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Review Article

A Review on Green Chemistry and Catalysis

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ABSTRACT

Green chemistry, also known as sustainable chemistry, refers to the development of chemical products and processes that minimize or eliminate the usage and production of harmful compounds. They only utilize environmentally friendly chemicals and chemical procedures. It is built on twelve principles that can be used to develop or reproduce molecules, materials, reactions, and processes that are safer for human health and the environment from the ground up. Green Chemistry decreases the environmental impact of chemical processes and technologies, as demonstrated in this article. The goal of this review is to learn more about the role of catalysts in green chemical synthesis for a more sustainable future. In the ecologically friendly synthesis of novel and existing compounds, catalysis plays a critical role. Catalyzed processes require less energy to produce and produce fewer by-products, co-products, and other waste items, indicating increased efficiency. Catalysts can be created in such a way that they are not harmful to the environment. Catalysts come in a variety of shapes and sizes, and some of them have positive effects in the chemical industry.

INTRODUCTION

Primarily, green chemistry is characterized as reduction of the environmental damage accompanied by the production of materials and respective minimization and proper disposal of wastes generated during different chemical processes. According to another definition, green chemistry is a new technique devoted to the synthesis, processing, and application of chemical materials in such manner as to minimize hazards to humankind and the environment. New chemistry is required to improve the economics of chemical manufacturing and to enhance the environmental protection. The green chemistry concept presents an attractive technology to

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chemists, researchers, and industrialists for innovative chemistry research and applications. Hence, there is an essential need to improve the synthetic and engineering chemistry either by environmentally friendly starting materials or by properly designing novel synthesis routes that reduce the use and generation of toxic substances by using modern energy sources.

There are twelve green chemistry principles that have been created By EPA's Paul Anastas and John Warner, who described their significance in practice in their Green Chemistry Theory and Practice book, published in 1998. Green chemistry principles call for the elimination or reduction of dangerous or harmful compounds from the synthesis, manufacture, and application of chemical products, reducing or eliminating the use of substances harmful to human health and the environment. "Reducing Risk" and "Minimizing the Environmental Footprint" are two of the principles. In the past, various chemical industries have been associated with risk. Hazardous chemicals to humans and the potential of environmental pollution were linked to new chemical products, giving synthetic chemical materials a "bad name." Energy use, climate change, crisis, and depletion of natural resources are all factors in the environmental footprint.

1. Atom Economy
2. Less Hazardous Chemical Syntheses
3. Designing Safer Chemical
4. Safer Solvents and Auxiliaries
5. Design for Energy Efficient
6. Use of Renewable Feedstock
7. Reduce Derivatives
8. Catalysis
9. Design for Degradation
10. Real-time analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

The Principles of Green Chemistry:

Fig No. 01 Principles of Green Chemistry

- **The "better to prevent than to cure" principle:**

It is beneficial to a priori prevent the generation of waste instead of later on treating and cleaning up waste.

- **The "atom economy" principle:**

Synthetic production routes have to be planned in a way maximizing the incorporation of all the compounds used in the synthesis into the desired product.

- **The "less precarious chemical synthesis" principle:**

Wherever feasible, such synthetic methods have to be aspired, which resort to and generate compounds of no or only insignificant noxiousness to the environment and human health.

- **The "designing safer chemicals" principle:**

Chemicals should be developed in a way acting their desired functionality, while, at the same time, considerably reducing their toxicity.

- **The "safer solvents and safer auxiliaries" principle:**

Expenditure of auxiliary substances, such as solvents, separation agents, and others, should be avoided wherever possible; if not possible, harmless auxiliaries should be used.

- **The "design for energy efficiency" principle:**

The environmental and economic impact of energy demands for chemical processes should be analyzed in terms of followed by optimizing the required energy input. Wherever practicable, chemical synthesis should be carried out under mild process conditions, hence, at ambient temperature and pressure.

- **The "renewable feed stocks" principle:**

Whenever feasible in technological and economic terms, synthetic processes should resort to such raw materials and feed stocks, which are renewable rather than limited.

- **The "derivative reduction" principle:**

Redundant derivatization, e.g., protection/ deprotection, the use of blocking groups, or temporary modiffcation of physical/chemical processes, requires additional reagents and often contributes to additional waste generation. Therefore, wherever possible, they should be avoided or reduced to a minimum.

- **The "catalysis" principle:**

Generally, catalytic reagents are intrinsically superior to stoichiometric reagents; these catalysts should be as selective as possible.

- **The "degradation" principle:**

Chemical products have to be designed in such a way that, at the end of their life span, they do not resist in the biosphere, but disintegrate into nontoxic degradation product.

- **The "real-time analysis for pollution prevention" principle:**

Advanced analytical methods have to be developed, which permit the real-time, in-line process monitoring and control well before hazardous substances are generated.

- **The "accident prevention by inherently safer chemistry" principle:**

Compounds and the compound's formula applied in a chemical process should be chosen in a way minimizing the risk of chemical accidents, encompassing the release of chemicals, detonations, formation.

Concept of Pharmaceutical Green Chemistry:- Pharmaceuticals are the most dynamic segment of the chemical business. It is at the vanguard of major shifts toward "greener" feedstock, cleaner solvents, alternative methods, and new concepts . All of these measures will improve the pharmaceutical industry's environmental credentials while also lowering costs and materials for manufacturing processes, paving the way for long-term sustainability. Green chemistry is a Hippocratic oath for chemists, and a new generation of scientists and technologists is being formed to analyse the processes and materials used in production and development efficiently in order to protect natural resources and the environment . If no hazardous substances are used or produced, the risk is zero, and there is no need to be concerned about removing hazardous substances from the environment or limiting exposure to them. "Green chemistry is about reducing waste, raw materials, risks, energy, environmental impact, and cost," as the phrase goes.5 Scientific Areas for Practical Applications of Green chemistry The areas proposed for special focus under the green chemistry.

Benefits of Green Chemistry

Benefits to Human:

- Cleaner air: Less release of hazardous chemicals to air leading to less damage to lungs
- Cleaner water: Less release of hazardous chemical wastes to water leading to cleaner drinking and recreational water.
- Increased safety for workers in the chemical industry
- less use of toxic materials
- less personal protective equipment required, less potential for accidents (e.g., fires or explosions)
- Safer consumer products of all types

Benefits to Environment:

- Many chemicals end up in the environment by intentional release during use (e.g., pesticides), by unintended releases (including emissions during manufacturing), or by disposal.
- Green chemicals either degrade to innocuous products or are recovered for further use.
- Plants and animals suffer less harm from toxic chemicals in the environment.
- Lower potential for global warming, ozone depletion, and smog formation
- Less chemical disruption of ecosystems
- Less use of landfills, especially hazardous waste landfills Economy and business
- Higher yields for chemical reactions, consuming smaller amounts of feedstock to obtain the same amount of product.
- Fewer synthetic steps, often allowing faster manufacturing of products, increasing plant capacity, and saving energy and water.
- Reduced waste, eliminating costly remediation, hazardous waste disposal, and end-of-the- pipe treatments.
- Allow replacement of a purchased feedstock by a waste product-better performance so that less product is needed to achieve the same function.
- Reduced use of petroleum products, slowing their depletion and avoiding their hazards and price fluctuations
- Reduced manufacturing plant size or footprint through increased throughput

BENEFITS OF GREEN CHEMISTRY

- Business benefits of green chemistry include: improved resource efficiency and lower raw material and utility bills
- Reduced waste treatment and disposal costs.
- Ability to capitalize on the environmental technology marketplace by designing new, 'greener' products
- Improved health and safety for staff and customers
- Environmental benefits include: fewer raw materials and natural resources used.
- Lower levels of chemicals released to the environment
- Cleaner production technologies
- Reduced emissions and product impacts

Fig No. 02 Benefits of Green Chemistry

Green Chemistry's Latest Trends:- The green program's core goals are achieved through many prominent trends in the design, development, and use of chemical products and processes that decrease or eliminate the use or production of substances that are dangerous to human health and the environment."

- Catalytic and biocatalytic reaction research in order to obtain highly.
- Searching for new raw materials that are both harmless and renewable, such as biomass.
- Developing and evaluating new non-toxic, renewable reaction media, such as water, ionic liquids, and supercritical fluids.
- Developing and evaluating new reaction conditions, such as microwave, ultrasound, and light reaction.

Green chemistry is the utilization of a set of principles that will help reduce the use and generation of hazardous substances during the manufacture and application of chemical products. Green chemistry aims to protect the environment not by cleaning up, but by inventing new chemical processes that do not pollute. It is a rapidly developing and an important area in the chemical sciences. Principles of green chemistry, developments in this field and some industrial applications are discussed.The terms

‘Environmental Chemistry’ and ‘Green Chemistry’ are two different aspects of environmental pollution studies.. Green chemistry seeks to reduce pollution at source, whereas environmental chemistry focuses on the study of pollutant chemicals and their effect on nature.

CATALYSIS:

1. Role of Catalysis: Green chemistry is an area of chemistry that focuses on the discovery and use of environmentally friendly chemicals and processes. Catalysis is a key component of green chemistry. Green chemistry, often known as environmentally benign chemistry or sustainable chemistry, minimises toxicity. Its objective is to design and execute pollution avoidance solutions other than waste management that reduce waste, save energy, and reduce natural resource depletion. Green chemistry is considered environmentally friendly because it is thought to reduce carbon emissions and pollution. Catalysis has aided in the reduction of pollution in our environment. Catalysts have been used to improve air quality by removing and controlling NOx emissions, reducing the use of Volatile Organic Compounds (VOCsi), developing alternative catalytic technology to replace the use of chlorine or chlorine-based intermediate in chemical synthesis and waste minimization, and developing alternative catalytic technology to replace the use of chlorine or chlorine-based intermediate in chemical synthesis and waste minimization. Catalysis allows for more efficient and selective reactions, resulting in the elimination of vast volumes of by-products: and other waste chemicals.

As noted above, the waste generated in the manufacture of organic compounds consists primarily of inorganic salts.This is a direct consequence of the use of stoichiometric inorganic reagents in organic synthesis. In particular, fine chemicals and pharmaceuticals manufacture is rampant with antiquated ‘stoichiometric’ technologies. Examples, which readily come to mind are stoichiometric reductions with metals (Na, Mg, Zn, Fe) and metal hydride reagents (LiAlH4, Phloroglucinol from TNT.NaBH4), oxidations with permanganate, manganese dioxide and chromium (VI). reagents and a wide variety of reactions, e.g. sulfonations, nitrations, halogenations, diazotizations and Friedel-Crafts acylations, employing stoichiometric amounts of mineral acids (H2SO4, HF, H3PO4) and Lewis acids (AlCl3, ZnCl2,BF3)

The solution is evident: substitution of classical stoichiometric methodologies with cleaner catalytic alternatives. Indeed, a major challenge in (fine) chemicals manufacture is to develop processes based on H2, O2, H2O2, CO, CO2 and NH3 as the direct source of H, O, C and N. Catalytic hydrogenation, salt processes. The generation of copious amounts of inorganic salts can similarly be largely circumvented by replacing stoichiometric mineral acids, such as H2SO4, and Lewis acids and stoichiometric bases, such as NaOH , KOH, with recyclable solid acids and bases, preferably in catalytic amounts (see later).

catalyst
PhCOCH3 + H PhCH(OH)CH3
Heterogeneous 100%

catalyst
PhCH(OH)CH3 + ½ O2 PhCOCH3+ H2O
Homo/heterogeneous

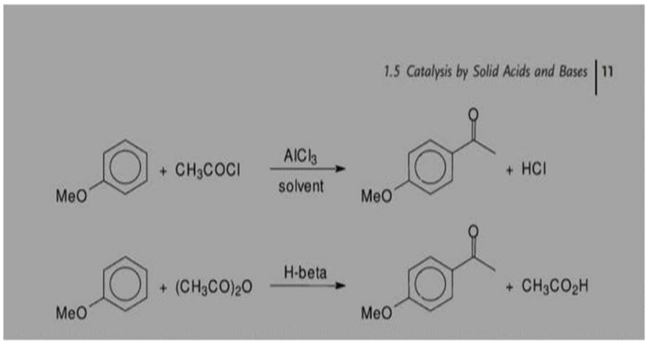
catalyst
PhCH(OH)CH3 + CO PhCH(CH3)CO2H
Homogeneous 100%

For example, the technologies used for the production of many substituted aromatic compounds have not changed in more than a century and are, therefore, ripe for substitution by catalytic, low-salt alternatives. An instructive example is provided by the manufacture of hydroquinone Traditionally it was produced by oxidation of aniline with stoichiometric amounts of manganese dioxide to give benzoquinone, followed by reduction with iron and hydrochloric acid (Bechamp reduction). The aniline was derived from benzene via nitration and Bechamp reduction. The overall process generated more than 10 kg of inorganic salts (MnSO4, FeCl2, NaCl, Na2SO4) per kg of hydroquinone. This antiquated process has now been replaced by a more modern route involving autoxidation of p-diisopropyl benzene (produced by Friedel-Crafts alkylation of benzene), followed by acid catalysed rearrangement of the bis-hydroperoxide, producing <1 kg of inorganic salts per kg of hydroquinone. Alternatively, hydroquinone is produced (together with catechol) by titanium silicalite (TS-1) catalysed hydroxylation of phenol with aqueous hydrogen peroxide (see later). Biocatalysis has many advantages in the context of green chemistry, e.g. mild reaction conditions and often fewer steps than conventional chemical procedures because protection and deprotection of functional groups are often not required. Consequently, classical chemical procedures are increasingly being replaced by cleaner biocatalytic alternatives in the fine chemicals industry.

2. Catalysis by Solid Acids and Bases: As noted above, a major source of waste in the (fine) chemicals industry is derived from the widespread use of liquid mineral acids (HF, H2SO4) and a variety of Lewis acids. They cannot easily be recycled and generally end up, via hydrolytic work-up, as waste streams containing large amounts of inorganic salts. Their widespread replacement by recyclable solid acids would afford a dramatic reduction in waste. Solid acids, such as zeolites, acidic clays and related materials, have many advantages in this respect. They are often truly catalytic and can easily be separated from liquid reaction mixtures, obviating the need for hydrolytic work-up, and recycled. Moreover, solid acids are non-corrosive and easier (safer) to handle than mineral acids such as H2SO4 or HF. Solid acid catalysts are, in principle, applicable to a plethora of acid-promoted processes in organic synthesis. These include various electrophilic aromatic substitutions, e.g. nitrations, and Friedel-Crafts alkylations and acylations, and numerous rearrangement reactions such as the Beckmann and Fries rearrangements. A prominent example is Friedel-Crafts acylation, a widely applied reaction in the fine chemicals industry. In contrast to the corresponding alkylations, which are truly catalytic processes, Friedel-Crafts acylations generally require more than one equivalent of, for example, AlCl3 or BF3. This is due to the strong complexation of the Lewis acid by the ketone product.

The commercialisation of the first zeolite-catalysed Friedel-Crafts acylation by Rhone-Poulenc (now Rhodia) may be considered as a benchmark in this area. Zeolite beta is employed as a catalyst, in fixed-bed operation, for the acetylation of anisole with acetic anhydride, to give p- methoxyacetophenone. The original process used acetyl chloride in combination with equivalents of AlCl3 in a chlorinated hydrocarbon solvent, and generated 4.5 kg of aqueous effluent, containing AlCl3, HCl, solvent residues and acetic acid, per kg of product. The catalytic alternative, in stark contrast, avoids the production of HCl in both the acylation and in the synthesis of acetyl chloride. It generates 0.035 kg of aqueous effluent, i.e. more than 100 times less, consisting of 99% water, 0.8% acetic acid and <0.2% other organics, and requires no solvent. Furthermore, a product of higher purity is obtained, in higher yield (>95% vs. 85– 95%), the catalyst is recyclable and the number of unit operations is reduced from twelve to two. Hence, the Rhodia process is not only environmentally superior to the traditional process, it has more favorable economics. This is an important conclusion; green, catalytic chemistry, in addition to having obvious environmental benefits, is also economically more attractive. Another case in point pertains to the manufacture of the bulk chemical, caprolactam, the raw material for Nylon 6. The conventional process volves the reaction of cyclohexanone with hydroxylamine sulfate (or another salt), producing cyclohexanone oxime which is subjected to the Beckmann rearrangement in the presence of stoichiometric amounts of sulfuric acid or oleum. The overall process generates ca. 4.5 kg of ammonium sulfate per kg of caprolactam, divided roughly equally over the two steps.

Homogeneous:



Acid and base catalysed reactions are important in the oil refining and petrochemical sectors, as well as in the production of a wide range of speciality chemicals like medicines, agrochemicals, and flavors and perfumes. In liquid-phase homogeneous systems or on inorganic supports in vapour phase systems, many of these processes require the use of conventional Brnsted acids (H2SO4, HF, HCl, p-toluene-Sulfonic acid) or Lewis acids (AlCl3, ZnCl2, BF3). Similarly, NaOH, KOH, NaOMe, and KOBut are examples of common bases. As a result of their subsequent neutralisation, The formation of inorganic salts that eventually find their way into aqueous streams.

Additional advantages of using solid acids and bases as catalysts include:

-Separation and recycling are made easier, resulting in a faster process and lower production costs.

-Solid acids, such as H2SO4, HF, are safer and easier to handle than their liquid equivalents. Very corrosive and necessitates the use of costly construction materials.

-Trace levels of (neutralized) catalyst contamination in the product are often avoided. When the latter is a dependable.

-Granular chemicals are safer and easier to operate than their liquid counterparts.

3. Catalytic Reduction: Selective catalytic reduction (SCR) is a means of converting nitrogen oxides, also referred to as NOx with the aid of a catalyst into diatomic nitrogen (N2), and water (H2O). A reductant, typically anhydrous ammonia (NH3), aqueous ammonia (NH4OH), or a urea (CO(NH2)2) solution, is added to a stream of flue or exhaust gas and is reacted onto a catalyst. As the reaction drives toward completion, nitrogen (N2), and carbon dioxide (CO2), in the case of urea use, are produced. Selective catalytic reduction of NOx using ammonia as the reducing agent was patented in the United States by the Engelhard Corporation in 1957. Development of SCR technology continued in Japan and the US in the early 1960s with research focusing on less expensive and more durable catalyst agents. The first large-scale SCR was installed by the IHI Corporation in 1978.Commercial selective catalytic reduction systems are typically found on large utility boilers, industrial boilers, and municipal solid waste boilers and have been shown to reduce NOx by 70-95%. Catalytic hydrogenation is unquestionably the workhorse of catalytic organic synthesis, with a long tradition dating back to the days of Sabatier who received the 1912 Nobel Prize in Chemistry for his pioneering work in this area.It is widely used in the manufacture of fine and specialty chemicals and a special issue of the journal Advanced Synthesis and Catalysis was recently devoted to this important topic. According to Roessler

, 10–20% of all the reaction steps in the synthesis of vitamins (even 30% for vitamin E) at Hoffmann-La Roche (in 1996) are catalytic hydrogenations.

An illustrative example is the synthesis of an intermediate for the Roche HIV protease inhibitor, Saquinavir. It involves a chemo- and diastereo selective hydrogenation of an aromatic while avoiding racemisation at the stereogenic centre present in the substrate. The chemo selective hydrogenation of one functional group in the presence of other reactive groups is a frequently encountered problem in fine chemicals manufacture. An elegant example of the degree of precision that can be achieved is the chemo selective hydrogenation of an aromatic nitro group in the presence of both an olefinic double bond and a chlorine substituent in the aromatic ring. Although catalytic hydrogenation is a mature technology that is widely applied in industrial organic synthesis, new applications continue to appear, sometimes in unexpected places.

4. Catalytic Oxidation: It is probably true to say that nowhere is there a greater need for green catalytic alternatives in fine chemicals manufacture than in oxidation reactions. In contrastto reductions, oxidations are still largely carried out with stoichiometric inorganic(or organic) oxidants such as chromium(VI) reagents, permanganate, manganese dioxide and periodate. There is clearly a definite need for catalytical ternatives employing clean primary oxidants such as oxygen or hydrogen peroxide. Catalytic oxidation with O2 is widely used in the manufacture of bulk petrochemicals. Application to fine chemicals is generally more difficult, however, owing to the multifunctional nature of the molecules of interest. Nonetheless, in some cases such technologies have been successfully applied to the manufacture of fine chemicals. An elegant example is the BASF process for the synthesis of citral, a key intermediate for fragrances and vitamins A and E. The key step is a catalytic vapor phase oxidation over a supported silver catalyst, essentially the same as that used for the manufacture of formaldehyde from methanol. This atom efficient, low-salt process has displaced the traditional route, starting from -pinene, which involved, inter alia, a stoichiometric oxidation with MnO2. The selective oxidation of alcohols to the corresponding carbonyl compounds is a pivotal transformation in organic synthesis. As noted above, there is an urgent need for greener methodologies for these conversions, preferably employing O2 or H2O2 as clean oxidants and effective with a broad range of substrates.

5. Catalytic C–C Bond Formation: Another key transformation in organic synthesis is C–C bond formation and a important catalytic methodology for generating C–C bonds is carbonylation. In the bulk chemicals arena it is used, for example, for the production of acetic acid by rhodium-catalysed carbonylation of methanol. Since such reactions are 100% atom efficient they are increasingly being applied to fine chemicals manufacture. An elegant example of this is the Hoechst-Celanese process for the manufacture of the analgesic, ibuprofen, with an annual production of several thousands tons. In this process ibuprofen is produced in two catalytic steps (hydrogenation and carbonylation) from p-isobutylactophenone (with 100% atom efficiency. This process replaced a more classical route which involved more steps and a much higher E factor. In a process developed by Hoffmann-La Roche for the anti-Parkinsonian drug, lazabemide, palladium-catalysed amide carbonylation of 2,5-dichloropyridine replaced an original synthesis that involved eight steps, starting from 2-1.8 Catalytic C–C Bond Formation.

The best oxidation is no oxidation. methyl-5-ethylpyridine, and had an overall yield of 8%. The amidocarbonylation route affords lazabemide hydrochloride in 65% yield in one step, with 100% atom efficiency.

6. **Hydrolysis**: Hydrolytic processes provide the baseline loss rate for any chemical in an aqueous environment. Although various hydrolytic pathways account for significant value only the reactant species water provides - that is, H+, OH-, and H20 - but the complete picture includes analogous reactions and thus the equivalent effects of other chemical species present in the local environment, such as SH- in anaerobic bogs, Cl in sea water, and various ions in laboratory buffer solutions. Methods to predict the hydrolysis rates of organic compounds for use in the environmental assessment of pollutants have not advanced significantly since the first edition of the Lyman Handbook (Lyman et al., 1982). Two approaches have been used extensively to obtain estimates of hydrolytic rate constants for use in environmental systems. The first and potentially more precise method is to apply quantitative structure/activity relationships (QSARs). To develop such predictive methods, one needs a set of rate constants for a series of compounds that have systematic variations in structure and a database of molecular descriptors related to the substituents on the reactant molecule. The second and more widely used method is to compare the target compound with an analogous compound or compounds containing similar functional groups and structure, to obtain a less quantitative estimate of the rate constant.[3] Predictive methods can be applied for assessing hydrolysis for simple one-step reactions where the product distribution is known. Generally, however, pathways are known only for simple molecules. Often, for environmental studies, the investigator is interested in not only the parent compound but also the intermediates and products. Therefore, estimation methods may be required for several reaction pathways.

7. **Renewable Raw Materials**: Another important goal of green chemistry is the utilisation of renewable raw materials, i.e. derived from biomass, rather than crude oil. Here again, the processes used for the conversion of renewable feedstocks – mainly carbohydrates but also triglycerides and terpenes – should produce minimal waste, i.e. they should preferably be catalytic. In the processes described in the preceding section a biocatalyst – whole microbial cells or an isolated enzyme – is used to catalyse a transformation (usually one step) of a particular substrate. When growing microbial cells are used this is referred to as a precursor fermentation. Alternatively, one can employ de novo fermentation to produce chemicals directly from biomass. This has become known as white biotechnology, as opposed to red biotechnology (biopharmaceuticals) and green biotechnology (genetically modified crops). White biotechnology is currently the focus of considerable attention and is perceived as the key to developing a sustainable chemical industry. Metabolic pathway engineering is used to optimise the production of the required product based on the amount of substrate (usually biomass-derived) consumed. More recently, de novo fermentation is displacing existing multistep chemical syntheses, for example in the manufacture of vitamin B2 (riboflavin) and vitamin C. Other recent successes of white.

CONCLUSION

Understanding the importance of green chemistry, which is basic requirement in today's pharmaceutical industries. The approach will help to avoid the utilization of the toxic chemicals leading to various hazards in the industry. These conventional methods can be replaced easily by the methods which utilize nontoxic and environment friendly techniques for the synthesis of same. Microwave Assisted Synthesis and Sonochemistry are new techniques that adopted instead of conventional methods as conventional methods requires use of harmful chemical and catalyst The approach will definitely help in the synthesis by keeping the environment safe.

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