multiple steps

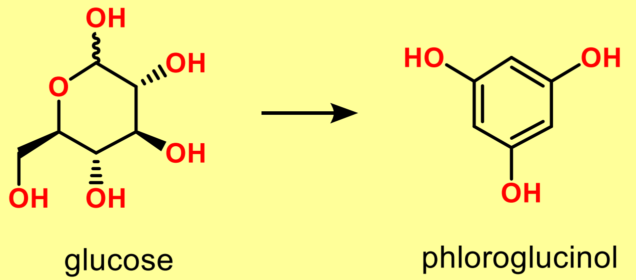
(a) $HNO_3$, $H_2SO_4$; (b) $Na_2Cr_2O_7$, $H_2SO_4$; (c) $Fe^0$, HCl; (d) $H_2SO_4$

**+ $Cr_2(SO_4)_3$ + $2KHSO_4$ + $9FeCl_2$ + $3NH_4Cl$ + $CO_2$ + $8H_2O$**

| + $Cr_2(SO_4)_3$ | + $2KHSO_4$ | + $9FeCl_2$ | + $3NH_4Cl$ | + $CO_2$ | + $8H_2O$ |
|---|---|---|---|---|---|
| 392 | 272 | 1143 | 160 | 44 | 144 |

**EA = 126/2282 = ca. 5%**

**E Factor = ca. 40**

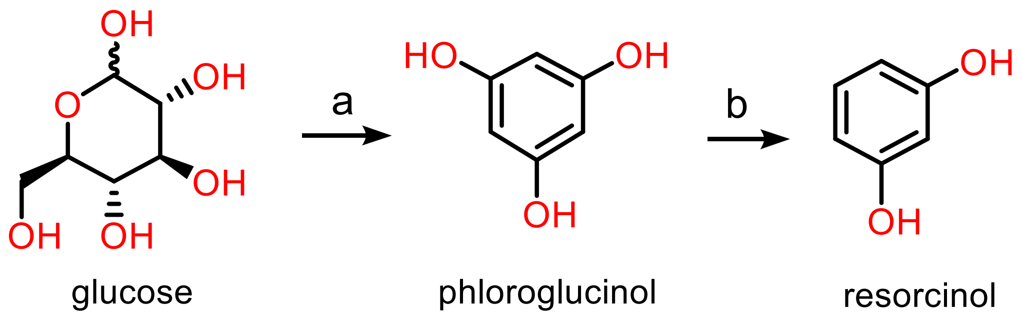



Advantages
- nontoxic glucose
- no toxic waste
- single step

(a) *E. coli* W3110serA(DE3)/pJA3.131A

# Resorcinol.

Manufacturing Route from Renewables:




(a) *E. coli* W3110serA(DE3)/pJA3.131A; (b) $H_2$, $Rh/Al_2O_3$

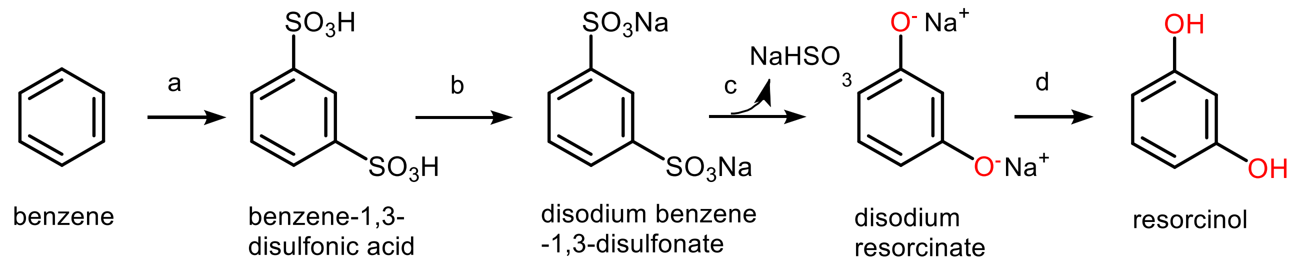
- Renewable feedstocks
- Nontoxic glucose
- Short synthetic sequence
- Mild reaction temperatures.
- Salt waste stream minimized
- Explosion risk minimized
- Use of contract manufacturing

current market price: $ 6.50/kg

2009 manufacturing cost: $ 3.80/kg

# Resorcinol (2).

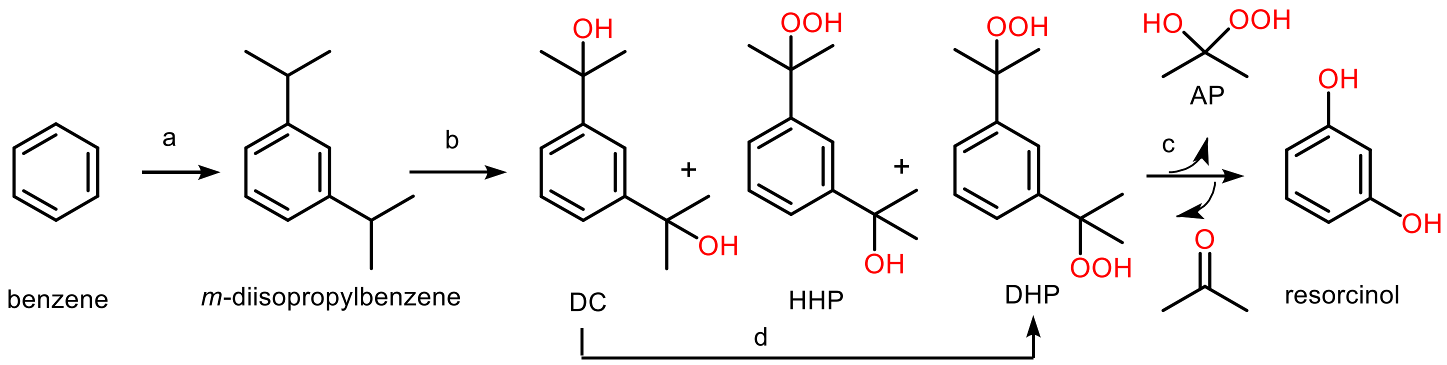
## INDSPEC Manufacturing Route




Challenges
- benzene
- high temperature
- salt byproduct

(a) $SO_3$; (b) NaOH; (c) NaOH fusion, 350 °C; (d) $H_2SO_4$

## Sumitomo Manufacturing Route

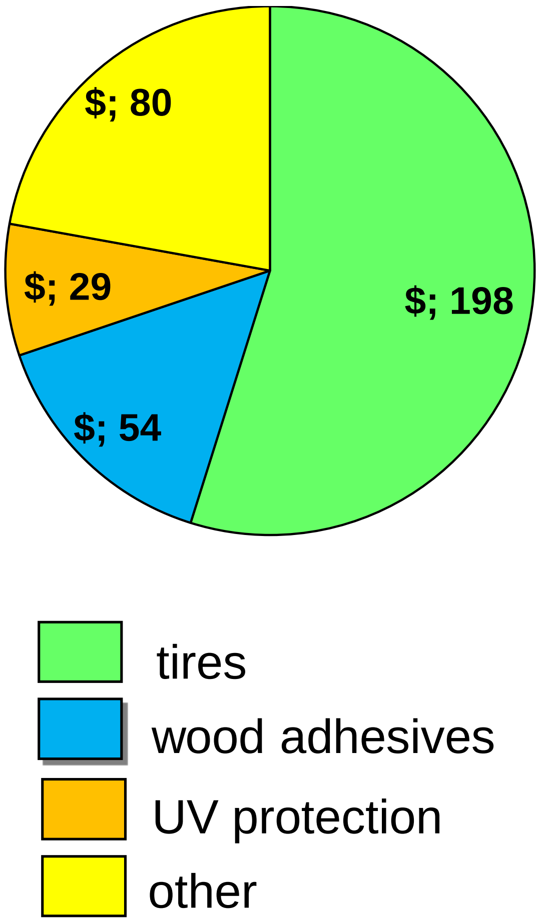



Challenges
- benzene
- yield issue
- detonation risk

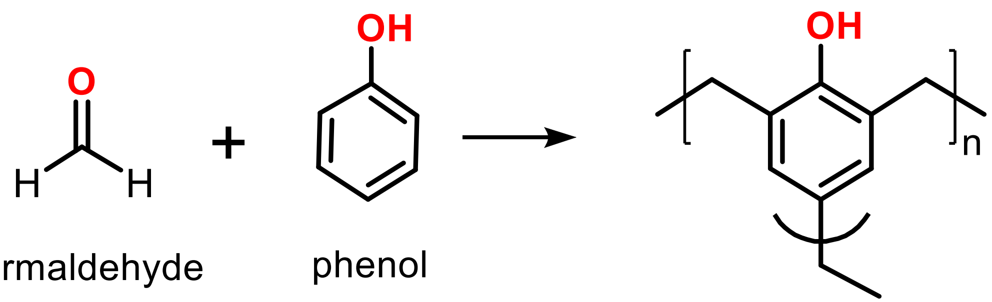
(a) propylene, HZSM-12; (b) $O_2$, NaOH; (c) $H_2SO_4$, heat; (d) $H_2SO_4$, $H_2O_2$

# Resorcinol Market.

| Application | Major Buyers |
|---|---|
| - **Adhesives for tires and fiber-reinforced rubber goods** | - **Goodyear**<br>- **Michelin**<br>- **Bridgestone**<br>- **Continental**<br>- **Others** |
| - **Wood adhesives requiring room-temperature curing, structural integrity, waterproofing** | - **Hexion**<br>- **Georgia-Pacific**<br>- **Dynea**<br>- **National Casein** |
| - **UV screening agents**<br>- **Dyestuffs**<br>- **Pharmaceuticals**<br>- **Other miscellaneous** | - **Akzo Nobel**<br>- **ISP**<br>- **Others** |



## Phenol-Formaldehyde Adhesive Resins



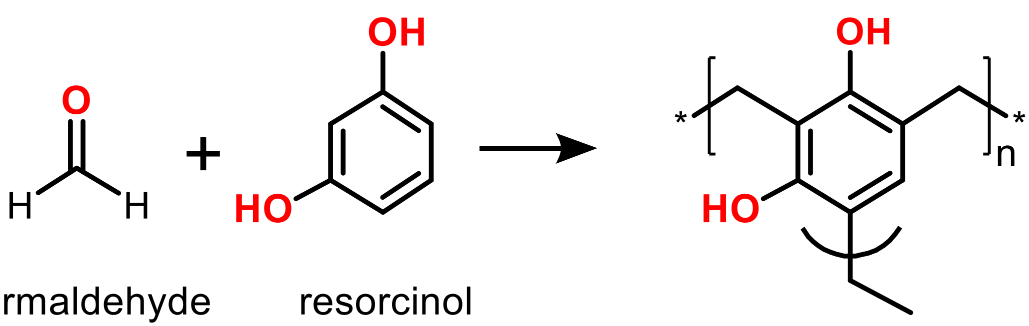

formaldehyde phenol

phenol-formaldehyde polymer

Problems:

- rising phenol prices
- rising resorcinol prices
- rising methanol prices
- formaldehyde toxicity

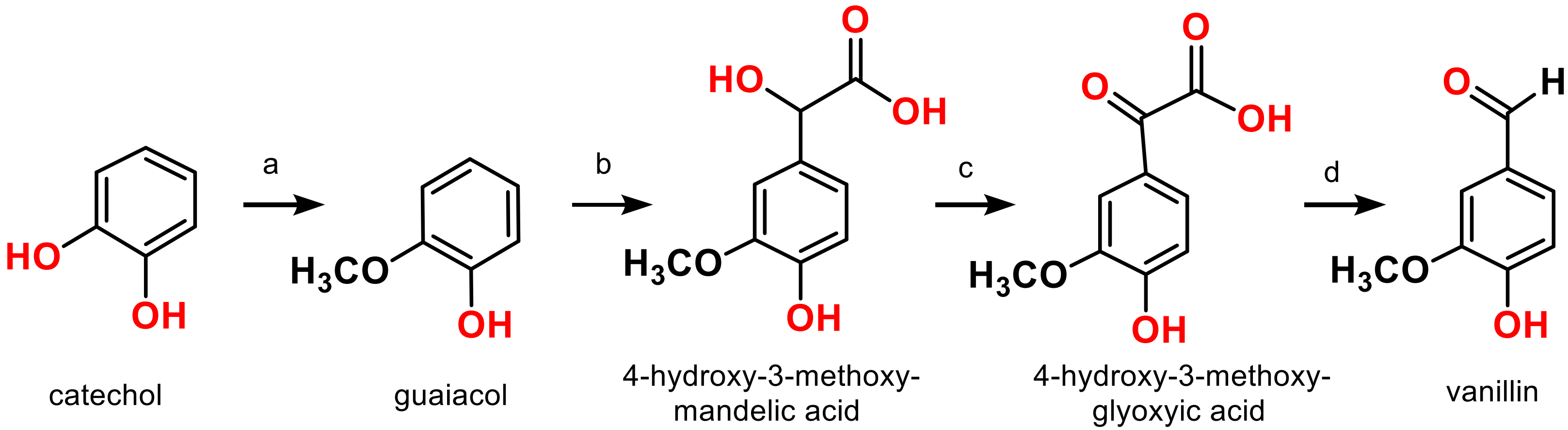
## Resorcinol-Formaldehyde Adhesive Resins



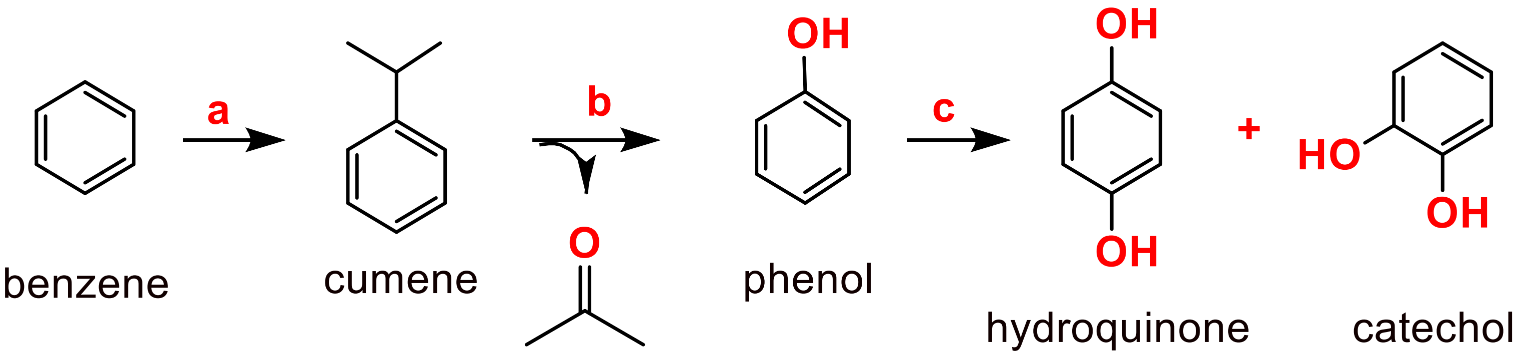

formaldehyde resorcinol

resorcinol-formaldehyde polymer

# Vanillin and Catechol Manufacture.

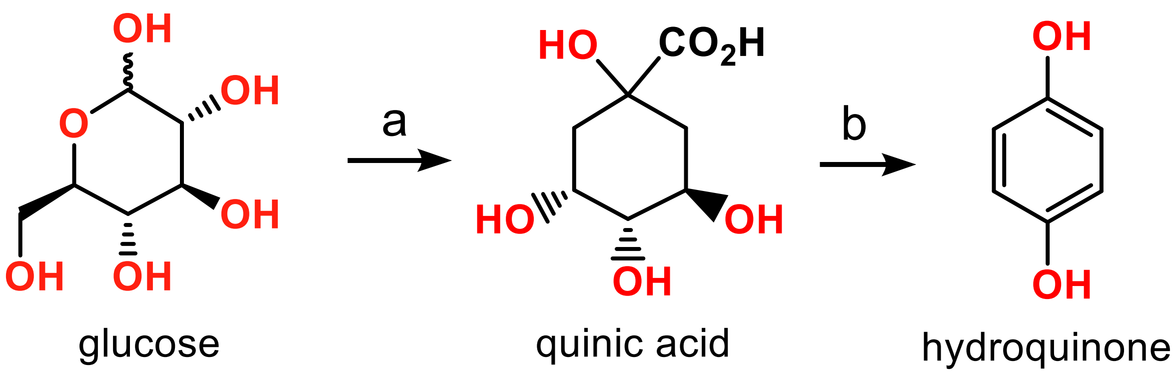



(a) MeOH, $H_3PO_4$; (b) glyoxylic acid, NaOH; (c) $O_2$; (d) $H^+$




(a) propene, $H_{n+2}P_nO_{3n+1}$, 200 atm., 200 °C; (b) $O_2$; 90-120 °C; (c) 60-70% $H_2O_2$, $H_3PO_4/HClO_4$.

# Synthesis of Aromatics from Renewables.




(a) microbial synthesis; (b) HOCl or $Ag_3PO_4/K_2S_2O_8$

## Quinic Acid

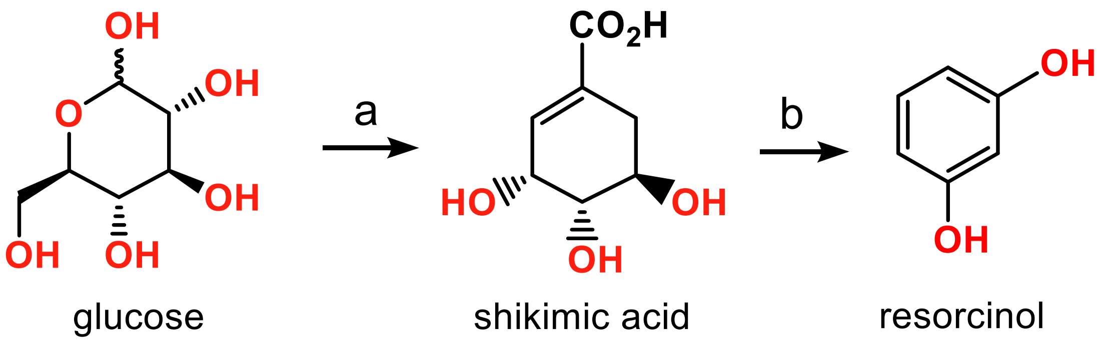
Isolated from *Cinchona* tree bark primarily in Zaire.

Starting material for the original Gilead synthesis of Tamiflu.

Biologically active component in extract of *Uncaria tomentosa* (cat's claw) bark.

Cat's claw extract stimulates the immune system and accelerates DNA repair.

# Synthesis of Aromatics from Renewables (2).




(a) microbial synthesis; (b) $H_2O$, 330 °C.

## Shikimic Acid

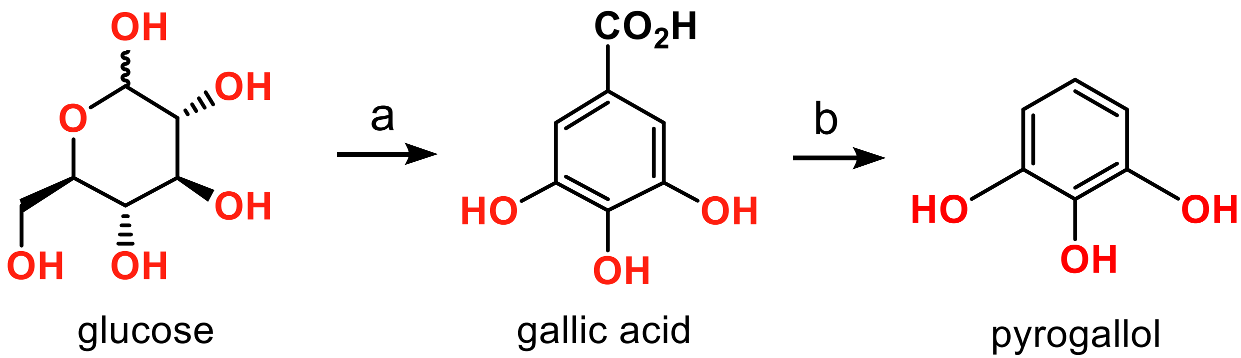
Extracted from star anise in China.

Starting material for the synthesis of Tamiflu.

As Tamiflu came out of clinical trials in 1998, shikimic acid cost $ 50,000/kg.

The manufacturing cost of microbe-synthesized shikimic acid is $ 20/kg.

# Polyhydroxybenzenes.




(a) *E. coli* KL7/pSK6.161; (b) *E. coli* RB791*serA*::*aroB*/pSK6.234.

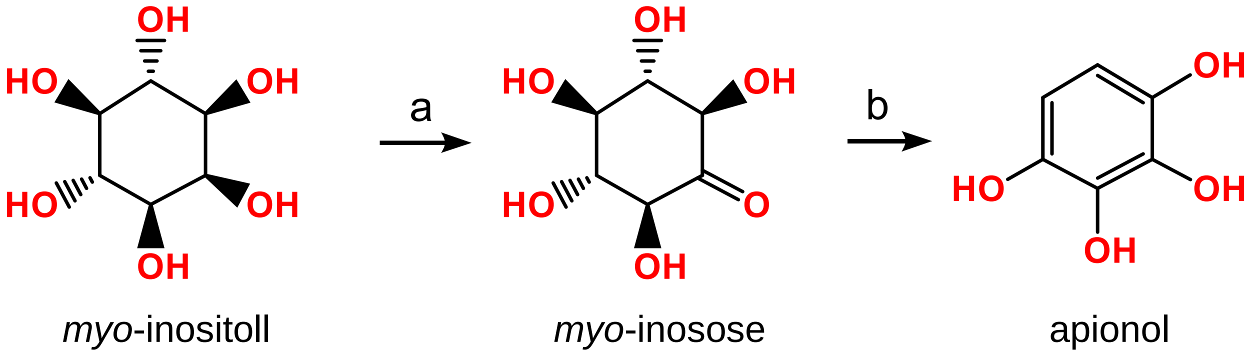
## Gallic Acid:

Isolated from a wasp carapace in China.

Powerful antioxidant.

Most favorable toxicological profile of the large-volume antioxidants (BHA, BHT, TBHQ) .

# Polyhydroxybenzenes (2).




(a) *Gluconobacter oxydans* ATCC 621; (b) $H^+$, $H_2O$.

Apionol:

Natural product found in trace quantities in wood grain distillate.

Powerful antioxidant.

*myo*-Inositol (Vitamin B7):

A supplement used in aquaculture and animal feed applications.

Can be derived from phytic acid or microbially synthesized from glucose.

POLITECNICO DI MILANO

# CFC Substitution.

# CFC and Related Concerns.

**CFCs** Chlorofluorocarbons
**HCFCs** Hydro chlorofluorocarbons
**HFCs** Hydrofluorocarbons

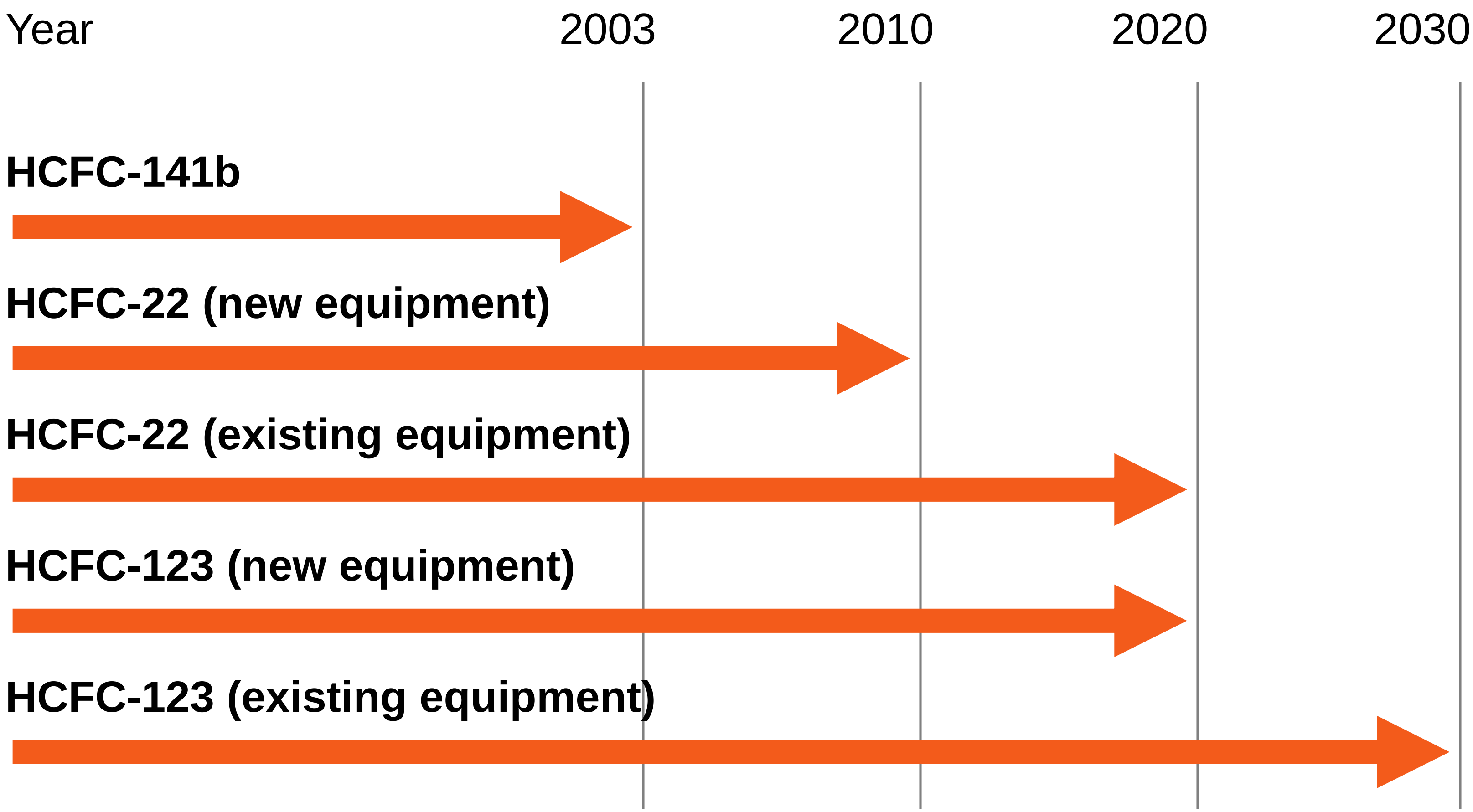
Release of these refrigerants to the atmosphere causes:

- **Ozone depletion**
- **Global warming**

| Refrigerant | Ozone Depletion Potential | Global Warming Potential ($CO_2$=1) | A. L. |
|---|---|---|---|
| CFC-11 | 1 | 3,400 | 59 |
| CFC-12 | 1.0 | 7,100 | |
| HCFC-22 | 0.05 | 1,600 | 18 |
| HCFC-123 | 0.02 | 90 | |
| HFC-134a | 0.0 | 1,200 | |

# Phase-out of CFC and HCFC.

- CFC production halted:
  **January 1, 1996**



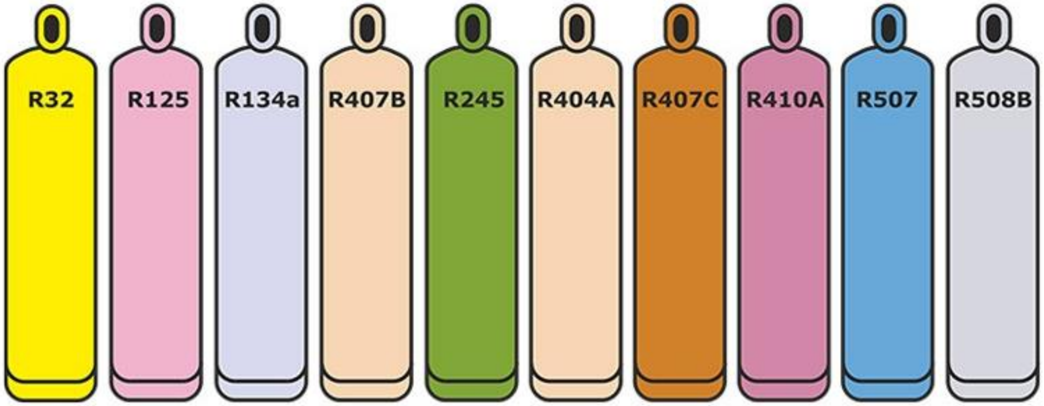
# Possible Substitutes?

**HFC** *(hydrofluorocarbon)*

- HFCs Are Ozone-Safe
- HFCs Contribute to Global Warming
  - ***N.B. Phase down of HFC refrigerants announced in 2015 as part of the US Federal Government's emissions.***

**Hydrocarbons**

- Zero Ozone Depletion
- Potentially Dangerous
  - *Toxic*
  - *Flammable*
  - *Explosive*



POLITECNICO DI MILANO

# Substitution of Chemicals: Pesticides.

# Substitution of Chemicals: Pesticides.

Definition of Pesticides

- **Any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest (harmful, destructive or troublesome insects, animals, weeds and plants, fungi, molds, or microorganisms - bacteria and virus).**

Classes of Pesticides (by type of pest)

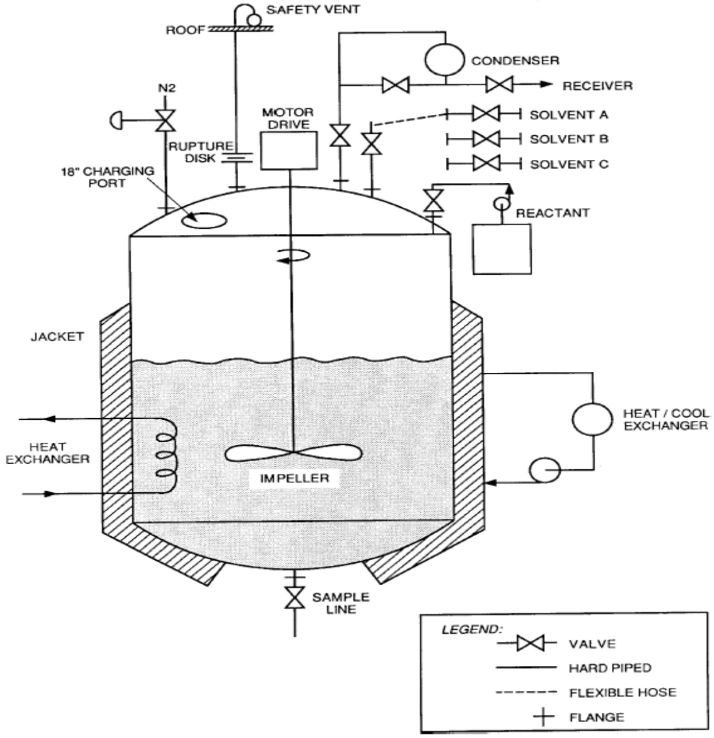
- Insecticides
- Herbicides
- Disinfectants
- Rodenticides
- Algicides
- Molluschicides
- Piscicides
- Fungicides
- Avicides

# Pesticides.

## Pesticides are just chemicals; the same but different!

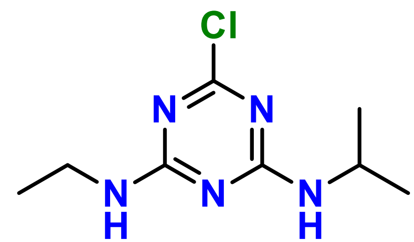
- Manufactured as a purposefully toxic chemicals.
- Occupational exposures occur across varied life-cycle.
- Formulated for specific targets and methods.
- Dermal is a major route of exposure.
- Insecticides are easily absorbed through intact skin.
- Identifiable chemical classes with similar toxic effects.
- Different regulatory agencies and approaches.

Continuously Stirred Tank Reactor:

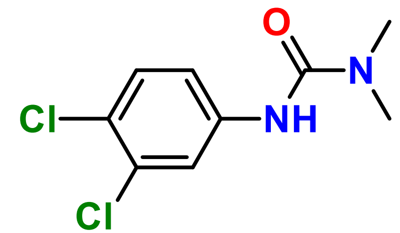


# Traditional Insecticides: Low Selectivity of Target.

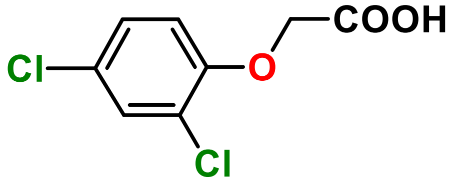
- Concern Common Systems
  - Main target: nervous system
  - Other targets: mitochondrion
- Risk for Organisms not target
  - Useful Insects
  - Fishes, mammals
  - Mans



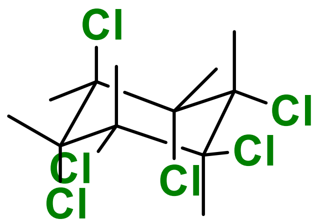

Atrazine



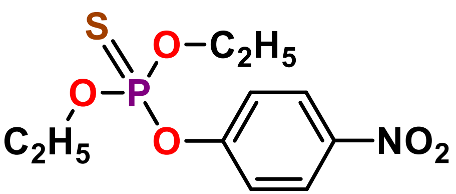

N,N-dimethyl 1-(3,4-Dichlorophenyl)urea




2,4-Dichlorophenoxyacetic acid

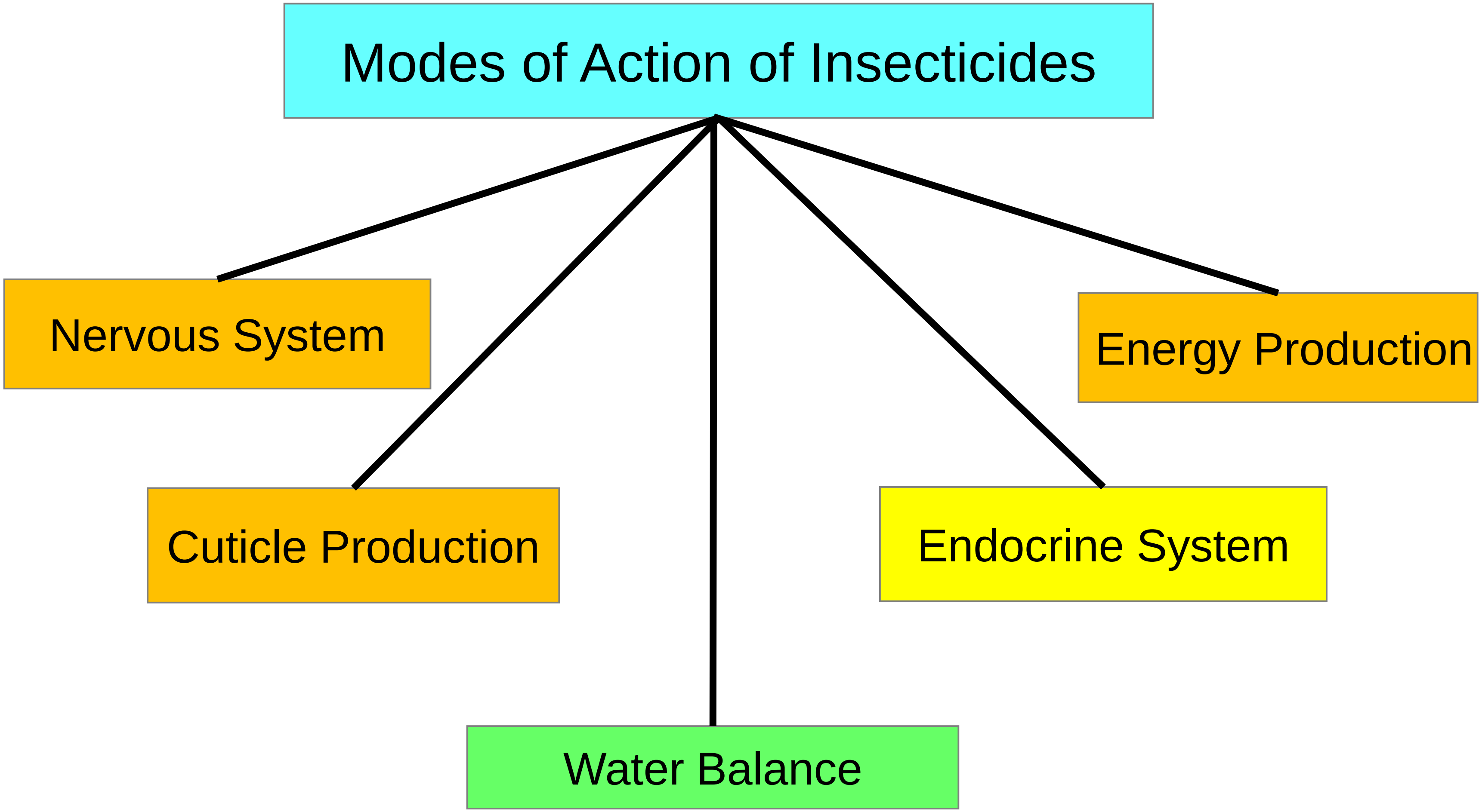



hexachlorocyclohexane




O,O-Diethyl
O-(4-nitrophenyl) phosphate
Methyl parathion

# Modes of Action of Insecticides.



# Insecticides Acting on Nervous System as Target.

- Organochlorine
  - DTT, linden, cyclodienes
  - Alter the ionic permeability of nerve membranes
- Organophosphates and Carbamates
  - malathion, parathion, carbaril
  - Inhibits acetyl cholinesterase and increase the acetylcholine levels
- Rotenone
  - Inhibits the mitochondrial electronic transport at the level of complex I.

# Insecticides Influence Important Functions Connected to Long-term Health.



- Mitochondrial Energy Disrupters
  - Uncouples oxidative phosphorylation and electron transport; an effect linked to symptoms of Parkinson disease
  - A primary target of rotenone but a further target of organophosphates?
- Detoxification by CYP Monooxygenases
  - Insecticides included organophosphates can adversely affect the detoxification systems
- Endocrine Disrupter
  - Linked to cancer and reproductive disorders?

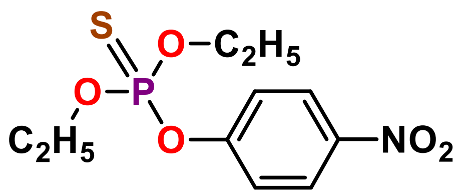
# Exposure to Pesticides.

Different potentials for exposure across phases of life-cycle.

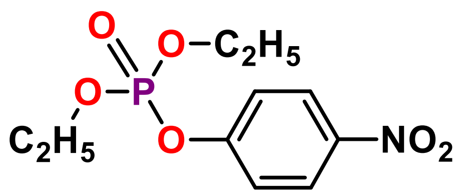
- **Manufacturing**: Creating the active ingredient. (Closed systems).
- **Formulating**: Make physical form + additives. (Semi-enclosed).
- Packaging: Putting in containers. (Open - automated).
- Transporting: Shipping. (Closed - except for accidental spills).
- Mixing /Loading: Commercial applicators only (Open or closed).
- **Applying**: Delivery to target site or pest. (Open).
- **Residues**: Reentry into treated areas and consumption. (On or off target).

# Post-harvest Hazards to Pesticide Residues.

1. Toxic metabolites or breakdown products




Parathion




Paraoxon

2. Dermal is the highest route of exposure to harvesters.
3. Responsibility for off-site hazards . . .
   - from drift, run-off
   - accidental exposures (esp. to children)
   - first responders to spills
   - incidental exposures (esp. in homes)
   - residuals on consumed food
4. OPH enzymes can be used to detoxificate the residues.

# Toxicity Categories for Pesticides.

| Toxicity Categories | I | II | III | IV |
|---|---|---|---|---|
| **Signal Words** | Danger Poison | Warning | Caution | Caution |
| **Oral $LD_{50}$ mg/kg** | <50 | 50 – 500 | >500 – 5000 | >5000 |
| **Oral $LD_{50}$ for a 70kg person** | a "pinch" or < 1 teaspoon | 1 teaspoon to 1 tablespoon | 1 ounce to 1 pint | more than 1 pint |
| **Inhalation $LC_{50}$** | <0.2 mg/L (<200 mg/m$^3$) | 0.2 – 2 mg/L (0.2 – 2 g/m$^3$) | 2 – 20 mg/L (2 – 20 g/m$^3$) | >20 mg/L (>20 g/m$^3$) |
| **Skin Effects** | Corrosive | Severe | Moderate | Mild/Slight |
| **Eye Effects** | Irreversible Corneal Opacity | Reversible within 7 days | Irritation but no Corneal Opacity | No Irritation |

# Safer Alternatives: General Non-Toxic Pesticides.



Boric acid: safer than synthetic pesticides but can still cause irritation and poisoning if exposed to large amounts

Diatomaceous earth or Crushed bug mixture

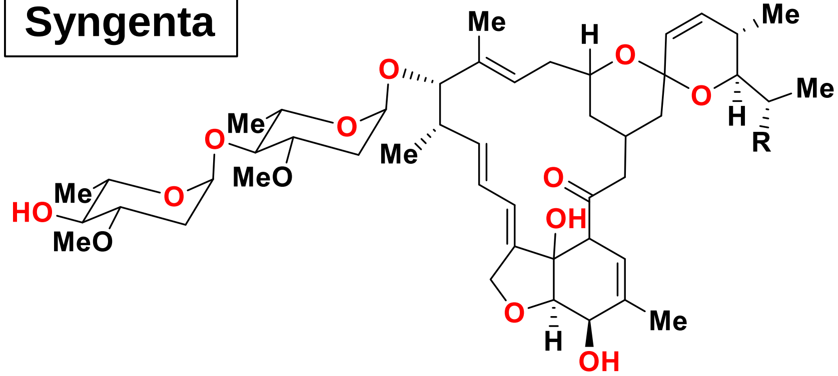
Natural insecticides:

- Spearmint hot pepper (*Capsicum frutescens*) horseradish onion spray: for plants
- Bay leaf essential oil: for flies and ticks
- Buttermilk wheat flour water mixture: for spider mites
- Bowls of beer: for snails and slugs
- Camphor essential oil: for mosquitoes
- Cedar essential oil: for fleas, mosquitoes and moths
- Citronella: for flies, ticks, mosquitoes
- Citrus essential oils: for flies and ticks
- Eucalyptus essential oil: for flies and ticks
- Garlic (*Allium sativum*) oil: for fleas, flies and mosquitoes
- Lavender essential oil: for flies, ticks, mosquitoes and lice
- Neem (*Azadirachta indica*) oil: for flies, mosquitoes and lice
- Pennyroyal essential oil: for flies, ticks and mosquitoes
- Rose geranium essential oil: for ticks Rosemary essential oil: for mosquitoes ……….

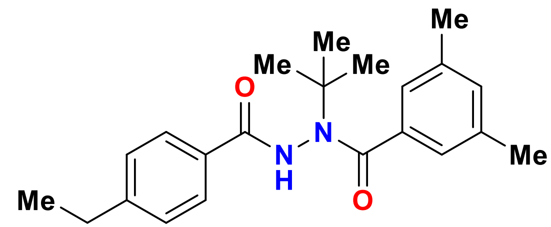
# Successful Pesticides from Natural Products: NOT Bio-pesticides.

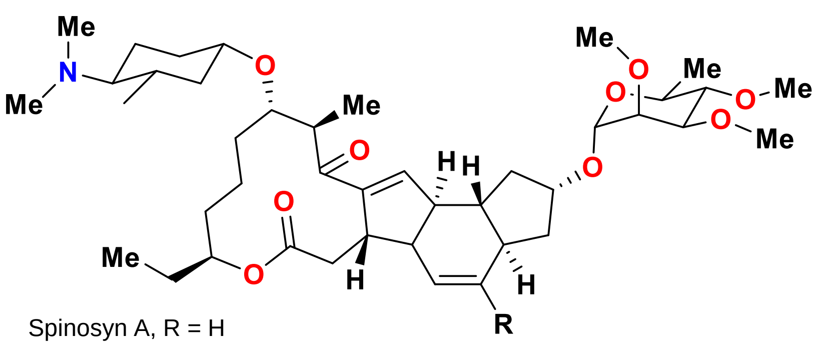


**Avid® – Syngenta**



**Tebufenozide (Mimic®, Confirm®) - Dow**

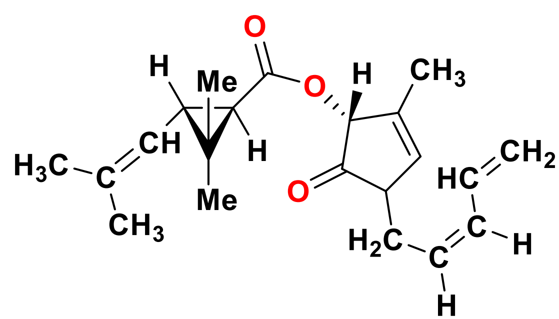




Spinosyn A, R = H
Spinosyn D, R = $CH_3$

**Spinosad (Entrust®, Conserve®, SpinTor®, Success®, Tracer®) – Dow Agro**

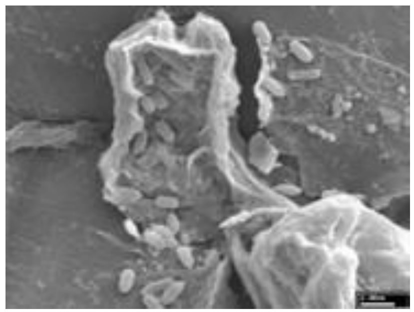
**Pyrethrins**



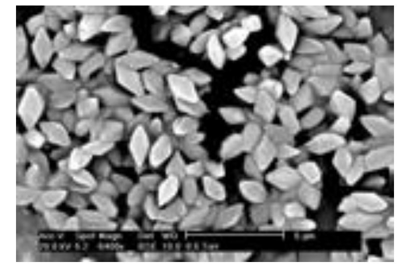
(Z)-(*S*)-alcohol ($^1$*R*)-*trans*-acid

# MICROBIALS (e.g., bacteria, virus, fungi).

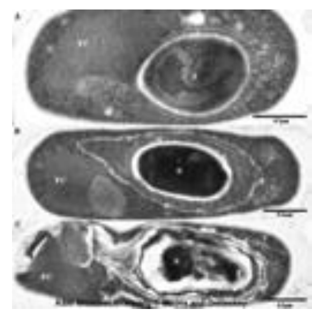
Bacteria: e.g., *Bacillus*, *Pseudomonas fluorescens*

*Bacillus thuringiensis*
(Bio-insecticide)

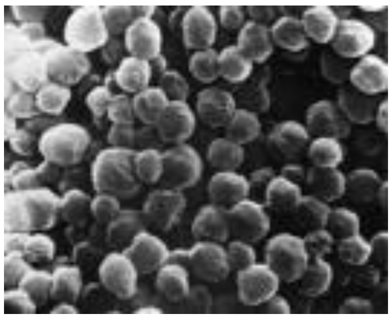


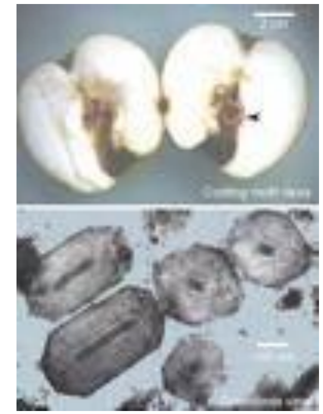
*Bacillus subtilis*
on powdery mildew
spore
(Bio-fungicide)



# MICROBIALS (e.g., bacteria, virus, fungi) (2).

Virus: e.g., NPV, GV





Codling moth (*Cydia pomonella*) granulosis virus

Gypsy moth (*Lymantria dispar* ) killed by nuclear polyhydrosis virus

School of Industrial and Information Engineering

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POLITECNICO DI MILANO

# Chemical Substitution: Anti-foulant
## (algae and seaweed; barnacles and diatoms).


Prof. Attilio Citterio

Dipartimento CMIC “Giulio Natta”


https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

# Chemical Pesticides for Bio-foulants.

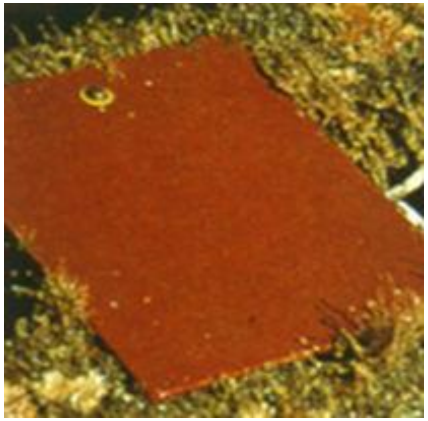
- Insecticides
- Herbicides
- Disinfectants
- Rodenticides
- Algaecides
- Molluschicides
- Pisicidies
- Fungicides
- Avicides

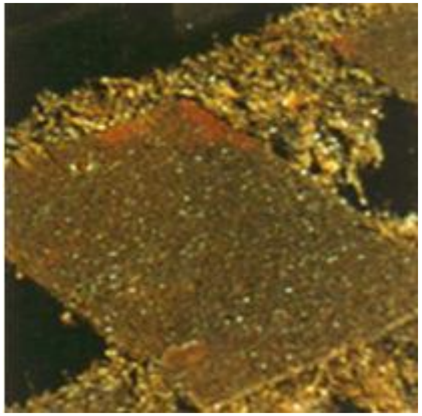
*Foulant Types*:

- Soft Bio-Foulants (algae and seaweed)
- Hard Bio-Foulants (barnacles and diatoms)

# Anti-foulants.

- Fouling: the unwanted growth of plants and animals on a ship's surface
- Anti-foulants are compounds used to control the growth of marine organisms
- Usually mixed with the paint as it is applied to the hull of boats
- Slowly leach form the surface of the hull






http://www.scranton.edu/faculty/cannm/green-chemistry/english/downloads/environmental.pdf

# Costs of Fouling.

## Economic Costs:

- Increased fuel consumption, 3 billions $ /year
- Increased time in Dry-dock, 2.7 billions $ /year
  - To clean ship
  - For being out of service

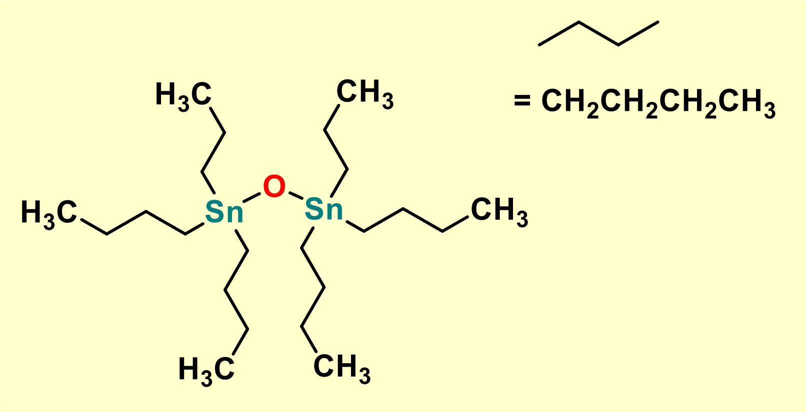
## Environmental Costs:

- Increased consumption of fossil fuels (a nonrenewable resource)
- Increased formation of carbon dioxide (a greenhouse gas)
- Increased formation of other atmospheric pollutants (nitrogen oxides, sulfur oxides, unburned hydrocarbons, ozone etc.).

# Organotin Anti-foulants.

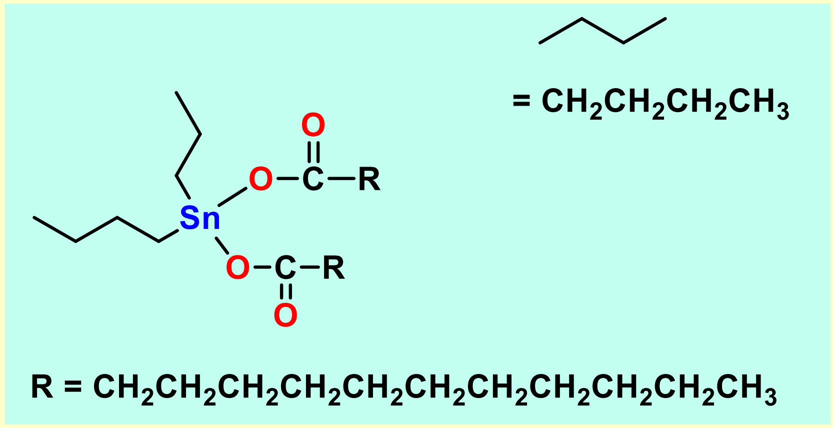
Tributyltin Oxide

(TBTO)




Dibutyltin dilaurate

(DBTL)



# Environmental Concerns of TBTO.

- Half-life ($t_{1/2}$) of TBTO in seawater is > 6 months
- Bio-concentration: $10^4$
- Chronic toxicity :
  - ✓ Thickness of oyster shells
  - ✓ Sex changes in whelks
  - ✓ Imposex in snails
  - ✓ Immune system in dolphins and others?

Directive 99/33/EC(11), as: - harmful in contact with skin,- toxic if swallowed,- irritating to eyes and skin,- toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed,- very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

# Ban on Organotin Anti-foulants.

- US -Organotin Antifouling Paint Control Act of 1998 (OAPCA)
  - The treaty specifies the start of the ban to begin on January 1, 2003. This ban will prohibit the application or re-application of TBT coatings to underwater structures. The treaty also specifies January 1, 2008 for the complete ban of TBT coatings, requiring that structures must have all the coating removed or overlay a protective barrier to prevent the leakage of organotin biocides.
- Ban by Japan (2000).
- International Maritime Organization (IMO) complete ban on 1/1/03.

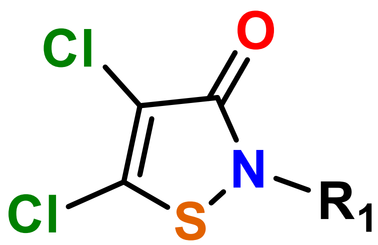
# Environmentally Preferable Anti-foulants.

## Ideal Properties:

- ✓ Rapid degradation
- ✓ Nonhazardous environmental concentrations
- ✓ Limited bioavailability
- ✓ Toxic only to target organisms
- ✓ Minimum Bio-concentration.

# New Anti-foulant (Sea-Nine 211).

- "Rohm and Haas" Presidential Green Chemistry Challenge Award - 2000
- Low Bio-concentration (BCF = 13)
- Rapid bio-degradation to nontoxic products (½ life < 1hour)
- Acutely toxic to a wide range of marine organisms (effective anti-foulant)
- Environmental Conc. < Acute Toxicity level
- No Chronic Toxicity
- Rapid partitioning to the sediment (low bio-availability).




**$R^1$ = n-$C_8H_{17}$**

Active ingredient

**4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI)**

# Environmental Risk (ER) and Risk Quotient (RQ).

- ER = f(toxicity and exposition)
  - DCOI limits the ER limiting the exposition

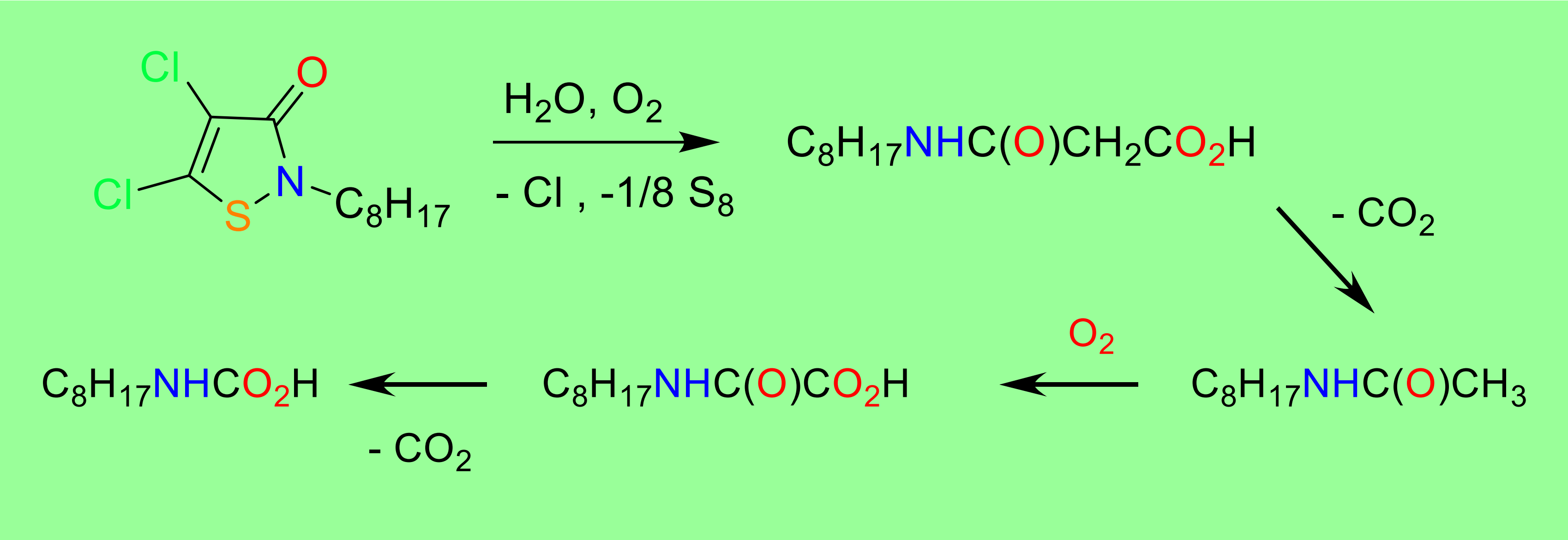
- RQ = PEC/PNEC
  - DCOI RQ = 0.024-0.36
  - TBTO RQ = 15-430

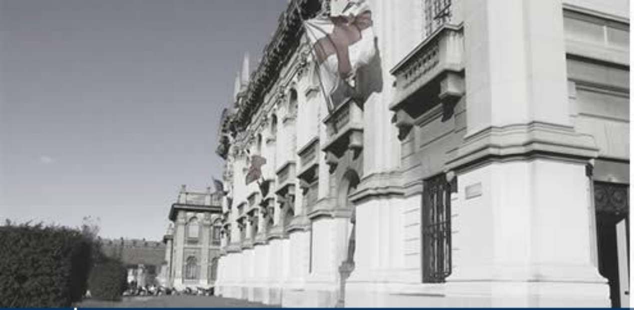
where PEC (predicted environmental concentration)

PNEC (predicted no-effect environmental concentration)

# Biodegradation of DCOI.

- The S-N (sulfenamide) bond is active towards ionic and redox reactions
- DCOI biodegradate to low toxicity amide products:





School of Industrial and Information Engineering
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Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

# Chemical Substitution: Anti-scalants.

Prof. Attilio Citterio
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https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

# Mineral Scale Build up and Anti-scalants.

Scale Build Up in Industrial Water Handling Processes:

- Results in reduced water flow though pipes,
- Reduced heat transfer in boilers and condensers,
- Pump failures.
- Scale consists of insoluble inorganic compounds such as calcium carbonate, calcium phosphate, calcium sulfate, and barium sulfate.

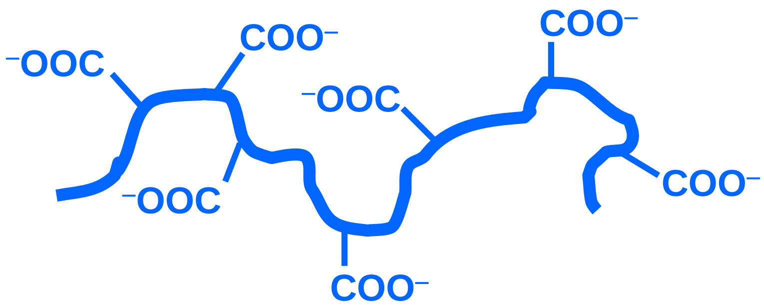
Anti-scalants

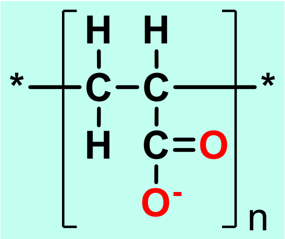
- Prevent scale formation entirely or
- Permit the scale to be deposited in such a way that it is easily removed by the fluid flowing along the pipe or heat transfer surface.
- Anti-scalants complex with the cations present in water to prevent formation of insoluble inorganic solids.

# Polyacrylate Anti-scalants.

Polyacrylate (PAC) is one of the most common scale inhibitors.

PAC is a poly-anion:




Polyelectrolytes:

- Are polymers with bound positive or negative charges
- Are also called macro ions or poly-ions
- Can be poly-anions or poly-cations
- Are generally water soluble polymers if their structure is linear.

# PAC as an Anti-scalant or Dispersant.

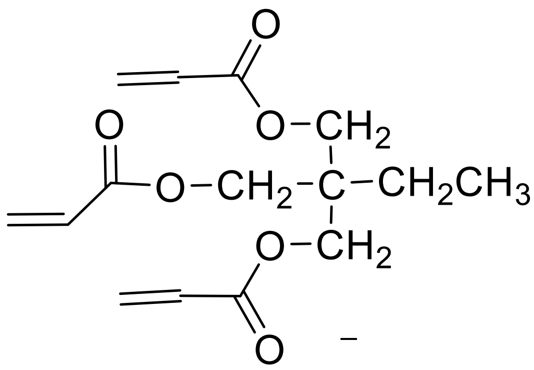
- Polymeric anti-scalants are generally low molecular weight polymers.
- Polymeric dispersants consist of higher molecular weight fractions.
- Dispersants do not stop the formation of scale, but instead are able to keep the scale particles suspended in the bulk fluid by imparting a negative charge to the particles.
- PAC comprises 5% of many laundry detergent formulations because of its dispersant properties.

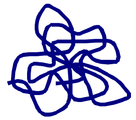
Crosslinked PAC:

- A crosslinked form of the sodium salt of polyacrylic acid is used as a superabsorbent material in diapers and other personal hygiene products.
- Crosslinked PAC has a great affinity for water, but is unable to dissolve and will instead swell in aqueous solution.
- Because of the presence of the charged groups on the polymer chain of a polyelectrolyte, the polymer will be highly expanded in aqueous solution.

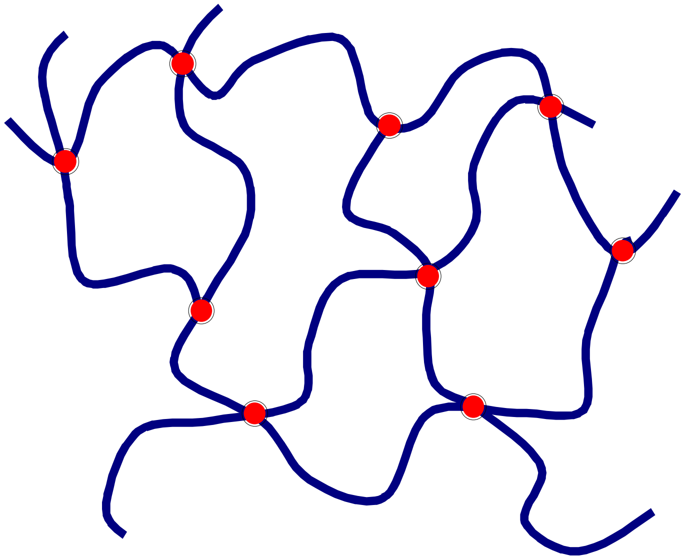
# Crosslinked Polymer (Dry and Swollen).

Crosslinking Agent



Dry Crosslinked Polymer



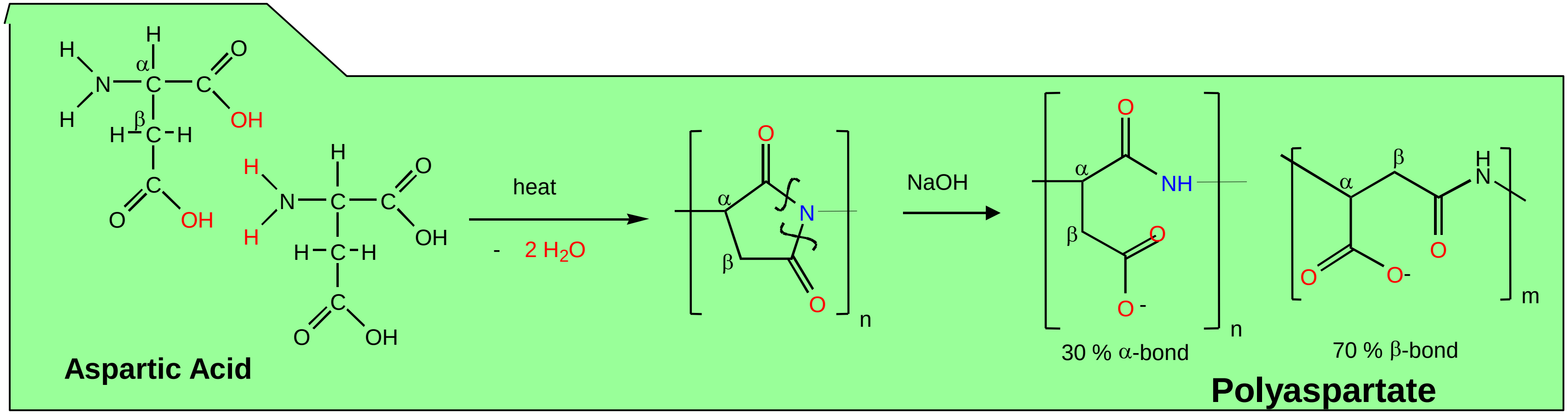
Swollen Crosslinked Polymer

# PAC and the Environment.

- PAC is nontoxic and environmentally benign, but it is not biodegradable.
- Because it is widely used for many applications, it poses an environmental problem from a landfill perspective.
- When PAC is used as an anti-scalant or a dispersant, it becomes part of wastewater.
- PAC is nonvolatile and not biodegradable, so the only way to remove it from the water is to precipitate it as an insoluble sludge.
- The sludge must then be landfilled.

# A Substitute: Thermal Polyaspartate.

- Donlar Corporation developed an economic way to produce thermal polyaspartate (TPA) in high yield and with little or no waste products.
- Polyaspartate is a biopolymer synthesized from L-aspartic acid, a natural amino acid.
- Polyaspartate has similar properties to the polyacrylates and so it can be used as a dispersant, or an anti-scalant, or a super absorber.
- Polyaspartate is biodegradable.



School of Industrial and Information Engineering

Course 096125 (095857)

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POLITECNICO DI MILANO

# Biomicry: Innovation Inspired by Nature.

Prof. Attilio Citterio

Dipartimento CMIC “Giulio Natta”

https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

# Better Products from Natural Specialty.

Biomimicry is a simple idea that may someday catch on in a big way. Simply put, biomimicry is the belief that the future of material design and use can be found in the design of the natural world around us.

- Spider Web (thread strength)
- Slug mucous (adhesive)
- Abalone Shell (protective shell)
- Barnacle (adhesives)
- Lotus flower (waterproofing)
- Geckos (small hairs as glue)
- Venus Flower basket (better fiber optic cables).

# Targets Based on Consolidated Solution.

Humans may have a long way to go towards living sustainably on this planet, but 10-30 million species with time-tested genius have figured it out and maybe we can learn a few things from them?

This is the real news of biomimicry: After 3.8 billion years of research and development, failures are fossils, and what surrounds us is the secret to survival. In biomimicry, we look at nature as model, measure, and mentor.

**Biomimicry introduces an era based not on what we can extract from organisms and their ecosystems, but on what we can learn from them.**

Instead of harvesting or domesticating, biomimics consult organisms; they are inspired by an idea, be it a physical blueprint, a process step in a chemical reaction, or an ecosystem principle. Borrowing an idea is like copying a picture-the original image can remain to inspire others.

# Three Types of Biomimicking.

## 1. Mimicking form: What's the design?

- Physical form can be inspired - Mimic form of owl feather: silence/fiber

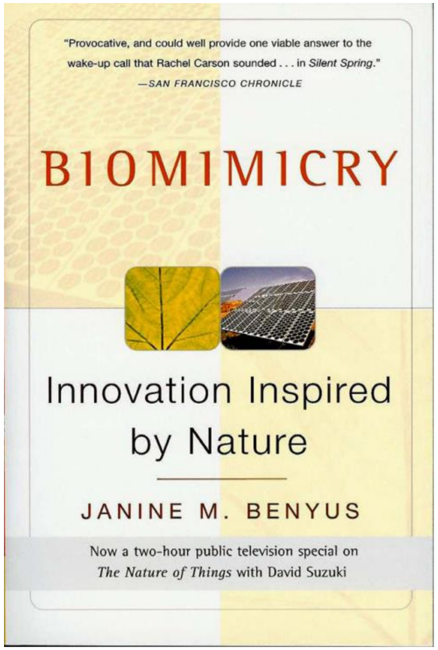
## 2. Mimicking process: How is it made?

- Self-assembles at body temperature
- Without toxins or high pressures
- Nature's chemistry
- Green chemistry

## 3. Mimicking ecosystems: How does it fit?

- Owl – Ecosystem - Biome - Biosphere
- Product - Larger economy - Biosphere
- Restore / deplete the earth and its people?

*database.biomimicry.org;*



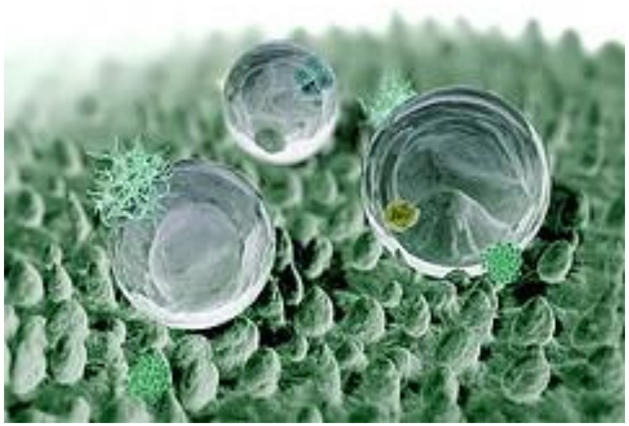
# Velcro.

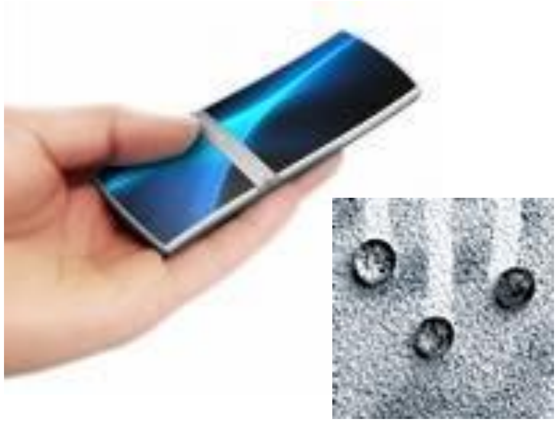
Velcro fastening was invented in 1941 by Swiss engineer George de Mestral, who took the idea from the burrs that stuck to his dog's hair. Under the microscope he noted the tiny hooks on the end of the burr's spines that caught anything with a loop - such as clothing, hair or animal fur. The 2-part Velcro fastener system uses strips or patches of a hooked material opposite strips or patches of a loose-looped weave of nylon that holds the hooks.

# Gecko Tape.


Gecko Tape is a material covered with nanoscopic hairs that mimic those found on the feet of gecko lizards. These millions of tiny, flexible hairs exert van der Waals forces that provide a powerful adhesive effect. Applications include underwater and space station uses. Tape sneakers and gloves were extensively commercially applied.

# Lotus Effect Hydrophobia.





The Lotus Effect: The surface of lotus leaves are bumpy, and this causes water to bead as well as to pick up surface contaminates in the process. The water rolls off, taking the contaminates with it. Researchers have developed ways to chemically treat the surface of plastics and metal to evoke the same effect. Applications are nearly endless, and not just making windshield wipers and car wax jobs obsolete.

# Self-Healing Plastics.

Consider the body's power to heal itself of scrapes and cuts. The value of the same sort of process in light polymer composites that can be used to produce things like aircraft fuselage becomes obvious. The new composite materials being developed are called self-healing plastics. They are made from hollow fibers filled with epoxy resin that is released if the fibers suffer serious stresses and cracks. This creates a 'scab' nearly as strong as the original material. Such self-healing materials could be used to make planes, cars and even spacecraft that are lighter, more fuel efficient, and safer.

# Artificial Photosynthesis.

Photosynthesis is the way that green plants use chlorophyll to convert sunlight, water and carbon dioxide into carbohydrates and oxygen. The quest to reproduce the process technologically is called Artificial Photosynthesis, and is envisioned as a means of using sunlight to split water into hydrogen and oxygen for use as a clean fuel for vehicles as well as a way to use excess carbon dioxide in the atmosphere. The process could make hydrogen fuel cells an efficient, self-recharging and less expensive way to create and store energy applicable in home and industrial systems.

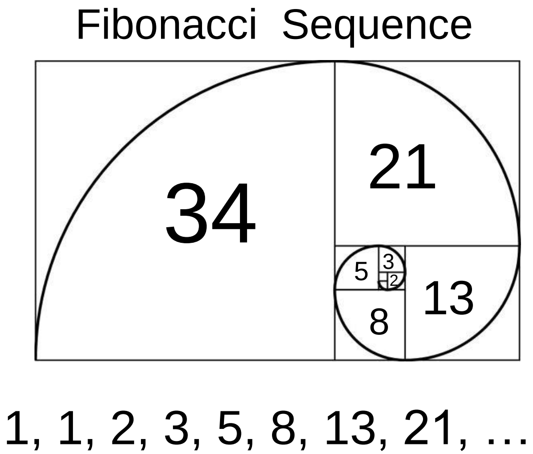
# Friction - Reducing Sharkskin.

Inspired by the evolved ability of shark's skin to reduce drag by manipulating the boundary layer flow as the fish swims, researchers are developing coatings for ship's hulls, submarines, aircraft fuselage, and even swimwear for humans. The material made their appearance at the Bejing Olympics!

# Butterfly - Inspired Displays.

By mimicking the way light reflects from the scales on a butterfly's wings, the Qualcomm company has developed Mirasol Displays that make use of the reflected light principle with an understanding of how human beings perceive that light. Using an interferometric modulator [IMOD] element in a two-plate conductive system, the display uses near-zero power whenever the displayed image is static while at the same time offering a refresh rate fast enough for video. Perfect for 'smart' hand-held devices, already deployed in many, and a battery-saver extraordinaire!

# The Golden Streamlining Principle.




A company called PAX Scientific out of San Rafael, California has been developing air and fluid movement technologies based on such beautiful and recurring natural designs as the Fibonacci sequence, logarithmic spirals and the Golden Ratio. These shapes align with the observation that the path of least resistance in this universe isn't a straight line. Put all this together and you get the "Streamlining Principle," being applied to fans, mixers, impellers and such that move air and liquids around in systems. Such fans on motors, compressors and pumps of all sizes and in all applications could save at least 15% of all the electricity consumed in the US.