Green Chemistry

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Definition

- **Green chemistry**, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances*.
- 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**.
  - *As defined by United States Environmental Protection Agency
  - ** Anastas, P. T.; Warner, J.C. Green Chemistry: Theory and Practice, Oxford University Press,1998

Green chemistry is about :

Waste

Hazard

Risk

Energy

Cost

Reducing

Improving

Renewability

Reusability

Atom utilization

Energy efficiency

Principles of Green Chemistry

- 1.PREVENTION

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

Waste and the chemical industry

Industry	**Tonnage**	**Ratio (kg of byproduct/kg of product)**
Oil refining	10^6 - 10^8	<0.1
Bulk chemicals	10^4 - 10^6	1-5
Fine chemicals	10^2 - 10^4	5-50
Pharmaceuticals	10 - 10^3	25-100+

Pharmaceuticals and chemical industries though have a lesser waste production compared to other industries like oil refining, have an opportunity of reducing the waste further since the amount of waste per kg of product is relatively higher

2. Atom Economy

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

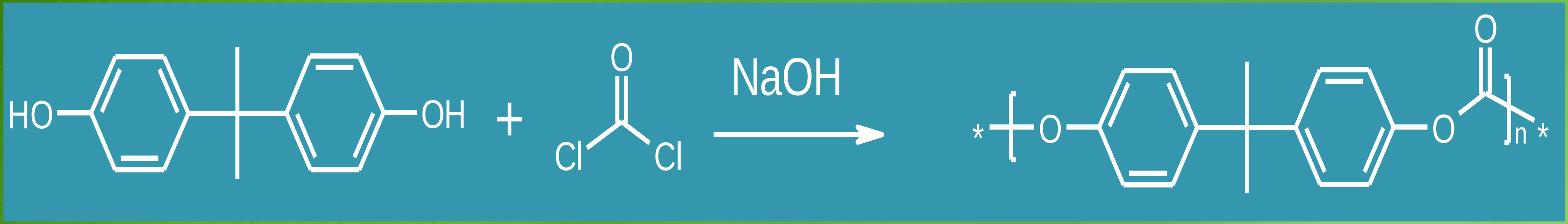
- **Atom economy** (**atom efficiency**) describes the conversion efficiency of a chemical process in terms of all atoms involved (desired products produced).
- In an ideal chemical process, the amount of starting materials or reactants equals the amount of all products generated and no atom is wasted.

% atom economy= (MW of desired product/MW of all reactants) *100

3. Less Hazardous Chemical Synthesis

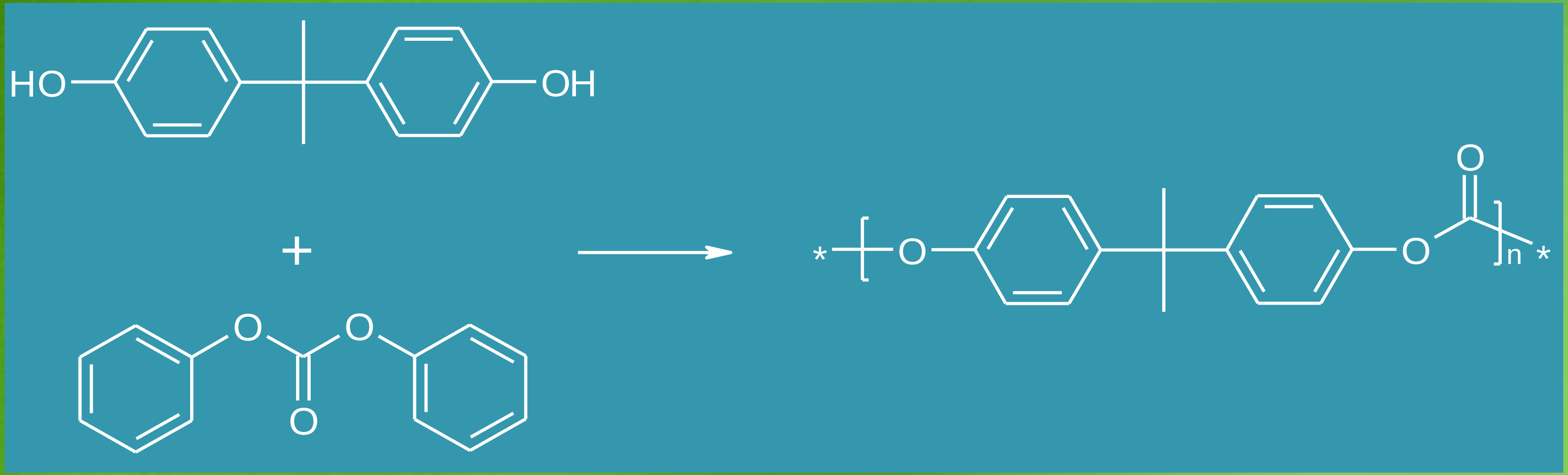
Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Polycarbonate Synthesis using Phosgene



- Disadvantages
  - Phosgene is highly toxic and corrosive
  - Requires large amount of CH_2cl_2
  - Polycarbonate gets contaminated with chlorine impurities

Polycarbonate Synthesis using solid state process



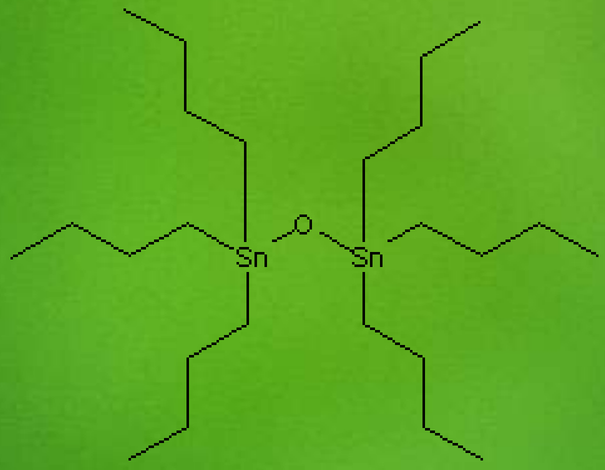
- Advantages
  - diphenylcarbonate synthesized without phosgene
  - Eliminates use of CH_2Cl_2
  - Higher-quality polycarbonates without chlorine impurities.

Komiya *et al.*, Asahi Chemical Industry Co.

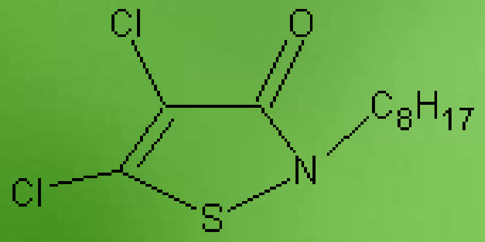
4. Designing Safer Chemicals

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

- Tributyltin oxide is usually used mixed with paints as an antifoulants for ships. This chemical is usually toxic to marine organisms and also bio-accumulate.
- Sea-Nine® 211, 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOI), is now used which is relatively less toxic.



Tributyltin Oxide



4,5-dichloro-2-n-octyl-4-isothiazolin-3-one

DCOI

http://academic.scranton.edu/faculty/CANNM1/environmentalmodule.html

5. Safer Solvents and Auxiliaries

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

Preferred

- Water
- Acetone
- Ethanol
- 2-Propanol
- 1-Propanol
- Ethyl acetate
- Isopropyl acetate
- Methanol
- Methyl ethyl ketone
- 1-Butanol
- *t*-Butanol

Useable

- Cyclohexane
- Heptane
- Toluene
- Methylcyclohexane
- Methyl t-butyl ether
- Isooctane
- Acetonitrile
- 2-MethylTHF
- Tetrahydrofuran
- Xylenes
- Dimethyl sulfoxide
- Acetic acid
- Ethylene glycol

Undesirable

- Pentane
- Hexane(s)
- Di-isopropyl ether
- Diethyl ether
- Dichloromethane
- Dichloroethane
- Chloroform
- Dimethyl formamide
- N-Methylpyrrolidinone
- Pyridine
- Dimethyl acetate
- Dioxane
- Dimethoxyethane
- Benzene
- Carbon tetrachloride

Pfizer solvent replacement table

Red solvents	Green solvents
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or diethyl ether	2-MeTHF or *tert*-butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or *tert*-butyl methyl ether
Chloroform, dichloroethane or carbon tetrachloride	Dichloromethane
Dimethyl formamide, dimethyl acetamide or N-methylpyrrolidinone	Acetonitrile
Pyridine	Et_3N (if pyridine is used as a base)
Dichloromethane (extractions)	EtOAc, MTBE, toluene, 2-MeTHF
Dichloromethane (chromatography)	EtOAc/heptane
Benzene	Toluene

- Ionic solvents:
- Room temperature ionic liquids(RTILs) can be used as substitutes for aromatic solvents in chemical reactions and separation processes.
- RTILs are organic salts with melting points below 100^0 C, often below room temperature, have no vapour pressure and composed of entirely cations and anions.
- Exhibit good solvent properties and often facilitate chemical reactions without being transformed in the process.
- Have negligible vapour pressure and miniscule flammability.

- Exhibit high thermal stability and wide working temperatures.
- Owing to multitude of possible combinations of cation and anion, they are susceptible to numerous permutations that allow various physical and chemical properties to be adjusted at will.
- Eg: 1-butyl-3-methylimidazoliumhexafluorophosphate, and some imidazolium tetrafluoroborates

Philip E.Rakita, Ozark Fluorine Specialities

6. Design for Energy Efficiency

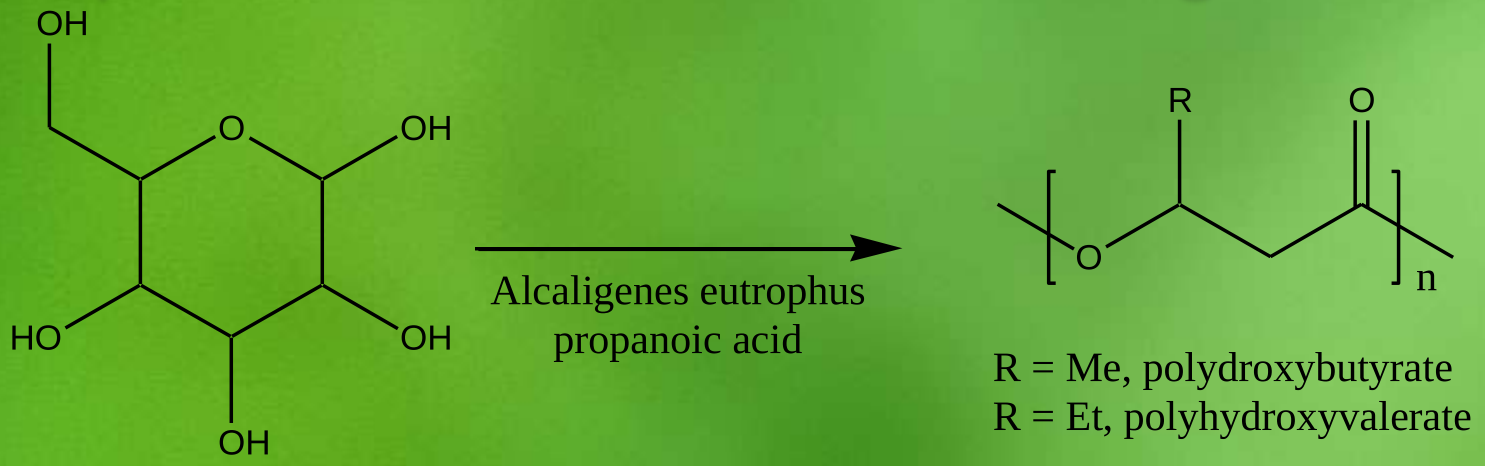
Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

- Use of alternate, recyclable and more efficient energy resources.
- Use of light energy as a source for photochemical reactions.
- Use of microwave chemistry for more efficient energy utilization

7. Use of Renewable Feedstocks

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

- Fermentation of glucose in the presence of bacteria and propanoic acid gives Polyhydroxy alkanoates (PHAs).
- The PHAs are similar to polypropene and polyethene but however are biodegradable.



- PLA (polylactic acid) is another plastic that is being made from renewable feedstocks such as corn and potato waste.

8. Reduce Derivatives

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

- An increase in the number of synthetic steps would eventually reduce the overall yield and atom economy.
- Protecting groups are generally used because there is no direct way to solve the problem without them.
- Attempts to reduce the number of steps and derivatization is considered important.

9. Catalysis

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

- A green catalyst has advantages such as:
  - Readily separated
  - Readily regenerated & recycled
  - Long service life
  - Very high rates of reaction
  - Robust to poisons
  - High selectivity
  - Works under milder conditions

- Certain chemicals are used as green catalysts which reduce the incidence of toxic chemicals formed in a reaction by converting them to less toxic or harmless substances.
- Oxidation catalysts, called Fe-TAML® (tetra-amido macrocyclic ligand) activators, are made from elements found in nature and work with hydrogen peroxide to convert harmful pollutants into less toxic or harmless substances*.

*Terrence J. Collins;Teresa Heinz Professor of Green Chemistry

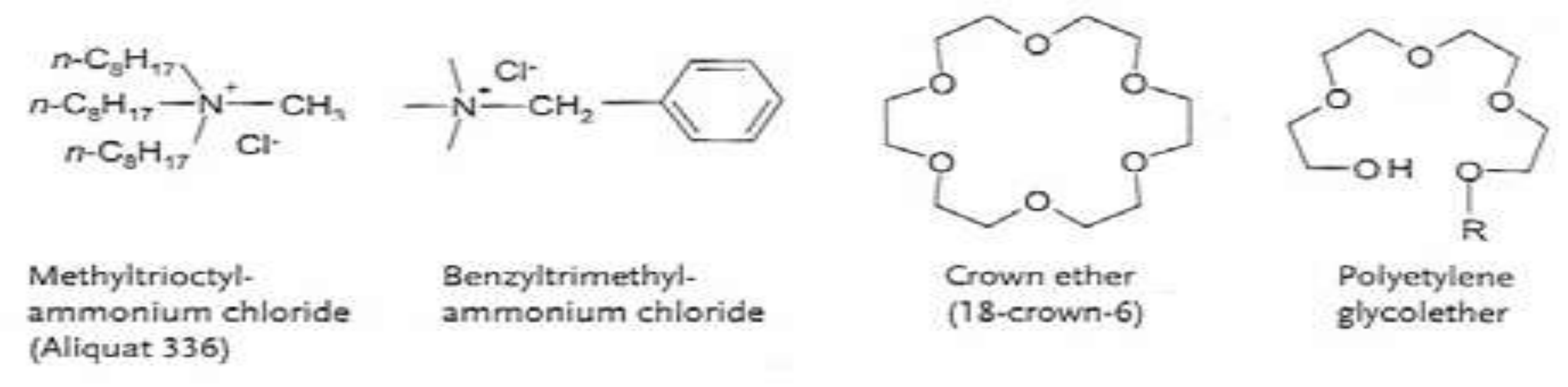
Biocatalysis:

- Enzymes or whole-cell microorganisms are used.
- Benefits include:
  - Fast reactions due to correct orientations
  - Orientation of site gives high stereospecificity
  - Substrate specificity
  - Water soluble
  - Naturally occurring
  - Moderate conditions
  - Possibility for tandem reactions

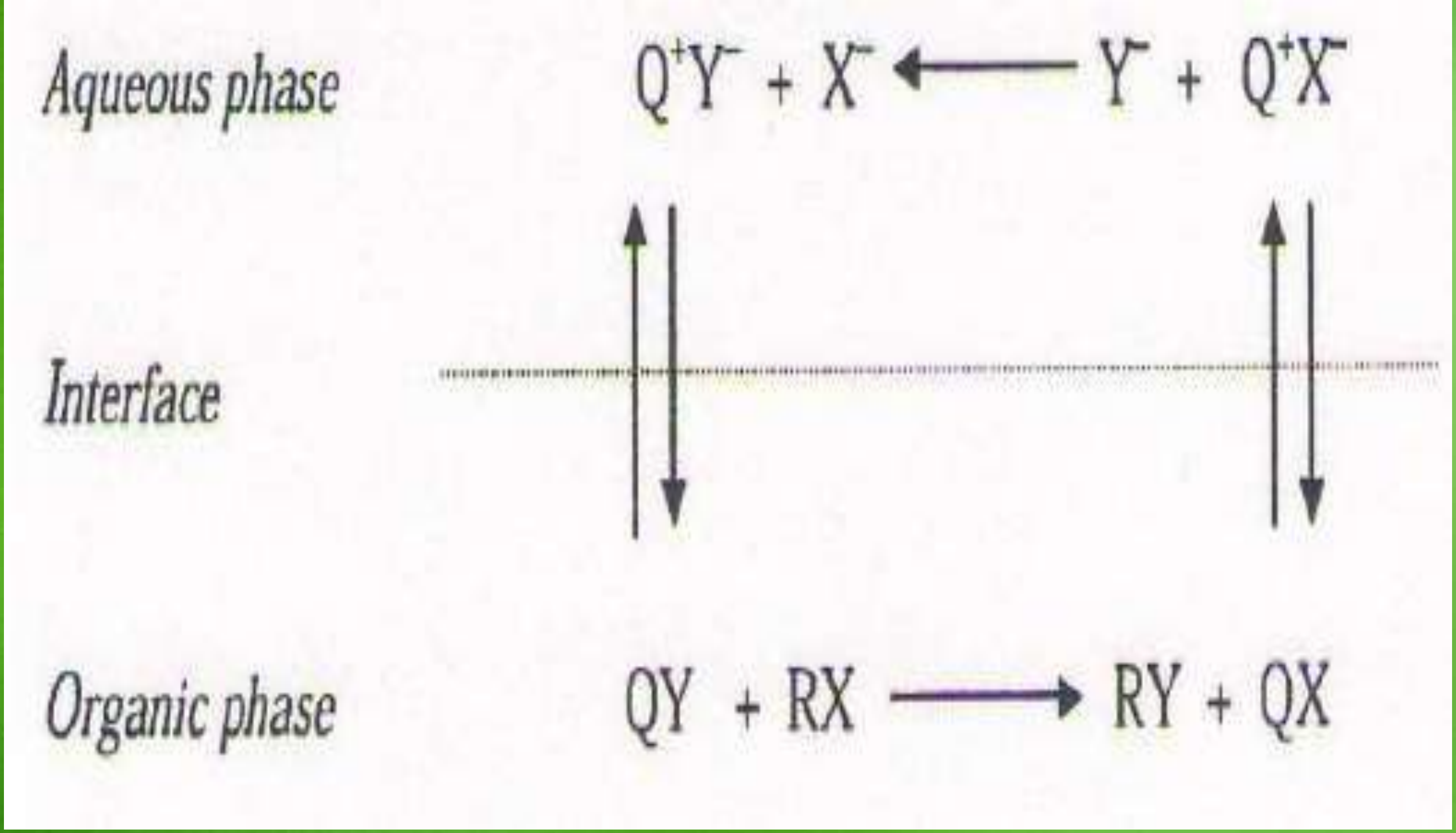
Phase Transfer Catalyst:

- A phase transfer catalyst is a catalyst which facilitates the migration of a reactant in a heterogeneous system from one phase into another phase where reaction can take place.
- Ionic reactants are often soluble in an aqueous phase but are insoluble in an organic phase unless the phase transfer catalyst is present.
- Advantages of PTC
  - Elimination of organic solvents
  - High yields and purity of products
  - Simplicity of the procedure
  - Highly scalable
  - Low energy cosumption and low investment cost
  - Minimization of industrial waste

- Quarternary ammonium or phosphonium salts are most widely used PTCs.
    - Eg: methyltrioctyl ammoniumchloride (Aliquat 336 or Adogen 464),
    - Tetra-n-butylammonium bromide (TBAB)
    - Triethylbenzylammonium chloride (TEBA)
    - Cetyltrimethylammonium bromide (cetrimide)
    - benzyltrioctyl ammoniumchloride,
    - polyethylene glycoether,
    - crown ethers



- Mechanism of phase transfer by PTC:

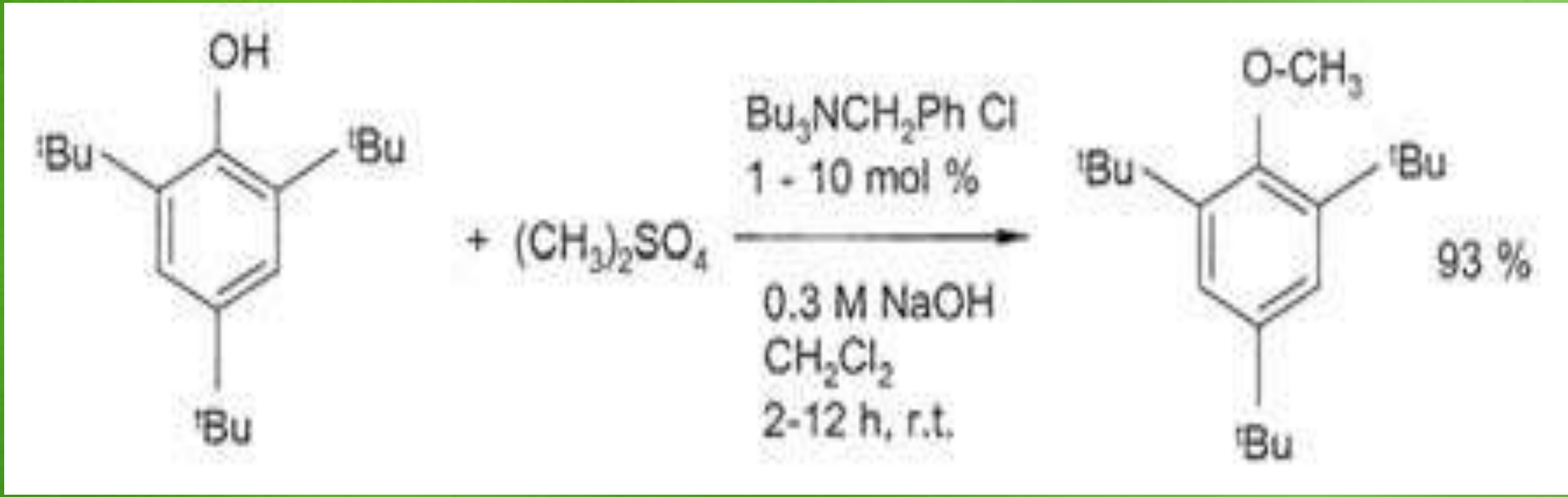


Applications of PTCs:

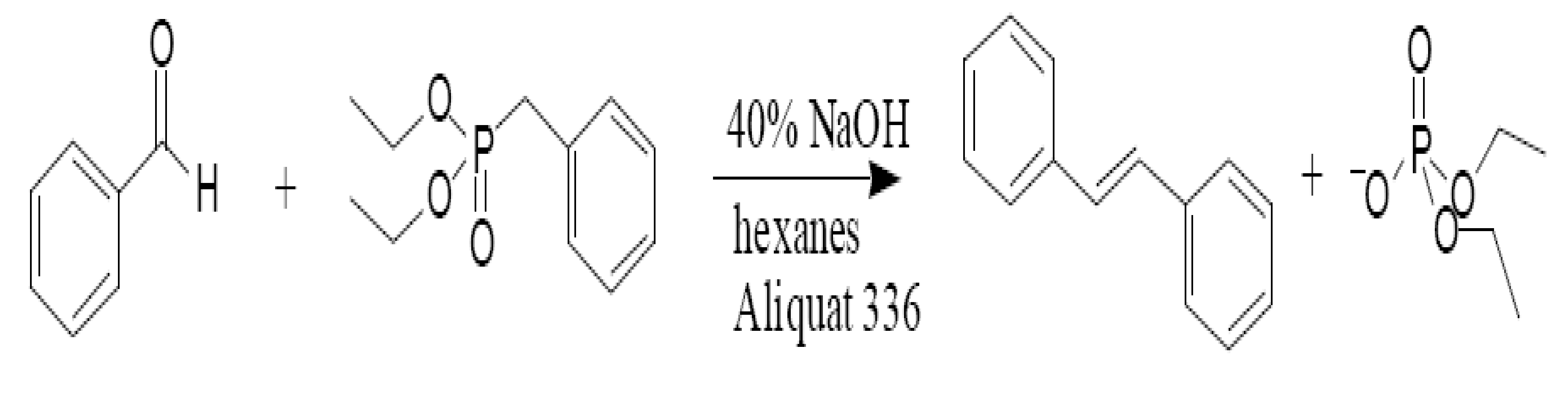
- In nucleophilic substitution reactions
- Synthesis of fine chemicals
- In perfumery and fragrance industry
- Is synthesis of drugs like dicyclonine, phenoperidine, oxaladine, ritaline etc.
- Provides liberty of use of cheaper and easily available raw materials like potassium carbonate and aqueous sodium hydroxide thereby obviating the need of severe anhydrous conditions, expensive solvents and dangerous bases such as metal hydrides and organometallic reagents.

Williamsons ether synthesis by PTC:

- High-yield etherification
- No need for excess pre-formed alkoxide
- Usually short cycle time and easy workup
- Non-dry mild reaction conditions



- Wittig reaction by PTC
- Aliquat 336 (N-Methyl-N,N-dioctyloctan-1-ammonium chloride) is used as PTC.



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.

- Plastics, long chain hydrocarbons, CFCs have longer persistence.
- Chemicals such as DDT bioaccumulate.
- Drugs such as antibiotics build up in water streams.
- Design of degradable chemicals is the need of the hour.
- Polylactic acid:
  - Manufactured from renewable resources such as corn or wheat;
  - 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.

- In the process of a chemical reaction, analysing when a reaction is exactly complete can save a lot of energy, waste and time.
- Overdoing a reaction may result in energy wastage and under-doing the same may result in material wastage.
- An advanced and sophisticated analytical tool helps reduce this pollution

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.

- Use of potential toxic, hazardous and highly inflammable chemicals may result in accidents which eventually lead to pollution and danger to plant and animal life.
- U.S. Public Interest Research Group Reports (April 2004) find that chemical industry has had more than 25,000 chemical accidents since 1990
- More than 1,800 accidents a year or 5 a day.
- In Bhopal gas tragedy, release of 40 tons of Methyl isocyanate (MIC) took the lives of 15000 people leaving hundreds of thousands seriously affected.

THANK YOU