

REVIEW ARTICLE**GRAY CHEMISTRY VERSES GREEN CHEMISTRY:  
CHALLENGES AND OPPORTUNITIES****Sanjay K. Sharma<sup>a</sup>, Ashu Chaudhary<sup>b\*</sup> and R.V. Singh<sup>c</sup>**<sup>a</sup>Computational and Green Chemistry Research Laboratory,

Department of Chemistry, Institute of Engg. &amp; Technology, Alwar, India

<sup>b\*</sup>Department of Chemistry, Indian Institute of Technology Delhi, New Delhi-110016<sup>c</sup>Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

E-mail: ashu\_chaudhary77@yahoo.com

**ABSTRACT**

*Green Chemistry is placed in the frontier areas of research and has been focused for considerable recent research. Green Chemistry, the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances is an overarching approach that is applicable to all aspects of chemistry. From feedstocks to solvents, to synthesis and processing green chemistry actively seeks ways to produce materials in a way that is more benign to human health and the environment. The current emphasis on green chemistry reflects a shift away from the historic "command-and-control" approach to environmental problems that mandated waste treatment, control and clean up through regulation and towards preventing pollution at its source rather than accepting pollution at its source. Rather than accepting waste generation and disposal as unavoidable, green chemistry seeks new technologies that are cleaner and economically competitive. Utilizing green chemistry for pollution prevention demonstrates that power and beauty of chemistry: through careful design, society can enjoy the products on which we depend while benefiting the environment.*

*All synthetic processes involve the use of different solvents. Unfortunately many of the solvents are used in industry and retail are volatile organic compounds which inevitably lead to environmental damage, through pollution, risks to human health and to resource depletion, we need to develop and apply more environmentally friendly approaches.*

*So, all traditional and old synthetic routes are more or less "Grey" in their working and obviously give adverse effects to the mankind and all living beings. Green chemistry provides "Green" paths for different synthetic routes using non-hazardous solvents and environmental-friendly chemicals.*

*The fundamentally attractive concept of green chemistry is solvent free reactions. Solvent free reactions can be accelerated by microwave activation and this combined clean technology approach to "greening" chemical reactions. The two most widely studied "new" alternative solvents at present are ionic liquids and supercritical fluids.*

*An attempt has been made to introducing a new emerging Green face of multidimensional chemistry. The major aim of this article is to provide / discuss the emerging trends in environment management and evolve sustainable management strategies to solve the burning environmental problems.*

**Key Words:** *Green chemistry, solvent free reactions, microwave chemistry, atom economy, and electrochemistry.*

**INTRODUCTION**

The economic benefits of green chemistry are central drivers in its advancement. Industry is adopting green chemistry methodologies because they improve the corporate bottom line. A wide array of operating costs is decreased through the use of green chemistry. When less waste is generated, environmental compliance costs go down. Treatment and disposal become unnecessary when waste is eliminated. Decreased solvent usage and fewer processing steps lessen the material and energy costs of manufacturing and increase material efficiency. The

environmental, human health, and the economic advantages realized through green chemistry are serving as a strong incentive to industry to adopt greener technologies.

The American Chemical Society (ACS), US Environmental Protection Agency (EPA) and Royal Society of Chemistry have been working in this field for the betterment of the environment globally. Royal Society launched "Green Chemistry Network" to educate people and to provide a common platform to all teachers, students, researchers and common people to share their views to generate awareness about this burning global problem.

Developed countries like UK, Japan, USA, Germany are very much aware about this new "Green" Stream of Chemistry. But we are (in India) far behind and still there is a good scope of developing Green approach with more scientific way in a managed and articulate manner.

Here, in this paper we are discussing the challenges and opportunities in the field of Green chemistry in Indian context. Also, we are providing a fair discussion about comparison of "Grey Chemistry" and "Green Chemistry".

### **Evaluation of the concept:**

To maintain our current standard of living and improve our quality of life, society has come to depend on the products of the chemical industry. The 20<sup>th</sup> century has been highly successful in this regard. However, with the advent of the 21<sup>st</sup> century, the public is equally aware of the hazardous substances used and generated by the chemical processes. Our environment, which is endowed by nature, needs to be protected from ever increasing chemical pollution associated with contemporary lifestyles and emerging technologies. Developments in water treatment, waste disposal methods, agricultural pesticides and fungicides, polymers, materials sciences, detergents, petroleum additives and so forth have all contributed to the improvement in our quality of life. But all these advances come with a price tag – of pollution.

Soon after the World War II, within just 15 years, the world witnessed what economists call the Post-War Economic Boom. During this period the western world not only saw enormous economic growth but also enormous environmental problems. By 1960, it was impossible to breathe in most Western cities. Since the 1960's a number of events all over the globe have raised concern about the toxic chemicals being released into the environment. The occurrence of major incidents such as the Exxon Valdez oil spill, the Union-Carbide (DOW) Bhopal disaster, large – scale contamination of the Rhine River, the progressive deterioration of the Rhine River, the progressive deterioration of the aquatic habitats and conifer forests in the Northeastern US, Canada and parts of Europe or the release of radioactive material in the Chernobyl accident, etc. and the subsequent massive publicity due to the resulting environmental problems has highlighted the potential for imminent and long-term disasters in the public's conscience. More than 3500 people were killed in December 1984 when poisonous gas leaked from a pesticide factory in Bhopal, India. The accident was caused by Water entering a storage tank holding 40 tons of Methylisocyanate provoking a runaway reaction and explosion. Therefore, enormous amount of scientific and technological investment had to be made in the 1970's onwards to deal with the environmental crisis.

### **Sustainability and Cleaner Production:**

To combine the technological progress with environmental safety is one of the key challenges of the millennium. Cleaner technology is a new dimension that is emerging rapidly at both national and international level. Cleaner production has been identified as a key method for reconciling environment and economic development. The basic idea of cleaner production is to increase production efficiency while at the same time eliminate or at least minimize wastes and emissions at their source rather than treat them at the end of pipe after they have been generated. The concept of cleaner production, pollution prevention or waste reduction is still relatively young, although the concepts involved are much older. Both cleaner production and sustainability came into focus with the publication of 'our common future'.

This report provided a focused definition for the concept of sustainable development : "A process of change in which the exploitation of resources, the direction of investment, the orientation of the technological development and instituted change are all in harmony and enhance both current and future potential to meet human need and aspiration". According to the World Commission on Environment and Development, Brundtland Commission on Environment and Development, Brundtland commission 1987, Sustainable development is "Development that meets the needs of the present without compromising the ability of future generations to meet their own needs." Sustainable development<sup>2-4</sup> demands change, requires doing more with lesser resource input and less waste generation. Instead of end-of-pipe technology, it requires pollution prevention philosophy, which is : "First and foremost, reduce waste at the origin-through improved housekeeping and maintenance, and modification in product design, processing and raw material selection. Finally, if there is no prevention option possible, treat and safely dispose off the waste."

### **Green Chemistry and Eco-efficiency:**

In the efforts to move towards 'Sustainable Development', chemistry nowadays is at the forefront of the development of clean production processes and products. Chemistry is no doubt determinant to understand and protect our environments as the world's future is strongly dependently on the chemical processes adopted. Chemistry plays an integral part of our lives and is all around us in the clothes we wear, the food, air and buildings etc. Sustainability, eco-efficiency and green chemistry are new principles that are guiding the development of next generation of products and processes.<sup>5,6</sup> "Green chemistry is considered an essential piece of a comprehensive program to protect human health and the environment. It its essence Green Chemistry<sup>7-12</sup> is a science based, nor regulatory and economically driven approach to achieving the goals of environmental protection and sustainable development.

In order to be eco-friendly, or green, organic synthesis<sup>13-16</sup> must meet, if not all, at least some of the following 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 bio-degradable, avoid auxiliary substances, reduce energy requirements, use renewable materials, use catalysts rather than stoichiometric reagents. These requirements can be easily met by the concept of green chemistry.

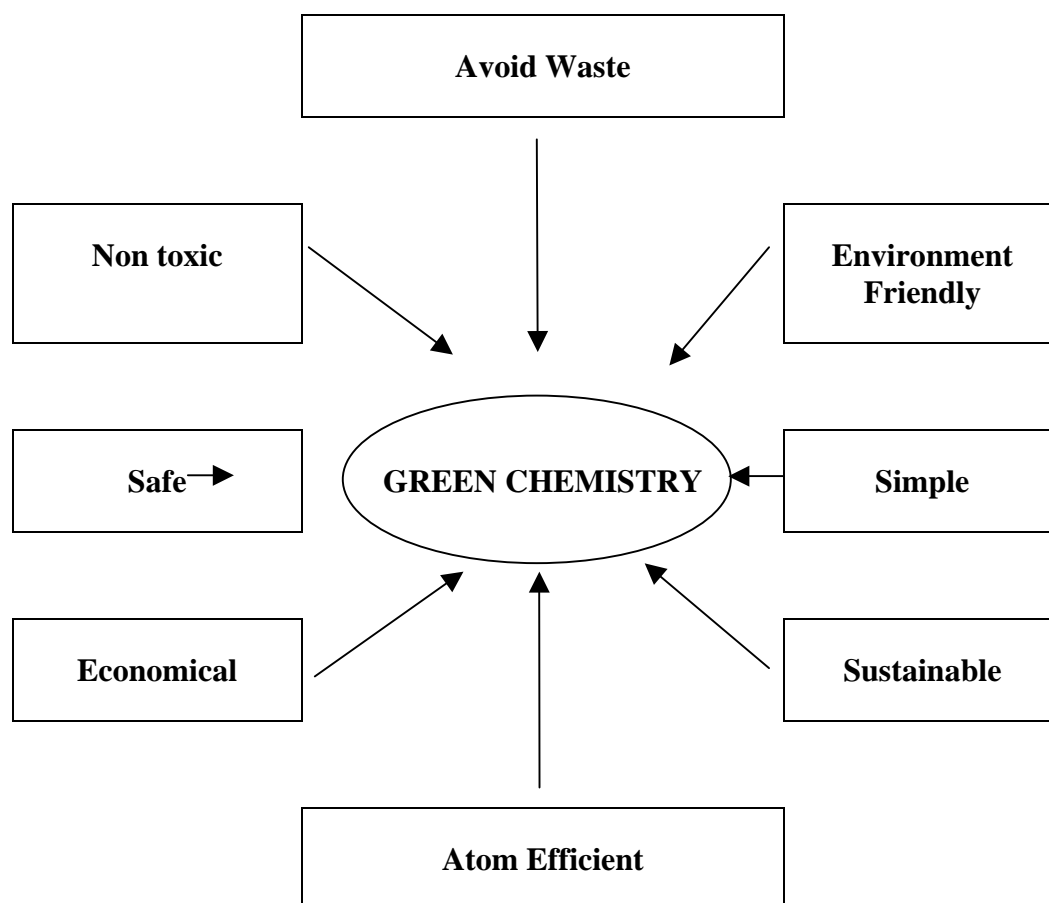
### **GREEN CHEMISTRY: THE NEED OF THE DAY**

Green chemistry is one of them, which involves modified engineering, practices, bioremediation, eco-friendly reaction media and concept of atom economy leading to almost zero waste. It clearly differentiates the *grey* synthetic processes with that of *green* natural processes having strategic objectives with social and environmental benefits<sup>17</sup>.

Green strategies include the replacement of organic solvent by water, altogether elimination of a solvent, the substitution of environmentally benign substances to replace toxic heavy metals, development of solid support reagents and catalysts for synthesis, launching of eco-friendly methods of organic synthesis, designing of products, which can be recycled or safely disposable, use of dry media reactions and many other important aspects. The overall strategy is to virtually eliminate toxic persistent substances from the environment by allowing no further release or by collecting and destroying the existing deposits. Harmful synthetic products either should be replaced by green products or should be synthesized by environment friendly techniques.

*Just in time production* approach for hazardous substances essentially required for any commercial production is an excellent example of inherently safer chemistry. The use of biocatalyst is promising avenue for this purpose. An inherently safer production process using a biocatalytic approach has been developed which allow generating just the amount of MIC (methyl isocyanate), need for conversion into some agrochemicals. Devising waste free

process involves the use of solid-state catalyst, which in many cases can be chosen so that yield of the commercial product is maximized and undesirable by product is minimized. The change of reactant or solvent for a reaction to one that is less toxic, often by using a different reaction to produce the desired product is nothing but Green Chemistry. The use of supercritical fluids [supercritical carbon dioxide] solvents can replace organic solvents, which are often hazardous toxic, flammable and even explosive. Super critical CO<sub>2</sub> can replace now banned CFC and other aromatic hydrocarbons as solvents in the production of number of commercial organic polymers<sup>18</sup>.



**Fig. 1**

Green chemistry has launched the *concept of atom economy*. The objective is to conduct chemical reaction where all the atoms that go into process come out either incorporated in the products or marketable side products. It combines the goals of environmental benignity with synthetic elegance in the design of methods for producing compounds. Green chemistry places special emphasis on the synthesis of new substances and the corresponding industrial process. Examples include the replacement of classical synthesis in organic chemistry for ethanol, ethanoic acid and amino acid. The use of microorganism for the synthesis of drugs and chemical disposal with the help of genetically manipulated living system has been considered safe<sup>19</sup>.

*Green methods* to save vegetation from pests are to saw transgenic crops, engineered to be resistant to specific insects. The genetic engineering can slash the volume of insecticides that farmers need to dump on the land every year genetically engineered plants produce a steady supply of own insecticide. Crops can be genetically engineered to produce Bt, and insecticidal protein. Thus Bt. Cotton, Bt Maize, Bt. Potato have begin to hit the fields. Green

alternatives to conventional chemical insecticides are considered viz. bacterial and viral insecticides, which control insect by infecting them with bacterial diseases.

*Green Products*, like derivatives of  $\beta$ -methoxy acrylic acid, a class of natural products having fungicidal properties are being envisaged to replace conventional fungicides. One such derivative is [ICIA 5504] is likely to be come the most useful anti-fungal agent and possesses an extremely low toxicity. Light activated herbicides are becoming increasingly popular. These chemicals are use in solar energy to produce toxic compounds that kill the weeds. Amino lemlinic acid is an important member, which is precursor to magnesium tetra pyrrol, which in turn is a precursor to chlorophyll biosynthesis. When a weed is spread with aminolevulinic acid, it produces abnormally large amount of magnesium tetra- pyrrol, a part of which is used up in synthesis of chlorophyll and leftover remain unused. The unused magnesium tetrapyrrol absorbs light energy and undergoes photochemical reaction to procure a highly reactive form of oxygen called singlet oxygen. Singlet oxygen is a power full oxidizing agent that can trigger free radical chain reaction amongst the biomolecules present in the tissue of plants. The free radicals can destroy cell membranes, enzymes, nucleic acids, proteins and weeds are killed. Breeding for stress resistance species for water deficient soil and revegetating the uncultivated land are the areas of immense interest of Green Agricultural Chemists.

*Recycling of waste* is an important dimension of waste management. Waste management is an area where we can help ourselves, win our won battles and stand at our own feet. The food of single cell protein manufactured from refuse, chemicals from cellulose wastes, alternative fermentation products and single cell protein [SCP] production have been explored and examined. The production of genetically engineered microorganism for waste utilization is now attainable objective. The waste of biological or chemical process will become the feed stock of the next process so that energy, carbon content and water are fully conserved. The developments of an alternative recycling strategies are being encouraged under the domain of Green Chemistry to ensure resources for the future. The best way to minimize waste and to avoid the burdensome costs associated with waste was to produce the hazard components in the risk equation by developing environmentally benign chemical synthesis right from the stand including the design of safer chemicals as end products. The new approach is to move up the pipeline towards the point of pollutant creation. Generally, saying or even eliminating the generation of wastes accomplishes this approach.

## INTRODUCTION AND PRINCIPLES OF GREEN CHEMISTRY

*"Industrial vomit.....fills our skies and seas pesticides and herbicides filter into our foods. Twisted automobile carcasses, aluminium cans, non-returnable glass bottles and synthetic plastics form immensde middens in our midst as more and more of our detritus resists decay. We do not even begin to know what to do with our detritus resists decay we do not even begin to know what to do with our radioactive wastes – whether to pump them into the earth, shoot them into outer space, or pour them into the oceans. Our technological powers increase, but the side effects and potential hazards also escalate."*

**-Alvin Toppler, Furture Shock 1970**

In the glorious days of 1950's and 1960's chemists envisioned chemistry as the solution to a host of society's needs. Indeed, they created many things which improve the quality of life on earth like dyes, plastic, cosmetics and other materials. At the same time chemistry brought about medical revolution i.e. through antibiotics which conquered infectious disease. All these things prove DuPont Slogan. *"Better things for better living through chemistry"*.

But there are some adverse outcome due to discovery of drugs, insecticides, herbicides, fertilizers etc. which causes a cancerous grip of the air, water, soil and noise pollution on earth that grabbed this world like an octopus, e.g. DDT which accumulated in birds, and

causes egg shell thinning and nesting failures results in decline of that species. Refrigerant like CFCs depletes the ozone layer remarkably which protects our earth from harmful UV rays of sun. So there are several advantages and disadvantages of chemistry, but there is main advantages of chemistry the beginning of green chemistry by the middle of 20th century.

The term " GREEN CHEMISTRY" was coined by Professor Paul Anastas, who is known as the father of green chemistry, at US Environmental Protection Agency Green Chemistry is the effort of reducing or eliminating the use of or generation of hazardous substances in the design, manufacture and application of chemical products.<sup>20</sup>

Green Chemistry is defined as environmentally benign chemical synthesis. It is science based, non regulatory and economically driven approach to achieving the goals of environmental protection.<sup>21-26</sup> The ultimate value of green chemistry lies in its applicability for the new millennium. So the challenge to reduce the waste, the toxicity of chemical and the amount of energy used, while still providing the goods that society needs, is overcome through green chemistry.

Green Chemistry has been referred by a number of alternate name like 'Clean Chemistry', 'Atom Economy', 'Bengh by Design Chemistry', 'sustainable chemistry', 'Eco-friendly chemistry' and 'Environmentally Benign Chemistry'. While Green Chemistry encompasses human health and the environment. The discovery and development of fundamental chemical transformations that are harmful to the environment will be the driving force that moves this area forward.

Green Chemistry is the utilization of a set of principles that reduce or eliminate the uses or generation of hazardous chemicals in the design, manufacture and application of chemical products. It describes an area of research arising from scientific discoveries about pollution and covers the following areas :

- (i) Development of environmentally improved routes to products.
- (ii) Use of sustainable resources.
- (iii) Design of new green chemicals.
- (iv) Use of biotechnology, alternative and innovative technology for industrial processes.

Green chemistry involves the design and redesign of chemical synthesis<sup>24</sup> and chemical products to prevent pollution and thereby solve environmental problems. It is the use of chemical principles and methodologies for source-reduction which is the most desirable form of the pollution prevention. It incorporates pollution prevention practices in the manufacture of chemicals and promotes industrial ecology. It is a new way of looking at chemicals and minimizes any negative environmental effects.

The *twelve principles* of Green Chemistry can be applied to almost every part of chemistry, that includes synthesis of molecules with a desired structure and property, catalysis of a process, less polluting reaction conditions etc.

#### **1. Prevention**

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

#### **2. Less hazardous chemical synthesis**

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

**3. Designing Safer Chemicals** Chemicals products should be designed to affect their desired function while minimizing their toxicity.

#### **4. Atom economy**

Synthetic methods should be designed to minimize the incorporation of all materials used in the process into the final product. A very good example<sup>28</sup> is the BHC company synthesis of Ibuprofen, which creates less waste and fewer by products (Fig. 1). The % economy for the three step catalytic green synthesis (BHC) Vs the six step brown

synthesis (BOOTS) in 77% and 40% respectively. Considering the fact that acetic acid generated in steps 1 of green synthesis is recovered the % atom economy climbs to 99% from 77%.

**5. Safer solvents and auxiliaries** The use of auxiliary substances (solvents, separation, agents, etc.) should be minimized whenever possible and should be made innocuous when used.

**6. 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.

**7. Use renewable feedstocks** Raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

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

**9. Catalysis** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. Using catalytic reagents creates opportunities for increased selectivity, better yield, and feasibility of non feasible reaction.

**10. 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.

**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.

**12. Inherently safer chemistry for accident prevention** Substances and the form of a substance used in chemical process should be chosen to minimize the potential for chemical accidents including releases, explosions and fires.

Green Chemistry has changed our life style in many ways. Like now a days dry cleaning of clothes is done with the use of liquid CO<sub>2</sub> and a surfactant, thereby eliminating a need of halogenated solvents like PERC (per chloroethylene Cl<sub>2</sub>C=CCl<sub>2</sub>)<sup>29</sup>. This technology is known as micell Technology. In the same way, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is used with some activators like TAML<sup>30</sup> activators as a bleaching agents rather than the use of halogenated compounds.

## SCOPE OF GREEN CHEMISTRY

Newer, environmentally friendly, waste-minimization, remediation (clean-up) and restoration strategies can be based on physical, chemical or biological approaches<sup>31</sup>. Examples of green chemistry / technology that have been developed encompass most all areas of chemistry including organic, biochemistry, inorganic, polymer, toxicology, environmental physical, industrial etc. The principle of green chemistry can be applied broadly to areas like synthesis, catalysis<sup>32</sup>, reaction conditions, analysis and monitoring, extraction, separations, computational chemistry and process modeling etc. An emerging area of increasing importance in green chemistry is that of analytical chemistry and all of its associated activities. Green chemistry is also applicable to all sectors of the chemical industry ranging from pharmaceuticals and specialty chemicals to the high volume manufacture of bulk chemicals. The growing public sentiment in support of our environment, the focus of the industry has shifted to reduce or eliminate the use of water and organic solvents during manufacturing and processing. This involves 'closed loop system' leading to reduction and / or recycling, switching to "solvent free" processes or "solvent alternatives".

The key to achieving the goal of reducing the generation of environmentally unfriendly waste and the use of toxic solvents and reagents is the widespread substitution of "solochiometric" technologies by greener catalytic alternatives. The first two involve 100% atom efficiency while the latter is slightly less than perfect owing to the co-production of molecular water. The longer trend is towards the use of the simplest raw materials - H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, NH<sub>3</sub>, CO and CO<sub>2</sub> in catalytic low salt processes. For many years catalysis<sup>33</sup> sprouted life and led to evolution. Today catalysis is one of the powerful tools of the chemical industry. Similarly, the widespread substitution of classical mineral and Lewis acids by recyclable solid acids, such as zeolites and acidic clays, and the introduction of recyclable solid bases, such as hydrotalcites (anionic clays) will result in a dramatic reduction of inorganic waste. Because of the deleterious effects that many organic solvents have on the environment and/or health, media such as halogenated hydrocarbons (e.g. chloroform, dichloromethane) are being phased out of use and benign replacements are being developed. A possible alternative for the use of organic solvents is the extensive utilization of water as a solvent. Traditionally, water is not a popular reaction medium for organic reactions due to the limited solubility of many substrates and also to the fact that a variety of functional groups is reactive towards

Water. But recently, there has been a revival of interest in water as a solvent<sup>34, 35</sup> and chemistry in aqueous medium, as it offers many advantages for a clean green chemistry. The addition of surfactants can strongly modify the attitude of water to solubilize organic molecules.

An important incentive for the use of supercritical fluids (SCFs)<sup>33</sup> in synthetic chemistry comes from this increasing demand for environmentally and toxicologically benign processes for the production of high value chemicals. Although SCF<sub>8</sub><sup>36</sup> were discovered more than 100 years ago, it wasn't until the 1970s that they were used commercially to decaffeinate coffee. Since then, SCF media have been used successfully to extract analysis from a variety of complex compounds through manipulation of system pressure and temperature. By comparison conventional methods (e.g. Soxhlet extraction and vacuum isolation) are more complicated and time and energy intensive. In general, conventional methods have a tendency to generate crude extracts consisting of deteriorated constituents or to prematurely remove volatile components. SCF extraction has also been applied to environmental remediation such as removing PCBs and other organics from water and soil. Supercritical carbon dioxide (SC-CO<sub>2</sub>) is an attractive alternative because it is inexpensive and poses no threat to the environmental or human health<sup>37</sup>. However, depending on the application, a variety of other



SCF<sub>3</sub> have been used for applications as diverse as extraction, chromatography, inorganic and organic synthesis, catalysis, materials, processing and even dry cleaning. In ScCO<sub>2</sub> based processes, simple pressure release leads to the isolation of solvent free clean products and the non-toxic CO<sub>2</sub> can be readily recycled. Furthermore, the replacement of potentially hazardous organic solvents with ScCO<sub>2</sub> can help to increase the inherent safety of a process as the risk of explosion or ignition is greatly reduced in the presence of large amounts of inert CO<sub>2</sub>. The use of SCFs for catalytic processes has also been shown to overcome many of the chemical engineering, and environmental difficulties associated with conventional process. Homogeneous catalysis is generally preferred to heterogeneous, catalysis because it offers greater rates and selectivities. However, the drawback of this methodology is the difficulty in separating products. By comparison, reactions involving SCFs offer the best opportunity for separation of reaction products and removal of solvent from the system accomplished through simple system depressurization.

Promoting a reaction photochemically rather than thermally is greener, since light is the green reagent par excellence. Photochemistry<sup>38</sup> offers an inexhaustible source of new chemistry via chemical reactions of the excited state, which are much faster and little dependent on conditions, affording a large freedom of choice. Similarly, reactions by a microwave have an advantage of less or no solvent, very little time, no side products and better yields with better selectivities compared to those carried out by conventional means.

Much of the industrial chemistry takes place in organic solvents, or involves apolar compounds. Biocatalysis<sup>39</sup>, in contrast involves aqueous environments. The range of reactions that can be carried out with whole cells is enormous, given the range of microorganisms that have already been isolated or remain to be discovered. Microbial cells can be employed as very effective reactors for the conversion of substrates to products, operating in mixed aqueous – a polar systems. Optimized for the best space time yields attainable at lowest costs. Biodegradation of toxic pollutants in the wastewater treatment technologies, by using microbes is well known. Just as light, heat and moisture can degrade many materials, biotechnology relies on naturally occurring, living bacteria to perform a similar function. Some bacteria naturally "feed" on chemicals and other wastes including some hazardous materials. They consume those materials, digest them, and excrete harmless substances in their place. According to William K. Reilly, former head of the Environmental Protection Agency, "The use of biotechnology to solve environmental problems, could be - should be - an environmental breakthrough of staggering positive dimensions".

Mention of fuel cells<sup>40</sup> and most people thoughts will probably turn to them being the future energy source for cars, buses etc. However, the average consumers first encounter with fuel cell may be through the domestic vacuum cleaner. Manhattan. Scientific teaming up with electrouse to develop a new line centered on a small lightweight hydrogen fuel cell. The saving on CO<sub>2</sub> emissions have not been calculated but the product is expected to be quieter, lighter and of course cordless<sup>41</sup>. Fuel cell vehicles could be a part of the solution to smog, global warming and other ecological problems that conventional cars cause. The technology, which was first used during the Apollo moon project in the 1960, mixes hydrogen fuel and oxygen from air using electrochemical process to produce the electricity that powers the car. Far from harming the environment, running on an inexhaustible power source, its only by products are heat and water so pure that the Apollo astronauts drink it. The two Japanese automakers. Toyota Motor and Honda Motor launched the biggest step yet towards the mass marketing of FCVs.

### **EMERGING GREEN TECHNOLOGY**

In current aspects development of more sustainable products and energy efficient processes with reducing waste are discussed in emerging green technologies. By using these

technologies energy input reduces, improvement of selectivity, shortening of reaction time occurs. Some reactions which are not possible with single heating, can be possible with solid support. Use of energy sources like light, microwave, ultrasound and electricity and more clean and efficient. Particularly for bulk chemicals, development of much more energy efficient processes provides significant commercial benefits. Emerging techniques, in the overall development of "Green Chemistry", can be categorised in the following parts :

### 1. Photochemistry

Light is environmentally benign, leaving no residue to be removed in the workup of a reaction. A photochemical reaction occurs when an atom or molecules absorb light [Gratthuss - Draper law]. Further on photon of light can activate only on molecules [Stark - Einstein law] when a photon is absorbed by a molecule or atom it must transfer all its energy to atom or molecule and promoted to higher energy state. The energy required for promotion from ground state to lowest excited state falls in ultraviolet and visible region of electromagnetic spectrum. Light can catalyze some reactions that are difficult or impossible in other ways (e.g. cycloaddition<sup>43</sup>). Solar furnace is used for isomerisation, catalytic cyclisation and purification of water<sup>44</sup>. Dithianes, benzyl ethers and related compounds have been cleaved by the use of visible light with a dye<sup>45</sup>. A combination of visible light and water was used in cyclization to produce substituted pyridines with almost no byproducts<sup>46</sup>. Oxidation of hydrocarbons in zeolites with blue light gives improved selectivity<sup>47</sup>. Photo oxidation of cyclohexane in the presence of titanium dioxide gave 85.4% cyclohexanone, 2.6% cyclohexane and 12% carbon dioxide<sup>48</sup>. Acylhydroquinones can be produced from 1,4-benzoquinone and aldehyde using light from a sunlamp<sup>49</sup>. In contrast to the usual acylation with an acid chloride, this process produces no byproduct salt (*Fig.2*).

Benzonitrile in methanolic potassium hydroxide can be hydrolyzed to benzamide in 96% yield using an oxophosphorpyrin catalyst with light >420 nm at 20°C<sup>50</sup>. Photo redox reactions can be carried out with semiconductors. Irradiation of nitrobenzene in the presence of zinc oxide particles in alcohol produce phenyl hydroxyl amine in 73% yield<sup>51</sup>. Solar light induced photocatalytic oxidation of benzyl alcohol using heteropolyoxometalate catalyst of the type  $[S_2M_{18}O_{62}]^{4-}$  was reported<sup>52</sup>. The photo reactions between 1,4-quinones and aldehyde (photo-Friedel-Craft acylation of quinones), yielding acylated hydroquinones as sole products, were investigated under artificial and solar irradiation conditions<sup>53</sup>. A photochemical method to remove uranium from a phosphate containing waste in high yield is reported by Evans et.al.<sup>54</sup>.

### 2. Electrochemistry

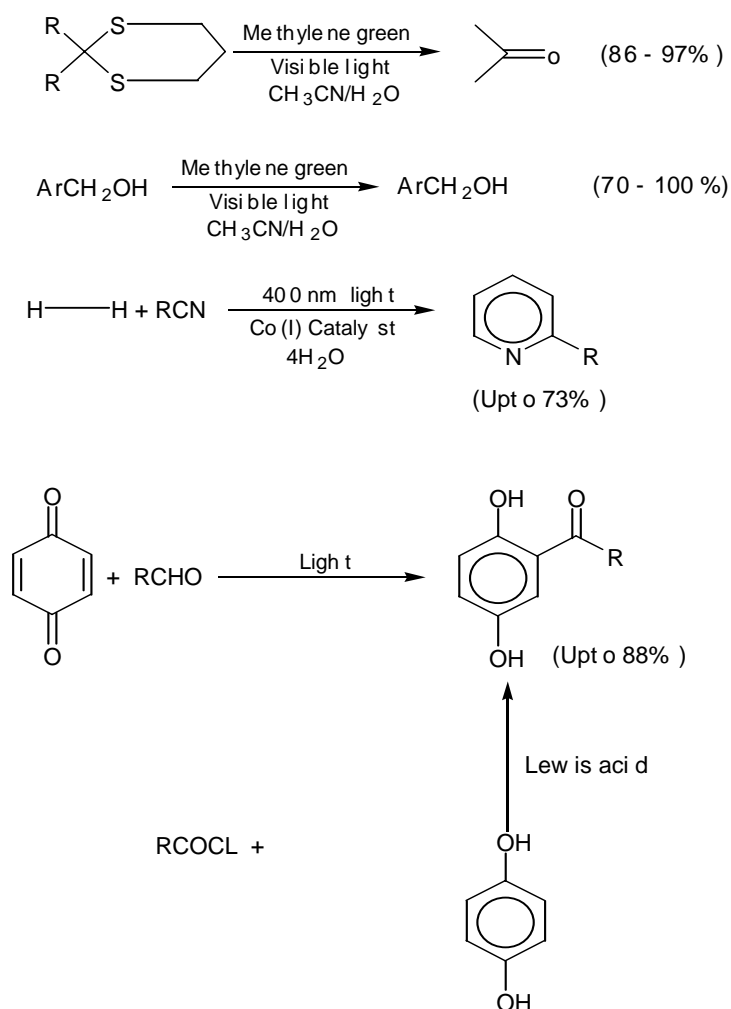
Electrochemistry is widely used in industry for example in effluent treatment, corrosion prevention and electroplating as well as in electrochemical synthesis. Electrochemical synthesis is a well established technology for major processes such as aluminum and chlorine production. So now a days interest is increasing for clean synthesis of fine chemical by using electrochemistry. The basis of electrochemical synthesis is the electrochemical cell of which there are many types, both batch and continuous flow, with a multitude of electrode variation. Lead, cadmium, zinc and carbon electrodes are quite after used.

The only large volume application in organic chemistry appears to be the hydrodimerization of acrylonitrile to form adiponitrile (200000 tons/ year) which is then reduced to the hexamethylenediamine or hydrolysed to adipic acid for the preparation of Nylon 66<sup>55</sup>. Electrochemistry can be used to regenerate an expensive or toxic reagent in situ. It is used to generate sodium hypiodite and sodium hydroxide continuously for the epoxidation of 2-methylnaphthoquinone<sup>56</sup>, yield is 100% and no waste is produced (*Fig.3*).

Electricity can be used in oxidation and reductions instead of reagents. When iodine is reduced to hydroiodic acid in this way<sup>57</sup>, no waste products are formed. Naphthalene can be oxidized to naphthoquinone with 98% selectivity using a small amount of cerium (III) that forms is reoxidized to cerium (IV) electrically<sup>58</sup>.

Substituted aromatic compounds can be oxidized to the corresponding phenols electrically with a platinum electrode in trifluoroacetic acid, triethylamine and methylene chloride<sup>59</sup>. An oxidation using a nickel hydroxide electrode is done<sup>60</sup>. Hydrogenation of edible oils using a cell with a Nafion membrane with a ruthenium anode on one side and a platinum or palladium black cathode on the other produced less of the undesirable trans-isomers than conventional hydrogenations<sup>61</sup> (Fig.4). Electrochemistry also provides a way to produce radicals and anions.<sup>62</sup>

Synthesis of 3-bromothiophene through 2,3,5-tribromothiophene provides an example of the obvious environmental beneficial of an electrochemical route compared to a conventional process because the use of metal reducing agent is avoided and no bromine is wasted. The electrochemical hydrogenation of water immiscible olefins and acetylenes is enhanced by concurred ultrasonication<sup>63</sup>. Tetramethyl adipic acid, a starting monomer for several technically important polymers is synthesized by direct carbon-carbon bond formation between the saturated primary carbon atom of pivalic acid using a sonoelectrical fenton process<sup>64</sup>.



**Fig. 2**

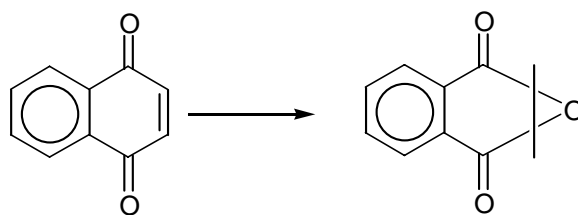


Fig. 3

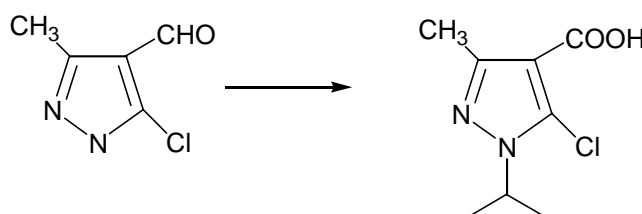


Fig. 4

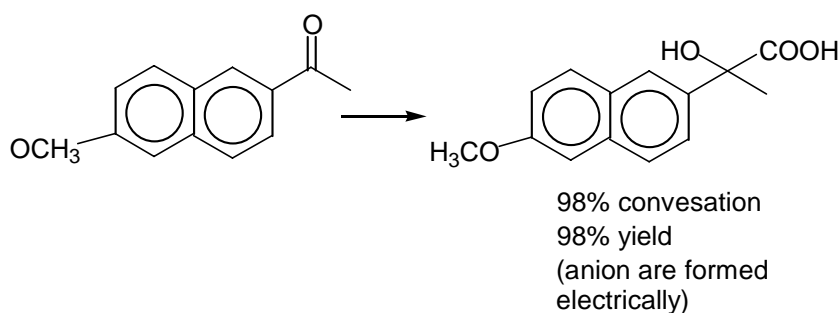


Fig. 5

Electrochemistry is used on a large scale in the production of organic and inorganic compounds. Reduction of carboxylic acids, nitro compounds and nitrile has been widely reported. Oxidation of aromatics and methyl aromatics has also been studied. Other inorganic compound like chlorine and sodium hydroxide etc. are manufactured using electrochemical technology. Electrochemical treatment processes can provide valuable contribution to the protection of environment through the minimization of waste and toxic materials in effluents. Electrochemical treatment of distillery effluents using catalytic anode was reported by Manishanker et.al.<sup>65</sup>.

### 3. Sonochemistry

Ultrasound is defined as sound of a frequency, which is beyond human hearing i.e. above 16 KHz. It has been reported that chemical reactivity of a system increases on irradiating it with power ultrasound. The study of effects of ultrasound on chemical reactivity is termed as sonochemistry. Some important applications of ultrasound in chemical synthesis are given as:

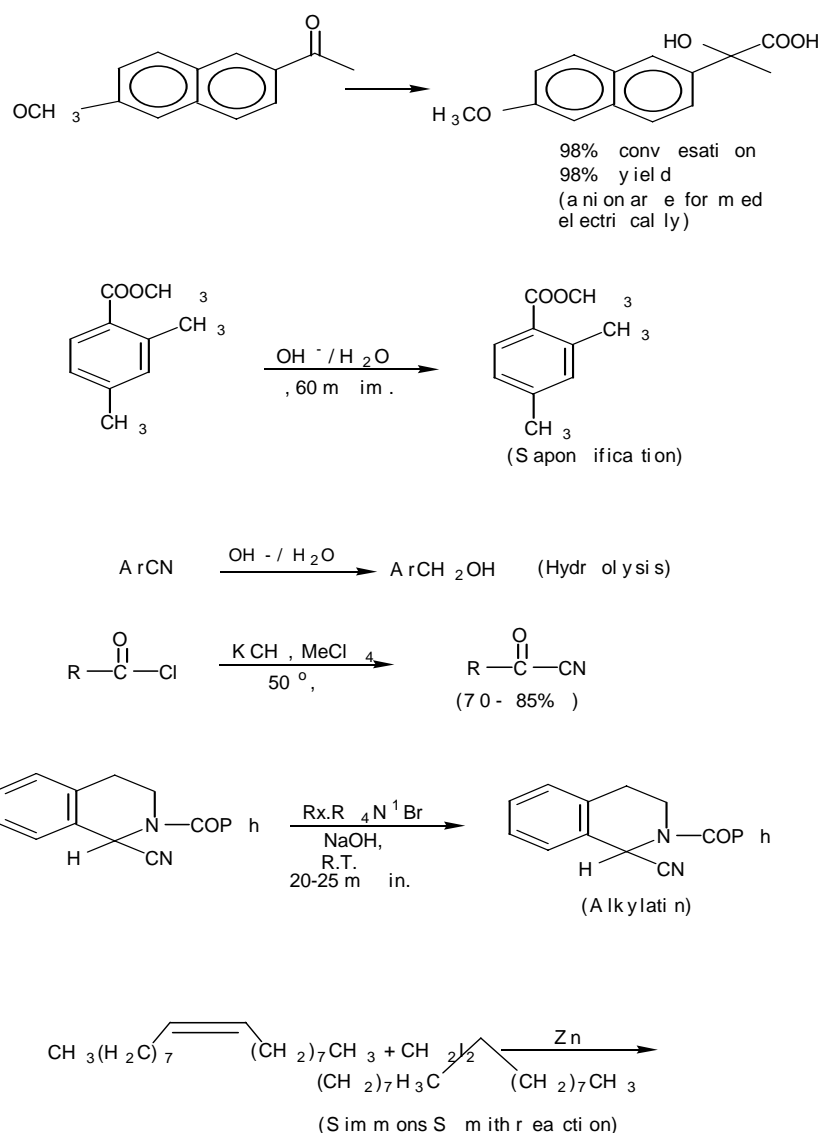


Many other examples of sonochemistry assisted organic synthesis like addition reaction, oxidation, reduction, hydroboration, coupling reactions, etc. have been reported<sup>66-71</sup>. An improved synthesis of chalcones under ultrasound irradiation has been reported by Li et.al.<sup>72</sup>. The yields were 52-97% and 83-98% respectively with pulverized KOH and KF-Al<sub>2</sub>O<sub>3</sub>.

catalysts in alcoholic solvent. An improved preparation of ionic liquids by ultrasound has been reported<sup>73</sup>. of sonication with other techniques e.g. phase transfer and photocatalysis, gives best results. Ultrasound technique is also useful in treatment of various pollutants. Sonochemical degradation of toxic halogenated organic compounds volatile pollutants in natural ground water<sup>74</sup>, 2,4,6-trichlorophenol in presence of TiO<sub>2</sub> Catalyst<sup>75</sup>, textile dyestuff<sup>76</sup> have been reported.

#### 4. Microwave Chemistry

Microwaves have wave length between 1cm and 1m (frequencies 30 GHz to 300 Hz). These are similar to frequency of radar and telecommunication devices. In order to avoid interference with these systems, the frequency of radiation that can be emitted by household and industrial microwave oven is regulated and most of the appliances operate at a fixed frequency of 2450 MHz. In 1986 two pioneering publications<sup>78</sup> appeared, that described several synthetic organic reactions conducted in domestic microwave oven.



**Fig.6**

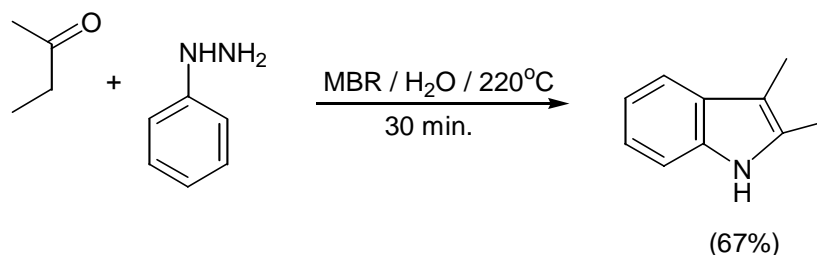
Ultra sound : 91% yield, no exothermic, no iodine  
No ultrasound ; 50% yield, unpredictable exothermic, iodine

Ultrasonic synthesis gives excellent yield compared to other reactions. Combinatin The use of microwave energy<sup>79</sup> instead of convential heating, often results in good yields in very short time. Lewis<sup>80</sup> stated enhancement of a chemical reaction in microwave as compared to conventional heating. Reaction can mainfest in several ways including:

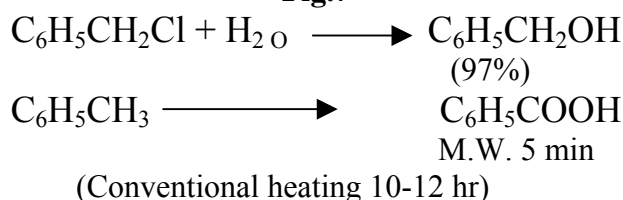
- Highly accelerated reaction time
- Improved yield in many cases
- Stereo / regioselectivity in some cases
- Reduction in side products.
- Limited amount of solvents needed as reaction medium.
- Successful product formation in some reactions that fail under conventional conditions.
- Simplification and improvement of classical synthetic method etc.

A recent survey shows that mere than a thousand publications have appeared on microwave mediated chemical reactions<sup>81</sup>. Microwave heats some certain substances not others due to selective absorbtion of microwave by polar molecules. Reactions can be classified in two catagories in microwave : (a) Reaction with solvent (b) Solvent free reactions.

Various type of reactions are conducted in microwave. 2,3-Dimethyl indole was obtained with 67% yield from phenylhydrazine and butane -2- one at 220°C for 30 min<sup>82</sup>(Fig.7).

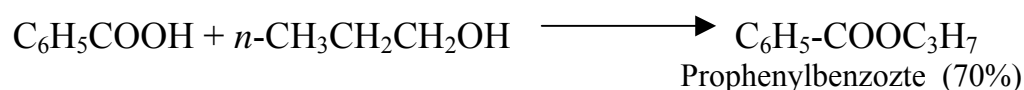


**Fig.7**



Hydralysis of benzyl chloride into benzyl alcohol takes 3 min in microwave while conventional method takes 35 min<sup>83</sup>.

Various types of oxidation<sup>84-86</sup> can be carried out in MW, e.g. In microwave some organic reactions can be carried out with the use of organic solvent like esterification of alcohol<sup>87</sup>, esterification of benzyl ethers using  $\text{Ln Br}_3$ <sup>88</sup>. Fries rearrangement<sup>89</sup>, orthoester claisen rearrangement<sup>90</sup>, Diels-Alder reaction, decarboxylation<sup>91</sup>, Chalcones synthesis, aziridine synthesis<sup>92,93</sup>.



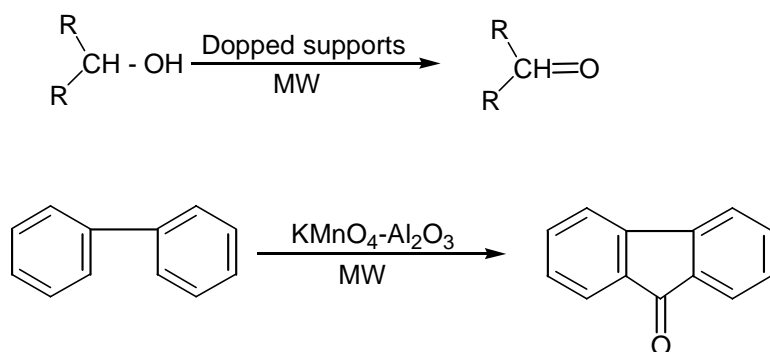


Fig. 8

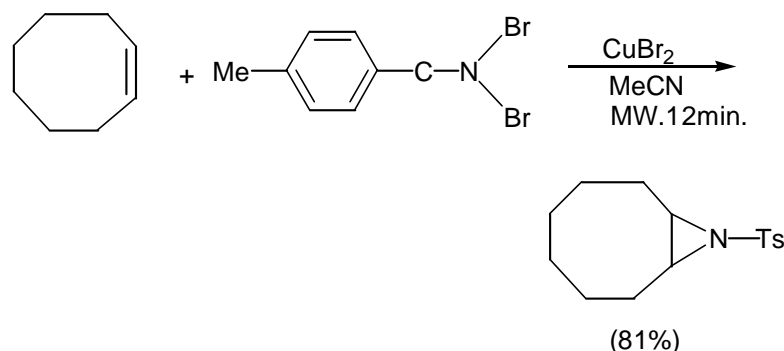
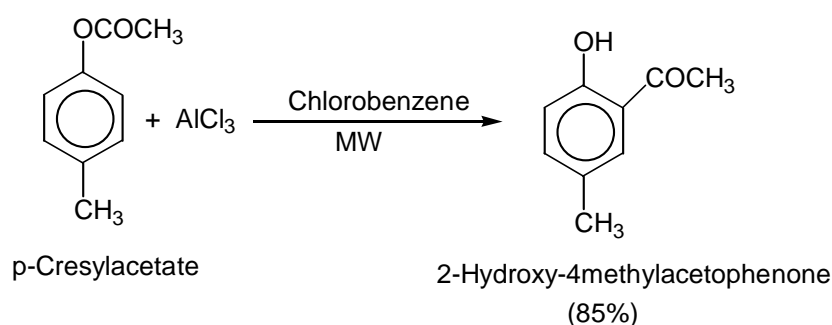
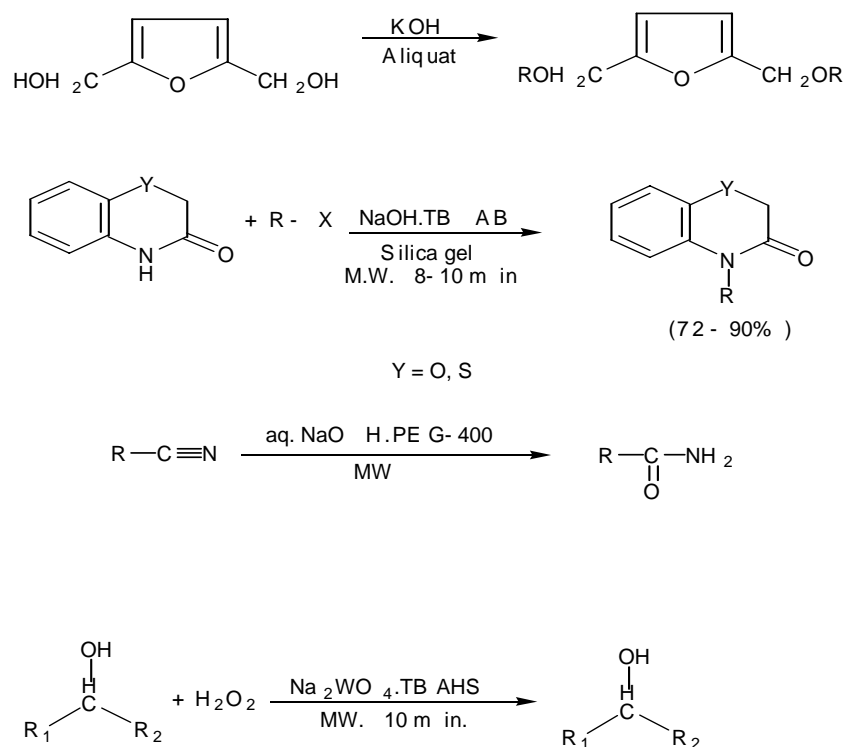


Fig. 9

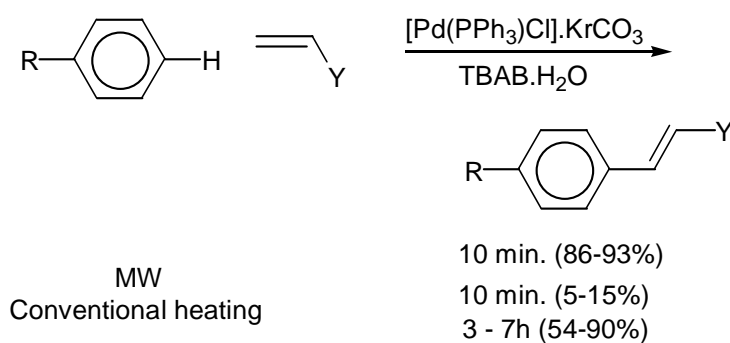
Hydrogenation of  $\beta$ -lactams using ammonium formate as hydrogen donor and Pd/C as catalyst has been described by Bose and co-workers<sup>94</sup>. Using solid support various organic reactions<sup>95,96</sup> can be carried out in microwave. Cyclo condensation of N(carbo trifluoro methyl) ortho arylene diamine<sup>98</sup> on clay KIO in dry media under MW irradiation for 2 min. give high yield while by classical heating only traces of heterocycles are observed<sup>97</sup>.

Condensation of  $\beta$ -formyl enamides with cyano methylenes under microwave irradiation is catalyzed by basis alumina to afford fused pyrimidines in excellent yields in very short time<sup>99</sup>. Hantzsch dihydropyridine synthesis<sup>100</sup> and oxidation of  $\beta$ ,  $\beta$ -disubstituted enamines over  $\text{KM}_2\text{O}_4\text{Al}_2\text{O}_3$ <sup>101</sup> is also reported in MW with shorter time and high yield as compared<sup>102</sup>, thiadiazepines synthesis<sup>103</sup>, carbohydrate glycosylations<sup>104</sup> can be carried out in MW by using solvent.

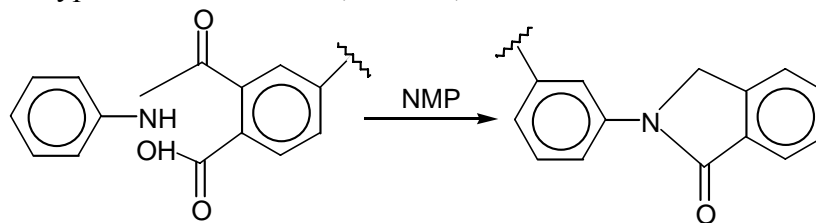
Reaction of carboxylic acid with benzyl halides does not occur when heated conventionally but could be performed in MW by using phase transfer catalyst some important organic reactions like ester synthesis<sup>105, 106</sup>, ether synthesis<sup>107</sup>, N-alkylation of benzoxazinones and benzothiazinones<sup>107</sup>, hydrolysis of nitriles<sup>108</sup>, oxidation of primary and secondary alcohol<sup>109</sup> can be done in MW.

**Fig. 10**

Heck cross coupling reaction<sup>110</sup> can be done in same way under solventless liquid-liquid phase transfer catalytic conditions in presence of potassium carbonate.

**Fig. 11**

Aromatic aldoximes were converted to the corresponding nitriles in the presence of a molecular sieve type modified zeolite, Ersorb, under solvent free condition<sup>111</sup>(Fig.12).

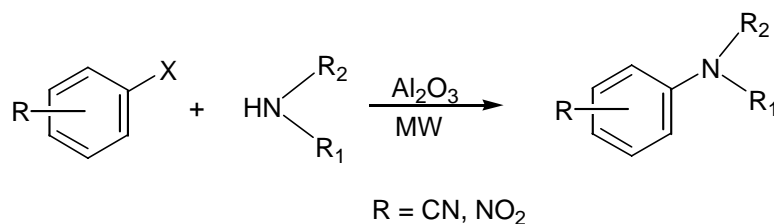


NMP, N-methyl pyrrolidinone

**Fig. 12**

A novel and efficient synthesis of N-arylamines by the reaction of activated aryl halides with secondary amines in the presence of basic  $\text{Al}_2\text{O}_3$  under microwave irradiation in solvent free conditions in reported<sup>112</sup>(Fig.13).



**Fig. 13**

A fast, highly efficient and environmentally friendly, solvent procedure under microwave irradiation using silica gel supported reagents for the synthesis of melamines is also developed<sup>113</sup>. There are some reactions which takes place in MW under solvent free conditions. Like deactivated and sterically hindered phenols have been acetylated with acetic anhydride using iodine as catalyst in an ecofriendly process<sup>114</sup>.

Traditionally synthesis of molecules involves use of chemicals, which are hazardous and also put at risk both the human beings and environment. Also, tightening and more universal legislation over the use of hazardous chemicals may indirectly hinder or prevent manufacturing of many important chemical products. Green chemistry as applied to chemical processes can be environmentally benign (in terms of reduction of energy, auxiliaries, waste, etc.) and should always lead to simplification of processes in terms of chemicals used and steps involved. Thus, if we can develop an efficient chemical synthesis (economically and technologically viable), which incorporates human and environmental good as its core principles, then we truly have sustainable green chemical processing.

### **SOLVENT FREE MICROWAVE ASSISTEDSYNTHESIS (ENVIRONMENT - FRIENDLY ALTERNATE )**

*The combination of solvent free procedures and microwave irradiation can be used to carry out a wide range of reactions with in short reaction times and with high conversions and selectivity. Yields and purity of the products as proved by GC analysis are generally improved when compared to those obtained by conventional heating. This approach is efficient, easy-to-perform, economic and less polluting as avoiding solvents. Some specific, non-purely thermal, effects of the radiation are often evidenced depending on the reaction mechanism and enhancement in polarity during the reaction progress.*

#### **Background Informations**

Among the most promising ways in procedures for Green Chemistry, solvent free techniques hold a strategic position as solvents are very often toxic, expensive, and problematic to use and to remove. It is the main reason for the development of such modern technologies. These approaches can also enable experiments avoiding the use of strong mineral acids (i.e. HCl, H<sub>2</sub>SO<sub>4</sub> for instance) that can in turn cause corrosion safety, mainpulation and pollution problems as wastes. These acids can be replaced advantageously by solid, recyclable acids such as clays (montmorillonites).

#### **Reactivity**

Accelerations of reactions can result from increasing concentrations in reactants when a diluting agent such as a solvent is avoided. As concentrations in reactive species are optimal, reactivity is notifceably increased and only mild conditions can be required. In several cases difficult reactions using solvents can be easily achieved under solvent free conditions. Another important advantage lied in the fact that higher temperatures, when compared to classical conditions, can be used in open vessels without the limitation imposed by solvent boiling points.

#### **Selectivity**

The layout of reacting systems can be increased when high concentrations/aggregation of charged species are involved. It can lead to some modifications in mechanisms resulting in a

decrease in molecular dynamics and induce subsequent special selectivities (stereo - regio - or enantioselectivity). Weak interactions can appear (such as T-stacking) which are usually masked by solvents, inducing further benefic consequences on selectivity.

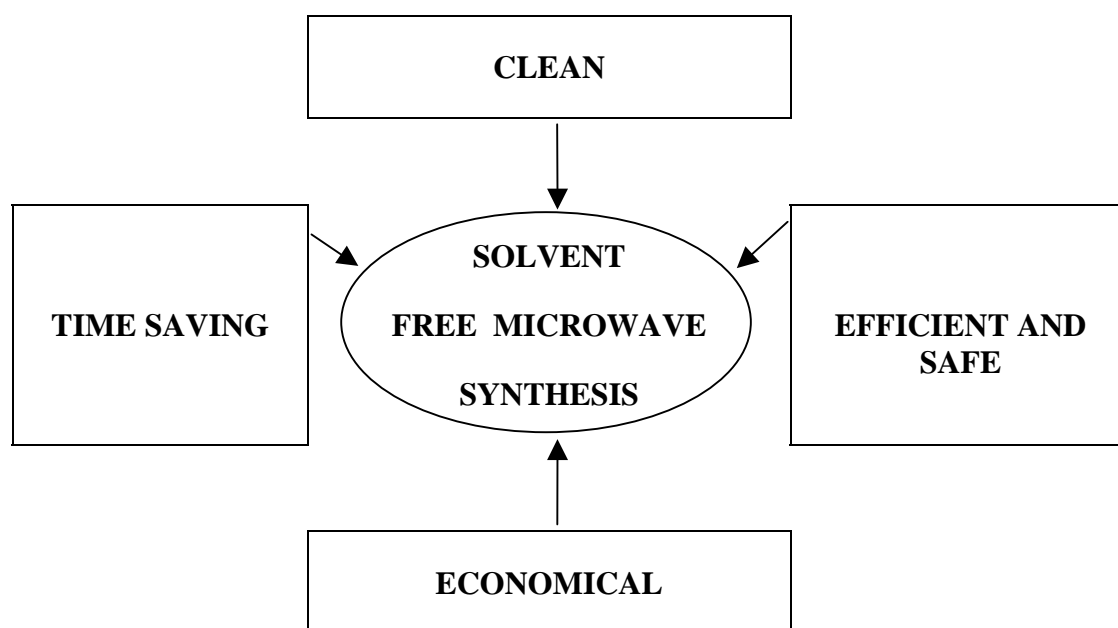


Fig. 14

### Reactions on Solid Mineral Supports<sup>115</sup>

Reactants are previously impregnated onto solid mineral supports such as aluminas, silicas and clays as neat liquids or via their solutions in an adequate organic solvent and further solvent removal. Reaction in "Dry media" is then performed between individually impregnated reactants, possibly under heating. At the end of reaction, organic products are easily removed by elution with diethyl ether or dichloro-methane and a simple filtration to eliminate the solids.

### Solid-Liquid Phase Transfer Catalysis (PTC)<sup>116</sup>

Reactions occur between neat reactant in quasi-equivalent amounts in the presence of a catalytic quantity of tetraalkylammonium salts or cation complexing agents. When the reaction is performed in the absence of solvent, the liquid organic phase consists of the electrophilic reagent then possibly the reaction product (Fig.1). Nucleophilic anionic species can be generated in situ by reacting their conjugated acids with solid bases of increased strength due to ion-pair exchange with  $R_4N^+X^-$ .

### Reactions without any solvent support, or catalyst<sup>117, 118</sup>

The heterogeneous reactions are carried between neat reactants in quasi equivalent amounts without any adduct. In the case of solid-liquid mixtures, the reaction implies either solubilization of the solid in the liquid phase or adsorption of the liquid on the solid surface as an interfacial reaction.

### Advantages of Microwave Exposure

From the interactions between materials and electromagnetic waves, the heat is produced according to an original process characterized by a heating taking place in the core of the materials without superficial overheating, with a subsequent very homogeneous temperature.

**Specific Effects of Microwaves** Microwaves can be used to promote many chemical syntheses. The materials-wave interactions produce some heating of the reaction medium by

polar molecules (solvents, reagents or complexes, solid supports). To these purely thermal effects can be added specific effects due to MW radiation.

### SYNTHESIS UNDER MICROWAVES<sup>120</sup> APPLICATIONS

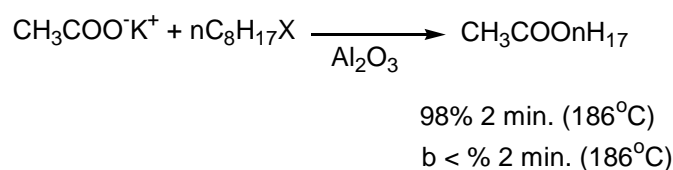
- Thermal reactions, which need high temperatures for long reaction times. Microwaves will bring acceleration of reactions, lower decomposition of products and consequently enhanced yield.
- Equilibrated reactions, with displacement of equilibrium by vaporization of small polar molecules.

### BENEFITS

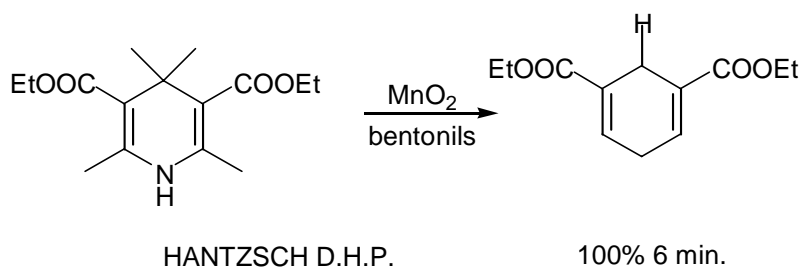
- Very rapid reactions.
- Higher degree of purity achieved due to short residence time at high temperatures.
- No local overheating, minor decomposition & minor occurrence of secondary reactions.
- Yield often better.
- Short reaction time.

### STRIKING EXAMPLES OF SOLVENT-FREE SYNTHESIS UNDER MICROWAVES<sup>119, 121, 122, 123, 124</sup>

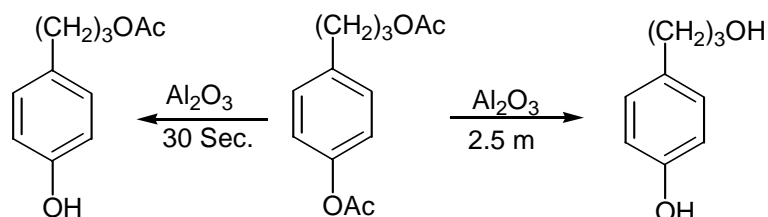
#### ○ Alkylation :

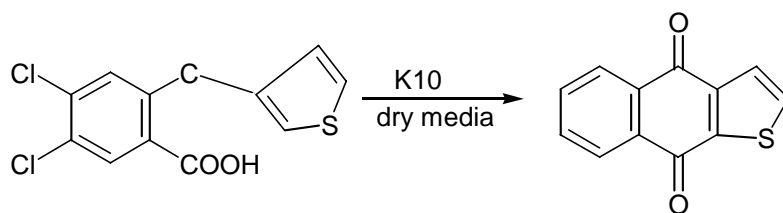


#### Oxidation:



#### Deacetylation



**Synthesis of Fused Anthraquinones Using Clay Under Microwaves :**

Classical method : PCl

5(1.5 eq) AlCl,  
1.5 eq Nitrobenzene

**Classical method :** PCl (1.5eq)AlCl, 1.5 eq Nitrobenzene  
4 Hrs.                      140°C                      70%

**Dry Media Condition :**

3 min.	320°C	MW	92%
1 hr.	320°C	Δ	4.1%

**Solvent-Free Esters Saponification**<sup>124,122</sup>

R	R <sup>1</sup>	Time (min.)	Final Temp. °C	Yield %	Time (min.)	Final Temp °C	Yield (%)
Ph	Me	1	205	96	1	205	90
Ph	nOct	2	210	94	2	210	72
	Me	2	240	87	2	240	38
	nOct	4	223	82	4	223	0

- Easy Saponification of Hindered Esters due to solvent free PTC<sup>+</sup> MW coupling
- M.W. specific effect is clearly substrate dependent

## CONCLUSIONS

When coupling to microwave irradiation, solvent free technique revealed to be of special efficiency as furthermOre clean and economic procedures. Serious improvements and simplifications over conventional methods originate from the repidity, the enhancements in yields and purities of products.

Non-purely thermal specific MW effects can be involved essentially when non-polar solvents, or better solvent free conditions, are concerned with polar mechanisms (more polar transition states when compared to their ground states) and for difficult reactions, which necessitate high energy of activation (late transition state according to Hammond postulate). In all cases, accurate controls of temperature and microwave emitted power are necessary to ensure reproducible and safe reactions.

## ACKNOWLEDGEMENT

The work of Singh research laboratory in this area of microwave chemistry during last eight years has been supported by C.S.I.R. New Delhi and U.G.C. Delhi. We wish to thank all members of microwave synthesis lab of Prof. Kidwai, Department of Chemistry, University of Delhi. for their essential contribution to microwave chemistry. One of the authors (A. Chaudhary) is thankful to Prof. A.K.Singh, Department of Chemistry, Indian Institute of Technology Delhi and Prof. D. Kishore, Department of Chemistry, Banasthali University for supporting this work. One of the authors (SKS) is very grateful to Dr. V. K. Agarwal, (Chairman) IET Group of Institutions, Alwar for providing him the opportunity to establish a *Computational & Green Chemistry Research Laboratory* at IET, Alwar.

## REFERENCES

1. G.H. Brundtland (chairman), World Commission on Environment and Development, Our common future, U.K. : Oxford University press, Oxford, 400 (1987)
2. T. Callins, *Towards sustainable chemistry Science*, **291**, 5501 (2001)
3. L. Desimone and F. Popoff, *Eco-efficiency : The business link to sustainable development*, MIT Press, Cambridge MA (2000)
4. O. Hutzinger, *Env. Sci., Poll. Res.*, **6**, 123 (1999)
5. R. Sanghi, '*Better living through sustainable green chemistry, current science*, **79**, 1662 (2000)
6. P. Anastas and J.C. Warner, *Green chemistry : Theory and Practise*. Oxford Science publications Oxford (1998).
7. T.J. Collins, Green Chemistry, *Macmillan, Encyclopedia of Chemistry*, New York, (1997)
8. P. Tundo and M. Selva, *Green Chemistry : Designing Chemistry for the Environment*, Williamson Eds. ACS Sym Series No.626, 81 (1996)
9. S.L. Wilkinson, "Green". Is practical, Even Profitable. No longer a luxurg. Green Chemistry becomes a central strategy for sustainable firms', *chem. Eng. News*, **75**, 35, (1997)
10. P.T. Anastas, Green Chemistry and the Rule of Analytical Methodology Development, *Critical Rev. Anal. Chem.* **29**, 167 (1999)
11. P.T. Anastas and C.A. Farris (Eds.), *Benign by Design : Alternative Synthetic Design for Pollution prevention*, A.C.S. Symposium. Ser N557. Washington DC, (1994)

12. D.C. Neckers D. H. Volamom and C. Von Bunau, *Adv. Photochem.*, 25 (1999).
13. K. Faber, *Bio transformations in Organic Chemistry : Text book* : 3rd completely rev. ed; springer verlag : Berlin; New York. (1997).
14. R. Sanghi, Microwave Irradiatum - A way to eco-friendly Green Chemistry, *Resonance*, 5, 3, 77 (2000)
15. P.A. Grieco, *Organic Synthesis in water*, Ed. Blackie, London, (1988).
16. P.G. Jessop and W. Leitner (Eds), *Chemical Synthesis in Supercritical Fluids* Wiley - VCH Weinheim.
17. P.T. Anastas and T.C. Williamsion, *Green Chemistry : Grontiers in Chemical Synthesis and processes*. Oxford University Press Oxford (1988).
18. P. Tundo and P.T. Anastas, *Green Chemistry : Challenging Perspectives*, Oxford University, Press Oxford (2000).
19. R. Ryan Dupont, L. Theodore and K. Ganesan, *Pollution Prevention*, Lewis Publishers New York (2000).
20. P.T. Anastas and J.C. Warner, "*Green Chemistry : Theory and Practice*", Oxford University Press, Oxford (1998).
21. T.J. Collins, "*Green Chemistry, Encyclopedia of Chemistry*", Macmillan, New York (1997).
22. A. Bhattacharya *Prog. Polym. Sci.*, 25, 371(2000).
23. S.L. Willikinson, *Chem. Eng. News*, 75, 35 (1997).
24. P.T. Anastas, *Critical Rev. and Chem.*, 29, 167 (1999).
25. P.T. Anastas and C.T. Farris (eds.), "*Benign by Design : Alternative Synthetic Design for Pollution Prevention*", ACS Symp., Washington, D.C. 557 (1994)
26. C.E. Wayne and R.P. Wayne "*Photochemistry*" Oxford University Press, Oxford (1996)
27. A. Bomben, M. Selva and P. Tundo *J. Chem. Res. (s)*, 448 (1997).
28. M.C. Cann and M.E. Connelly, *Real-World Cases in Green Chemistry*, American Chemical Society, Washington (2000).
29. Micell Technologies, Website : [www.micell.com](http://www.micell.com) accessed Dec.(1999).
30. J.A. Hall, L.D. Vuocolo, L.D. Suckling, C.P. Horwity, R.W. Allison, L.J. Wright and T. Collins. "*Proceedings of the 53rd APPITA Annual Conference*", April 1999, Rotorua, New Zealand.
31. C.A. Eckert et.al., 'Clean solutions for chemical synthesis', *Chem and Industry* 3, 94 (2000).
32. J.A. Armer, 'Energy efficiency and the Environment : Opportunities for catalysis, *J. Appl Cat A.*, 3, 194 (2000)
33. P.E. Savage, 'Heterogeneous catalysis in supercritical water; *Catalysis today*, 62, 167, (2000).
34. R.A. Sheldon et.al. 'Green catalytic oxidation of alcohols' in Water', *Science*, 286, no.5485, 1636, (2000).
35. S.A. Galena, *Chem. Soc., Rev.*, 26, 233 (1997).
36. M. Poliakaff et.al., 'A supercritical success story', *Chem and Indus*, 19, 750, (1999).
37. C.M. Wai, F. Hunt and X. Chem., 'Chemical Reaction in supercritical CO<sub>2</sub>' *J. Chem. Ed.*, 75, 12, 1641 (1999).
38. O.M. Alfano et.al., 'Photocatalysis in water environment using artificial and solar light,' *Catalysis Today*, 58, 2, 199 (2000).

39. Pdogano et.-al., 'continuous green biocatalytic processes using ionic liquids and supercritical carbon dioxide', *Chem commun*, 692 (2002).
40. B. Cook et.al., 'Fuel Cells power for the future,' *Education in chem*, **36**,5,123, (1999).
41. G.L.N. News letter, **9**,3, April (2001).
42. The ultimate "Green Car", 3 Dec. *The Hindustan Times, Reuters Tokyo* Dec.2, Japan Launches fuel cell cars (2002).
43. (a) V. Rammurthy and K.S. Shanze "*Organic photochemistry*", Dekker, New York (1997).
44. J.H. Krieger and M. freemantle, *Chem. Eng. News*, **7**, 15 (1997).
45. G.A. Epling and O. Wang, "*Benign by design*". (eds.) P.T. Anastus and C.T. Farris ACS Symb. 577, Washington DC, 64 (1994).
46. B. Heller and G. Dehme, *J. Chem. Sec. Chem. Commen*, 197 (1995).
47. P. Zurer, *Chem. Eng. News*, **1**, 5 (1996).
48. P. Pichat *Catal, today*, **19**, 313 (1994).
49. G.A. Kraus, M. Kirihara and Y. Wu "*Benign by Design*" (eds.) P.T. Anastas and C.T. Farris, ACS Symp. 577. Washington DC, 76 (1994).
50. T. Lqaxashi, K. Konishi and T. Aida. *Chem. Lett*, 1039 (1998).
51. R. Rao, W.S. Dadson, T.C. Bauton and Y. hi, preprint papers, Natt, Mut. Acs Div. *Environ. Chem.*, 4118 (1994)
52. T. Ruther, A.M. Bond and W.R. Jackson, *Green Chemistry*, **5**, 364 (2003).
53. C. Schiel, M. Odgemouer. J. Ortner and J. Mattay *Green chemistry*, **3**, 224 (2001).
54. C.J. Evans, G.P. Nicholson D.A. Faith and M.J. Kan, *Green Chemistry*, **6**, 196 (2004).
55. J.D. Genders and D. Pietcher, *Chem Ind.*, 682 (1996);
56. N. Takano, M. Ogata and N. Takeno, *Chem. Lett*, 85 (1996).
57. G. Parkinson, *Chem, Eng.*, **103**, 23 (1996)
58. J. Utley, *Chem. Ind.*, 215 (1994).
59. K. Fujimoto, Y. Tokuda, H. Mackawa, Y. Matsubara T. Mizuno and L. Nishiguchi. *Tetrahedron*, **52**, 3889 (1996).
60. S. Chardon - Nobdat, I.M.F. De Oliveira. J.C. Moutet and S. Tingey, *J. Mol. Catal. A : Chem.*, **99**, 13 (1995).
61. N. An. J.K. Hong. P.N. Pintauro, K. Warner and W Neff. *J. Am. Oil. Chem., Soc.*, **75**, 917 (1998).
62. A.S.C. Chan, T.T. Huang. J.H. Wagenknecht and R.E. Miller. *J. Org. Chem.*, 60, 742 (1995)
63. M. Freemantle, *Chem. Eng. News*, **9**, 11(1997).
64. D.H. Bremner, A.E. Burgess and F.B. Li, *Green Chemistry*, **3**, 126 (2001).
65. P. Manishanrar, S. Viswanathan and C. Rani. *Green Chemistry*, **5**, 270 (2003).
66. J.M. Khurana, P.K. Sahoo and G.C. Murkop, *Synth. Commun.*, 2267 (1990).
67. D.S. Krislol, H. Klotz and R.C. Parker, *Tetrahedron helt.*, **22**, 407 (1981).
68. T. Ando, J. Kuwate and T. Hanatusa, *Synthesis*, 637 (1983).
69. J. Ezquema and J. Alvarez - Bullis, *J. Chem. Soc., Chem. Commun*, 54 (1984).
70. I. Mendez G.C. Trigo and M.M. Solhumber *Tetrahedron Lett.*, **27**, 3285 (1986)
71. V.K. Ahluwalia and Renu Aggarwal, "*Organic Synthesis : Special Techniques*". Narosa Publishing House, New Delhi, 116 (2001).
72. J.T. Li, W.Z. Yang, S.X. Wang : S.H. Li and T., Shuang, *Utrasonics Sonochemistry*, **9**, 237 (2002).

73. J.M. Hevegue, J.L. Luche. C. Petrier, R. Rouse and W. Bonarth, *Green Chemistry*, **3**, 126 (2001).
74. K.C. Teo, Y. Xu and C. Yang, *Ultrasonics Sonochemistry*, **8**, 241 (2001).
75. D. Reters, *Ultrasonics Sonochemistry*, **8**, 221 (2001).
76. A.B. Pandit, P.R. Gogate and S. Mujumdar. *Ultrasonics Sonochemistry*, **8**, 227 (2001).
77. G. T. Ezeanli - Guyer and N.H. Ince. *Ultrasonics Sonochemistry*, **10**, 231 (2003).
78. (a) R. Gedye, F. Smith, R. Westway, H. Ali L. Baldisera, L. Laborge and L.J. Ronsell, *Tetrahedron Lett.*, **27**, 279 (1986). (b) R.J. Giguere, T.L. Bray, S.M. Dunean and G. Majetich, *Tetrahedron Lett*, **27**, 4945 (1986).
79. (a) H.M. Kingston and S.J. Haswell (eds), "*Microwave Enhanced Chemistry: Fundamentals, Sample preparation and Applications*", American chemical society, Washington DC (1997).
80. L.R. Spauss and R.W. Trainer, *Aust., J. Chem.*, **48**, 1665 (1995).
81. R.N. Gedye. W. Rank and K.C. Westway, *Can., J. Chem.*, **69**, 700 (1991)
82. R.N. Gedye F.E. Smith and K.C. Westaway, *Can. J. Chem.*, **66**, 17 (1988).
83. R.S. Varma and R.K. Saini, *Tetrahedron Lett.*, **38**, 2623 (1997).
84. A. Loupy, D. Monteux, A. Petit, J. Aizpurar, E. Doninquilz and C. Plomu, *Tetrahedron Lett.*, **37**, 8177 (1996).
85. R.N. Gedye, F. Smith, K. Westaway, H. Ali, I. Baldisera, L. Laberga and J. Rousel, *Tetrahedron Lett.*, **27**, 279 (1986).
86. J. Gulin and G. Guncheng, *Synth. Commun.*, **24**, 1045 (1994).
87. V. Sridar and V.S. Sundara Rao, *Indian J. Chem.*, **33**, 184 (1994).
88. A. Srikrishna and S. Nagaraju. *J. Chem. Soc., Perken Trans.* **1**, 311 (1992).
89. G.B. Jones and B.J. Chapman, *J. Org. Chem.*, **58**, 5558 (1993).
90. B.M. Chanmda, R. Vyas and A.V. Bedckar, *J. Org., Chem.*, **66**, 30 (2001).
91. A. Saoudi, J. Hemelin and H. Benhaona, *J. Chem., Res (S)*, 492 (1996).
92. A.K. Bose, B.K. Banik, K.J. Barakal and M.S. Manhas *Syn. Lett.*, 575 (1993).
93. I. Almena. A. Diaz - Qrtiz, E. Diez-Barra, A. Hos and A. Loupy. *Chem. Lett*, 1996, 333, S. Caddick, *Tetrahedron*, 10400 (1995).
94. B.C. Ranu, A. Hajra and U. Jana, *Tetrahedron Lett.*, **41**, 531 (2000).
95. F. Teier - Bouullet, R. Latouche and J. Hamelin, *Tetrahedron Lett.*, **34**, 2123 (1993).
96. K. Bougein, A. Loupy, A. Retit B. Daou and M. Soufiaoui, *Tetrahedron*, **57**, 63 (2001).
97. U. Sharma, S. Ahmed and R.C. Boruah, *Tetrahedron Lett*, 2001, **41**, 3493.
98. L. Ohberg and J. Westman, *Syn. Lett.*, **8**, 1296 (2001).
99. H. Benhaliliba, A. Derdour, J.P. Bazureau, F. Tesiler Bouullet and J. hamelin, *Tetrahedron Lett.*, **39**, 541 (1998).
100. M. Kidwai. P. Supra, K.R. Bhushan and P. Misra, *Synthesis*, **10**, 1509 (2001).
101. M. Kidwai, P. Sapra, P. Misra, R.K. Saxena and M. Singh, *Bioorg. Med. Chem*, **9**, 217 (2001).
102. C. Hlmousin, J. deophan, A. Petit, A. Loupy and G.J. Lukaes, *Carbohydr. Res.*, **16**, 327 (1997).
103. G. Bram, A. Loupy and M. Majdoub, *Synth, Commun.*, **20**, 125 (1990).
104. A. Loupy, A. Petit, M. Ramdani, C. Yuanaef M. Majdoub, B. Habiad and D. Villemin, *Lah., J. Chem.*, **71**, 90 (1993).
105. M. Majdoub, A. Loupy, A. Petit and S. Roudesli, *Tetrahedron*, **52**, 617 (1996).
106. P.M. Bendale and B.M. Khadilkar, *Synth. Commun.*, **30**, 1713 (2000).



- 107.D. Bogdal and M. Lukasiewicz, *Synlett*, 143 (2000).  
108.J.X. Wang, Z. Liu. Y. Hu. B. Wil and L. Bai, *J. Chem. Res (s)*, 484 (2000).  
109.A. Hegedus, A. Cwik, Z. Hell, Z. Hervath, A. Esek and M. Uzsoki, *Green Chemistry*, **4**, 618 (2002).  
110.J.S. Yadav and B.V. Subba Reddy, *Green Chemistry*, **2**, 115 (2002).  
111.V.K. Kurteva and Carlos A.M. Afonso, *Green Chemistry*, **6**, 183 (2004).  
112.N. Deka A.M. Moriotte and A. Boumedjel, *Green Chemistry*, **3**, 263 (2001).  
113.R. Smith, *Solid Supports and Catalysts in organic synthesis*, Ellis Horwood PTR Prentice Hall Chichester (1992).  
114.F. Toda, *Chem. Rek.*, **100**, 1025 (2000).  
115.Y. Sasson and R. Neumann, *Handbook of Phase Transfer Catalysis*, Blackie Academic and Professional (Chapman & Hall), London (1997).  
116.A. Loupy, *Modern Solvents in Organic Synthesis*, Wiley-VCH, Weinheim, to be edited (2002).  
117.P. Lidstrom, J. Tierney, B. Wathey and J. Westman, *Tetrahedron*, **57**, 9225, (2001).  
118.R.S. Varma, *Green Chem.*, **1**, 43 (1999).  
119.S. Deshayes, M. Liagre A. Loupy, J.L. Luche & A. Petit. *Tetrahedron*, **51**, 10851 (1999)  
120.R.S. Varma, in "*Microwaves in Organic Synthesis*" 181, Wiley-VCH, New York (2002).  
121.A. Stadler, C.O. Kappe, *J. Comb. Chem.* **3**, 624 (2001).  
122.R.S. Varma, D. Kumar, *Tetrahedron Lett.* **40**, 7665 (1999).  
123.R.S. Verma, D. Kumar, *J. Chem. Soc., Perkin Trans.* **1**, 1755 (1999).  
124.R.S. Verma, K.P. Naiker, *Tetrahedron Lett.* **39**, 8437 (1998).

(Received: 15 October 2007

Accepted: 14 January 2008

RJC-145)

### Invitation

**G**REEN CHEMISTRY is the need of today's life. It is our prime duty to save our planet from the *evil* Pollution. Chemists all over the World are fighting for this Noble cause.

We invite all researchers of *GREEN CHEMISTRY* to contribute their research finding to **RASĀYAN** and share their views mutually on a common platform here. We welcome the research papers of *GREEN CHEMISTRY*. We shall include such papers on priority.....**Come, let us save The Earth.**

*-Editor*

