

# Green Chemistry in Organic Synthesis

Nikita Ajinkay Bagade<sup>1</sup>, Ajinkay Rajendra Bagade<sup>2</sup>

**Abstract-** Organic chemistry has played a vital role in the development of various molecules that are used in medicine, agrochemicals and polymers. These molecules are synthesized in industries that adopt a synthesis process that is cost-effective; no attention is paid for the release of harmful chemicals. The development of concepts for "Green Chemistry" and the main principles of the field are reviewed. Examples of the application of these principles in various areas of chemistry is covered. Frequently used alternative solvents (green solvents – water, PEG, perfluorinated solvents, supercritical fluids) in preparative organic chemistry are described. Solvents such as water are of considerable importance because they are non-hazardous, easily renewable and reduce unnecessary waste of energy. Other recoverable solvents like acetone, alcohol, methanol etc. fall under green chemicals. Green chemistry also includes catalysts that promote chemical reactions without causing a dangerous effect and are renewable. All aspects of green chemistry, improving the level of research in chemistry and advanced techniques make experimental work easier for new researchers. This is a positive and harmless growth in the field of chemistry.

**Keywords-** Green chemistry, Principles of green chemistry, Green solvents, organic synthesis, Green approaches.

## I. INTRODUCTION

Green chemistry addresses our future challenges in working with chemical processes and products by inventing new reactions that can maximize desired products and minimize side products, designing new synthetic schemes that can simplify chemical manufacturing operations, and finding inherently greener solvents organic and ecological. ecologically sound. Green chemistry is defined as "The practice of chemical science and production in a manner that is safe, sustainable, and non-polluting to the environment and that consumes minimal amounts of materials and energy while producing little or no waste." When the chemical reaction, production, processing, use and eventual disposal of chemical products are found to cause harm, when done incorrectly have led to the practice of green chemistry.

The main goal of green chemistry and green chemical engineering is to modify or completely redesign chemical products and processes to minimize waste and the use or

generation of hazardous materials. Those who follow the 12 Principles of Green Chemistry acknowledge that they are responsible for any effects on the world that their chemicals or chemical processes may have. Green chemistry increases profits and promotes innovation while protecting human health and the environment. It is also economically regressive and inhibits profits.

A green signal allows you to continue. Thus "green chemistry" indicates a branch of chemistry that is acceptable and the most valuable. Green chemistry is a synthetic process that avoids many technical, environmental problems, hazardous atmosphere, and the formation of specific products with high yields, avoids the use of hazardous chemicals, achieves a more economical state, reduces the number of by-products, and creates an environment-friendly atmosphere.

## II. CONCEPT OF GREEN CHEMISTRY

The concept of green chemistry introduced environmentally sound synthetic protocols for the synthesis of heterocycles, which have had a significant impact in many areas, such as the use of green solvents, solvent-free synthesis, sustainable catalytic materials, reduced energy consumption, improved atom economy, optimized reaction yields, the use of alternative energy sources, the introduction of multicomponent reactions (MCRs), ionic liquids and the design of highly efficient and time-efficient reactions that operate at ambient temp. Pollution and increasing energy demands have prompted the design of new synthetic protocols that meet the requirements of green and sustainable chemistry to support the synthesis of organic products.

The concept of Green Chemistry emerged in the US as a general one scientific program based on the interdisciplinary cooperation of research groups in universities, independent research groups, scientific societies and government agencies, with members of each of these bodies having their own program dedicated to reducing the level of environmental pollution. Green chemistry includes a new approach to the synthesis, processing and application of chemical substances, thereby reducing the danger to human health and environmental pollution.

## III. PRINCIPLES OF GREEN CHEMISTRY

A. Prevention of waste generation:

**It is better to prevent the generation of waste materials and/or by-products than to process or clean them.**

It is better to prevent the creation of waste than to treat it after it has been created. An example is the production of phenol. That used to be made from benzene using sulfuric acid and sodium hydroxide in a multi-step process with a yield of 78%; the reaction can be expressed as: Sodium sulfite is a by-product; it can be used in other processes. However, if there is no demand, it would mean this may not be the most suitable reaction for the production of phenol.

Another example of green synthesis is the synthesis of ibuprofen. The traditional synthesis of ibuprofen produces 60% waste. It is better to prevent the generation of waste materials and/or by-products than to process or clean them.

Organic syntheses in the absence of solvents. This principle gave rise to so-called "grinding chemistry", in which reagents are mixed without a solvent, sometimes simply by grinding in a mortar.

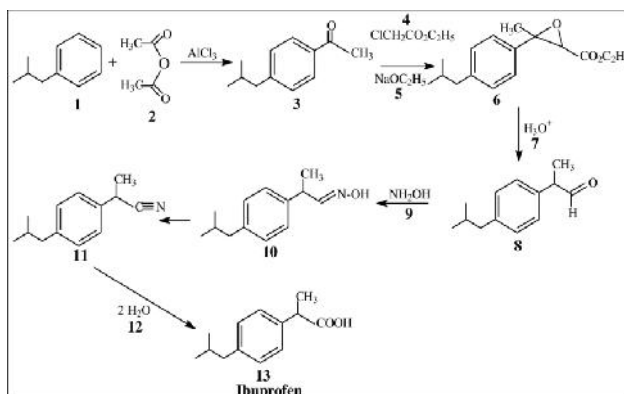


Fig: 02: Conventional method of synthesizing Ibuprofen

#### B. Atom Economy:

**Synthetic methods should be designed so that all products involved in the reaction process are included in the final product.**

Atom economy is a measure of the number of atoms from the starting material that are present in useful products at the end of a chemical process. Reaction byproducts that are not useful can lead to lower atom economy and more waste. Therefore, processes that maximize atom economy are preferred.

Atomic economy % =  $\frac{\text{Relative molecular weight of desired products}}{\text{Relative molecular weight of all reactants}} \times 100$

An example of a Diel Alder reaction with 100% atom economy

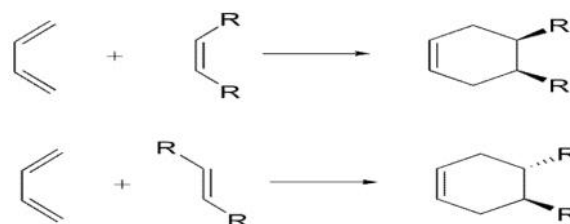


Fig: 01: Diels Alder reaction

The addition, condensation and rearrangement reactions will generally have higher atom economies than either elimination or substitution.



For example, the addition of chlorine to ethene, to form 1,2-dichloroethane (an important reaction in the manufacture of poly (chloroethene) (PVC)) has an atom economy of 100%:

However, if the product is hydrolyzed, the atom economy falls:



The first is an addition reaction; the latter is a substitution reaction.

#### C. 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.**

It is also important that the chemicals produced are safe for the environment. In all cases, the material should degrade into harmless products. Synthetic methods should, where possible, use or create materials with low human toxicity and environmental impact. For example, the synthesis of polycarbonate is carried out using phosgene ( $\text{COCl}_2$ ). To avoid phosgene, a dangerous chemical solid-state polymerization is carried out, which also leads to the formation of polycarbonate as part of green chemistry.

An example of this principle is the oxidation of cyclohexene to adipic acid with 30% hydrogen peroxide. Beneficial insects and predatory wasps are left unscathed by

Spinosad. The unique mode of action of Spinosad combined with a high degree of activity on the targeted pest, low toxicity to non-target organisms (including many beneficial arthropods) and resistance.

The management properties make Spinosad an excellent new tool for integrated pest control. Spinosad is an example of a technological development that shows how the creation and production of safer chemicals is possible. The means to achieve this goal are changes in chemical structure

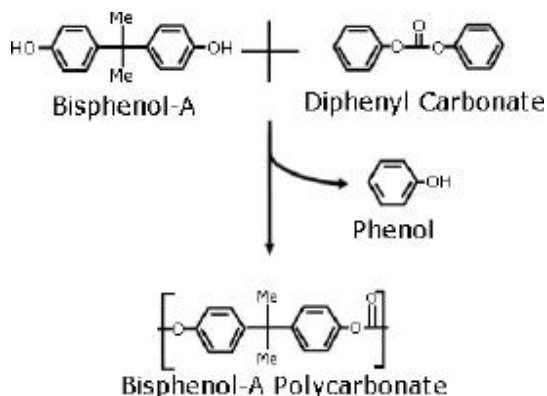


Fig: 03: Greenchemistry method of synthesizing Polycarbonate

#### D. Designing Safer Products:

**Product design should be safe from the point of view of human health and the environment.**

Designing safer chemical targets requires knowledge of how chemicals work in our bodies and the environment. In some cases, some degree of toxicity to animals or humans may be unavoidable, but alternatives must be sought. The toxic chemicals used, such as DEET repellent as an insecticide, bisphenol-A as a fabric softener, and some acid catalysts, require replacement to be on the safer side. In designing such requirements, safer chemicals are an important part of green chemistry, e.g. Zeolite H-FER solid acid catalysts, as Safer Catalyst 21.

#### E. Safer Solvents and Auxiliaries:

**The solvent chosen for the reaction should not pollute the environment or be hazardous to human health.**

Many chemical reactions require the use of solvents or other agents to facilitate the reaction. They can also be associated with a number of hazards such as flammability and volatility. Solvents cannot be avoided in most processes, but should be chosen to reduce the energy required for the

reaction, have minimal toxicity, and be recycled if possible. Solvents are also major contributors to the overall toxicity profile and therefore constitute the majority of materials of concern related to the process. Water is also able to speed up the process even when the diene and dienophile are linked.

#### Green Solvents

Organic solvents used in numerous syntheses are quite dangerous for the environment. VOCs are released into the environment by evaporation or runoff in substantial quantities because they are used at much higher rates than the reagents themselves. A new approach to overcome this problem is to perform chemical reactions in the absence of such media, i.e. without solvents or using non-volatile solvents that are harmless to humans and the environment. The ideal "green" solvent should have a high boiling point and must be non-toxic, dissolve a range of organic compounds, cheap and of course recyclable. Obviously, such requirements strongly limit the choice of a substance or class of compounds as a green solvent. Considerable efforts by research groups worldwide have led to the development of good alternatives to common organic solvents, including supercritical fluids, ionic liquids, low melting point polymers, perfluorinated (flour) solvents and water.

Flour liquids have quite unusual properties, which include high density, high stability (mainly due to the stability of the C-F bond), low solubility, and extremely low solubility in water and organic solvents, although they are miscible with the latter at higher temperatures. temperature. The low solubility of perfluorinated solvents can be explained by their low surface tension, weak intermolecular interactions, high densities and low dielectric constants.

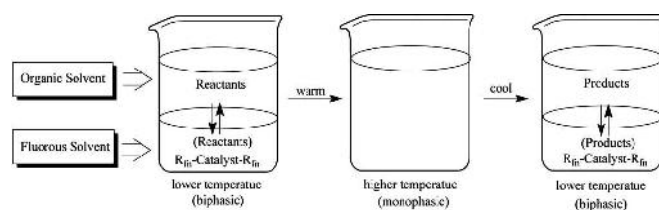


Fig: 04: organic syntheses in fluororous solvents

Water is the basis and carrier of life. For millions of years, water prepared the Earth for the development of life. Water is a solvent in which numerous biochemical organic reactions (and inorganic reactions) take place. All these reactions affect living systems and inevitably took place in an aqueous environment. On the other hand, modern organic chemistry was developed almost entirely on the premise that organic reactions must often be carried out in organic solvents.

Only in the last two decades or so have people refocused their attention on carrying out organic reactions in water.

#### *F. Design for Energy Efficiency:*

**The energy requirements involved in the chemical processes should be accounted for, in view of their influence on the environment and the economic balance, and the energy requirements should be diminished. If possible, the chemical processes should be carried out at room temperature and atmospheric pressure.**

The energy requirements of chemical processes should be recognized in terms of their environmental and economic impacts and should be minimized. If possible, synthetic methods should be carried out at ambient temperature and pressure. The reaction energy can be photochemical, microwave or ultrasonic radiation. Currently, there is a boom in the use of these green energy sources, and this is associated with a significant reduction in reaction time, higher yields and very often higher product purity.

#### *G. Use of Renewable Feedstocks:*

**The intermediates and materials should be renewable rather than depleting (which is the case with, e.g., crude oil) whenever this is technically and economically advantageous.**

The renewable feedstock of biomass forms the basis of many successful industries such as pulp and paper and the wood industry. Crops grown for fiber, oils or other materials provide the necessary raw material for such industries. One renewable source of hydrogen is obtained from biomass such as water, natural gas, oil, hydrocarbon and organic fossil materials. Recently, glycerin has become increasingly available as a byproduct of biodiesel production, and this renewable feedstock has improved the production of epichlorohydrin, a widely used chemical for the production of epoxy resins<sup>25</sup>. Some other solvents that can be distilled, purified, and reused, such as acetone, methanol, ethanol, acetonitrile, etc., are considered green solvents. Interest in biodiesel as an alternative fuel has surged due to recent regulations requiring substantial reductions in hazardous emissions from motor vehicles as well as high oil prices. Biodiesel is biodegradable in water and non-toxic. It produces far fewer hazardous emissions (leaks less Sulphur, 80% less carbohydrates and 50% less particulate matter) when burned compared to Petro diesel. Biodiesel can be used in modern diesel engines without the need for engine modification. With a flash point of 160 °C, biodiesel is classified as a non-

flammable liquid. This feature makes it much safer in motor vehicle accidents compared to diesel and Petro petrol's.

#### *H.Reduce Derivatives:*

**Derivatizations, such as protection/deprotection and various other modifications, should be decreased or avoided wherever possible since these stages require additional amounts of reagents and waste products could be formed.**

Unnecessary derivatization (use of blocking groups, protection/deprotection, and temporary modification of physicochemical processes) should be minimized or avoided if possible, as such steps require additional reagents and may generate waste. An alternative that has been explored in some processes is the use of enzymes. Because enzymes are highly specific, they can be used to target specific parts of a molecule's structure without the need for protecting groups or other derivatives. Enzymes are so specific that they can often react with one site of a molecule and leave the rest of the molecule alone, so protecting groups are often unnecessary.

An excellent example of the use of enzymes to avoid protecting groups and purification processes is the industrial synthesis of semi-synthetic antibiotics such as ampicillin and amoxicillin. In the first industrial synthesis, penicillin G (R=H) is first protected as its silyl ester [R = Si(Me)<sub>3</sub>], then reacts with phosphorus chloride at -40 °C to form chlorimidate 1 followed by hydrolysis to give the desired 6-APA, from which semi-synthetic penicillin's are produced

#### *I. Use of Catalysts:*

**It is well known that catalysts increase substantially the chemical process rates, without their consumption or insertion into the final products.**

However, a zeolite catalyst with acidic sites is now used again for the rearrangement. The zeolite is regenerated and saves the use and subsequent waste of sulfuric acid. Catalytic reagents are better than stoichiometric reagents. It has a higher activation energy that increases reaction selectivity, lowers the transformation temperature, increases the conversion product yield, and reduces reagent-based waste.

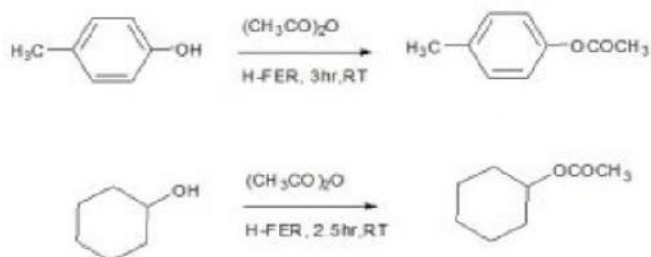


Fig: 05: Green chemistry method of synthesis reducing waste and increasing yield

#### *J.Design of Degradable Products:*

**The design of the final chemical products should be such that, after fulfilling their functions, these products should easily degrade to harmless substances that do not cause environmental**

This approach is illustrated by the creation of biodegradable "green" polymers. Conventional polymers such as polyethylene and polypropylene persist for many years after disposal. Built for the long haul, these polymers seem unsuitable for applications in which plastics are used for a short time before disposal. In contrast, biodegradable polymers (BPs) can be disposed of in a bioactive environment and degraded by the enzymatic action of microorganisms such as bacteria, fungi and algae. Global consumption of biodegradable polymers increased from 14 million kg in 1996 to an estimated 68 million kg in 2001. Target markets for BP include packaging materials (garbage bags, packaging, bulk foam, food containers, films, laminated paper), disposable non-woven fabrics (artificial fabrics) and hygiene products (diapers, cotton swabs), consumer goods (fast food containers, containers, egg cartons, razor handles, toys) and agricultural tools (mulch sheets, flower pots)

#### *K.Real Time Analysis for the Avoidance of Contamination. Increase in the Role of Analytical Chemistry in Green Technologies:*

**Analytical methodologies should be developed in such a way that the process can be monitored in real time.**

New analytical tools are needed to monitor industrial processes in real time and to prevent the formation of toxic materials. The growing field of process analytical chemistry is primarily focused on obtaining analytical data close to production operations. Real-time field measurement capability is required for continuous environmental monitoring, which would replace the conventional approach of sampling and transporting to a central laboratory.

The sensor in analytical chemistry will play a particularly important role, but in the future it is expected that traditional and instrumental analytical chemistry will also play a vital role in green technologies.

Environmental and industrial interest in biosensor technology has been driven by the need for faster, simpler, cheaper and better monitoring tools. Microfluidic analytical devices in which there are many sample handling processes integrated with the actual measurement step on a microarray platform, has recently received considerable interest. For obvious reasons, such devices are referred to as "lab-on-a-chip" devices. In this regard, complete assays, including sample pretreatment (eg, preconcentration/extraction), chemical/biochemical derivatization reactions, electrophoretic separations, and detection, were performed on single microarray platforms.

The dramatic miniaturization and integration of chemical assays make these analytical microsystems particularly attractive as "green analytical chemistry" screening tools and hold considerable promise for faster and easier on-site monitoring of priority pollutants. A large number of environmental applications of CE/EC microarrays have already emerged, including the rapid separation and detection of chlorophenols, nitroaromatic explosives, hydrazine and organophosphate pesticides.

The revolution in green chemistry has brought new challenges and exciting opportunities for analytical chemistry and for the development of greener analyzes in general.

It is worth noting at this point that Van Akan et al. developed the Eco Scale, a semi-quantitative tool for selecting an organic product based on economic and ecological parameters. A new post-synthesis analysis tool is introduced that evaluates the quality of an organic product based on yield, cost, safety, conditions and ease of processing/cleaning.

#### *L.Inherently Safer Chemistry for Accident Prevention:*

**The reagents used to carry out chemical processes should be chosen with caution in order to avoid accidents, such as the re-lease of poisonous substances into the atmosphere, explosions and fires.**

Safety can be defined as the control of recognized hazards to achieve an acceptable level of risk. The substances and form of the substance used in the chemical process should be chosen to minimize the possibility of chemical accidents, including spills, explosions and fires. Safer solvents such as water, liquid CO<sub>2</sub> or avoiding the use of solvents is part of

green chemistry. Diels–Alder reactions of pure reactive dienes and dienophiles are sometimes very energetic and therefore of limited preparative value. The addition of a limited amount of water in such a reaction makes it valuable by lowering its temperature, increasing the rate of formation, and producing a product of higher purity.

Oxidation of isatins to isatic anhydrides was achieved using a safe, cheap, stable and green urea/hydrogen peroxide complex oxidizing agent and ultrasound irradiation at room temperature. The oxidizing agent is safer than liquid hydrogen peroxide.

#### IV. ALTERNATIVE SOLVENTS IN ORGANIC SYNTHESIS-WATER

Water is the basis and carrier of life. For millions of years, water prepared the Earth for the development of life. Water is a solvent in which numerous biochemical organic reactions (and inorganic reactions) take place. All these reactions affect living systems and inevitably took place in an aqueous environment. On the other hand, modern organic chemistry was developed almost entirely on the premise that organic reactions must often be carried out in organic solvents. Only in the last two decades or so have people refocused their attention on carrying out organic reactions in water.

##### *Advantages*

##### *Costs*

Water is the cheapest available solvent on earth; the use of water as a solvent can make many chemical processes more economical.

##### *Safety*

Many organic solvents are flammable, potentially explosive, mutagenic and/or carcinogenic. Water, on the other hand, has none of these adverse properties.

##### *Synthetic efficiency*

In many organic syntheses, it may be possible to eliminate the need for protection and deprotection of functional groups, saving numerous synthetic steps. Water-soluble substrates can be used directly and this would be particularly useful in carbohydrate and protein chemistry.

##### *Simple operation*

In large industrial processes, the isolation of organic products can be done by simple phase separation. It is also

easier to control the reaction temperature because water has one of the highest heat capacities of any substance.

##### *Environmental benefits*

The use of water can alleviate the problem of organic solvent pollution because water can be easily recycled and is harmless when released into the environment (unless harmful residues are present).

Potential for new synthetic methodologies. Compared to reactions in organic solvents, the use of water as a reaction medium has been much less explored in organic chemistry. In addition, there are many opportunities to develop new synthetic methodologies that have not yet been discovered

#### V. WHERE DOES PUBLIC OPINION STAND ON CHEMISTRY?

Chemistry plays a key role in maintaining and improving the quality of our lives. Unfortunately, most people and governments do not fully appreciate this role. In fact, chemists, chemistry and chemicals are considered by many to be the source of environmental problems. A survey in the USA in 1994 showed that 60% of people have a negative attitude towards the chemical industry. At the same time, pharmaceutical and polymer chemistry have a better image, probably due to the nature of their products and their respective benefits. Public opinion is more negative towards the chemical industry than towards the Petro, wood processing and paper industries. The main reason is the opinion that the chemical industry has an adverse effect on the environment.

Only one third of the respondents believed that the chemical industry is interested in environmental protection and only one half admits that intensive work is being done to solve environmental problems. Negative public opinion is at odds with the enormous economic success of the chemical industry. The range of chemical products is vast and these products play an invaluable role in improving the quality of our lives. Millions of tons of waste products are generated during the production of these products, and solving this problem is a fundamental goal of industry, governments, education and society.

The challenge for chemists and other specialists related to the chemical industry and education is to create new products, new processes and a new approach to education in order to achieve societal, economic and environmental benefits that cannot be delayed longer. Changing public opinion is also important, but this is expected to take many

years. All of the above aspects form part of the green chemistry profession.

It is clear that after two centuries of development of modern chemistry and more than a century of industrial chemical production, mankind has reached an invisible point where two problems are clear: (i) without chemistry (meaning new materials, effective drugs, plant protection systems, dyes, computers, fuel etc.– the list could be extended) humanity cannot exist at its current stage of development and (ii) chemical production in its current form should not exist.

## VI. CONCLUSION

Green chemistry is one of the scientific fields. The green chemistry revolution provides enormous opportunities for the discovery and application of new synthetic approaches using alternative feedstocks, eco-friendly reaction conditions, energy minimization, and the design of less toxic and inherently safer chemicals. In this review article, we have seen many interesting examples of green chemistry that can be used in industry for the synthesis, processing and utilization of chemical compounds. The main goal of green chemistry is to design an ideal method or process that starts from non-polluting starting materials, gives rise to no secondary products, and requires no solvents during chemical conversion or for product isolation and purification.

Advances in green synthetic organic chemistry can lead to a greener future with green technologies, processes, and synthetic reaction conditions such as green solvents, green catalysts, solvent-free and less energy-intensive strategies, and microwave and ultrasound technologies. approaches that transform reactants into products with sustainability. The chemical industry and academic research mostly rely on hazardous catalysis and solvents. Alternative green solvents and green catalysis are therefore the future of our ecosystem in reducing or even eliminating the effects of these hazardous materials on the environment and can lead to optimized product yields in a shorter period of time, in accordance with all 12 principles of green chemistry.

All of us, by using the comforts of modern civilization, contribute to the pollution of the environment and owe it to mother nature. Educating future generations of chemists in green chemistry will contribute to solving a number of environmental problems on a national, regional and global scale and will enable specialists.

trained by us to be competitive in the global economy. By starting green chemistry education right now, we should go a long way toward fulfilling our mission and enjoy

the results of our efforts for future generations of chemists and chemists other specialists. In our opinion, this will inevitably happen in the very near future.

**The biggest challenge for green chemistry is to set its rules into practice.**

## REFERENCES

- [1] Jahangirian H, Lemraski EG, Webster TJ, Rafiee-Moghaddam R and Abdollahi Y: A review of drug delivery systems based on nanotechnology and green chemistry: green nanomedicine. *Int J Nanomed* 2017; 12: 2957-78.
- [2] Kaur G: Recent trends in green and sustainable chemistry & waste valorisation: Rethinking plastics in a circular economy. *Cur Opi in Green and Sus Chem* 2018; 9: 30-39.
- [3] Wiczerzak M, Namiesnik J and Kudlak B: Bioassays as one of the green chemistry tools for assessing environmental quality: A review. *Environ Int* 2016; 94: 341-361.
- [4] Pacheco-Fernández I and Pino V: Green solvents in analytical chemistry. *Current Opinion in Green and Sustainable Chemistry* 2019; 18: 42-50.
- [5] Wen J: H<sub>2</sub>O-controlled selective thiocyanation and alkenylation of ketene dithioacetals under electrochemical oxidation. *Green Chemistry* 2019.
- [6] Kozlov KS, Romashov LV and Ananikov VP: A tunable precious metal-free system for selective oxidative esterification of biobased 5-(hydroxymethyl) furfural. *Green Chemistry* 2019.
- [7] de Marco BA, Rechelo BS, Totoli EG, Kogawa AC and Salgado HRN: Evolution of green chemistry and its multidimensional impacts: A review. *Saudi Pharm J* 2019; 27(1): 1-8.
- [8] Poliakoff M, Leitner W and Streng ES: The 12 principles of CO<sub>2</sub> Faraday Discuss 2015; 183: 9-17.
- [9] Mulimani P: Green dentistry: the art and science of sustainable practice. *Br Dent J* 2017; 222(12): 954-61.
- [10] Jadhav K, Dhamecha D, Bhattacharya D and Patil M: Green and ecofriendly synthesis of silver nanoparticles: Characterization, biocompatibility studies and gel formulation for treatment of infections in burns. *J Photochem Photobiol B* 2016; 155: 109-15.
- [11] Colacino E: Mechanochemistry for “no solvent, no base” preparation of hydantoin-based active pharmaceutical ingredients: nitrofurantoin and dantrolene. *Green Chemistry* 2018; 20(13): 2973-77.

- [12] Mudge EM, Murch SJ and Brown PN: Leaner and greener analysis of cannabinoids. *Anal Bioanal Chem* 2017; 409(12): 3153-63
- [13] Vasilev, A.; Deligeorgiev, T.; Gadjev, N.; Kaloyanova, St.; Vaquero, J.J.; Alvarez-Builla, J.; Baeza, A.G. Novel environmentally benign procedures for the synthesis of styryl dyes. *Dyes Pigm.*, 2008, 77, 3, 550-555.
- [14] Toda, F., Schmeyers, J. Selective solid-state brominations of anilines and phenols. *Green Chem.*, 2003, 5, 701-705.
- [15] Bogdal, D.; Pielichowski, J.; Jaskot, K. Remarkable fast N-Alkylation of Azaheterocycles under microwave irradiation in dry media. *Heterocycles*, 1997, 45, 715-722.
- [16] Bogdal, D.; Pielichowski, J.; Jaskot, K. New method of N-alkylation of carbazole under microwave irradiation in dry media. *Synth. Commun.*, 1997, 27, 1553-1560.
- [17] Guzen, K.P.; Guarezemini, A.S.; Orfao, A.T.G.; Cella, R.; Pereira, C.M.P.; Stefani, H.A. Eco-friendly synthesis of imines by ultrasound irradiation. *Tetrahedron Lett.*, 2007, 48, 1845-1848.
- [18] Kiss, A.A.; Dimian, A.C.; Rothgenberg, G. Solid acid catalysts for biodiesel production --towards sustainable energy. *Adv. Synth. Catal.*, 2006, 348(1-2), 75-81.
- [19] Roche, D.; Prasad K.; Repic O.; Blacklock T.J. Mild and regioselective oxidative bromination of anilines using potassium bromide and sodium perborate. *Tetrahedron Lett.*, 2000, 41(13), 2083-2085.
- [20] Arcadi, A.; Biangi, G.; Di Giuseppe, S.; Merinel-Li, F. Gold catalysis in the reactions of 1,3-dicarbonyls with nucleophiles. *Green Chem.*, 2003, 5, 64-67.
- [21] Scott, G. 'Green' polymers. *Polym. Degr. Stab.*, 2000, 68(1), 1-7.