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A Green Route to Chemical Synthesis.

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ABSTRACT

Green chemistry, also called sustainable chemistry, is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances. Whereas environmental chemistry is the chemistry of the natural environment, and of pollutant chemicals in nature, green chemistry seeks to reduce and prevent pollution at its source.

Keywords: green chemistry, synthesis

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INTRODUCTION

One of the key challenges of the millennium is to combine the technological progress with the environmental safety. In the effort to move towards “Sustainable Development”, chemistry now a days is at the forefront of the development of clean production processes and products. One factor that is greatly speeding the incorporation of pollution prevention into industrial manufacturing processes is the development of green chemistry curriculum materials. The chemical industry is discovering that when their chemist are knowledgeable about pollution –prevention concepts, they are able to identify, develop and implement techniques that reduce pollution and cost . Green Chemistry [1] is the special contribution of chemists to the conditions for sustainable development. There is no doubt that the emerging area of green chemistry has identified scientific principles, approaches and methodologies [2] that have demonstrated the most positive aspects of chemistry. Chemical industries have adopted new eco-friendly techniques to survive in the market. Since its introduction in the early 1990’s, green chemistry [3-5] has spread throughout all aspects of chemical enterprise internationally. Green Chemistry is a revolutionary area for science and technology that seeks to unite government, academic and industrial communities by placing more emphasis on tending to environmental impacts at the earliest stage of innovation and invention. This approach requires an open and interdisciplinary view of material design, applying the principle that is better not generate waste in the first place rather than disposing or treating it afterwards [6]. In 2000, Daryle Busch former president of the American Chemical Society said ‘Green Chemistry represent the pillars that hold up our sustainable future. It is imperative to teach the value of green chemistry to tomorrow’s chemists.’

Principles Of Green Chemistry

Paul Anastas and John Warner have developed the Twelve Principles of Green Chemistry to aid one in assessing how green a chemical, a reaction or a process is. The principles of Green Chemistry are a significant beginning for the chemical profession in dealing with this novel concept for the betterment of the environment. The twelve principles of green chemistry are as follows:

Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

Atom Economy

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



Less Hazardous Chemical Syntheses

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

Designing Safer Chemicals

Chemical products should be designed to effect their desired function while minimizing their toxicity.

Safer Solvents and Auxiliaries

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

Design for Energy Efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

Use of Renewable Feedstocks

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

Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

Catalysis

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

Design for Degradation

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

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.

Inherently Safer Chemistry for Accident Prevention

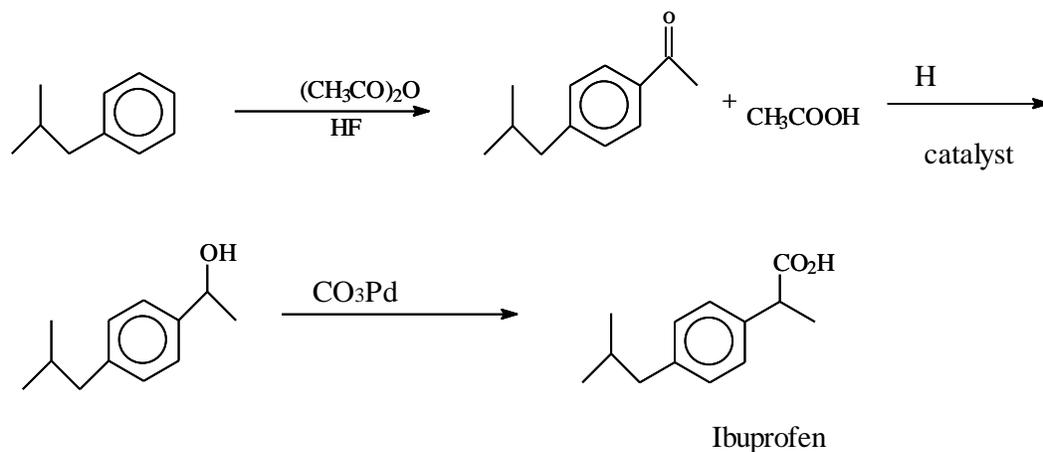
Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

GREEN ROUTE OF CHEMICAL SYNTHESIS

Green Chemistry involves the design and redesign of chemical syntheses[7,8] and chemical products to prevent pollution and thereby solve environmental problems. The research applications for the principle of green chemistry include:

Clean Synthesis [9] (e.g. new routes to important chemical reactions).

Green Chemistry Alternative Synthesis of Ibuprofen

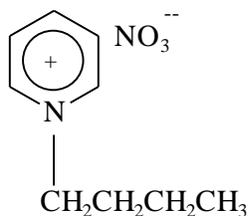


Enhanced atom utilization (e.g. more efficient methods).

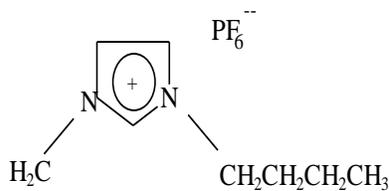
Replacement of stoichiometric reagents [10] (e.g. Catalytic oxidation using air as the only consumable source of oxygen).

New solvents and reaction media (e.g. use of supercritical fluids [11] and reactions in ionic liquids).

Ionic Liquids: Room-temperature solvents contain adjustable inorganic anion & organic cations



**1-Butylpyridinium
nitrate**

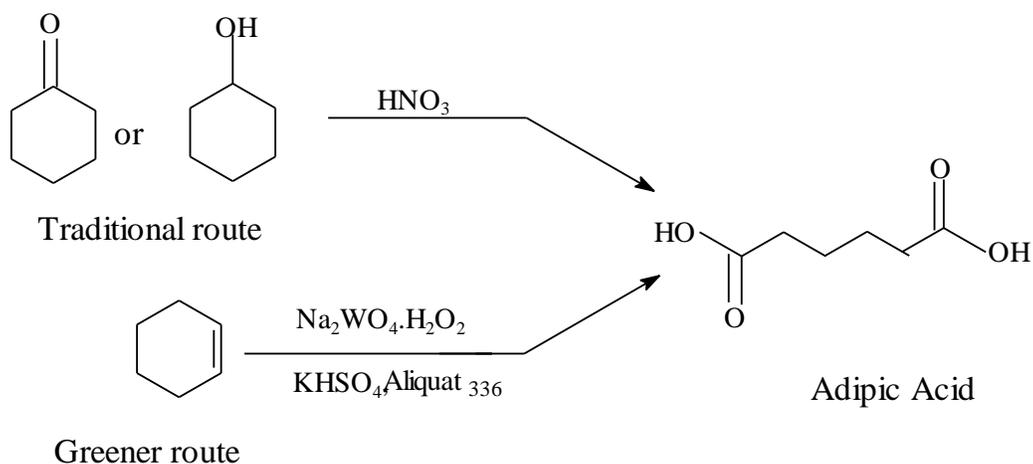


**1-Butyl-3-methylimidazolium
hexafluorophosphate**

Water based processes and products (e.g. organic reaction in high-temperature

Replacement for hazardous reagents (e.g. use of solid acids [12] as replacement of traditional corrosive acids).

Green Chemistry Alternative Synthesis of Adipic Acid replacing traditional acids

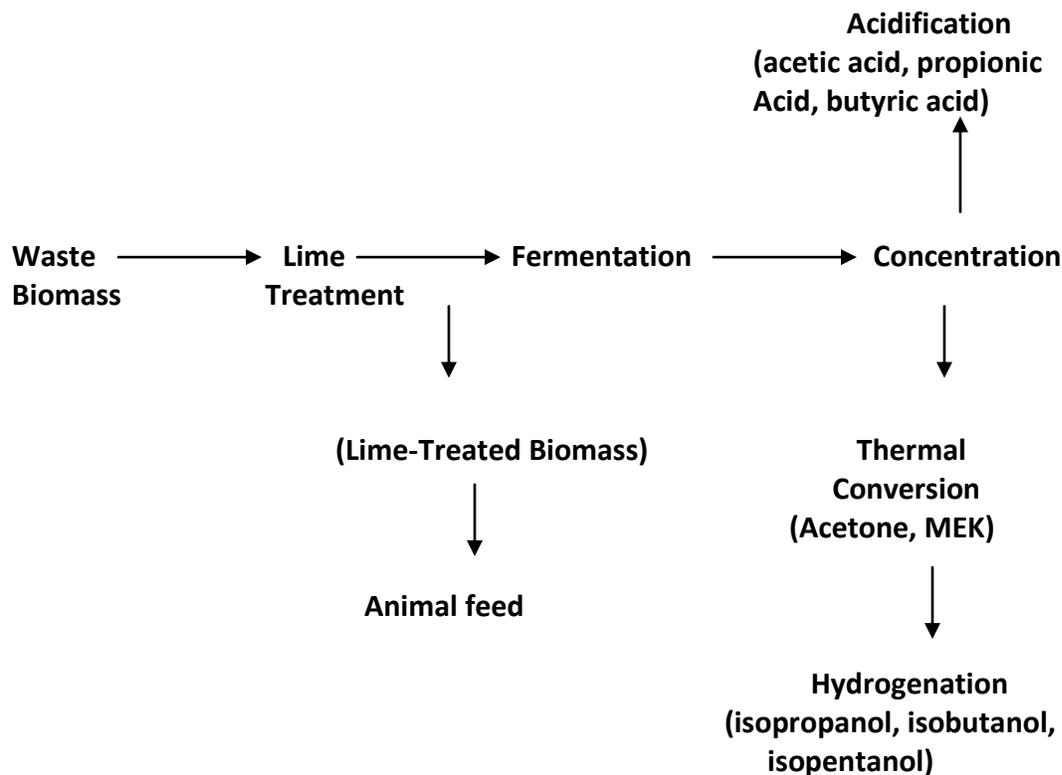


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Novel separation techniques [13].

Alternative feedstock (e.g. use of plant derived products as raw materials for the Chemical industry).

Alternative Feedstocks: Use of biomass in the synthesis of animal feed, chemical & fuels.



In order to be eco-friendly, or green, organic syntheses must meet at least some of the requirements: avoid waste, be atom efficient, avoid use and production of toxic and dangerous chemicals, produce compounds which perform better or equal to the existing ones and are biodegradable, reduce energy requirements, use renewable materials, use catalysts rather than stoichiometric reagents. The demand for solvents has declined over the past decade due to a combination of environmental concern and stricter legislation, as well as weak European and Asian economies. The trend from chlorinated solvents towards oxygenated solvents continues. An alternative for the use of organic solvents is the utilization of water as solvent. Water, in fact is not a popular reaction medium for organic reactions due to the limited solubility of many substrates and also that a variety of functional groups are reactive towards water. In spite of this, there has been a revival of interest in water as a solvent [14] as it offers many advantages for a clean green chemistry. Addition of surfactants can strongly modify the attitude of water to make organic molecules soluble.

Photochemistry offers an inexhaustible source of new chemistry via chemical reaction of the excited state, which are much faster. Photochemical reactions are greener than thermochemical reaction.

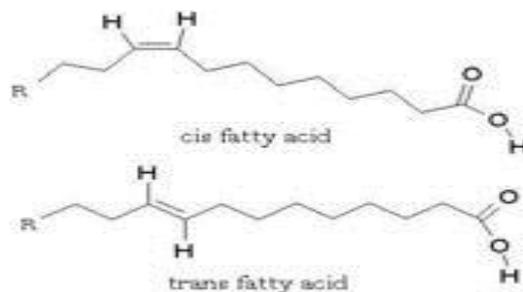
Microwave Chemistry has come up as a boon for eco-friendly conscious chemists. The microwave mediated organic reactions [15] have an advantage of using lesser or no solvent. It

takes place more rapidly, safely, and in an environmentally friendly manner, with high yield as compared to conventional methods.

Recent Developments and Examples

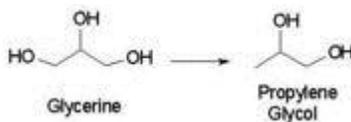
Creative and innovative skills of chemists have helped to develop new processes, synthetic methods, analytical tools, reaction conditions, catalysts, etc., under the green chemistry cover. Some of these are:

- In 1996, Dow Chemical won the 1996 Greener Reaction Conditions award for their 100% carbon dioxide blowing agent for polystyrene foam production. Polystyrene foam is a common material used in packing and food transportation. Seven hundred million pounds are produced each year in the United States alone. Traditionally, CFC and other ozone depleting chemicals were used in the production process of the foam sheets, presenting a serious environmental hazard. Flammable, explosive, and, in some cases toxic hydrocarbons have also been used as CFC replacements, but they present their own problems. Dow Chemical discovered that supercritical carbon dioxide works equally as well as a blowing agent, without the need for hazardous substances, allowing the polystyrene to be more easily recycled. The CO₂ used in the process is reused from other industries, so the net carbon released from the process is zero.
- In 2005, Archer Daniels Midland (ADM) and Novozymes N.A.. won the Greener Synthetic Pathways Award for their enzyme interesterification process. Novozymes and ADM worked together to develop a clean, enzymatic process for the interesterification of oils and fats by interchanging saturated and unsaturated fatty acids. The result is commercially viable products without *trans*-fats. In addition to the human health benefits of eliminating *trans*-fats, the process has reduced the use of toxic chemicals and water, prevents vast amounts of by products, and reduces the amount of fats and oils wasted.

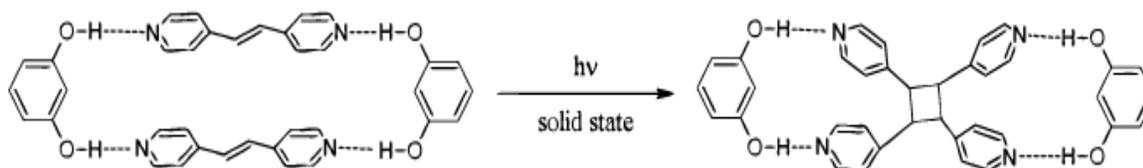


- In 2006, Professor Galen J. Suppes, from the University of Missouri–Columbia, was awarded the Academic Award for his system of converting waste glycerin from biodiesel production to propylene glycol. Through the use of a copper-chromite catalyst, Professor Suppes was able to lower the required temperature of conversion while

raising the efficiency of the distillation reaction. Propylene glycol produced in this way will be cheap enough to replace the more toxic ethylene glycol that is the primary ingredient in automobile antifreeze.

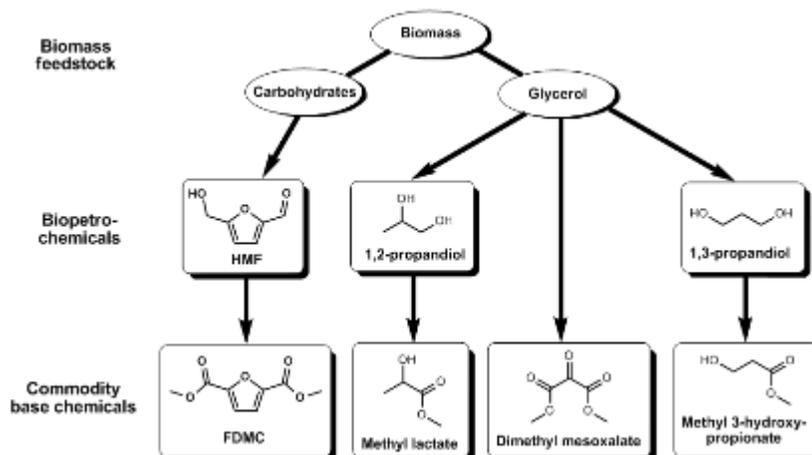


- Research is currently ongoing in the area of supramolecular chemistry [16] to develop reactions which can proceed in the solid state without the use of solvents. The cycloaddition of *trans*-1, 2-bis (4-pyridyl) ethylene is directed by resorcinol in the solid state. This solid-state reaction proceeds in the presence of UV light in 100% yield.



Cycloaddition of *trans*-1, 2-bis (4-pyridyl) ethylene

- The demand for non-ionic surfactant is growing and a new example of this is alkylglycoside, which is made from a saccharide. This product can be used as a replacement for alkylaryl sulphonate anionic surfactant in shampoos. Sodium silicate can be used as a more environmentally benign replacement for phosphorus containing additives in washing powder.
- Feedstock recycling of plastic wastes into valuable chemicals useful as fuels or raw materials [17]. The development of technologies that enables the conversion of biomass into value added chemicals is an essential step towards a more renewable chemical industry.



- The first bio-pesticide for sugarcane has been launched in Australia. The product is based on a naturally-occurring fungus that has been cultured on broken rice grains to provide a medium for distribution.
- Green Routes for Use of Organic Templates in Zeolite Synthesis [18].
- A novel and very effective wet chemical route for the preparation of metal dendritic nanostructures was developed by starting from VO_2 and Ag_2SO_4 (or K_2PdCl_4) in aqueous solution at room temperature [19].

CONCLUSION

Green is a strong color. Green is the color of chlorophyll, and green is the color of money. Being green has long been a battle cry of environmental activists, and being green has become an important marketing tool for businesses. And for chemists, it is becoming increasingly important to be green by applying the principles of green chemistry to all facets of the chemical sciences: basic and applied research, production, and education. Green chemistry is the utilization of a set of principles that will reduce or eliminate the use or generation of hazardous substances during the manufacture and application of chemical related products. Implementation of these principles will reduce waste from chemical processes leading to a cleaner environment and more cost effective use of starting materials. There is increasing political, economic, social and environmental demand for the introduction of this new clean technology, which will allow the rethinking and redesign of many chemical processes considered the industrial norm.

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