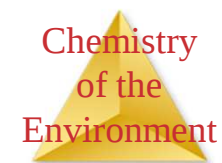
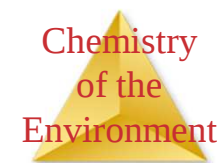


Green Chemistry

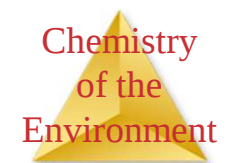


Syllabus

- Goals of green chemistry – Limitations
- Twelve principles of green chemistry with their explanations and examples
- Prevention of waste / byproducts
- Atom economy (maximum incorporation of materials used in the process)
- Minimization of hazardous / toxic products
- Prevention of chemical accidents
- Green synthesis – Designing a green synthesis



- Hazardous = Dangerous
- Benign = Caring, Kindly, Generally
- Paradigm = Pattern
- Spur = Encourage
- Ingenuity = Cleverness
- Innocuous = Harmless, safe
- Efficacy = Efficiency

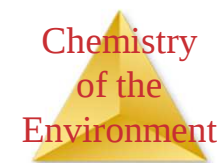


Brief History of Green Chemistry

- 1991** The phrase "Green Chemistry" invented by the chemist **Paul Anastas** of US Environmental Protection Agency (EPA)
- 1992** United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro. Agenda 21 was adopted.
- 1995** On President Bill Clinton's initiative, EPA started to give a yearly "the **U.S. Presidential Green Chemistry Challenge Award**"
- 1997** "The Green Chemistry Institute" is formed by Joe Breen in the United States (became part of ACS operations since 2001)
- 1998** Paul Anastas and **John C. Warner** published the book "Green Chemistry: Theory and Practice" (the book includes "**The Twelve Principles of Green Chemistry**")
- 1999** The Royal Society of Chemistry formed "The Green Chemistry Network" and started the journal "**Green Chemistry**"

What is Green Chemistry?

Green chemistry is the sustainable practice of chemical science and manufacturing within a framework of industrial ecology in a manner that is sustainable, safe, and non-polluting, consuming minimum amounts of energy and material resources while producing virtually no wastes



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

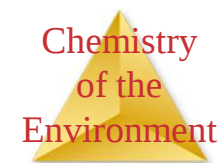


*Anastas and Warner
Green Chemistry: Theory and
Practice (1998)*

The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of substances hazardous to human health and the environment

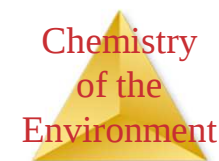
Fundamental and innovative chemical methods that accomplish pollution prevention through source reduction
“The use of chemistry for source reduction”

“Sustainable chemistry” is the design, manufacture and use of efficient, effective, safe and more environmentally benign chemical products and process

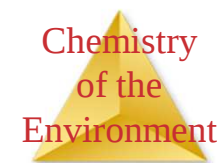


Green Chemistry is Sustainable

- **Economic:** At a high level of sophistication, green chemistry normally costs less in conventional economic terms (as well as environmental costs) than chemistry as it is traditionally practiced
- **Materials:** By efficiently using materials, maximum recycling, and minimum use of virgin raw materials, green chemistry is sustainable with respect to materials
- **Waste:** By reducing in so far as possible, or even totally eliminating their production, green chemistry is sustainable with respect to wastes



- Green Chemistry represents a major model that focuses on environmental protection at the design stage of product and manufacturing process
- It is an innovative way to deal with chemicals before they become hazards, with the goal of making chemicals and products “Benign by Design”
- Chemistry is an opportunity to encourage the next industrial revolution through human cleverness and creativity
- Advancing Green Chemistry is an opportunity to make a safer and more efficient world with less waste



Spirit of Green Chemistry

$$\text{Risk} = f(\text{hazard} \times \text{exposure})$$



Now

Minimize risk by minimizing hazard



Before

- **Reduced exposure:** The hazard remains, but exposure to it is reduced, such as by wearing safety goggles around an eye hazard
- **Reduced hazard:** The hazard is diminished or eliminated at its source; measures still may be taken to reduce exposure to remaining hazard



Reduction of What?



What is Green Chemistry?

Concepts & Ideas

12 Principles of Green Chemistry

1. Pollution Prevention
2. Atom Economy
3. Less Hazardous Chemical Synthesis
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



Challenges

Alternative feedstocks

- Move from petroleum to renewable or biologically derived sources
 - Petroleum chemistry => need oxidation chemistry
 - Sugar => need reduction chemistry
- CO₂ => need new catalysts

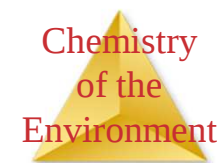
Alternative solvents

- No solvent (neat solution; grinding)
- Supercritical CO₂, ionic liquid...

Alternative synthetic pathways

- New catalysts (with more abundant metal)
- Move to biocatalysts (no toxic metals; intrinsically safer)
- Research into reuse and recycling catalysts still in infancy

The Twelve Principles of Green Chemistry



[1] Prevention

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

1. Pollution Prevention



What do we do to prevent pollution?

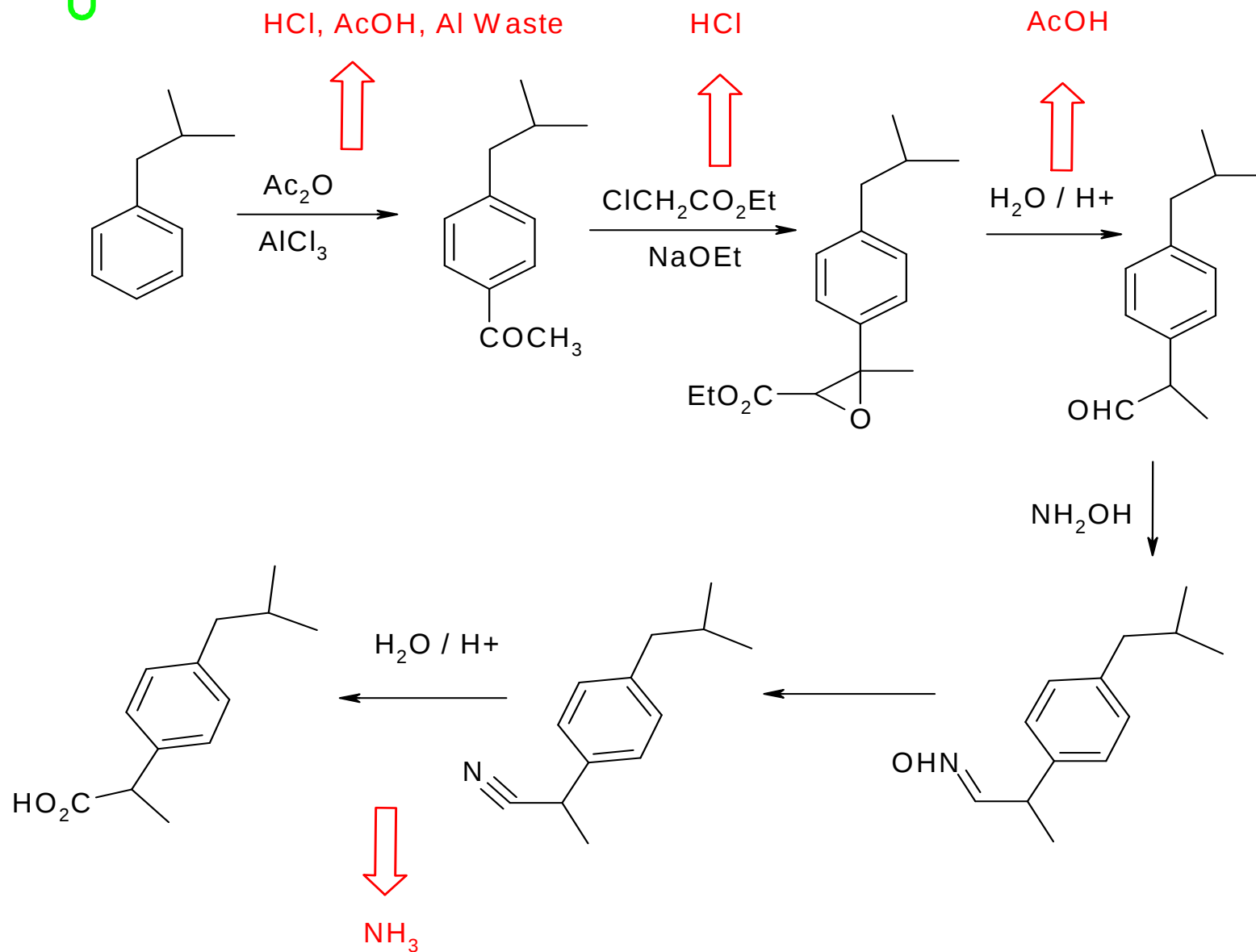
- Drive smaller, more efficient cars
- Take the commuter train
- Riding a bike
- Fix a leaky faucet
- Recycle paper or compost leaves

An ounce of prevention is worth a pound of cure.

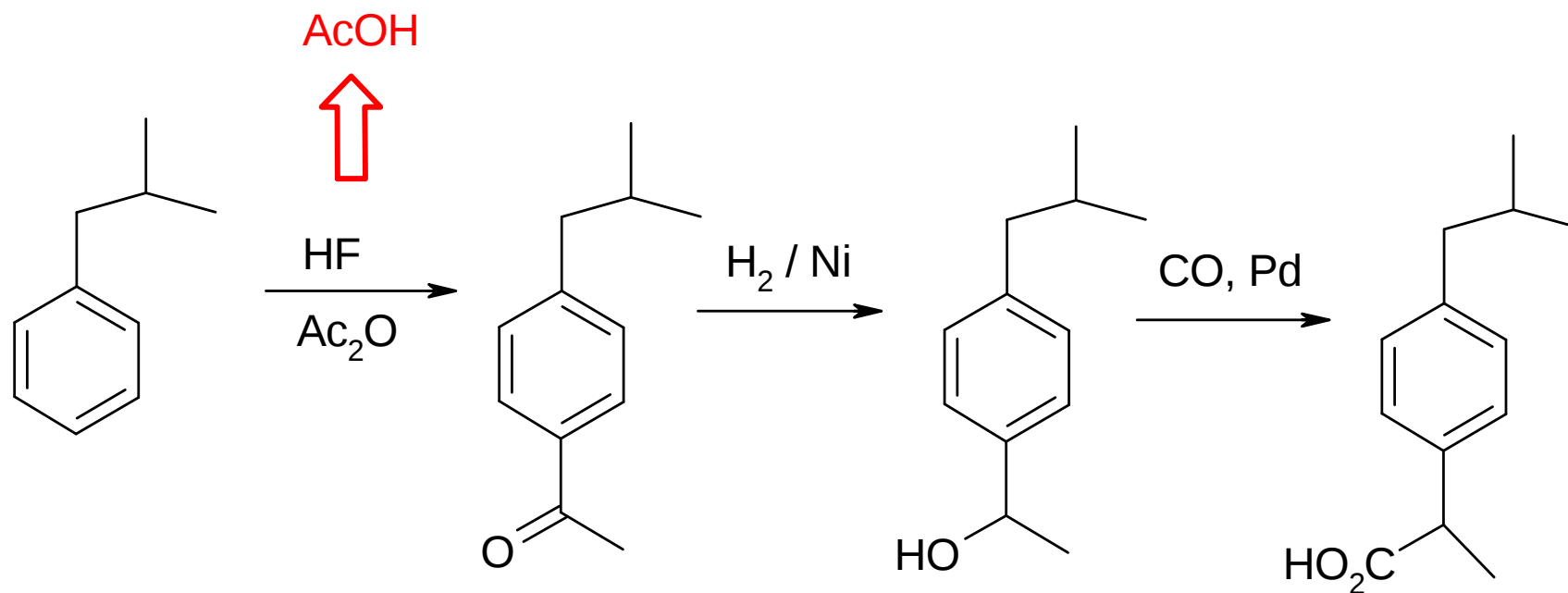
A chemist in a green chemistry lab is performing pollution prevention on a molecular level!



Classic Route to Ibuprofen



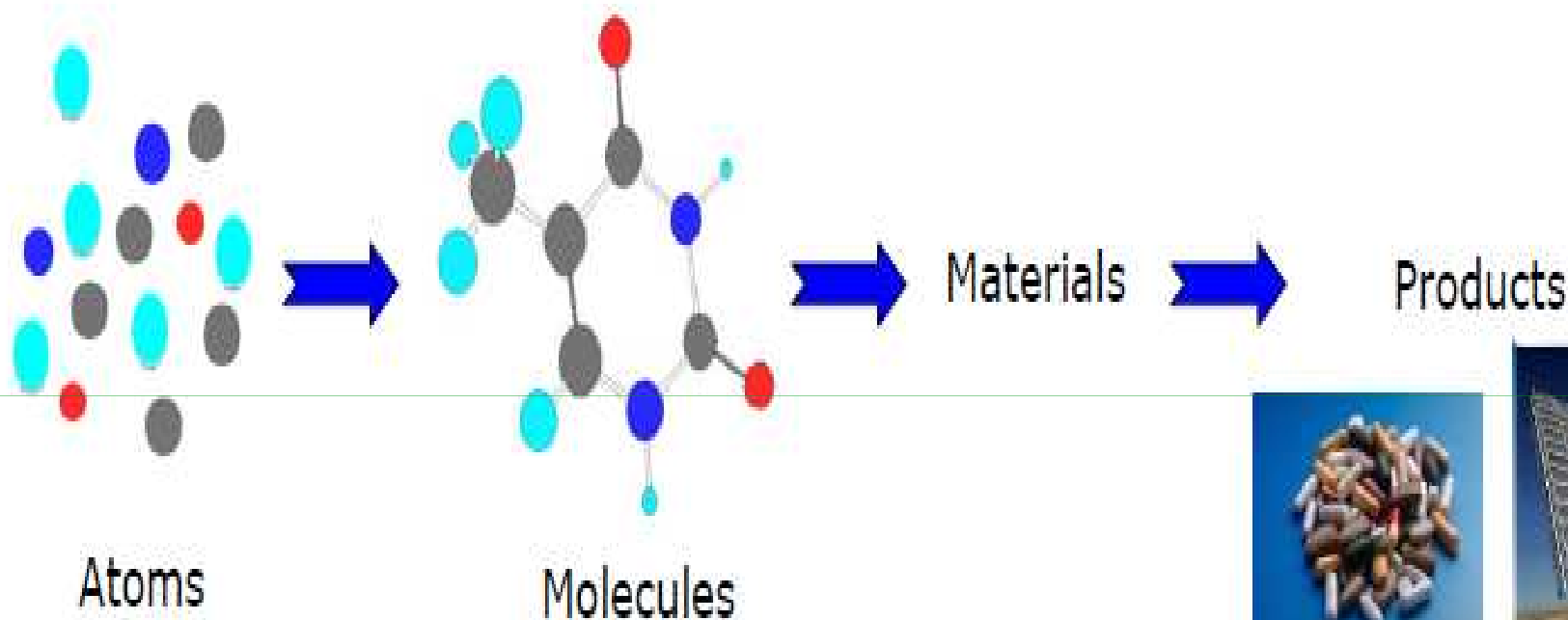
Hoechst Route To Ibuprofen



[2] Atom Economy

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

Where do products come from?

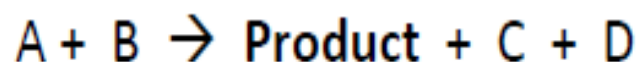


Atom Economy Focuses on:
Atoms → Molecules

2. Atom Economy

Waste not, want not!

A chemical reaction:



Cooking analogy:

Ingredients in $\rightarrow$ product out (any by-products??)

$$\text{Atom Economy} = (\text{FW of Product} \div \text{FW of Reactants}) \times 100\%$$

- Calculate the percentage atom economy in the formation of 1-iodopropane from 1-propanol according to the following reaction



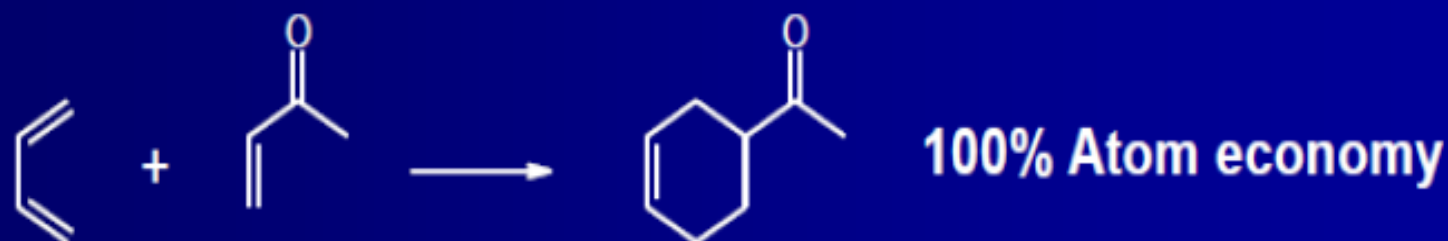
Formula of Reactants	Molar Mass of Reactants	Atoms used in Product	Sum of Molar Mass of Used Atoms	Unused Atoms	Sum of Molar Mass of Unused Atoms
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	60.1	3C, 7H	43.1	HO	17.0
NaI	149.9	I	126.9	Na	23.0
H_2SO_4	98.0	-	0	2H, S, 4O	98.0
Total Atoms in Reactants, 3C, 10H, 5O, Na, S, I	308.0	3C, 7H, I	170.0	HO, Na, 2H, S, 4O	138.0

Percentage Atom Economy =
 (molar mass used atoms / molar mass of all reactants) $\times$ 100
 = $(170.0/308.0) \times 100 = 55.2\%$

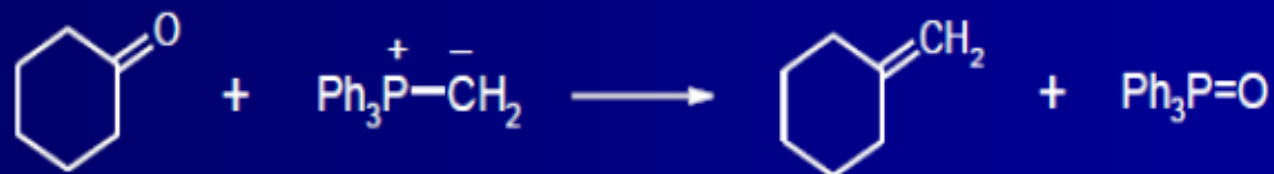


$$\text{Atom Economy} = \frac{\text{molecular weight of desired product}}{\text{molecular weight of all reactants}} \times 100\%$$

Diels-Alder Reaction



Wittig Reaction

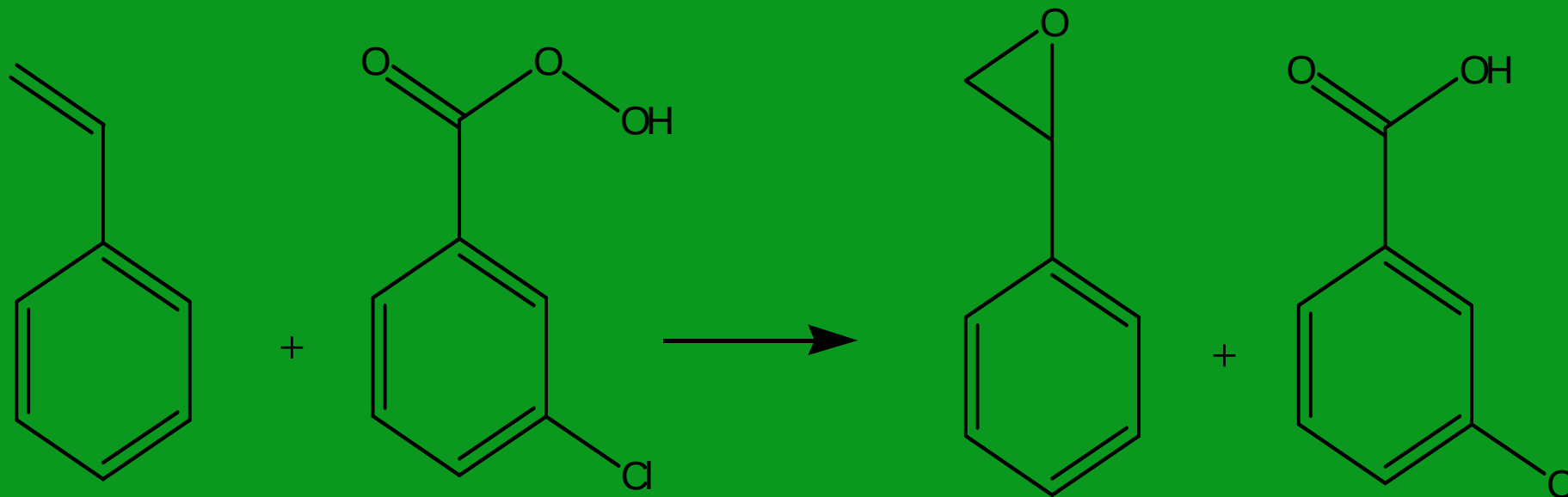


35% Atom economy

*The amount of **INPUT** is concerned! Different from **yield**!!*

Atom Economy

Balanced chemical reaction of the epoxidation of styrene



Assume 100% yield

100% of the desired epoxide product is recovered

100% formation of the co-product: m-chlorobenzoic acid

A.E. of this reaction is 23%

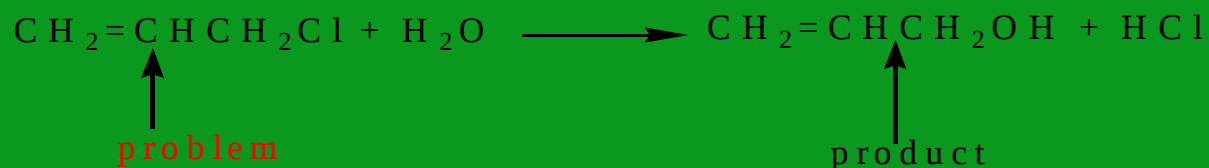
77% of the products are waste

- If the chemical reaction of the type
- $A + B \longrightarrow P + W$
- Find alternate A or B to avoid W
- Example 1:
- Disinfection of water by chlorination. Chlorine oxidizes the pathogens there by killing them, but at the same time forms harmful chlorinated compounds.
- A remedy is to use another oxidant, such as

**O₃ or supercritical water
oxidation**

Example 2 of green chemistry

- Production of allyl alcohol $\text{CH}_2=\text{CHCH}_2\text{OH}$
- Traditional route:** Alkaline hydrolysis of allyl chloride, which generates the product and hydrochloric acid as a by-product



- Greener route,** to avoid chlorine: Two-step using propylene ($\text{CH}_2=\text{CHCH}_3$), acetic acid (CH_3COOH) and oxygen (O_2)



- Added benefit:** The acetic acid produced in the 2nd reaction can be recovered and used again for the 1st reaction, leaving no unwanted by-product.

[3] Less Hazardous Chemical Synthesis

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

3. Less Hazardous Chemical Synthesis



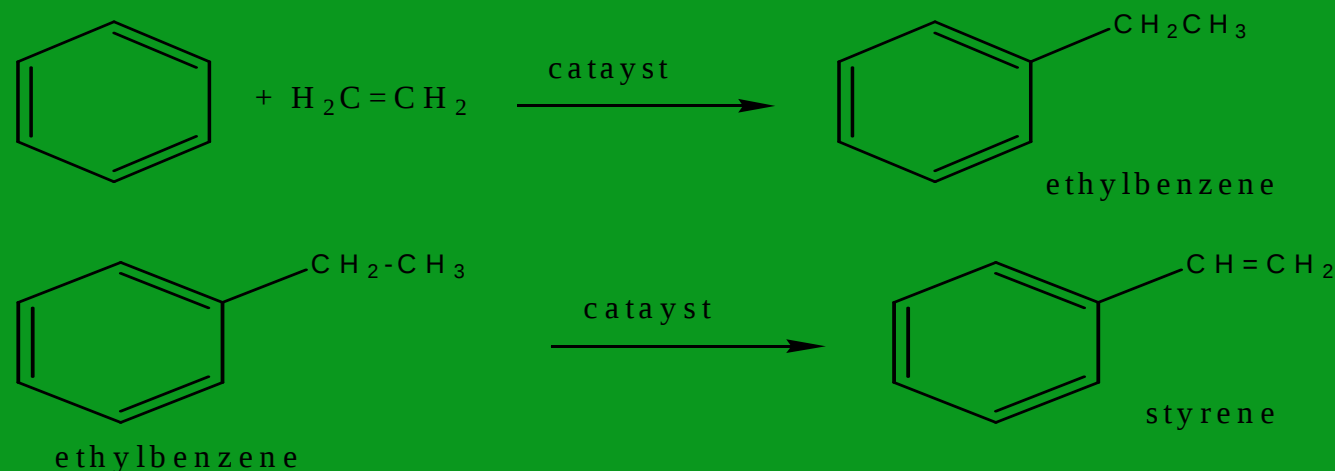
Function is related to hazard.
We do risky things all the time...

When chemists “do chemistry,” they have a choice in how they do it. Choosing the safer method in Chemistry is like using a screwdriver instead of a knife to tighten a screw. The knife might be able to tighten the screw, but it’s dangerous!



Example 3 of green chemistry

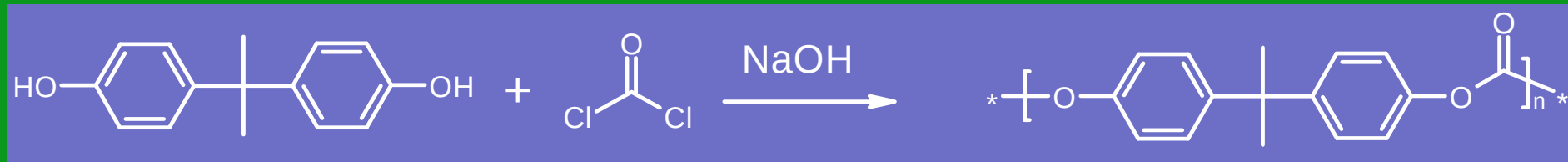
- Production of styrene (=benzene ring with $\text{CH}=\text{CH}_2$ tail)
- **Traditional route:** Two-step method starting with benzene, which is carcinogenic) and ethylene to form ethylbenzene, followed by dehydrogenation to obtain styrene



- **Greener route:** To avoid benzene, start with xylene (cheapest source of aromatics and environmentally safer than benzene)
- **Another option,** still under development, is to start with toluene (benzene ring with CH_3 tail)

Less Hazardous Chemical Synthesis

Polycarbonate Synthesis: Phosgene Process

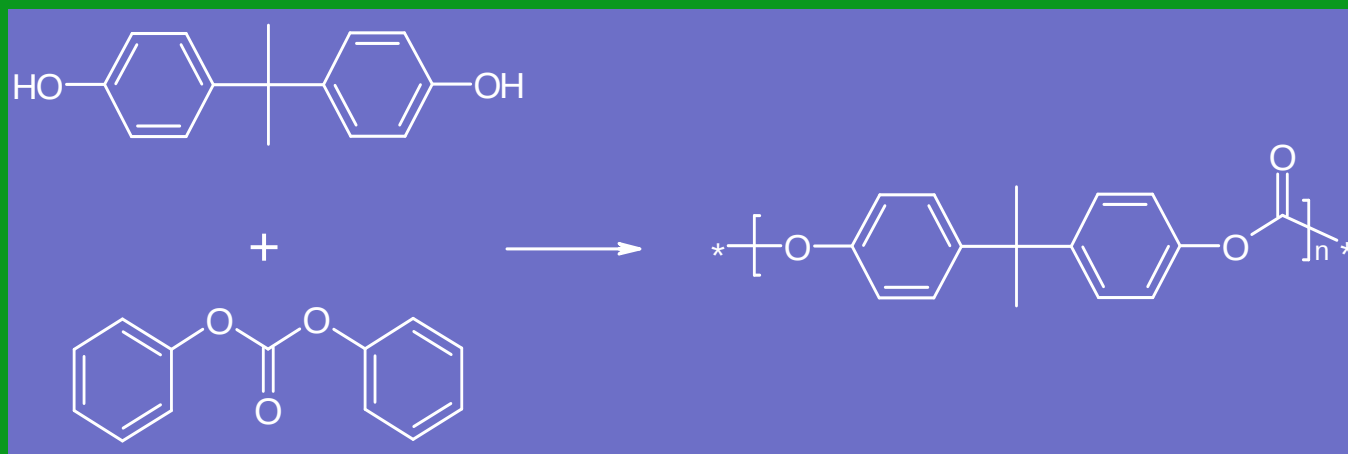


◆ Disadvantages

- 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

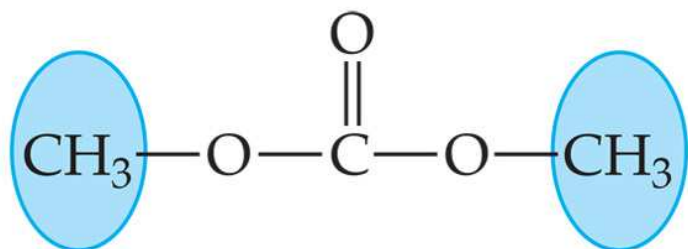
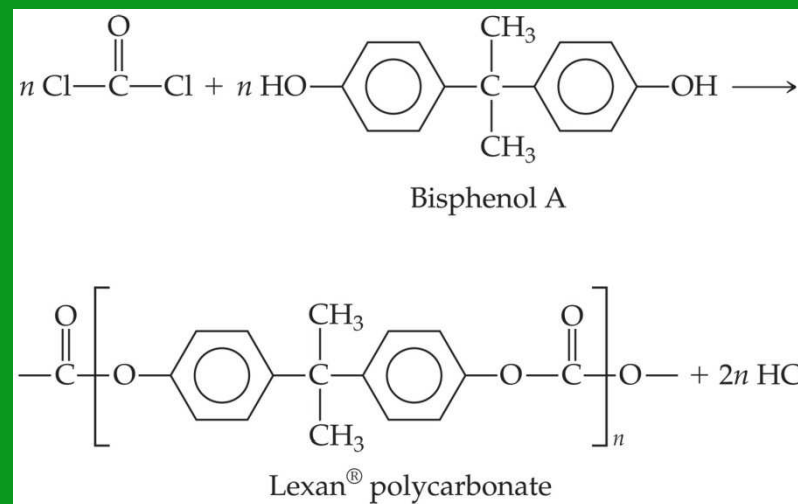


◆ Advantages

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

Reagents

- Phosgene, COCl_2 , is commonly used as a starting material for plastic polymers
- Phosgene is a highly toxic substance, and the by-products of many of its reactions are undesirable.



Dimethyl carbonate

A superior alternative might be dimethyl carbonate

[4] Designing Safer Chemicals

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

4. Designing Safer Chemicals

Chemists are molecular designers; they design new molecules and new materials. Green Chemists make sure that the things that we make not only do what they're supposed to do, but they do it safely. This means that it's not only important *how* chemists make something, it's also important that *what* they make isn't harmful.

In Chemistry: Function is NOT related to hazard.

Making safe, non-toxic products is the goal!



Designing Safer Chemicals

Case Study: Antifoulants (Marine Pesticides)

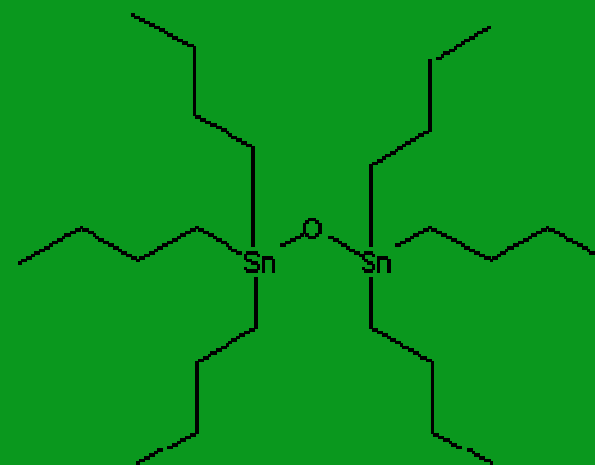


Designing Safer Chemicals: Case Study: Antifoulants

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

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.



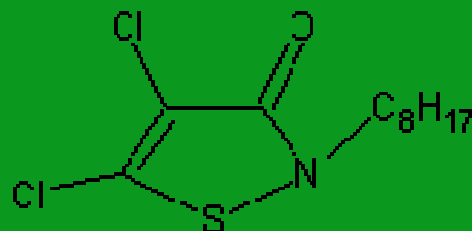
Tributyltin Oxide

Designing Safer Chemicals: Case Study: Antifoulants

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

Designing Safer Chemicals: Case Study: Antifoulants

- Sea-Nine® 211 works by maintaining a hostile growing environment for marine organisms. When organisms attach to the hull (treated with DCOI), proteins at the point of attachment with the hull react with the DCOI
- This reaction with the DCOI prevents the use of these proteins for other metabolic processes
- The organism thus detaches itself and searches for a more hospitable surface on which to grow
- Only organisms attached to hull of ship are exposed to toxic levels of DCOI
- Readily biodegrades once leached from ship (half-life is less than one hour in sea water)

[5] Safer Solvents and Auxiliaries

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

5. Safer Solvents and Auxiliaries

We use solvents for all kinds of things:

- Cooking
- Nail polish (lots of fumes!)
- Paints
- Cleaning products
- Decaffeinated coffee
- Chemical reactions



Many solvents are hazardous and toxic. There are safer alternatives!

What is a solvent?

A **solvent** is a substance (usually a liquid) that dissolves something else.

A **solute** is the substance that is dissolved in the solvent.

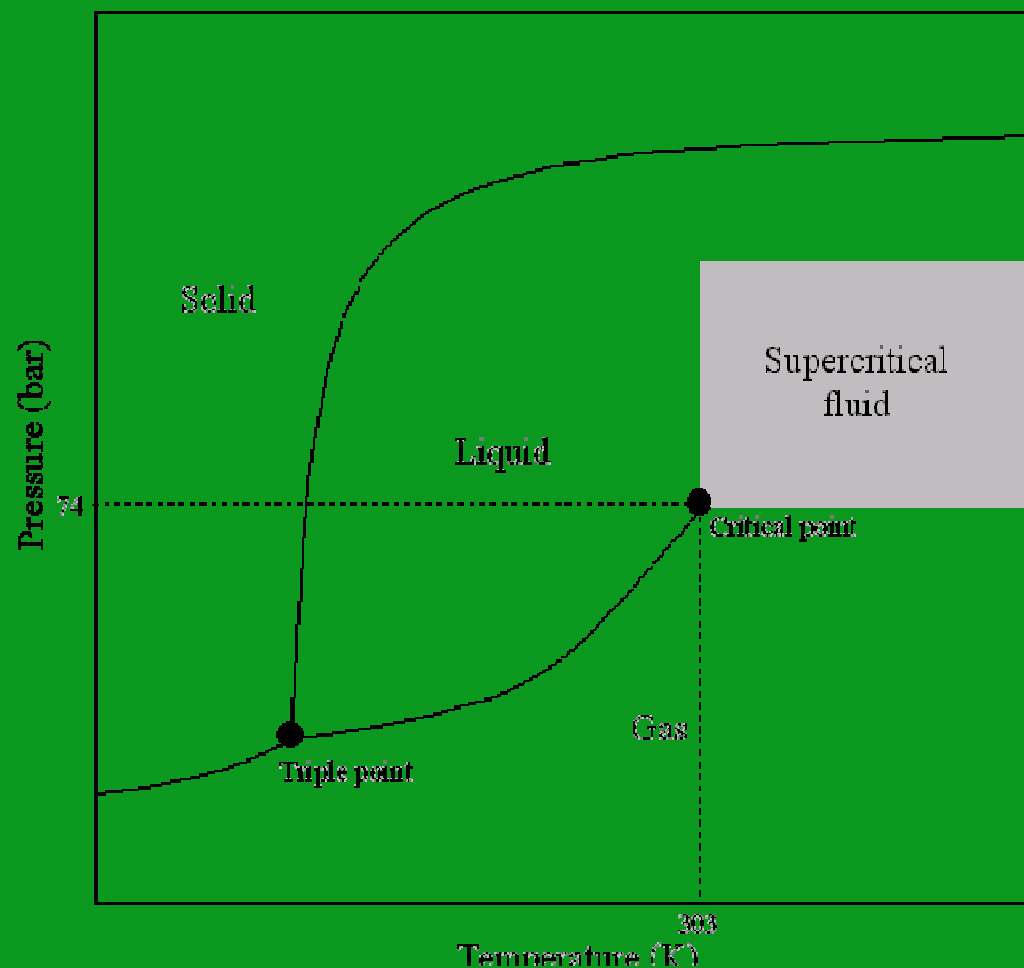
Example: If you dissolve sugar in water – which substance is the solvent and which is the solute?



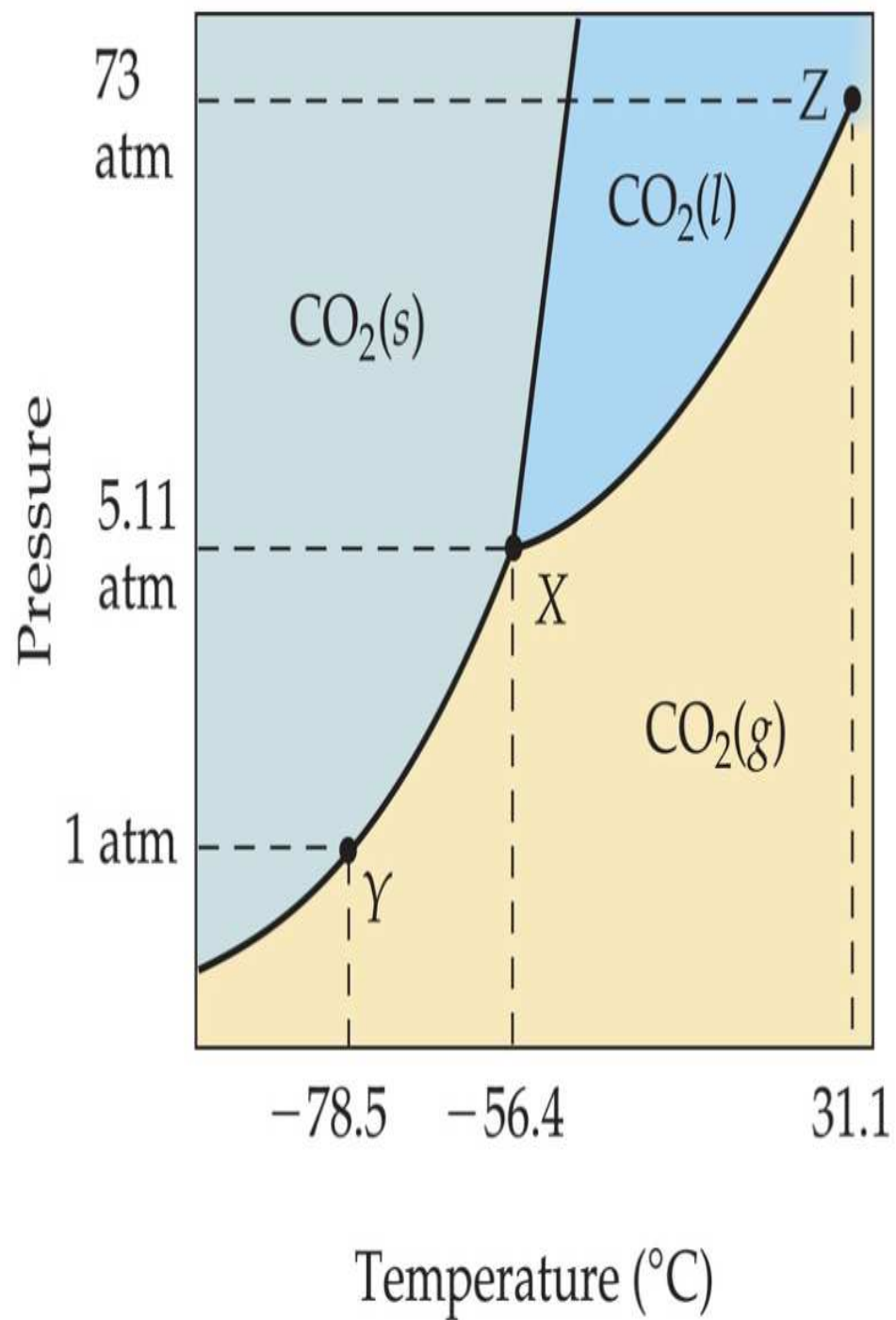
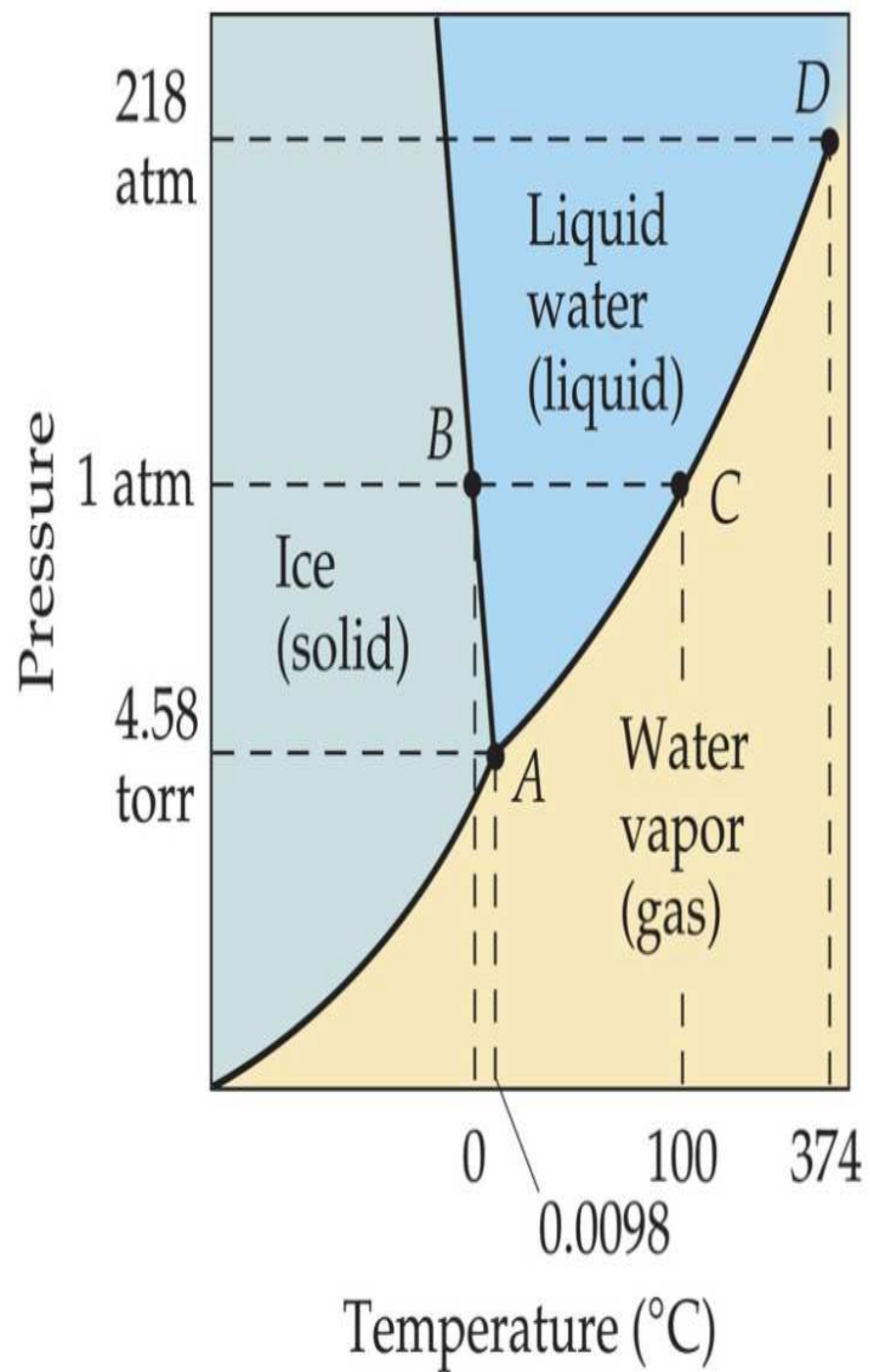
Safer Solvents

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

Safer solvents: Supercritical fluids



A SCF is defined as a substance above its critical temperature (T_c) and critical pressure (P_c). The critical point represents the highest temperature and pressure at which the substance can exist as a vapor and liquid in equilibrium.

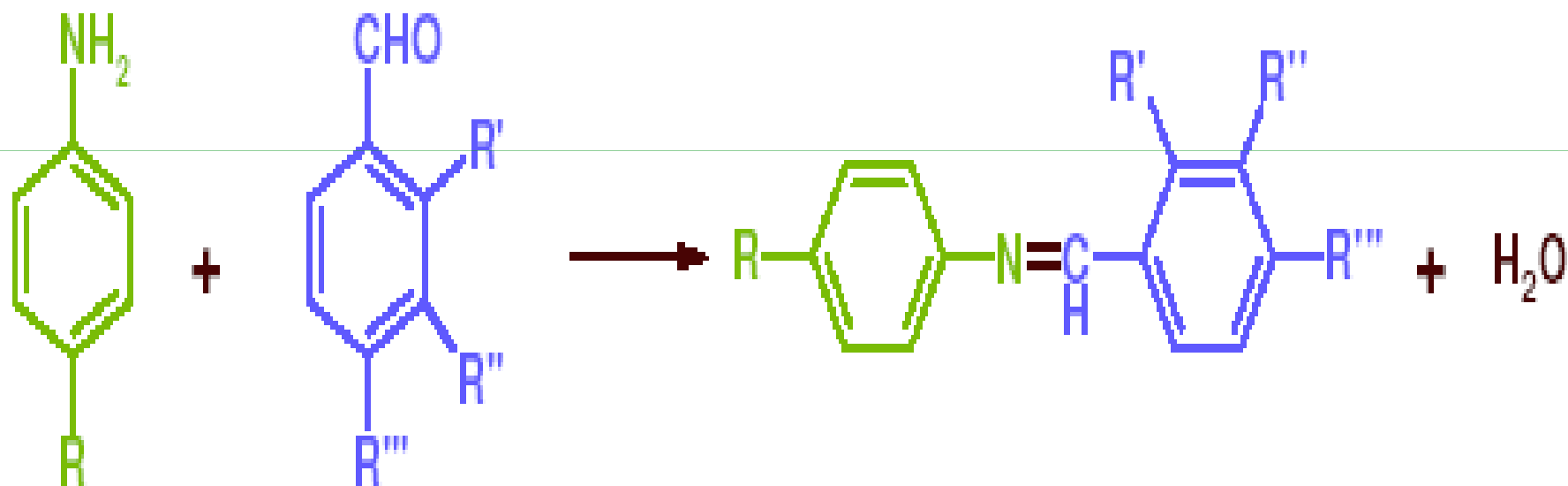


Supercritical Carbon Dioxide (scCO₂)

- Usually when liquids are heated they turn into a vapour and when vapour is compressed it condenses into a liquid
- However, if a vapour is heated above a certain critical temperature, the vapour cannot be liquefied no matter what pressure is applied
- At these temperatures the distinction between liquid and gas is blurred
- The material has similar properties to gas in that it expands to fill any space, however, it also has similar properties to a liquid and can be used as a solvent
- At this stage, the material is said to be a supercritical liquid

- Carbon dioxide forms a supercritical fluid at a pressure of 73 atm and a temperature of 31°C
- This relatively low temperature makes superficial carbon dioxide easy to work with
- Another useful feature is that its solvent properties can be altered by making slight adjustments to temperature and pressure
- scCO_2 is an environmentally friendly option also because it can be obtained as a by-product from other industries. It is also easy to recapture and rescue

A solventless reaction:



[6] Design for Energy Efficiency

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

6. Design for Energy Efficiency



We use lots of energy:

- Driving our cars
- Heating and cooling our houses
- Cooking food
- Drying our hair

Chemists also use lots of energy:

- Heating
- Drying
- Cooling

Energy is not only expensive – most of the time the power plant that creates the energy contributes to pollution.



Heating
Cooling
Stirring
Distillation
Compression
Pumping
Separation



Energy
Requirement
(electricity)



Burn fossil
fuel



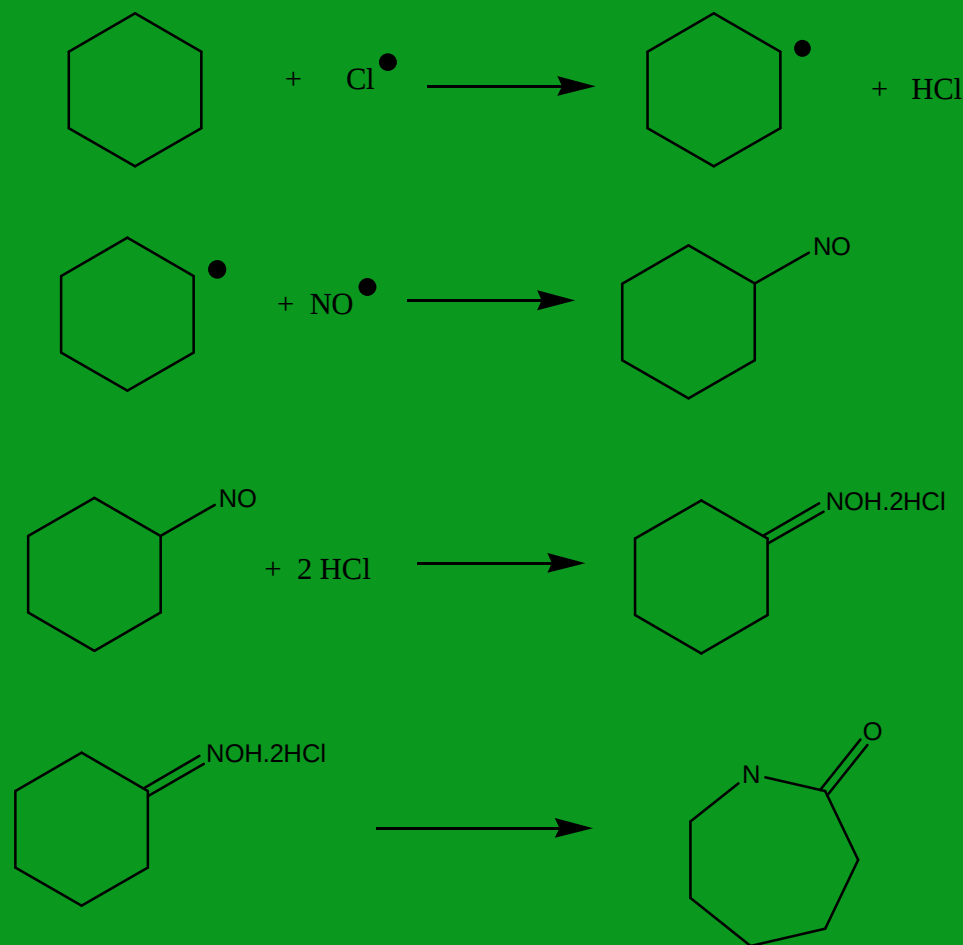
CO₂ to
atmosphere

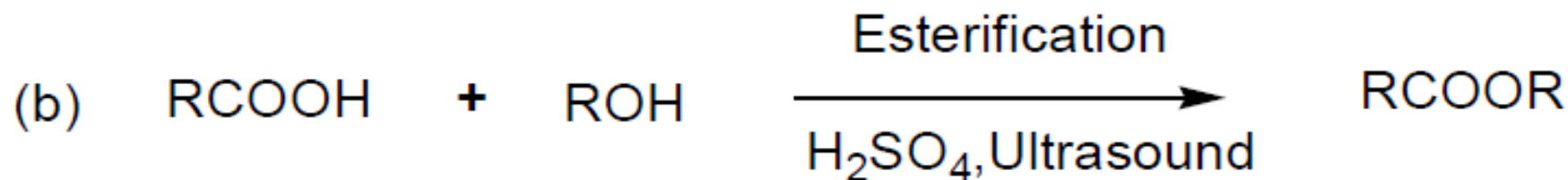
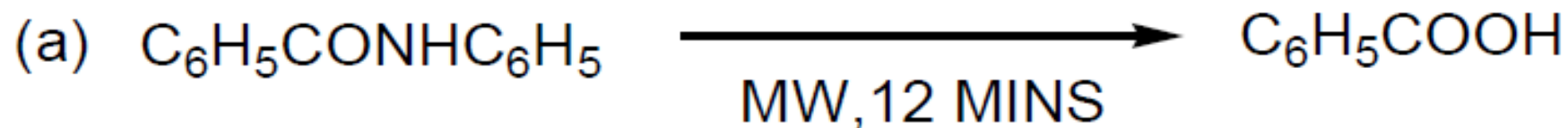


Global
Warming

Alternative energy sources: Photochemical Reactions

- Two commercial photochemical processes: From Cyclohexane to Caprolactam process using $\text{NOCl} \rightarrow \text{NO}^\bullet + \text{Cl}^\bullet$ (535nm)





- Wavelengths between 1 mm and 1 m
 - Frequency fixed at 2.45 GHz
- More directed source of energy
- Heating rate of 10°C per second is achievable
- Possibility of overheating (explosions)
- Solvent-free conditions are possible
- Interaction with matter characterized by penetration depth

[7] Use of Renewable Feedstocks

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

7. Use of Renewable Feedstocks



Why are gas prices so high?

One reason is that oil is not a renewable resource.

90-95% of the products we use (plastic bottles, pharmaceuticals, paint, non-stick coatings, fabrics, etc.) come from oil?



What will happen when we run out of oil and petroleum?

Green chemists look for alternative sources for making materials. Renewable feedstocks (corn, potatoes, biomass) can be used to make many products: fuels (ethanol and bio-diesel), plastics and more.



- Converting D-glucose into lactic acid using certain enzymes helps us to prepare aliphatic compounds from lactic acid
- E-coli converts D-glucose to catechol which acts as a starting material for aromatic compounds
- On the other hand isomaltulose which is widely available in biomass can be converted into glucosylmethyl furfural which can be used for production of many heterocyclic compounds

- Besides biomass cash crops is a new hope as ethanol from sugarcane has been derived successfully and now scientists are trying to use this “bio alcohol” as a source of vehicle for future
- Exhaust from Corn plant has been successfully utilized for preparing bio-degradable plastic

Raw Materials from Renewable Resources: The Bio Fine Process



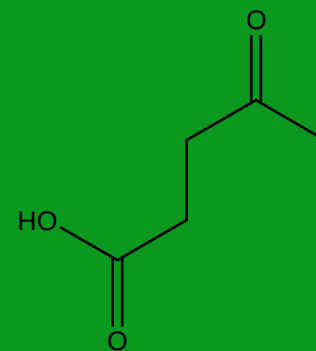
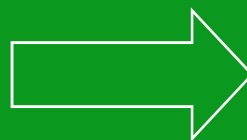
Paper mill
sludge



Agricultural
residues,
Waste wood

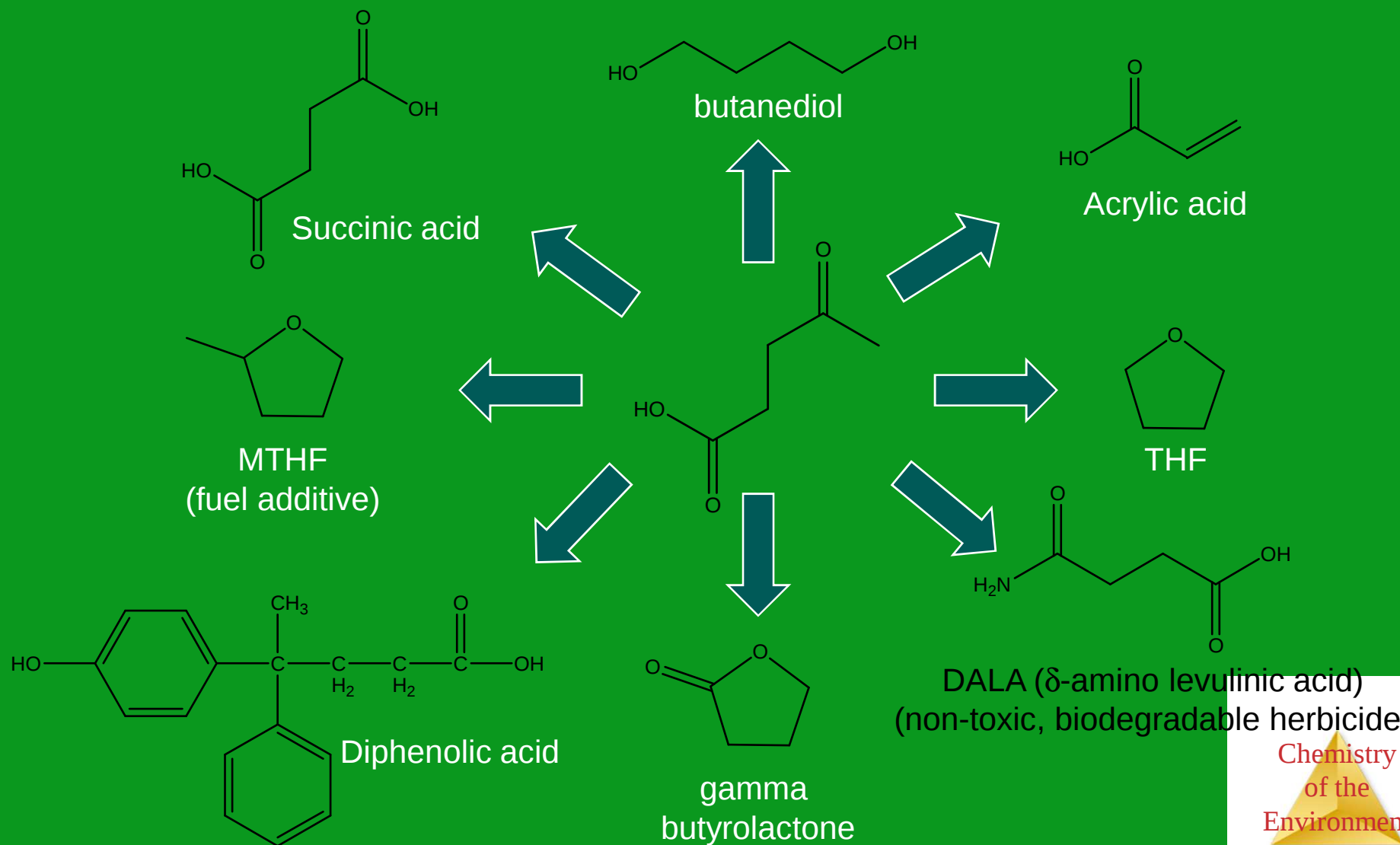


Municipal solid waste
and waste paper

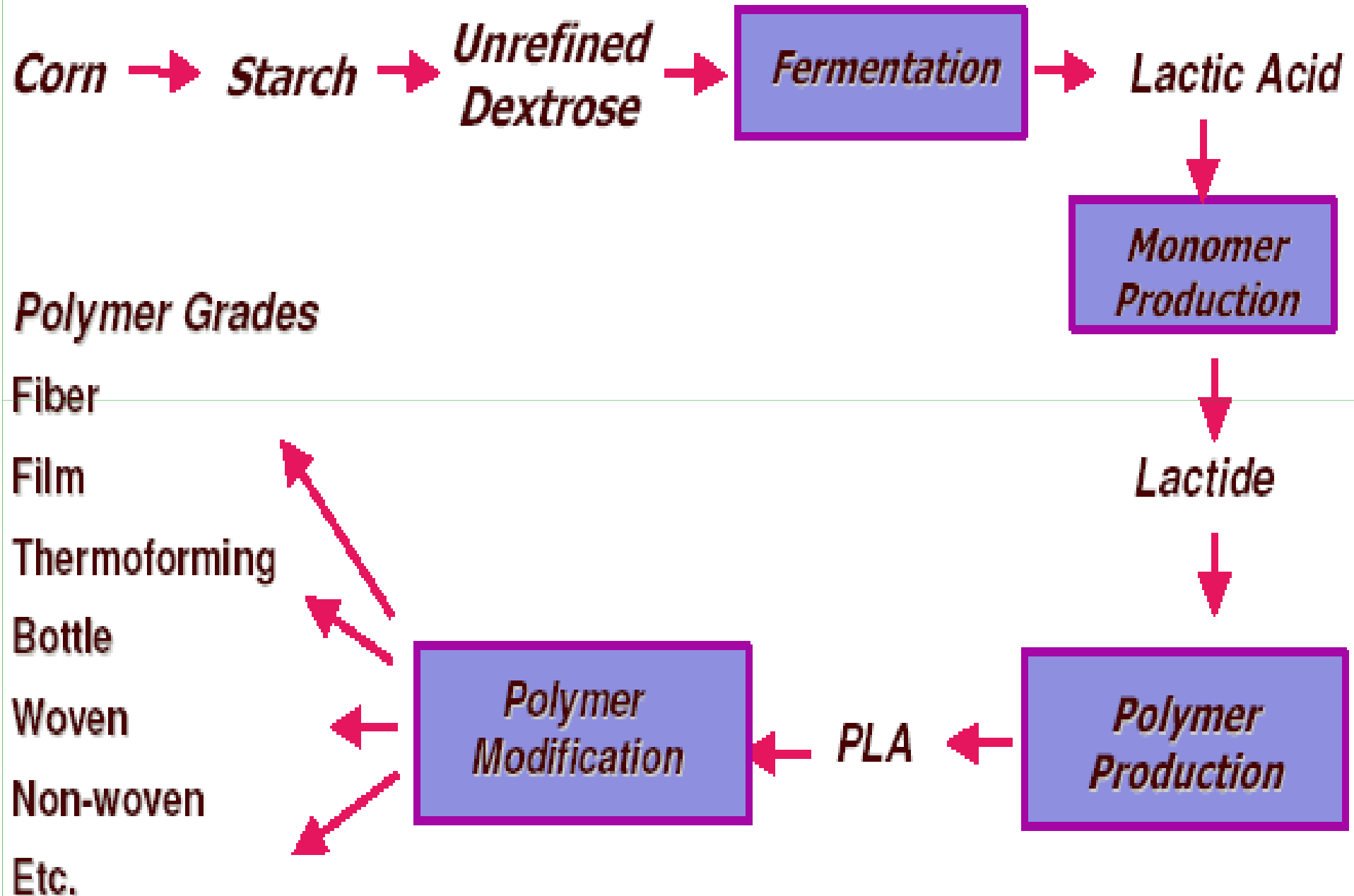


Levulinic acid

Levulinic acid as a platform chemical

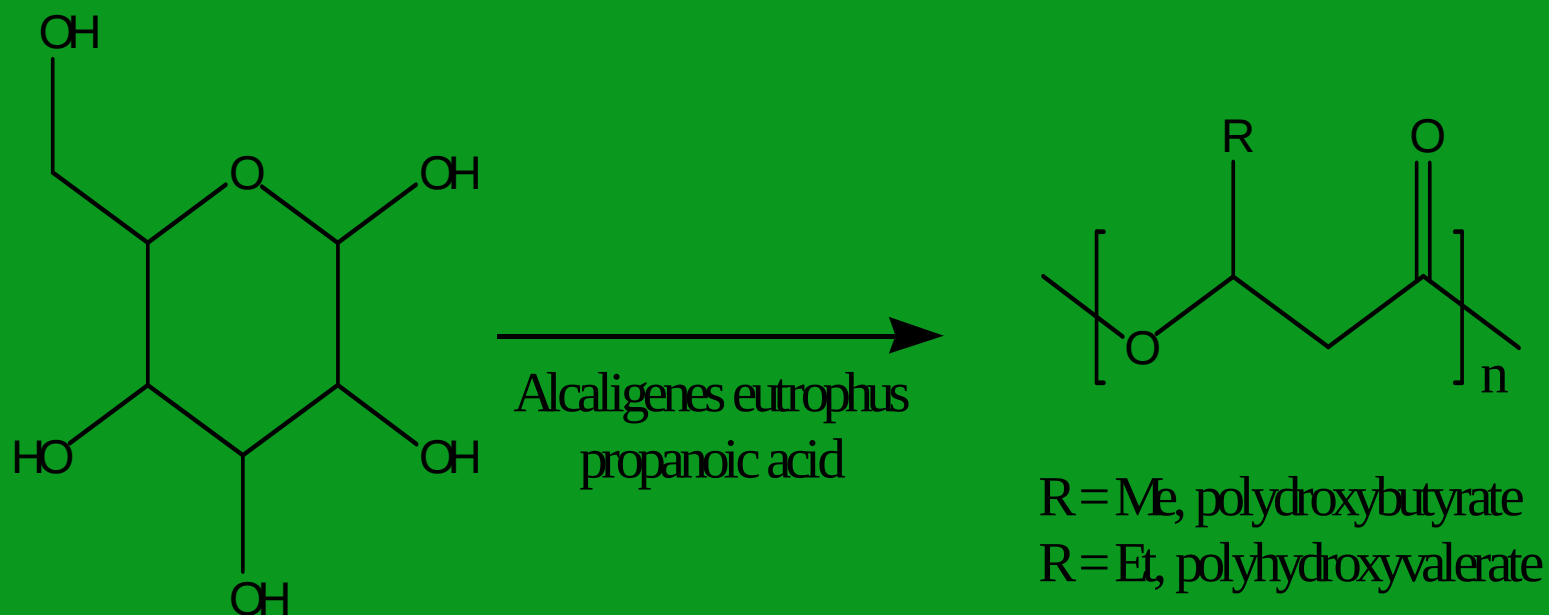


Poly lactic acid (PLA) for plastics production



Polymers from Renewable Resources: Polyhydroxyalkanoates (PHAs)

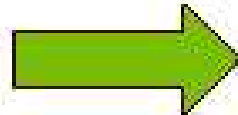
- Fermentation of glucose in the presence of bacteria and propanoic acid (product contains 5-20% polyhydroxyvalerate)
- Similar to polypropene and polyethene
- Biodegradable (credit card)



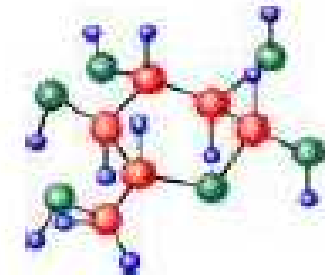
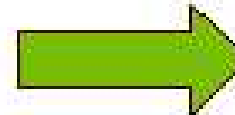
Polyhydroxyalkanoates (PHA's)



Sunlight



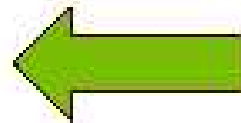
Crop



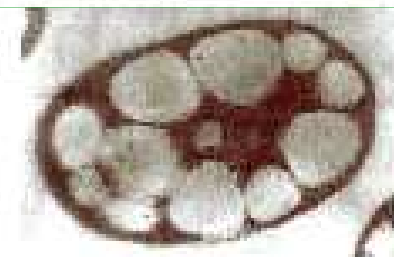
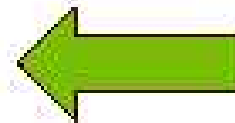
Sugar solution



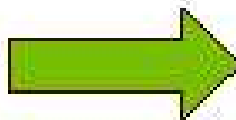
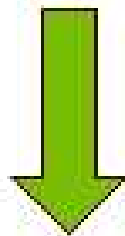
Plastic product



PHA



Fermentation



Biodegradation to CO₂ and H₂O

[8] Reduce Derivatives

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

8. Reduce Derivatives

Natural systems – Low energy, self-assembly

Chemistry – Traditionally high energy, high toxicity

Covalent versus non-covalent bonds



Protecting Groups

Two synthetic steps are added each time one is used

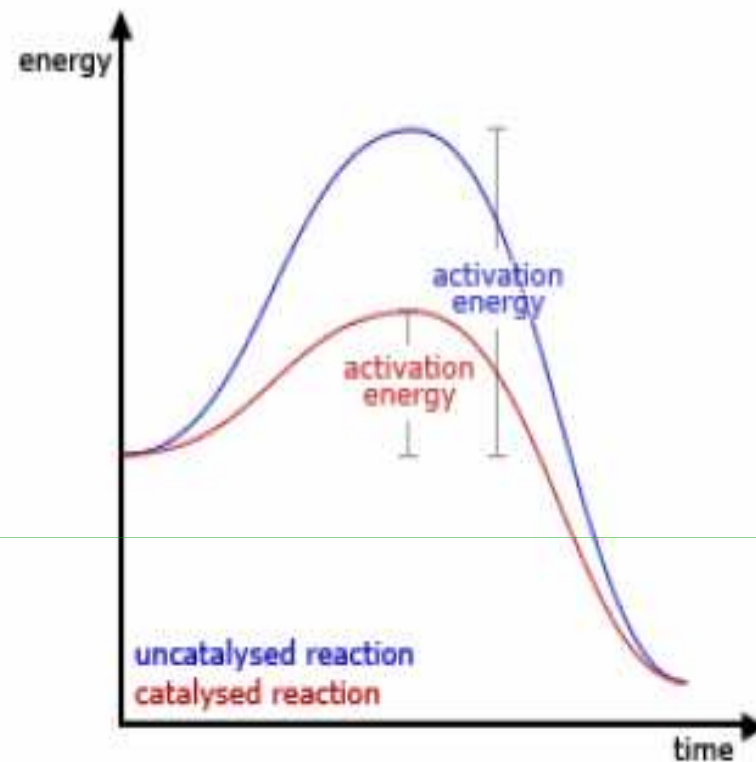
Overall yield and atom economy will decrease

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

[9] Catalysis

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

9. Catalysis



In chemistry and biology, **catalysis** is the acceleration (increase in rate) of a chemical reaction by means of a substance, called a **catalyst**, which is itself not consumed by the overall reaction.

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

- Using “green catalyst” is that its action mimics nature in respect that all natural synthesis is enzyme catalyzed reactions - Biocatalysts
- This not only helps in designing a highly stereo specific, stereo selective and enantio - selective product but also these reactions takes place under ambient conditions

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)

[10] Design for Degradation

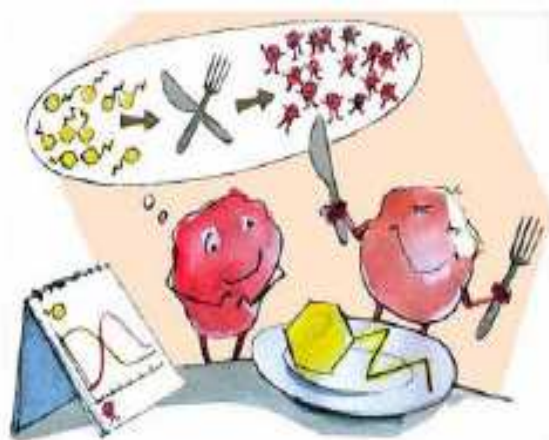
Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products

10. Design for Degradation



Recycling is one way of reducing waste... but, can we recycle everything?

What happens when we throw things away?



Design for degradation means that when green chemists design a new chemical (i.e., a pharmaceutical drug or medicine) or material (i.e., a new plastic) – they design it so that it breaks down at the end of its useful lifetime.

Persistence

- Early 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

Degradation of Polymers: Polylactic Acid

- ◆ Manufactured from renewable resources
 - Corn or wheat; agricultural waste in future
- ◆ Uses 20-50% fewer fossil fuels than conventional plastics
- ◆ PLA products can be recycled or composted

[11] 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

11. 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!

Analyzing a Reaction

What do you need to know, how do you get this information and how long does it take to get it?

[12] Inherently Safer Chemistry for Accident Prevention

Substance 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

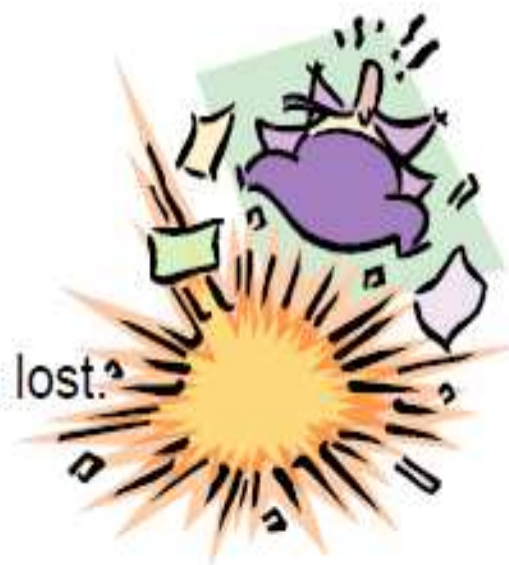
12. Inherently Safer Chemistry for Accident Prevention

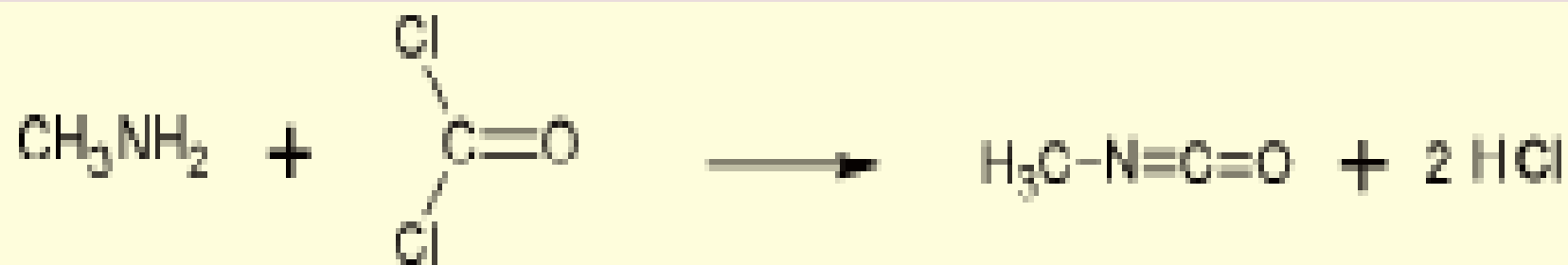
Tragedy in Bhopal, India - 1984

In arguably the worst industrial accident in history, 40 tons of methyl isocyanate (MIC) were accidentally released when a holding tank overheated at a Union Carbide pesticide plant, located in the heart of the city of Bhopal. 15,000 people died and hundreds of thousands more were injured.

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.

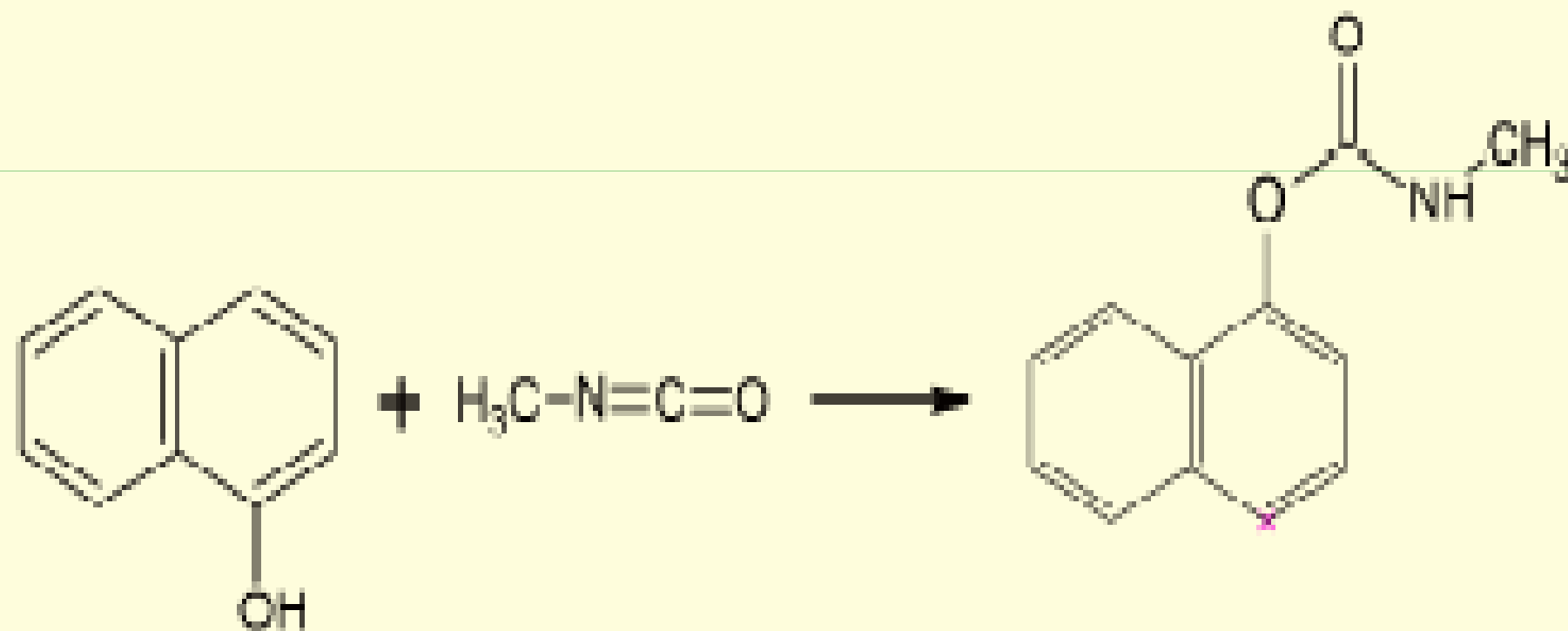




Methylamine

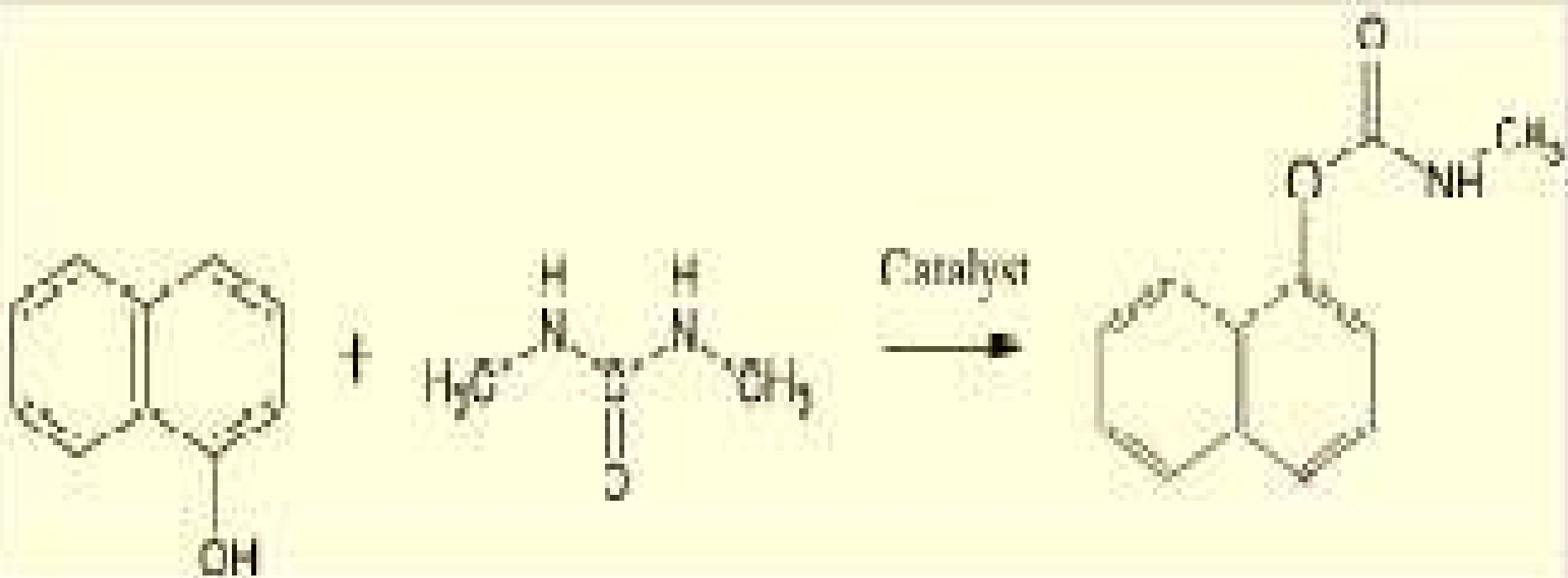
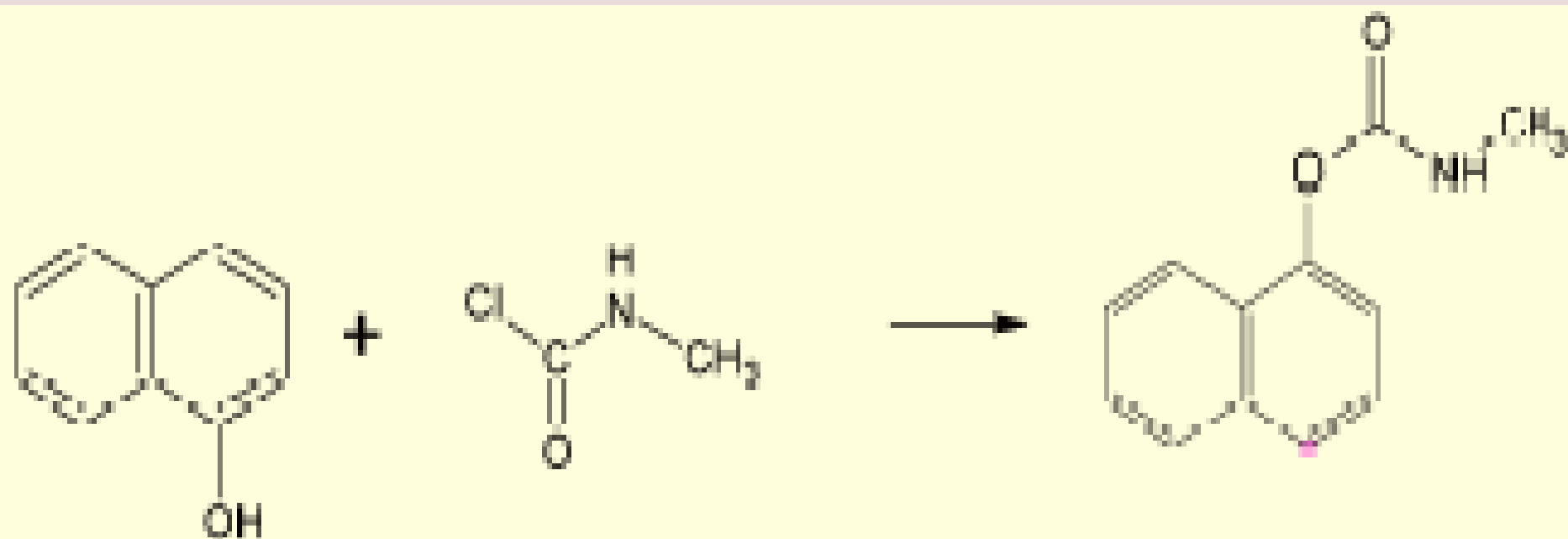
Phosgene

Methyl Isocyanate

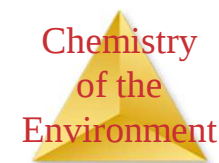


1-Naphthol

Carbaryl



Designing a Green Synthesis



➤ Atom Economy

- The yield in a chemical reaction is satisfactory without the formation of bi-products
- The reactions are focused to undergo addition reactions, rearrangements or pericyclic reaction where a single product is obtained which further increases the atom efficiency
- For reactions whose desired product is a chiral compound
- it is advisory to design such reactions which eliminates the formation of racemic mixtures
- Hence these type of synthesis should always be either highly stereo-specific or either highly stereo-selective



- (a) Use of “light” as a carrier of electrons which can eventually reduce the usage of other chemical agents which act as a carrier of electron and is obtained as waste products at the end of a redox reaction
- (b) Eliminating the un-necessary use of protection-deprotection methodologies
- (c) Replacement of soluble Lewis acids by mesoporous solids containing bound sulphonates in green synthesis

➤ Use of Renewable Feedstocks

- Converting biomass into starting material
- D-glucose → Lactic acid → Aliphatic compounds
- D-glucose → Catechol → Aromatic compounds
- Isomaltulose in biomass → Glucosylmethyl furfural → Heterocyclic compounds
- Ethanol from sugarcane → “Bioalcohol” as a source of vehicle for future
- Exhaust from Corn plant → Bio-degradable plastic

➤ Use of Catalysts (Catalysis)

- Maximize the yield of the desired products by developing such reactions which are catalyzed reactions whose catalyst can be extracted and further utilized for other reactions
- “Green Catalyst” → Enzyme catalyzed reactions
- Highly stereo specific, stereo selective and enantio - selective product
- These reactions takes place under ambient conditions



➤ Use of Green solvents

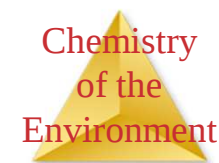
- Solvent in organic synthesis which is not only costly but is very harmful for those who is handling them also
- To minimize or eliminate these effects by using water as a solvent or the super critical carbon dioxide
- Other super critical fluids used in green chemistry are ethane, ethene, water, xenon etc

➤ Energy Efficiency

- Minimizing the energy requirements of industries by maximizing the efficiency of chemical conversion and decreasing the activation energy of the reactions by using recyclable catalysts can cut off the energy requirement of industries by half or even more
- Eliminating the use of energy consuming steps like distillation, crystallization, sublimation, ultra filtration etc
- Utilization of milder reaction conditions for carrying out a chemical reaction
- Incorporation of microwave energy which aims to achieve a high temperature at much faster rates
- Utilization of ultrasonic energy for certain reaction can eventually solve this problem

Conclusion

Green chemistry not a solution to all environmental problems but the most fundamental approach to preventing pollution



Conclusion

“It’s more **effective**,
it’s more **efficient**,
it’s more **elegant**,
it’s simply **better chemistry**,”



-- Paul Anastas

