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LABORATORY EXPERIMENTS AND DECOMPOSITION OF ENVIRONMENTAL HAZARDOUS CHEMICALS BY USING GREEN CHEMISTRY PRINCIPLES

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ABSTRACT :

The basic principles of Green Chemistry cover a wide range of issues for Organic Synthesis of chemical compounds: To design organic synthesis of process to maximize prevention of waste, atom economy, the use of less hazardous chemicals and safer or environmentally eco-friendly solvents, renewable raw materials, energy efficiency and catalysis. Also, Green Chemistry is interested for the best form of waste disposal and design for degradation of chemical products after use, complying with pollution, prevention measures and sustainable development. In the present paper we offer some important examples of Organic Synthesis with innovative "greener" techniques which has been used for teaching or/and applying in a chemical laboratory of a university. The "greener" organic synthesis of IBUPROFEN (active ingredient of many painkillers) is a typical example. The original synthetic route involved six consecutive steps and an overall atom efficiency of only 40%, while 60% of the mass of atoms ended up in waste products. The organic synthesis of Adipic acid (AA), a feedstock used to make nylon, using better oxidizing agents, a reaction without organic solvents and much less waste than the conventional route. Some examples of replacement of hazardous starting chemicals, the best selectivity and the "greener" synthetic route. Microwave assisted organic reactions is another example that can apply to teaching laboratories, as well as ultrasound-assisted organic synthesis.Organic chlorinated chemical solvents are the most hazardous environmental pollutants because of the low biodegradability and their accumulation potential in soil, water and biological tissues.

KEYWORDS : Environmental Energy, Green Chemistry, Synthesis, Microwaves Activation, Photocatalysis.

INTRODUCTION

Organic chemistry chemicals are the important starting materials for a great number of major chemical industries. The production of organic chemicals as raw materials or reagents for other applications is a major sector of manufacturing polymers, pharmaceuticals, pesticides, paints, artificial fibers, food additives, etc. Organic synthesis on a large scale, compared to the laboratory scale, involves the use of energy, basic chemical ingredients from the petrochemical sector, catalysts and after the end of the reaction, separation, purification, storage, packaging, distribution etc. During these processes there are many problems of health and safety for workers in addition to the environmental problems caused by their use and disposition as waste. Green Chemistry with its 12 principles would like to see changes in the conventional ways that were used for decades to make synthetic organic chemical substances and the use of less toxic starting materials. Green Chemistry would like to increases the efficiency of synthetic methods, to use less toxic solvents, reduce the stages of the synthetic routes and minimize waste as far as practically possible. In this way, organic synthesis will be part of the effort for sustainable development. one to three Green Chemistry is also interested for research and alternative innovations on many practical aspects of organic synthesis in the university and research laboratories of institutes. By changing the methodologies of organic synthesis health and safety will be advanced in the small scale laboratory level but also will be extended to the industrial large scale production processes through the novel techniques.

Basic Principals of Green Chemistry:

1) Atom Economy; Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product i.e. Reduce waste at the molecular level.
2) Prevention; It is better to prevent the production of waste than to treat or clean up waste after it has been created.
3) Less Hazardous chemical synthesis; wherever practicable, synthetic methods should be designed to use and generate substance that possesses little or no toxicity to human health and environment.
4) Design for energy efficiency; choose the least energy demanding chemical route. Ambient temperature and pressure are optimal.
5) Solvents and auxiliaries; Chose the safest solvents available for any given step and avoid whenever possible.
6) Designing Safer Chemicals; Chemical products should be designed to affect their desired function while minimizing their toxicity and environmental destiny throughout the design of the process.
7) Use of renewable feed stocks; Use chemicals which are made from renewable (i.e. Plant based) resources rather than chemicals originating from depleting resources.
8) Design for degradation; Design chemicals that degrade and break down into harmless products which do not persist in environment at the end of their function.
9) Catalysis; Use catalytic reagents (as selective as possible) rather than stoichiometric reagents in reactions.
10) Reduce derivatives; minimize the use of temporary derivation such as blocking group, protecting groups.
11) Safer chemistry for accident protection; Choose and develop chemical procedures andsubstances that are safer and minimize the potential for chemical accidents, explosions and fires. Here are some of the fields involved in everyday life where green chemistry has been applied to some extent.
12) Real time pollution prevention; Monitor chemical reaction in real time, in process andcontrol prior to the formation of hazardous substance.

Methodology:

a) **Microwave-assisted** heating under controlled conditions has been shown to be an invaluable technology in number of areas, from the organic synthesis on solid phase supported to the preparation of functional nonmaterials. The heating is due to the agitation of water molecules contained in the compound. Under the influence of the microwave, the water molecules will begin to change direction at the same frequency of 2.45×10^9 times per second corresponding to a frequency of 2.45 GHz. The microwave-assisted synthesis is used in the pharmaceutical, agrochemical and chemical related industries in the primary discovery and in development processes. Reduction of reaction times and the amount of solvent, increase in product yields, the saving energy for heating by focusing efficient energy on the sample and enhancing product purities avoiding possible side reactions. Moreover, the selectivity of certain manufacturing processes could be positively influenced by this technology [7]. In addition, microwave synthesis allows the discovery of new reaction pathways, which serve to expand "the chemical and the biological space". Two different approaches for microwave synthesis on a large scale have emerged: batch synthesis in larger multimode reactors or continuous/stop flow techniques [8]. The scale-up of microwave synthesis from the laboratory to process and production scale is a challenging area.

b) **The Photocatalysis** under visible light is different method use in wonderful chemistry. In the asymmetric organo catalysis has been extensively studied as a very useful technique of organ metallic catalysis. Light can be considered as an ideal reagent for environmentally eco-friendly, green chemical synthesis. Unlike many traditional reagents, light is abundant, non-toxic and generates do not waste.

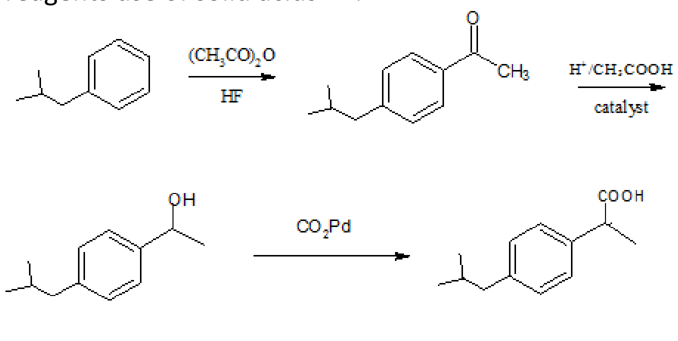
Nowadays, the development of photoredox catalysis initiated by visible light is of real importance. The one-electron reactions are often performed using, as photoredox catalysts, organo metallic complexes containing ruthenium or iridium. However, the toxicity of the ruthenium or the iridium salts as well as their future limited availability is the major weakness of these metal-based methods for the manufacturing of fine chemicals and pharmaceuticals. For example, the combination of a photocatalytic process and organocatalysis is an excellent method to develop enantioselective reactions [9].

c) Green Route Of Chemical Synthesis

Green Chemistry provides to design and redesign of chemical synthesis [12, 13] and chemical products to prevent pollution and to solve environmental problems. The research applications for the principle of green chemistry include: Clean Synthesis [14].

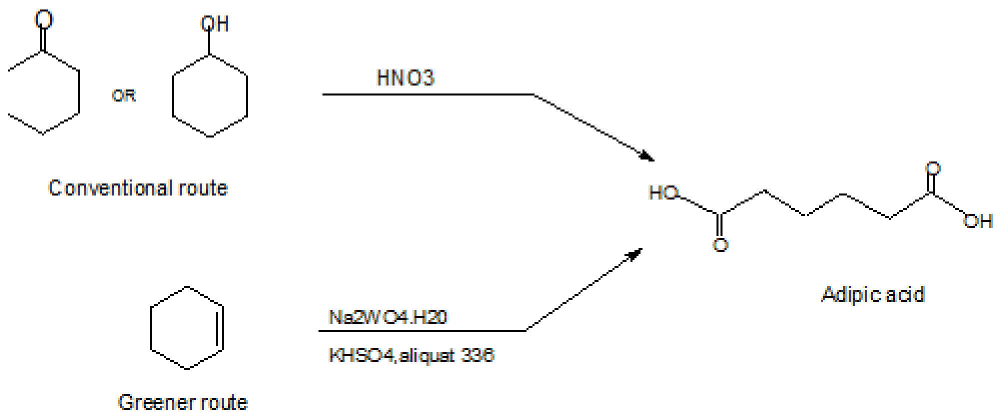
i) Green Chemistry Alternative Synthesis of Ibuprofen:

This method is a more efficient and enhanced atom utilization. The changing of stoichiometric reagents [15]for catalytic oxidation using air only consumable source of oxygen. Different type of new solvents and reaction use of supercritical fluids [16] and reactions in ionic liquids. In convertible reaction replacement for hazardous reagents use of solid acids [17].



Ibuprofen

ii) Green Chemistry Alternative Synthesis of Adipic Acid replacing Conventional acids:



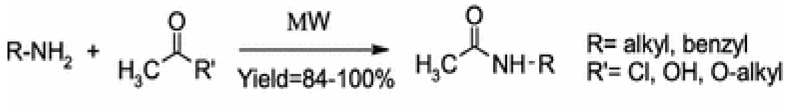
In above reaction greener route for the novel separation techniques [18].

Results and Discussion:

Microwaves assisted solvent – free amidation

To synthesize these lipophilic azapyridinomacrocycles we had to prepare a linker via an amidation reaction. The satisfactory results obtained under microwaves activation led us to develop a method to control the chemo- and regioselectivity in the amidation of polyamines. Previous studies have shown that microwave assisted amidation reactions result in a specific nonthermal microwave effect. This effect can be explained by an increase of the polarity of the dipolar transition state. The applications implement high power which leads to high temperatures, usually inconsistent with the control on selectivity in polyfunctional molecules.Thanks to the specific effect of microwaves, we have achieved the amidation reactions without solvent, in a few minutes at 2–25 W with excellent yields (85–100 %) [6].

The uncatalysed amidation under microwave-assisted solvent-free conditions of primary amines **1**, we performed the reaction with various esters as acyl donors **2** in a CEM Discover™ microwave synthesizer. Neat compounds were mixed in a sealed microwave reaction tube and irradiated under 25 W or 100 W for few seconds to few minutes. The reactions were monitored by GC–MS analysis and the purity of the desired products was evaluated by NMR spectroscopy. The desired compounds **3** were afforded with yields of 84–100%. Microwave-assisted amidation of primary amine under mild condition.



Conclusions:

Nowadays, green Chemistry plays as a very important role producing minimal waste by the development of inventive strategies from raw materials and renewable energy. For the different physicochemical activation techniques such as biotransformation, microwaves and photocatalysis are better for the environment by using less energy, emit less solvent and allow increasing efficiency in the preparation of new compounds. They are untold tools to complement the modern methods used in organic synthesis.

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