CH 101 ORGANIC

Syllabus:

Green Chemistry:		2 hrs
Spectroscopy :	UV	2 hrs
	IR	2 hrs
	NMR	3 hrs
Organic photochemistry		1 hrs
Pericyclic Reactions :		3 hrs
Macromolecules (polymers):		2 hrs
Bioorganic Chemistry:		x hrs

Chemistry is both a central science and an enabling science.

Chemistry plays a key role in

- **Conquering diseases**
- **Solving energy problems**
- **Solving environmental problems**
- **Providing the discoveries that lead to new industries**
- **Developing new materials and new technologies.**

The Major Challenges to Sustainability in the 21 st Century

- Population
- Energy
- Global Change
- Human Health
- Resource Depletion
- Food Supply
- Toxics in the Environment

Chemistry has the privilege of being singularly responsible for the tremendous advancements that humankind has made in different areas. Almost all fields have used chemistry in some form or the other for its betterment

However, industrial chemistry is not always benign, and it is also criticized for being responsible for a number of environmental problems. Thus there is need for sustainable development and practice of Green chemistry.

Green Chemistry

- Life style have been enhanced by chemistry, something chemists and students need to celebrate.

- Estimates from the United Nations put the world population as high as 10.7 billion people by 2050 - nearly doubled population creates a huge demand for chemical goods and services in the near future.

- Much of the growth of the chemical industry is likely to take place in the developing world, coincident with the rising population.

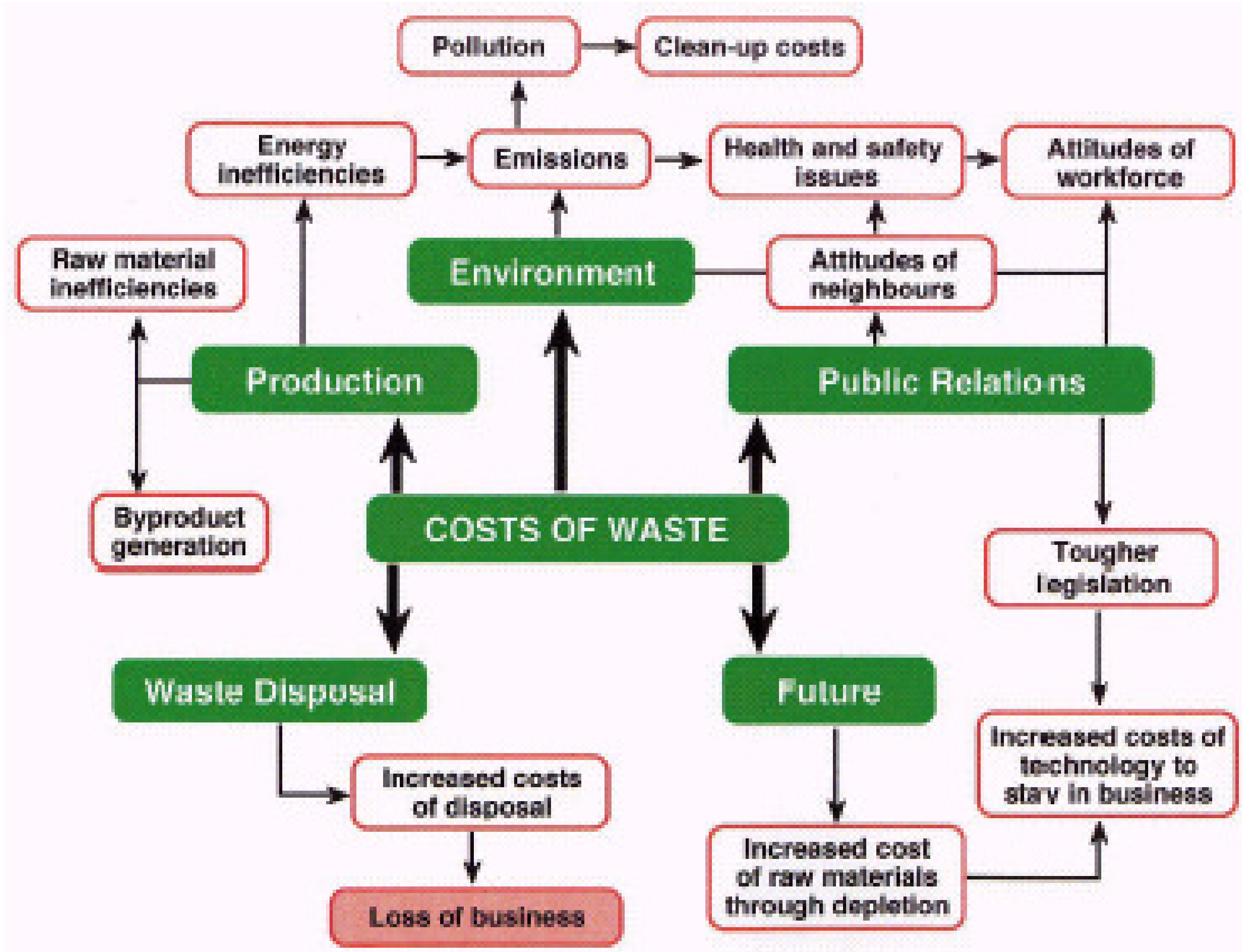
- Environmental problems such as ozone depletion, the Love Canal, Bhopal, Cuyahoga River, Changing Climate, Sea Level Change and the Loss of Biological Species are all too familiar examples of chemistry gone wrong.

DEFINITION OF CHOICE

Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. It also refers to the ***discovery of new chemistry*** and/or technology leading to prevention and/or reduction of environmental, health and safety impact at source.

– JH Clark, University of York, UK

An out and out interdisciplinary field of chemistry where chemical engineers also can contribute meaningfully.

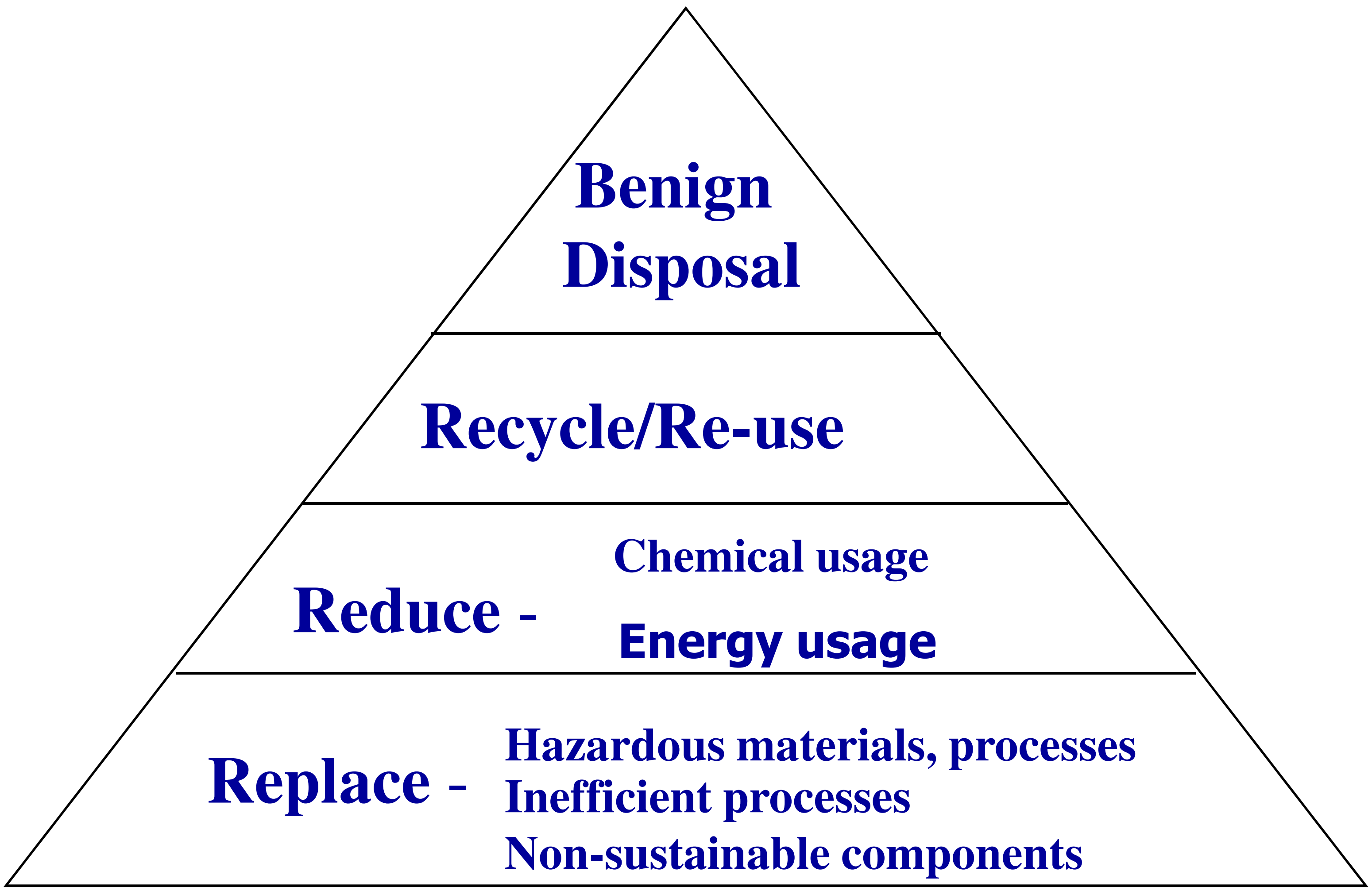


Pollution
Clean-up costs
Energy inefficiencies
Emissions
Health and safety issues
Attitudes of workforce
Raw material inefficiencies
Environment
Attitudes of neighbours
Production
Public Relations
Byproduct generation
COSTS OF WASTE
Tougher legislation
Waste Disposal
Future
Increased costs of technology to stay in business
Increased costs of disposal
Increased cost of raw materials through depletion
Loss of business

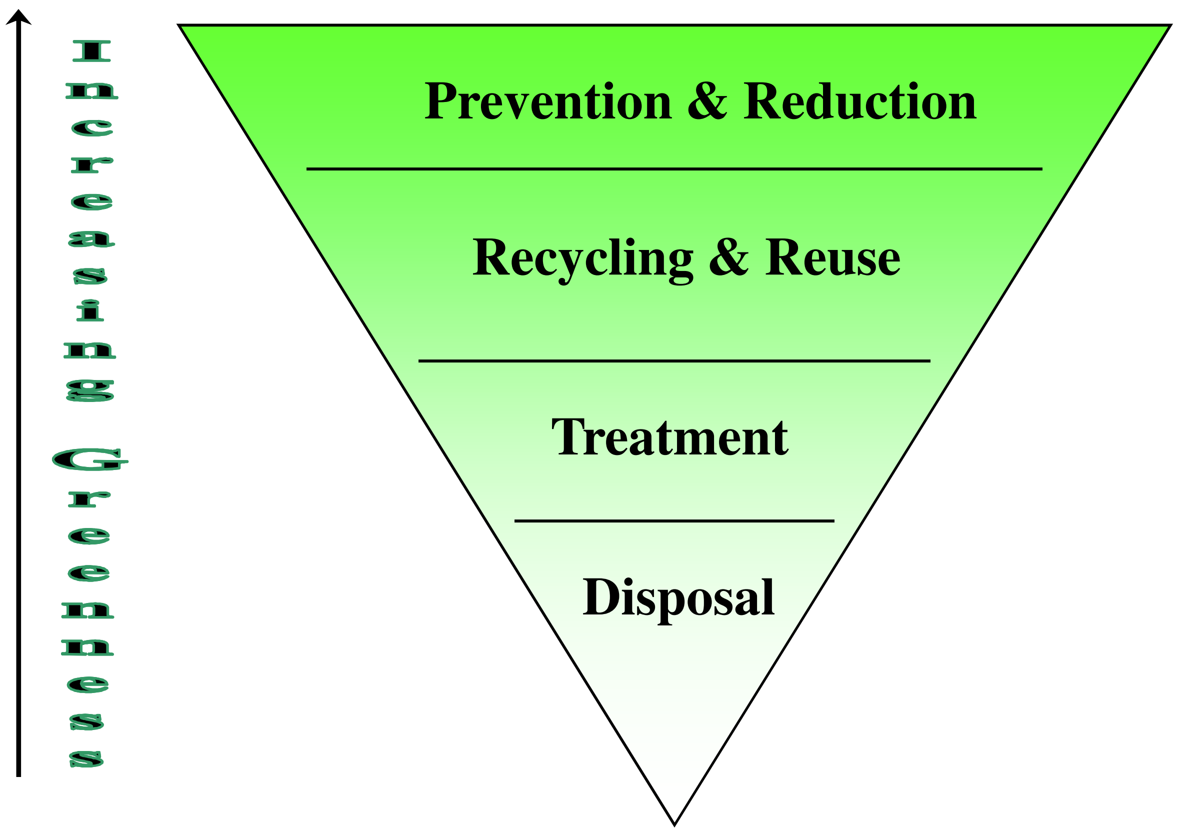
Fundamentals of Green Chemistry

- It is better to prevent waste than to treat or clean up waste after it is formed
- Atom economy
- Benign by design
- The raw material feedstocks should be renewable
- Performing reactions at ambient temperature and pressure
- Use of catalytic reagents (as selective as possible)
- Use of substances, which minimizing the chemical accidents
- Environmentally friendly and economically sound medium
- Design chemical products to break down into innocuous degradation products
- Unnecessary derivatization should be avoided whenever possible

What is Green Chemistry?



Pollution Prevention Hierarchy



Green Chemistry Is About...

Reducing

- **Waste**
- **Materials**
- **Hazard**
- **Risk**
- **Energy**
- **Environmental Impact**
- **COST**

PRODUCTIVE IMPROVEMENTS

The 24 Principles of Green Chemistry and Green Engineering

PRINCIPLES OF GREEN CHEMISTRY		PRINCIPLES OF GREEN ENGINEERING	
P	Prevent wastes	I	Inherently non-hazardous and safe
R	Renewable materials	M	Minimize material diversity
O	Omit derivatization steps	P	Prevention instead of treatment
D	Degradable chemical products	R	Renewable materials and energy inputs
U	Use safe synthetic methods	O	Output-led design
C	Catalytic reagents	V	Very simple
T	Temperature, Pressure ambient	E	Efficient use of mass,energy, space & time
I	In-Process Monitoring	M	Meet the need
V	Very few auxiliary substances	E	Easy to separate by design
E	E-factor, maximize feed in product	N	Networks for exchange of local mass & energy
L	Low toxicity of chemical products	T	Test the life cycle of the design
Y	Yes it's safe	S	Sustainability throughout product life cycle

Poliakoff et al., *Green Chem.*, 2008, 10, 268

Principle 1:

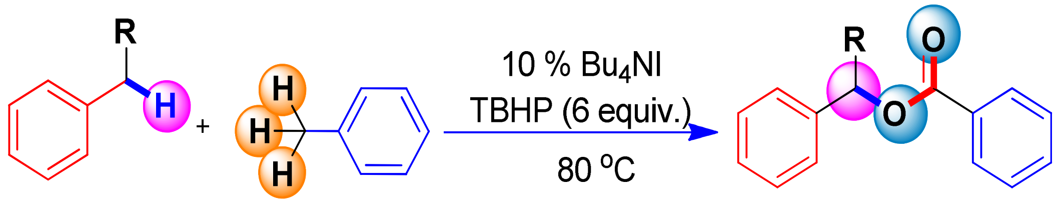
Prevent waste: **Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.**

Many strategies exist in chemical synthesis that go beyond converting reactant A to reaction product B.

In CASCADE reactions multiple chemical transformations take place within a single reactant, in multi-component reactions up to 11 different reactants form a single reaction product

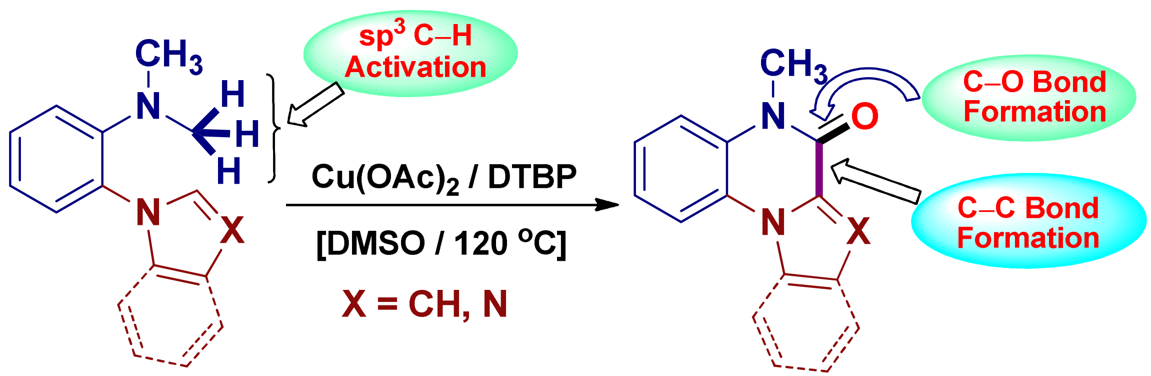
A cascade reaction or tandem reaction or domino reaction is a consecutive series of intramolecular organic reactions which often proceed via highly reactive intermediates.

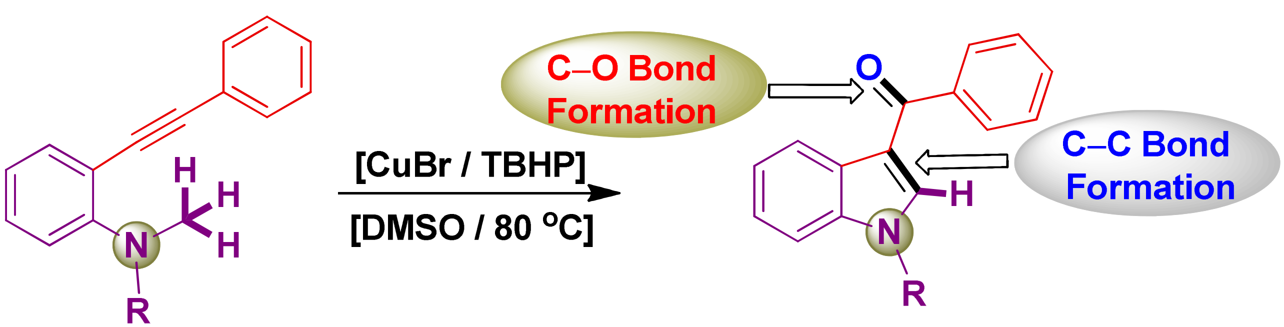
A Typical Reaction

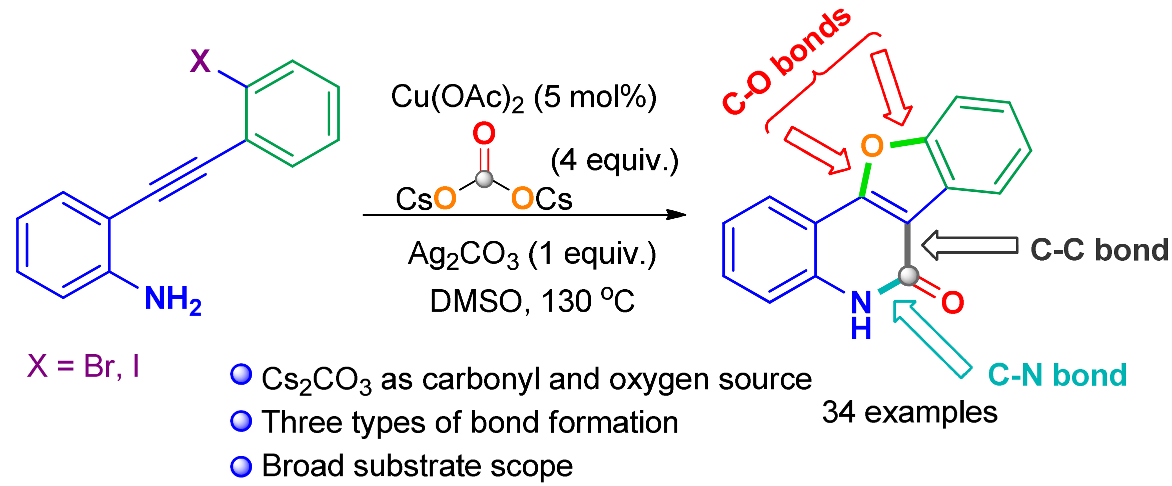


Chem Commun. **2013, *49*, 3031**

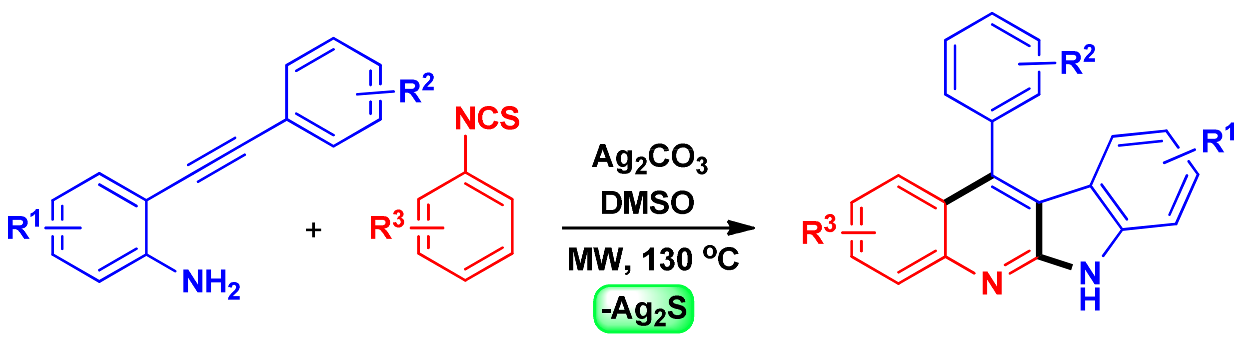
Examples of Cascade Reactions



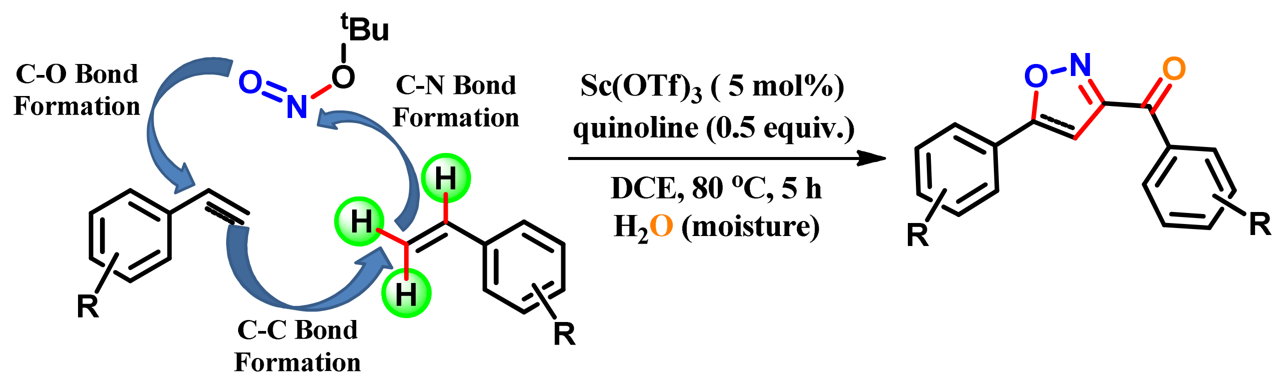




X
NH2
X = Br, I
Cu(OAc)2 (5 mol%)
(4 equiv.)
CsO OCs
Ag2CO3 (1 equiv.)
DMSO, 130 °C
C-O bonds
C-C bond
C-N bond
N H
34 examples
Cs2CO3 as carbonyl and oxygen source
Three types of bond formation
Broad substrate scope



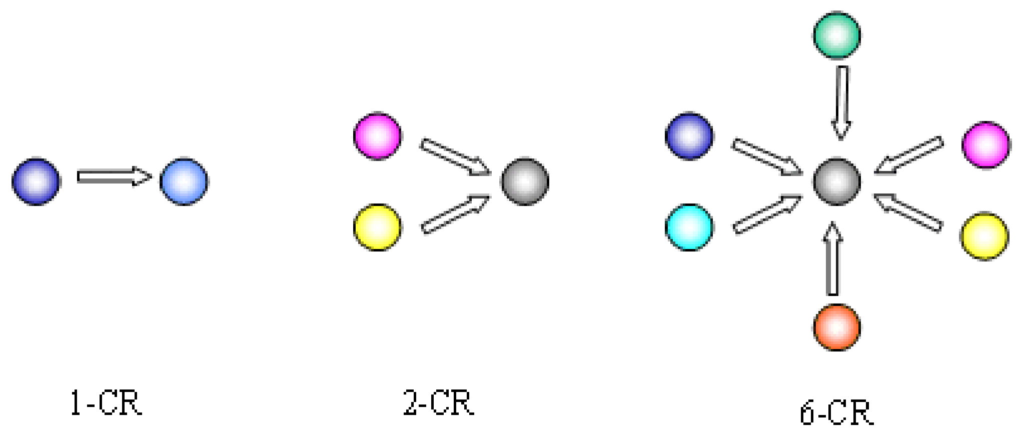
R1
NH2
R2
+
NCS
R3
Ag2CO3
DMSO
MW, 130 °C
-Ag2S
N
NH



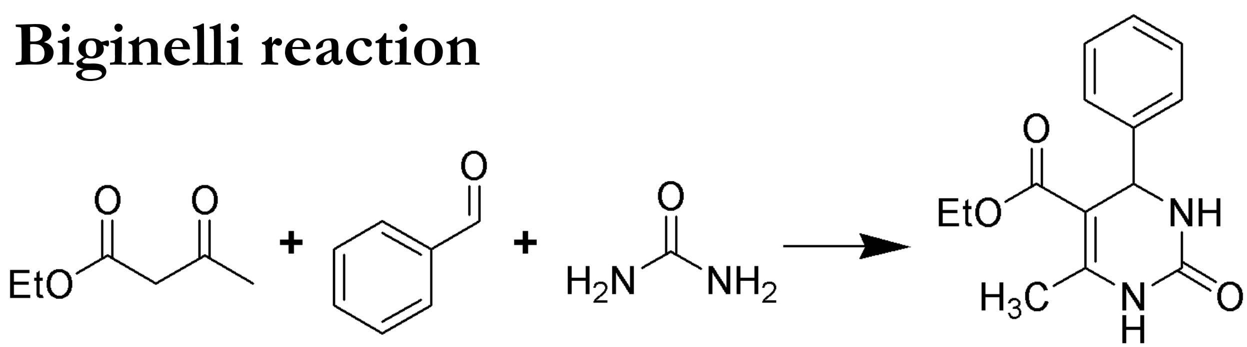
tBu
C-O Bond Formation
C-N Bond Formation
C-C Bond Formation
H
R
Sc(OTf)3 (5 mol%)
quinoline (0.5 equiv.)
DCE, 80 °C, 5 h
H2O (moisture)
O-N

Multicomponent reaction

In chemistry, a **multi-component reaction** (or **MCR**) is a chemical reaction where three or more compounds react to form a single product.



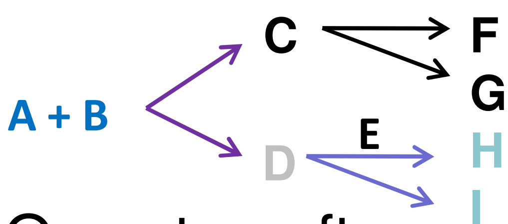
Biginelli reaction



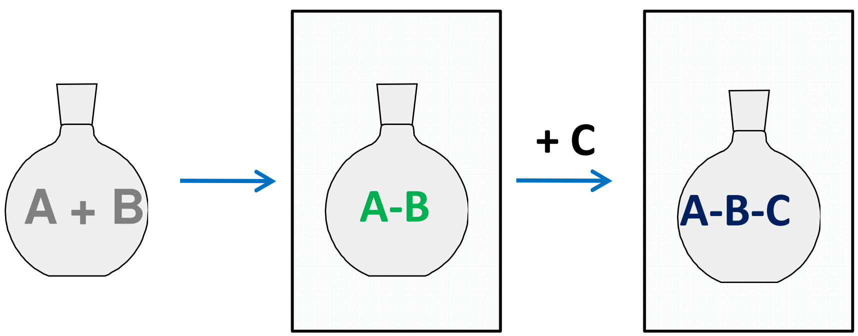
1 2 3 4

MULTICOMPONENT V/S MULTISTEP REACTIONS

- Multistep Reactions
  - Divergent Reactions

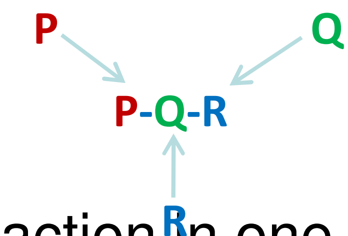


  - One step after another

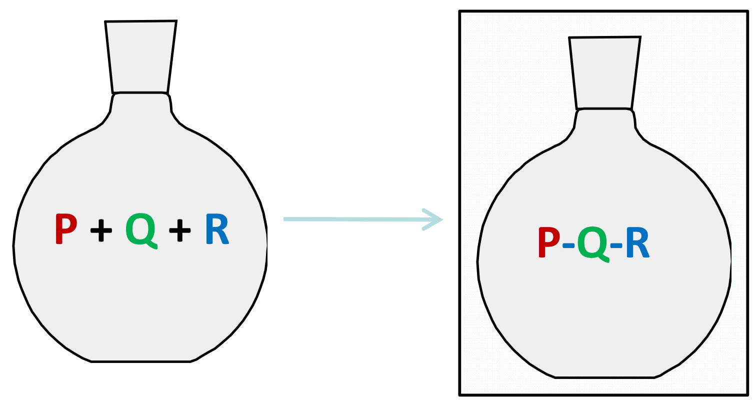


  - Low Efficiency
  - Low Diversity per Step

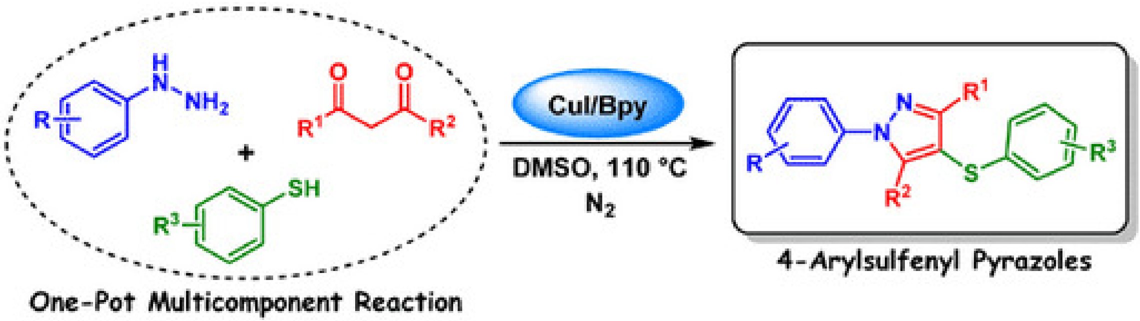
- Multicomponent Reactions
  - Convergent Reactions



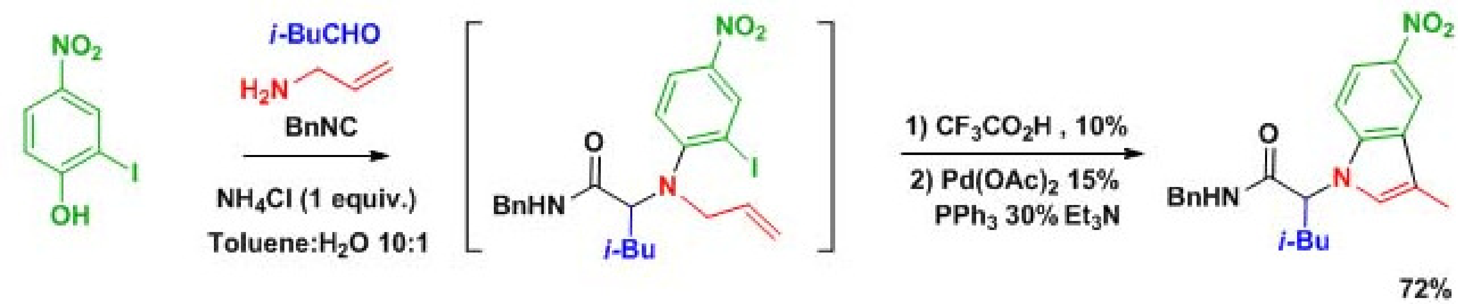
  - Reaction in one pot



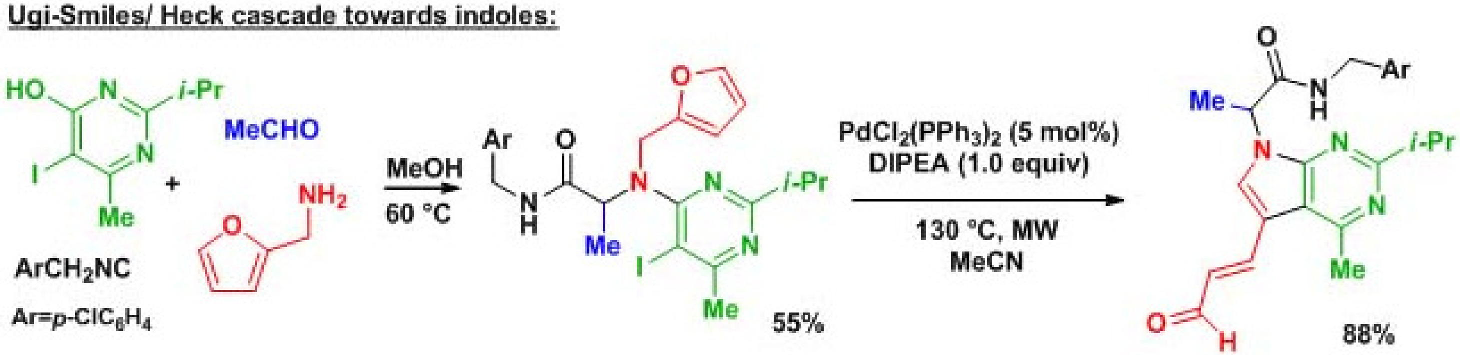
  - Higher Efficiency
  - High Diversity per Step

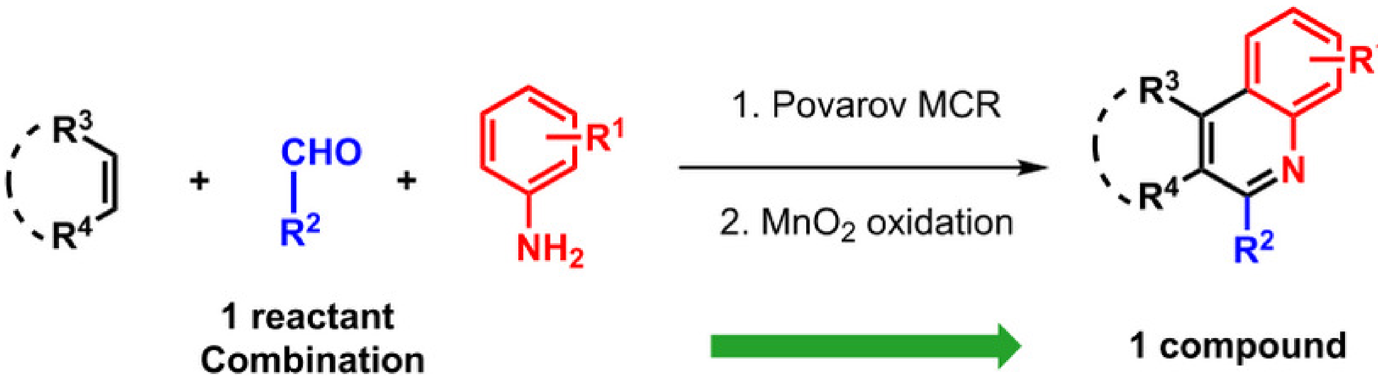


Ugi-Smiles/ Heck cascade towards indoles:

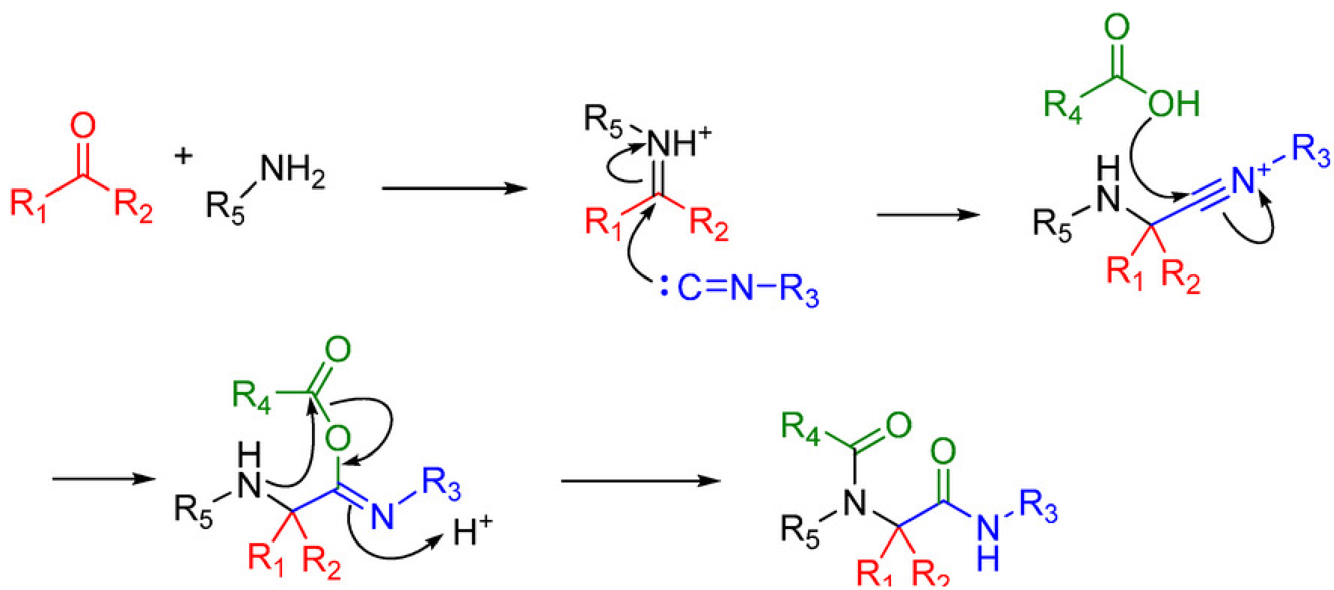


Ugi-Smiles/ Heck cascade towards indoles:





1. Povarov MCR
2. MnO2 oxidation
1 reactant
Combination
1 compound



Principle 2:

Design safer chemicals and products: **Design chemical products to be fully effective, yet have little or no toxicity.**

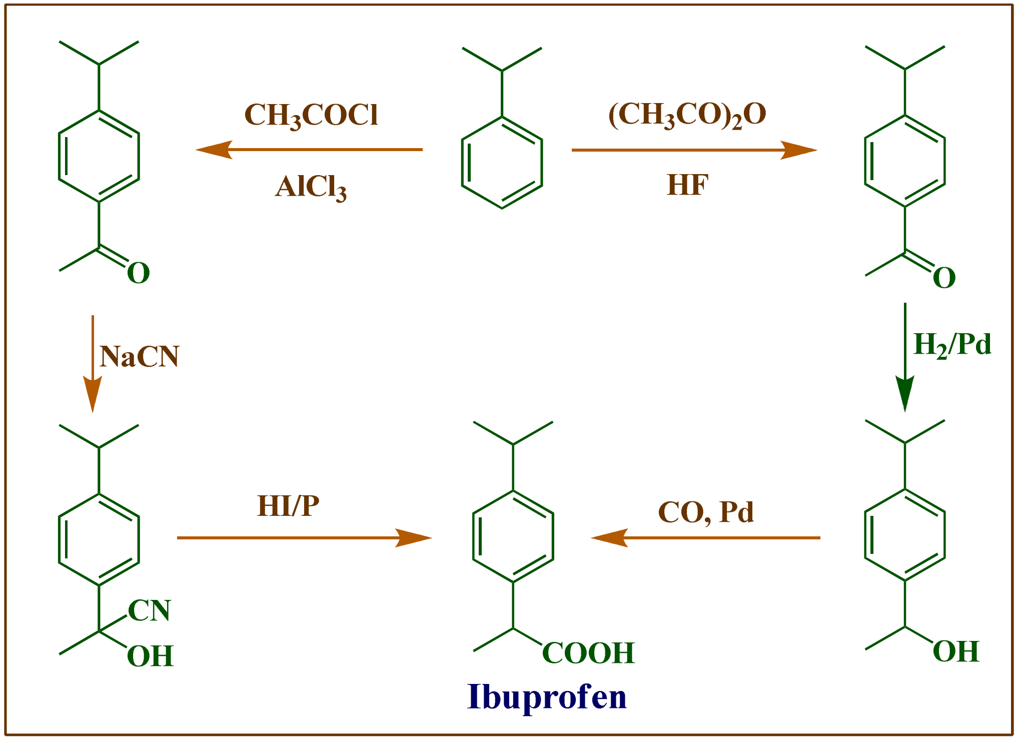
Chemicals include inorganic substances such as lead, mercury, asbestos, hydrofluoric acid, and chlorine gas, organic compounds such as methyl alcohol, most medications, and poisons from living things.

Principle 3:

Design less hazardous chemical syntheses: **Design syntheses to use and generate substances with little or no toxicity to humans and the environment.**

Green Chemistry - Heterogeneous Catalysis

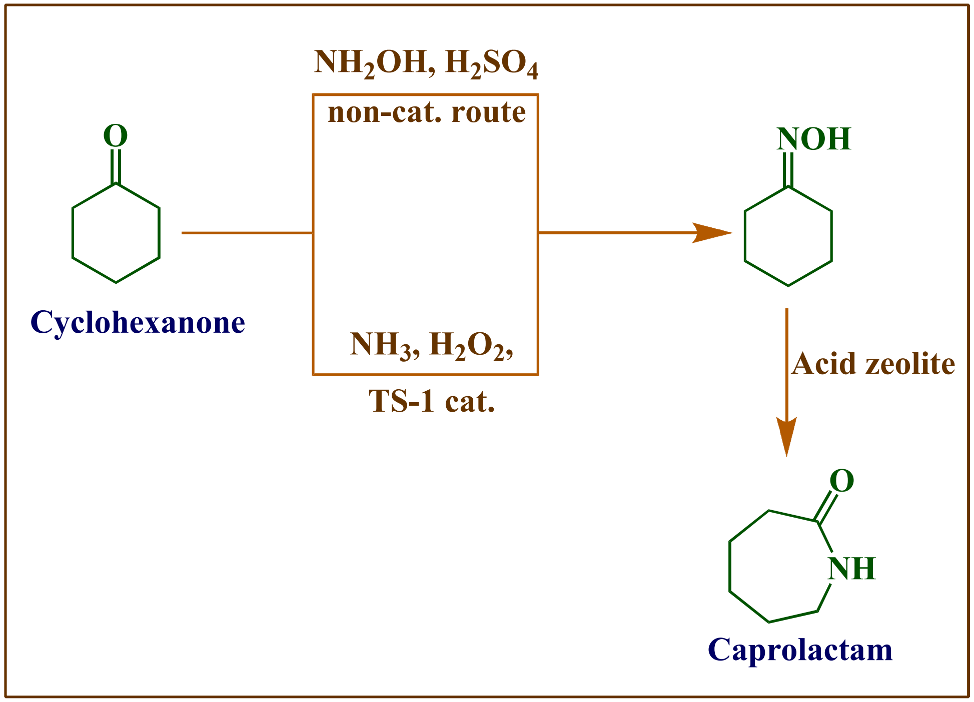
Synthesis of Ibuprofen



Traditional synthesis of ibuprofen is based on Friedel-Craft acylation. BHC (Boots Hoechst-Celanese, UK) developed a new cleaner process based on the use of HF as the Friedel-Craft catalyst. HF is being recovered and recycled

Green Chemistry - Heterogeneous Catalysis

Synthesis of Caprolactam, Starting material for the preparation of Nylon-6



Precursor of Nylon-6 4.5 billion KG required annually

In conventional synthesis, substantial amounts of ammonium sulphate is produced as a salt waste in both the oximation and rearrangement stages.

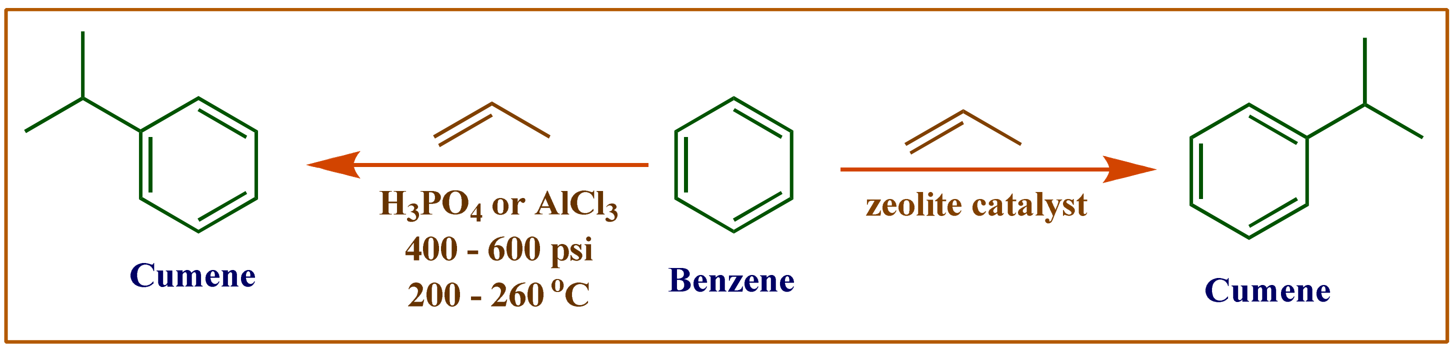
The liquid-phase ammoximation of cyclohexanone with a mixture of ammonia and aqueous hydrogen peroxide eliminates the co-production of ammonium sulphate. The heterogeneous catalyst employed is titanium silicalite TS-1 (redox molecular sieves).

Green Chemistry

Design a safer chemical process

It is better to adopt reactions that utilize non-toxic reagents and yield non-toxic product from the environmental and often economic perspectives.

Approximately 7 million metric tons of cumene are produced annually on a global scale. The traditional cumene synthesis employs alkylation of benzene with propene over a phosphoric acid or aluminium chloride catalyst. Both catalysts are corrosive and are categorized as hazardous wastes.



Mobil/Badger for production of cumene involves an environmentally benign catalyst, zeolite. The new process is carried out at atmospheric pressure, generates less waste and employs a non-corrosive catalyst.

Example 1 of green chemistry

Production of **allyl alcohol** $CH_2{=}CHCH_2OH$

Traditional route: Alkaline hydrolysis of allyl chloride, which generates the product and hydrochloric acid as a by-product

$$\underset{\uparrow \atop \text{problem}}{CH_2{=}CHCH_2Cl} + H_2O \rightarrow \underset{\uparrow \atop \text{product}}{CH_2{=}CHCH_2OH} + HCl$$

Greener route, to avoid chlorine: Two-step using propylene ($CH_2{=}CHCH_3$), acetic acid (CH_3COOH) and oxygen (O_2)

$$CH_2{=}CHCH_3 + CH_3COOH + \tfrac{1}{2}\, O_2 \rightarrow CH_2{=}CHCH_2OCOCH_3 + H_2O$$

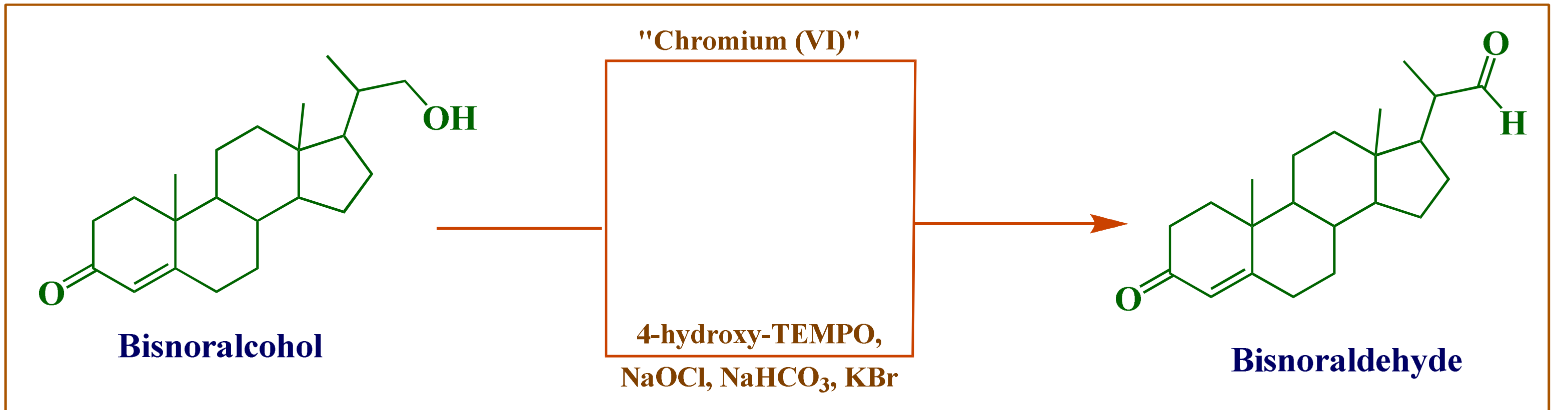
$$CH_2{=}CHCH_2OCOCH_3 + H_2O \rightarrow CH_2{=}CHCH_2OH + CH_3COOH$$

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.

Green Chemistry

Waste prevention

Waste prevention brings both environmental and economic benefits. A reaction needs to be designed in a way so as to minimize the generation of waste and other hazardous substances.



Pharmacia and Upjohn improved the manufacturing process of bisnoraldehyde, a key intermediate in the synthesis of progesterone and corticosteroids, by replacing heavy metal oxidant chromium (VI) by a bleach (NaOCl) and environmental benign 4-hydoxy-TEMPO catalyst system.

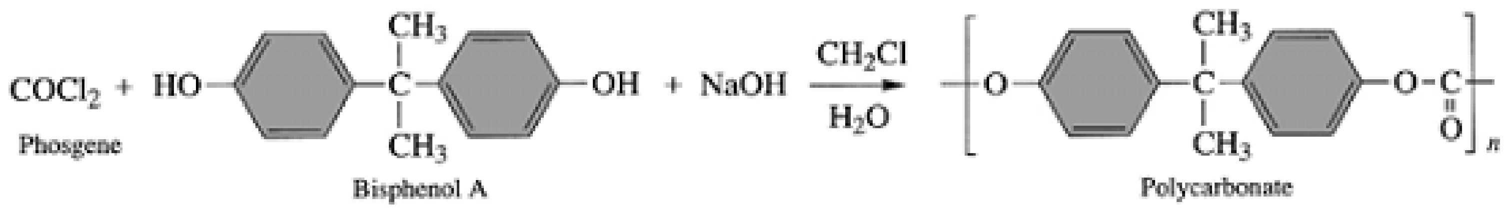

2.2 Liter Polycarbonate Bottle

POLICE
POLICE

Example 2 of green chemistry Production of **polycarbonate** (polymers)

Traditional route: Start with phosgene ($COCl_2$), which is extremely toxic, and end with methyl chloride (CH_2Cl), which is harmful, as a by-product.

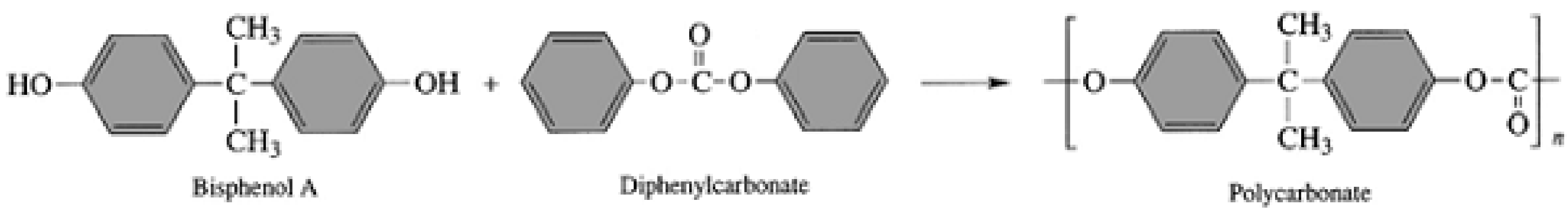
$$COCl_2 + \text{Biphenol A} + NaOH \rightarrow \text{Polycarbonate} + H_2O + CH_2Cl$$



Greener route, to avoid phosgene:

$$\text{Biphenol A} + \text{Diphenylcarbonate} \rightarrow \text{Polycarbonate}$$

(This process was developed by Ashai Chemicals Co. in Japan.)



Principle 4:

Use renewable feedstock: Use raw materials and feedstock that are renewable rather than depleting.

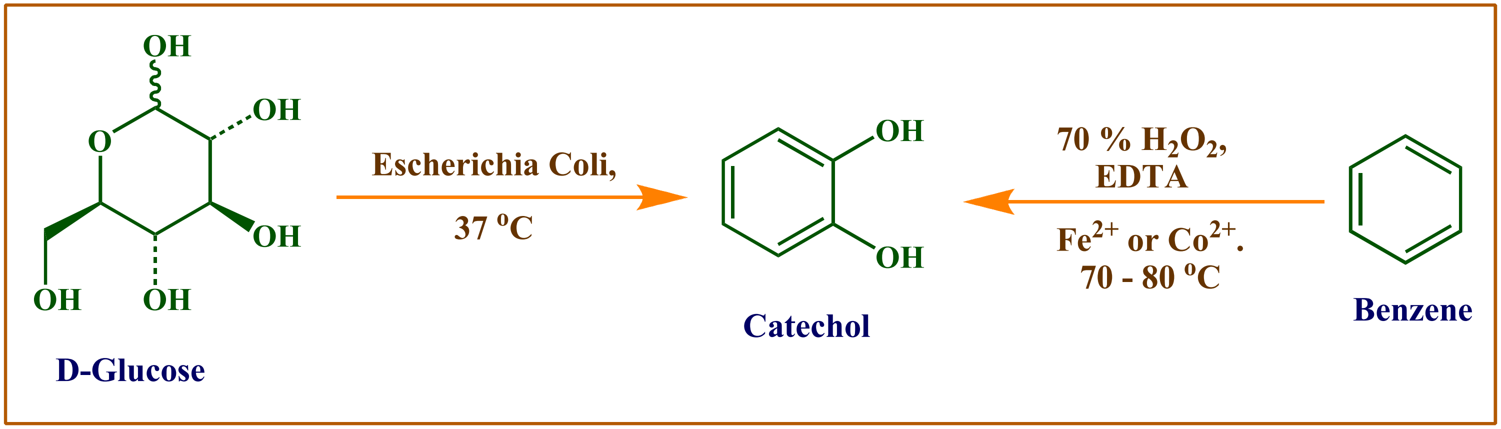
Renewable feedstock are often made from agricultural products or are the wastes of other processes;

CO_2 is renewable feed stock, oils and fats, glycerine.

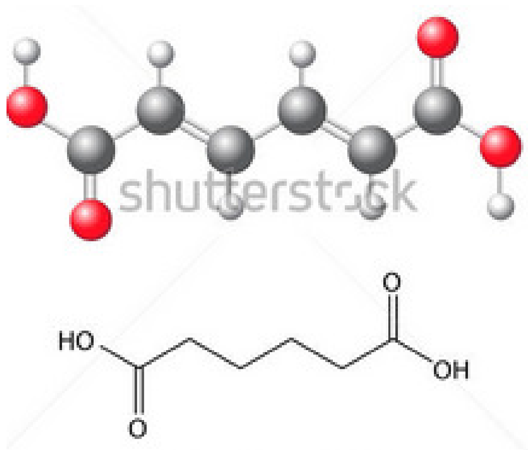
depleting feedstock are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

Renewable feedstocks

The utilization of benign, renewable feedstocks is a need component for addressing the global depletion of resources.

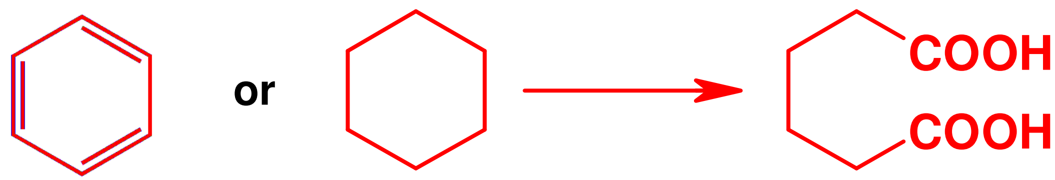


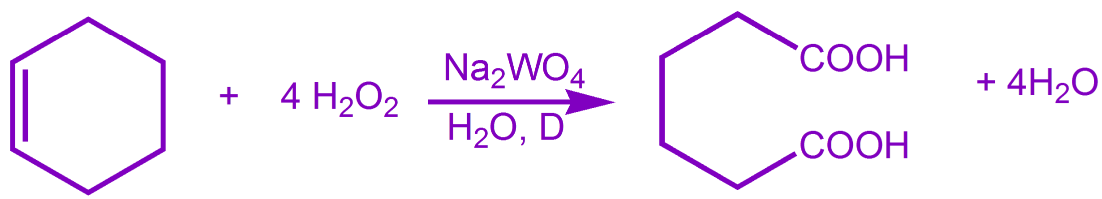
Using genetically-engineered *E.Coli*, catechol was obtained in a single step from D-glucose. The biocatalytic pathway eliminates the use of hazardous substances present in the synthesis of catechol and decreases the energy demands of the reaction.



About 2.5 billion kilograms of this white crystalline powder are produced annually, mainly as a precursor for the production of nylon.

Adipic Acid Synthesis

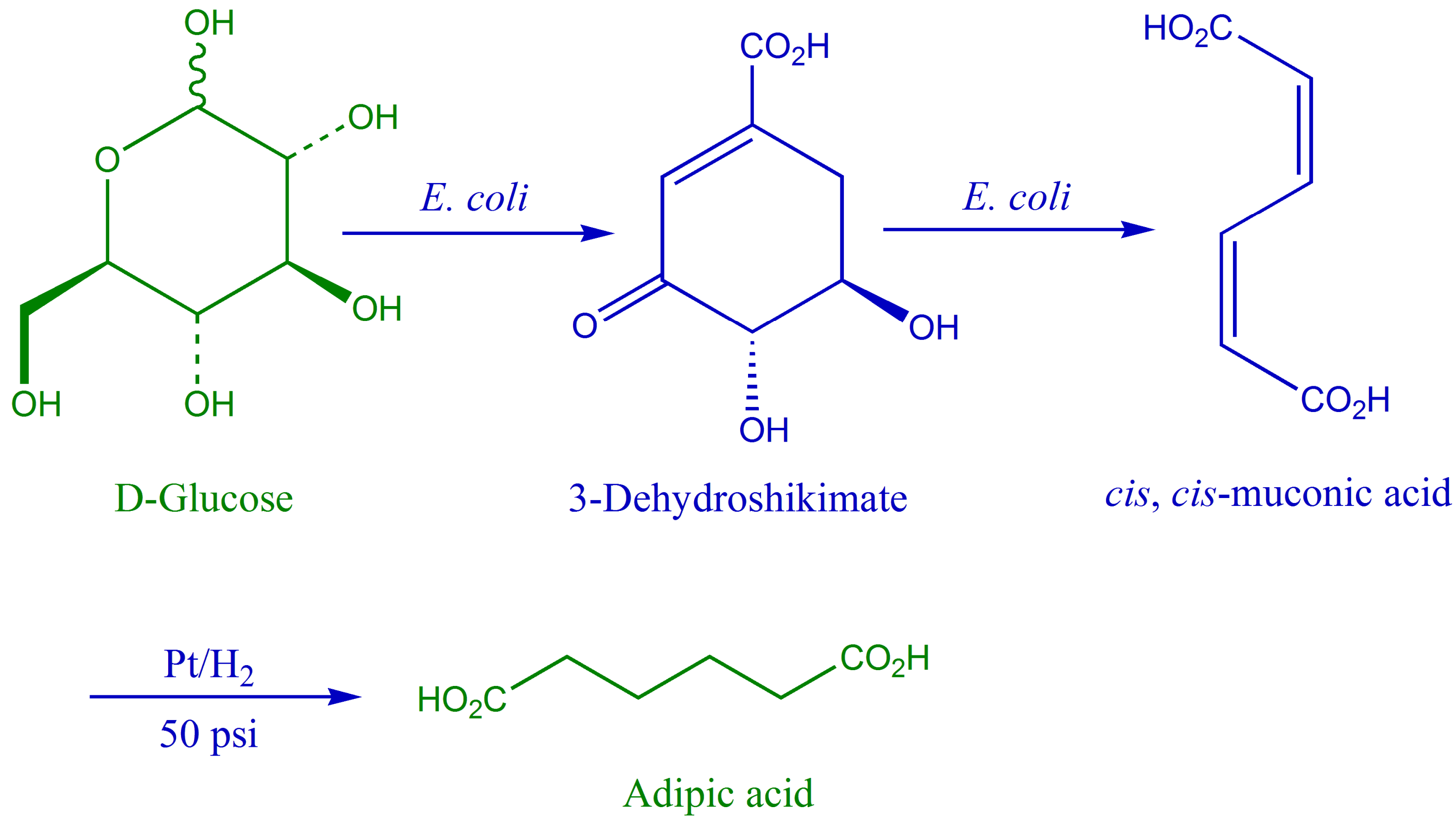




HNO_3 oxidation needed for conversion of ol/one mixture

Not environmentally friendly

Biocatalysed production of adipic acid



(Draths-Frost synthesis)

GC Advantages of D-F Synthesis

1. Highly choosy genetically engineered microbe used
2. Avoids using carcinogenic benzene
3. Eliminates N_2O formation
4. Uses glucose as a renewable source

An outstanding instance of *biocatalysis*. Although transition metal based catalysts also may be effective, the above is an attractive reaction. Commercially?

BIO-DEGRADABLE: IS IT GOOD?

- Non-Biodegradable
  None-Compostable
  Collection, Recycling
  Cleaning, Blendable
  Better Properties
  Thermal
  Hydrolytic Resist
  Anti-Microbial

- Bio-degradable
  Compostable
  Difficult to Collect, Recycle, Clean.
  Poorer Properties
  Thermal
  Hydrolysable
  Microbial Attack