Chemistry 471-671

Introduction to Green Chemistry

Contact Information

Timothy Dransfield (Atmospheric chemistry)
timothy.dransfield@umb.edu
S-1-85
7-6143

Jason Evans (Alternative energy)
jason.evans@umb.edu
S-1-84
7-6149

Bela Torok (Green synthesis)
bela.torok@umb.edu
S-1-132
7-6159

http://alpha.chem.umb.edu/chemistry/ch471

Human society is constantly facing such environmental issues and problems as ozone depletion, air pollution, global climate change, soil and water pollution, acid rain, the depletion of natural resources, and the accumulation of hazardous waste.

This course probes aspects of chemistry which are designed to benefit society and which search for pathways to minimize the environmental impact of human industry and technology.

Green Chemistry: Preventing Pollution
Sustaining the Earth

What makes a society sustainable?

There are several things to consider:

The environment

Human health

A stable economy

An efficient economy with respect to energy and resources

Social and political justice

In a sustainable society...

Technologies used for production of needed goods are not harmful to the environment or to human health

Renewable resources are used whenever possible

At the end of their use, non-biodegradable materials are recycled

Manufacturing processes are designed *either* so as to minimize waste products

Or

So that waste products are recycled or biodegradable

Is *Our* Society Sustainable?

Perhaps not without some changes...

Solid waste continues to accumulate in industrialized nations

There are demonstrable impacts of human industry on

air quality

water quality

soil quality

and by extension, on human health

Not to mention on animal and plant ecosystems

Green Chemistry

Green Chemistry works towards a sustainable society by:

Designing chemical products that are benign to both humans and the environment

Designing industrial processes that reduce or eliminate hazardous waste

Designing more efficient processes that minimize all waste materials

In 1990, at the EPS, UMB's Paul Anastas and John Warner defined Green Chemistry:
"The design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances."

They stressed the need for means to:
Reduce Waste
Reduce the consumption of resources
Reduce the consumption of energy

Since then, the idea has grown beyond that first definition, but the inspiration remains the same: preventing harm to people and the environment, rather than cleaning up the mess afterwards.

Anastas and Warner formulated the Twelve Principles of Green Chemistry

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

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

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

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

5) The use of **auxiliary substances should be made unnecessary** whenever possible, and innocuous when used.

Twelve Principles of Green Chemistry, continued

6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized.

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

8) Unnecessary **derivatization should be avoided** whenever possible.

9) **Catalytic reagents** are superior to stoichiometric reagents.

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

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

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

Discussion of some Principles:

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

This is the most fundamental aspect of Green Chemistry. It is not enough to be aware of waste and try to clean up. This is a fundamental shift in philosophy from all the preceding history of chemistry.

Discussion of some Principles:

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

Many synthetic routes produce unwanted by-products. Often these are toxic, and have to be dealt with as waste. This principle encourages the development of synthetic routes that maximize the yield of product and minimize the yield of waste. We will treat this more explicitly later, using an analysis based on **Atom Economy.**

Discussion of some Principles:

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

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

Together, stress that toxicity of reagents, catalysts, by-products *and* final products should be minimized. Note that principle 4 doesn't specify whether the compound is toxic to *humans*. For these principles (and several others), the story of DDT provides a useful cautionary tale.

Discussion of some Principles:

5) The use of auxiliary substances should be made unnecessary whenever possible, and innocuous when used.

What sort of auxiliary substances?

Solvents, drying agents, separating agents.

In almost all cases, these are used in larger quantities than the reagents themselves.

What happens to them when the reaction is over?

Discussion of some Principles:

6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized.

Many chemical reactions require heating or cooling, or pressures that differ significantly from ambient conditions. All of this requires energy, and that energy consumes resources and costs money. Green Chemists are encouraged not to forget this contribution to waste and cost-efficiency.

Discussion of some Principles:

7) A raw material feedstock should be renewable whenever technically and economically practical.

With a particular emphasis on modern problems, it is worth pointing out that the majority of organic chemicals are currently produced from petroleum. There is a boom in the industry to be the first to efficiently produce stock from biomass.

Discussion of some Principles:

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

A major failure of the chemical industry up to now has been the failure to consider the full lifetime of chemicals in the environment. Once we release them, what happens to them? How long do they take to decay, and what are their decay products? Again, the DDT example is particularly illustrative.

Atom Economy

Developed by Barry Trost at Stanford, and won him the 1998 Presidential Green Chemistry Award.

The idea is to focus our attention on principle 2 by asking “how many of the atoms of the reactants are incorporated into the final desired product, and how many are wasted?”

Atom Economy

A simple example:

Assume a one-step reaction to produce 1-bromobutane from 1-butanol.

$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH + NaBr + H_2SO_4 \rightarrow$

$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Br + NaHSO_4 + H_2O$

Let's compare the atomic mass of all the atoms which we used to the molecular mass of the desired product.

Atom Economy

Let's compare the atomic mass of all the atoms which we used to the molecular mass of the desired product.

% Atom Economy =

100% x (sum of molecular masses of desired products) / (sum of atomic masses of all atoms used)

% Atom Economy =

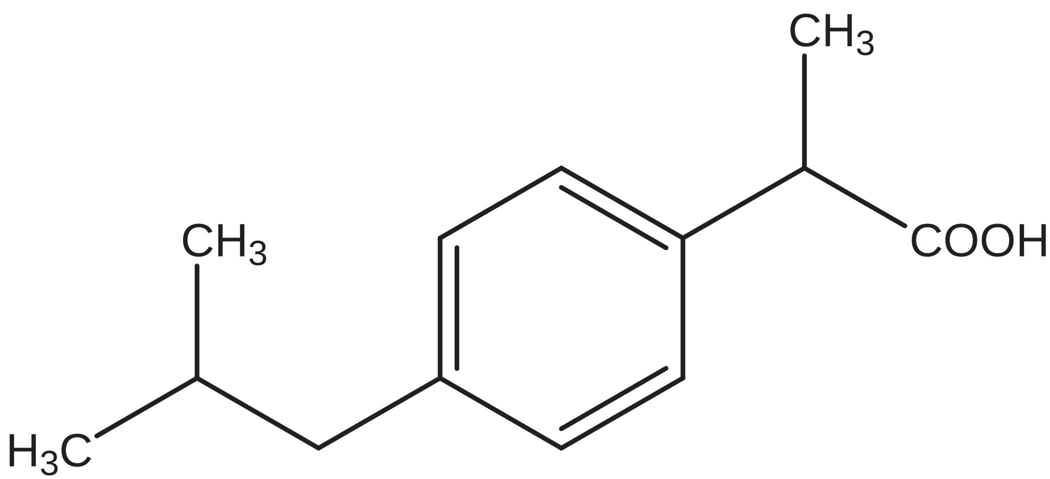
$(4*M_C + 12*M_H + M_{Br})/(4*M_C + 12*M_H + 5*M_O + M_{Br} + M_{Na})$

$\approx 100\% * (137/275) \approx 50\%$

That is, 50% of the atoms used are incorporated into the final product, and **50% are wasted**.

Atom Economy

A more involved example: the synthesis of ibuprofen.



A common analgesic and anti-inflammatory.

Brand names include Advil, Motrin and Medipren.

First synthesized by the Boots Company in Nottingham, England in 1960s.

Synthesis of Ibuprofen

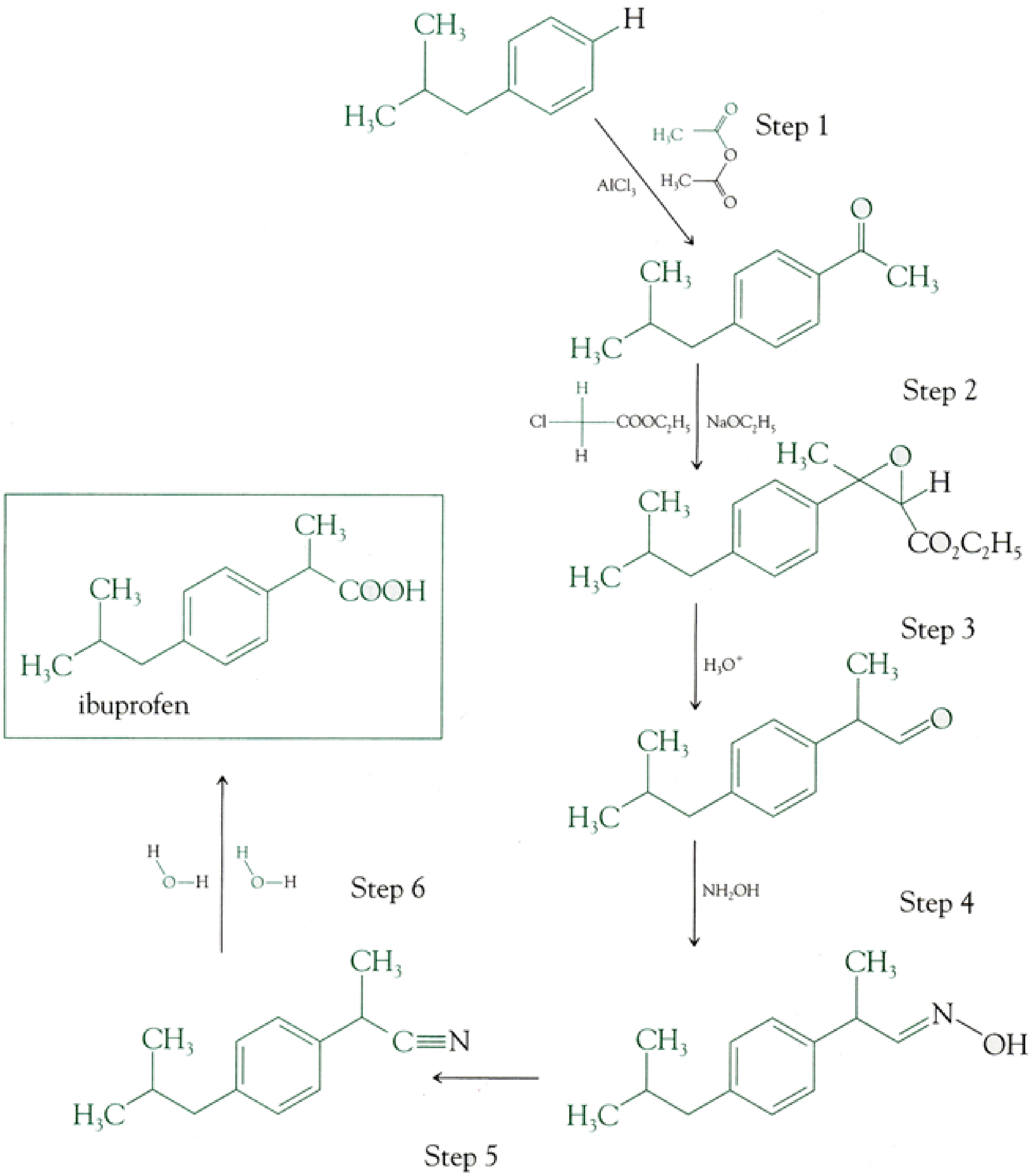


FIGURE In-1 The Boots Company synthesis of ibuprofen. [Source: M. C. Cann and M. E. Connelly, *Real-World Cases in Green Chemistry* (Washington, DC: American Chemical Society, 2000).]

Original Boots synthesis:

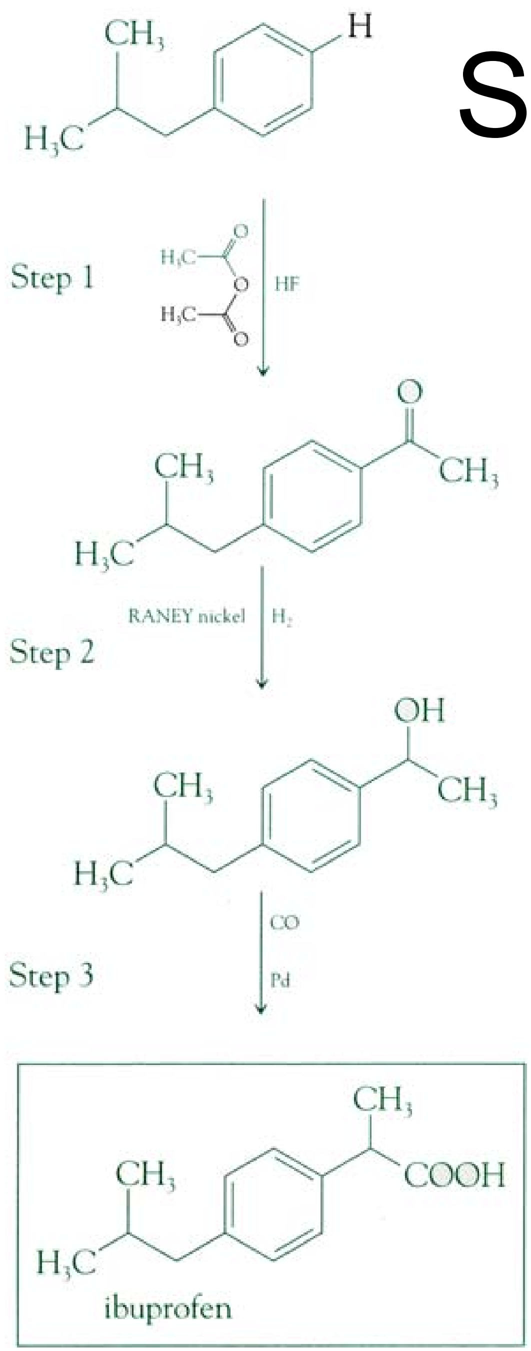
Six step synthesis

Multiple byproducts are formed

Atom Economy: 40%

That means a 60% waste of atoms. Consider: 30 million pounds of ibuprofen are produced each year.

Synthesis of Ibuprofen



BHC Synthesis (1997):

Three step synthesis

Very few byproducts

Atom Economy: 77%*

* - we don't include the mass of catalytic reagents in our calculations of atom economy

The acetic acid produced in step 1 is isolated and re-used, bringing atom economy to 99%.

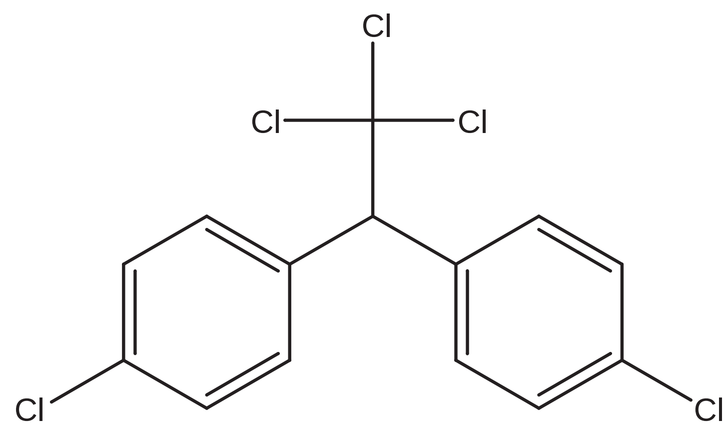
Eliminates much of the solvents, and the aluminum chloride catalyst.

FIGURE In-2 The BHC Company synthesis of ibuprofen. [Source: M. C. Cann and M. E. Connelly, *Real-World Cases in Green Chemistry* (Washington, DC: American Chemical Society, 2000).]

The Cautionary Tale of DDT

The birth of environmental activism can be seen in the response to the use of DDT as a pesticide.

DDT is *para*-dichlorodiphenyltrichloroethane:



Its widespread use came as a result of its efficacy in killing mosquitoes, body lice, and fleas. This greatly reduced the incidence of malaria, yellow fever, typhus and plague.

DDT

It was the first persistent insecticide which wasn't also toxic to humans. The 1948 Nobel Prize in medicine was given to Geigy scientist Paul Muller in recognition of the millions of lives saved during/following the war.

During WW1, 5 million deaths were caused by outbreaks of typhus. During WW2, the Allies used DDT liberally to prevent these deaths – the chemical was sprayed directly on civilians and Allied troops, and later at Dachau and Bergen-Belsen. Widespread aerial spraying was conducted in Gaudalcanal and the Pacific islands.

After WW2, DDT was widely used as an agricultural pesticide. As populations became resistant, farmers used higher and higher concentrations.

The problem: "persistent insecticide". DDT persists in soil for several years, and can become concentrated in a food chain.

DDT

This was most famously discussed in Rachel Carson's 1962 *Silent Spring*, discussing the decline in the American robin population as a result of the widespread use of DDT to combat Dutch Elm Disease.

Most animals can metabolize DDT through HCl elimination to form DDE (dichlorodiphenyldichloroethene). However, in some birds, the presence of DDE in the body interferes with the enzyme that regulates calcium distribution. This leads to eggshells which were too weak to withstand the weight of incubation.

Why is DDT so persistent in the environment?

- Low vapor pressure → low rate of evaporation
- Low reactivity
- Low photoactivity
- Low solubility in water

DDT

However... it IS soluble in organic solvents...
and thus, in animal fat. DDT and/or DDE have been
detected in the fat deposits of all birds and fish that have been analyzed, including those from desert regions or ocean depths. In North America, the average person has a 3 ppm concentration of DDT/DDE in their body fat.

Concerns regarding its possible long-term health effects on humans and its demonstrated damage to the life cycle of birds lead to bans in most Western countries. (US: 1973)

DDT

Many developing and tropical nations continue to use DDT to control mosquito populations

While other less-persistent insecticides are available, they are much less efficient

In South Africa, the introduction of replacement insecticides produced an increase from 8000 cases of malaria with 20 deaths in 1996 to 42000 cases with 340 deaths in 2000.

South Africa has since reverted to the judicious application of DDT

DDT

The lesson (which we'll see a lot):

Even chemicals designed with the best of intentions can have dramatic and unforeseen consequences on the environment and the biosphere

Green Chemists believe that it is the responsibility of chemists to take these possible outcomes in to consideration when designing chemicals, drugs, processes, technologies...

Green Chemistry at UMB

- It’s a philosophy, not a list of 12 Principles.

- It’s a science.

  And it underlies the way we think about ALL chemistry, not just synthesis

  That makes it very hard to cover in one course

Fall 2007 Topics Listing

Week 1: Green Chemistry, an Overview (Dransfield)

Weeks 2-4: The Chemistry of the Atmosphere (Dransfield)

What is the chemical fate of a molecule in the environment? How can we plan for this?

Weeks 5-7: Pragmatic Considerations of Alternative Energy (Evans)

Once we've determined a better solution, how do we implement it? What are the difficulties involved?

Weeks 8-10: Green Synthetic Methods (Torok)

How do we go about making better chemicals? How do we go about making the same chemicals ... but better?

Fall 2007 Topics Listing

Week 1: Green Chemistry, an Overview (Dransfield)

Weeks 2-4: The Chemistry of the Atmosphere (Dransfield)

- 2: The structure of the atmosphere, Tropospheric chemistry
- 3: Photochemical smog, Stratospheric chemistry,
- 4: The Greenhouse Effect, Climate Change

Weeks 5-7: Pragmatic Considerations of Alternative Energy (Evans)

5. Ethanol as fuel
6. Hydrogen as fuel
7. Solar and nuclear power

Weeks 8-10: Green Synthetic Methods (Torok)

- 8: Catalytic methods in synthesis
- 9: Synthesis in aqueous media
- 10: Unconventional energy sources in synthesis

Weeks 11-14: Specific Topics in Green Chemistry and Graduate Student Presentations

Topics, speakers and readings to be announced

Problem Sets:

- One per week
- Distributed on Tuesday
- Due the following Tuesday

Literature Analysis:

- Readings distributed on Tuesday
- Discussion on Thursday
- Discussion is **mandatory, and part of your grade**
- There will also be written assignments at the end of each sub-topic

For the undergraduate students in Chem 471:

weekly problem assignments	25%
weekly analyses of primary literature	25%
cumulative final exam	50%

For the graduate students enrolled in 671:

problem sets	20%
reading analyses	20%
cumulative final exam	30%
one 20 minute presentation	30%