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REVIEW ARTICLE

A REVIEW ARTICLE ON GREEN CHEMISTRY IN ORGANIC SYNTHESIS

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A Review Article on Green Chemistry in Organic Synthesis

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Abstract – The evolution of "Green Chemistry" concepts and the field's basic principles are discussed. There are examples of how these ideas are applied in many fields of chemistry. In preparative organic chemistry, the often employed alternative solvents (green solvents – water, PEG, per fluorinated solvents, supercritical liquids) are explained. Green chemistry's current and future advances in education and organic chemical technologies are discussed.

Keywords – Principles of Green Chemistry, Green Chemistry, Green Solvents, Organic Synthesis

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1. GREEN CHEMISTRY

In its most basic form, sustainable and green chemistry is just a new way of thinking about how chemistry and chemical engineering may be done. Various ideas have been developed over time that may be used to the design, development, and implementation of chemical goods and processes. By developing creative and inventive methods to decrease waste, preserve energy, and create substitutes for harmful chemicals, scientists and engineers can safeguard and benefit the economy, people, and the environment.

It's worth noting that the scope of green chemistry and engineering principles extends beyond concerns about chemical toxicity to include energy conservation, waste reduction, and life cycle considerations like the use of more sustainable or renewable feedstocks and product design for end-of-life or final disposal.

The usage of metrics may also be used to define green chemistry. Many methods to measure greener processes and products have been proposed, yet no standardised set of criteria has been created. These measures include those for mass, energy, hazardous substance reduction or removal, and environmental implications across the life cycle.

2. BASIC PRINCIPLES OF GREEN CHEMISTRY

The 12 principles outlined by Anastas and Warner form the foundation of green chemistry. These 12 green chemistry concepts are now widely regarded as the foundations for contributing to long-term sustainability. As shown in Table 1, the principles include directions for implementing new chemical products, syntheses, and procedures.

Table 1: The 12 principles of green chemistry proposed by Anastas and Warner

1	The "better to prevent than to cure" principle It is preferable to prevent trash formation in the first place rather than treating and cleaning up garbage later.
2	The "atom economy" principle Synthetic production methods must be designed in such a manner that all of the chemicals employed in the synthesis are fully incorporated into the target product.
3	The "less precarious chemical syntheses" principle Wherever possible, synthetic processes that use and create substances with no or minimal toxicity to the environment and human health should be pursued.
4	The "designing safer chemicals" principle Chemicals should be developed in a way affecting their desired functionality, while, at the same time, considerably reducing their toxicity
5	The "safer solvents and safer auxiliaries" principle Wherever feasible, auxiliary substances such as solvents, separation agents, and other chemicals should be avoided; if this is not possible, safe auxiliaries should be used instead.
6	The "design for energy efficiency" principle Energy needs for chemical processes should be examined in terms of environmental and economic effect, and then the needed energy input should be optimised. Chemical synthesis should be carried out under mild process conditions, such as at room temperature and pressure, wherever possible.

7	The “renewable feedstocks” principle Synthetic processes should use renewable rather than restricted raw resources and feedstocks wherever it is technologically and economically viable.
8	The “derivative reduction” principle Redundant derivatization, such as protection/deprotection, the use of blocking groups, or the temporary alteration of physical/chemical processes, necessitates the use of extra reagents and adds to the development of additional waste. As a result, they should be avoided or kept to a minimum whenever feasible.
9	The “catalysis” principle Catalytic reagents are preferable than stoichiometric reagents in general, and these catalysts should be as selective as feasible.
10	The “degradation” principle Chemical goods must be developed in such a manner that when they reach the end of their useful life, they dissolve into benign breakdown products rather than resisting in the biosphere.
11	The “real-time analysis for pollution prevention” principle Advanced analytical methods must be developed that allow for real-time, in-line process monitoring and control prior to the generation of hazardous chemicals.
12	The “accident prevention by inherently safer chemistry” principle Chemical compounds and their formulas should be chosen in a way that minimises the danger of chemical mishaps, which include chemical release, detonations, and fire creation.

2.1 It is better to prevent waste than to treat or clean up waste after its formation

This is one of the most often used process optimization recommendations; it outlines chemists' capacity to optimise chemical reactions to reduce the development of hazardous waste as a crucial step toward pollution control. Hazards connected with waste storage, transportation, and treatment might be reduced if waste creation is avoided.

This theory is simple to grasp and implement, and examples from both business and academics have demonstrated its importance, relevance, and viability. This pillar of green chemistry remains relevant; however, we must consider it in a larger perspective, moving away from a limited interpretation of waste based on its amount and toward a more general approach to the subject of "waste":

- We have to take waste's multidimensional nature into account.
- We need to shift from a "amount of trash per quantity of product" premise to a "quantity of

waste created per function given by the product" principle. In this environment, we must strive to improve product quality as well as functionality.

- When considering a product's whole life cycle, we must consider the fact that not only does the manufacturing process produce waste, but also "end-of-life waste" accumulates after the product's life span or consumption. This includes, first and foremost, the transformation of previously deemed waste resources into useful goods, as well as their recyclability.

Moving toward "zero-waste production" and "waste prevention" in general refers to the upgrading of industrial processes using clean manufacturing approaches. These strategies are designed to reduce gaseous emissions, effluents, solid residues, and noise output while also contributing to climate and environmental protection [1]. However, the most effective way to avoid waste formation is to simply stop making the desired product. In most cases, this will not be possible; nonetheless, it may be more cost-effective to create wholly new items with greater quality and longer endurance. To accomplish a given purpose, smaller quantities of such unique, better items are required. An alternate method is to prevent the product from becoming hazardous trash, for example, by making polymers biodegradable or converting to biodegradable plastics instead of extremely resistant petrochemical plastics a priori. According to these views, we need to rethink garbage as a dangerous substance that has to be disposed of by elevating waste to a valuable resource that can be used as a beginning material for the creation of new goods [2].

2.2 Maximize atom economy

Atom economics is a term used in the early 1990s to describe a method of evaluating the efficacy of chemical transformations on a per-element basis [3]. The notion of "atom economy" is based on the ratio of the total mass of atoms in the goal product to the complete mass of atoms in the starting materials, similar to well-known yield calculations. Planning chemical reactions that optimise the integration of all elements utilised in the process into the end product, resulting in a minimal number of lost atoms, is one method for reducing waste creation. As a result, choosing chemical conversion pathways that convert the majority of starting materials into desired products is more efficient and helps to reduce waste. This approach is currently widely applied in novel methods for generating diverse organic molecules, such as those used in biomedical and pharmacological research. [4]

The development of green chemistry is one element that is hastening the integration of pollution avoidance into industrial production processes. According to a different definition, chemical synthesis methods should

be designed to maximise the incorporation of various potentially hazardous materials, such as spinning precarious waste with cement and sand to produce a better paste for construction applications, or incorporating radioactive wastes as an immobilising material to produce a safe stabilised form of waste. In a similar line, mixing recycled poly(ethylene terephthalate) (PET) waste with cement paste shows promise for immobilising hazardous wastes such as radioactive borates[5].

2.3 Design less hazardous chemical synthesis

In synthetic organic chemistry, the concepts of green chemistry are concerned with achieving a successful chemical transformation in a new method, with a new molecule, or in a new order. Various researchers have shown that toxicity and the accompanying dangers and risks connected with chemical reactions are directly related to the matrix of materials present in the reaction vessel. In general, the chemistry underlying a process and the transformations that contribute to a chemical synthesis chain have a significant influence on the holistic toxicity spectrum of products or processes, as well as most other sustainability and green chemistry criteria. There is an exception in circumstances where a molecule is generated on purpose with the intent of displaying toxicity and/or biological activity. This scenario may be encountered, for example, in the case of different molecules created for pharmacological or agricultural purposes; such chemicals are hazardous and/or have an influence on living creatures.

A vital step in process development is the selection of compounds and materials to be employed to improve the efficacy of chemical transformations; scientists should devote more attention to the decision of which materials to put into reaction vessels. It is simple to ignore all other materials and focus all of our efforts just on the chemosynthetic route, which supplies us with the desired result. Discounting all other factors in a manufacturing process, on the other hand, leads to a hefty price to be paid, and we must eventually abandon this situation. Because chemists occasionally create harmful chemicals, the following concept is committed to the creation of molecules that are innately safer in nature [6].

2.4 Design safer chemicals and products

Chemical goods should be developed to perform their intended purpose while also being low in toxicity. New goods can be created that are fundamentally safer while yet being extremely effective for the intended use. Direct incorporation of radioactive spent liquid scintillation waste into cement combined with clay materials, for example, is considered an added value in the immobilisation of hazardous organic wastes in low-cost materials and natural clay to produce a safe stabilised product that is easy to handle, transform.[7].

2.5 Safer solvents and auxiliaries

This idea encourages the adoption of more environmentally friendly solvents and auxiliaries. It refers to any components that do not contribute directly to the structure of the reaction result but are nonetheless required for the chemical reaction or process to take place. Organic compound reactions often take place in liquid environments, where the solvent can facilitate improved contact between the reactants, stabilise or destabilise produced intermediates, or impact transition states. In addition, the solvent used determines whether downstream and regeneration procedures, as well as recycling or discarding strategies, are appropriate. Innovative approaches for the replacement of volatile organic solvents have become a major problem in green chemistry due to the environmental impact of chemical operations. Low toxicity, nonflammability, nonmutagenicity, nonvolatility, and universal availability are only a few of the requirements for a green solvent. Furthermore, these green solvents must be inexpensive, easy to handle, and recyclable. In the field of extractive recovery of microbial polyhydroxyalkanoate (PHA) biopolymers, which are common intracellular storage materials, prime examples are provided. For this extraction procedure, which is generally carried out with hazardous halogenated solvents, more and more people are turning to less damaging greener solvents or innovative solvent-free recovery technologies [8].

2.6 Design for energy efficiency

Typically, energy is used to improve human lives in significant ways. Coal, oil, and gas, which have long been utilised as energy sources, are in short supply, and their burning emits greenhouse gases. Both a shift toward renewable energy and energy-efficient architecture are required for continued improvement of life quality. Picking appropriate energy sources must go hand in hand with designing more efficient processes by selecting the most appropriate technology and unit activities. Using an electric motor using energy sources such as the sun and wind is more environmentally friendly than using fossil fuels. The most critical problems for engineers and designers to help society use energy more effectively are how energy is transformed to usable forms and where it is wasted.

As a result, green chemistry involves reducing energy losses such as mechanical friction, fluid drag, and undesired heat transfer by optimising refrigerator architecture and insulation or developing lighter cars with improved aerodynamic properties and reduced rolling resistance.

Furthermore, the influence of the geographical location of manufacturing plants must be considered while establishing a new production process: The ecological impact of different production scenarios for the same product, in this case bioplastics, clearly

demonstrates that different energy production technologies, resources for energy production, and the effect of available energy mixes in different countries all play a role in the environmental impact of a new process[9].

2.7 Use of renewable feedstocks

When technically and economically feasible, a raw material or feedstock should be renewable rather than depleting, according to green chemistry principles. Using renewable resources like microbial or plant biomass, which are part of nature's closed carbon cycle, is a viable alternative for making sustainable functioning bioproducts and contributing to the energy transition.

We now see a large number of current multidisciplinary collaborations involving the fields of agronomy, biochemical engineering, biotechnology, chemistry, microbiology, physics, toxicology, or engineering in the context of Green Chemistry Principle #7, which addresses the renewable feedstock thematic. These collaborations lead to the creation of next-generation fuels, polymers, and other materials that are critical for today's society, based on renewable resources and with low health and environmental effect. The present global dynamic of these advancements does, in fact, inspire hope for the future. Finding a way to turn raw wastes like spinney waste fibres into a mortar composite stabilised material might be a great use of this green chemistry principle. When transitioning from fossil to renewable feedstocks, it's important to remember that adding resource provision, transportation, storage, and other logistical considerations into the process design expands the process idea. However, such a shift in feedstock supply necessitates a fundamental shift in the structure of processes, technologies utilised, and industry and society's economic ideas [10].

2.8 Reduce derivatives

Many processes might be engineered to decrease the usage of extra chemicals and the waste generated as a result. It's typical to need to make a derivative of a molecule that has groups that aren't needed in the end product but make the synthesis or purifying process go faster. However, because these derivatives add atoms that are not absorbed into the final product but instead end up as trash, they have a poorer atom economy; this is in contradiction to Table 1's atom efficiency concept. Chemists are presently focusing their efforts to developing alternatives to several reactions that have historically needed protective groups.

2.9 Catalysis

The chemical process that is facilitated or accelerated by a catalyst is known as catalysis. Catalysts, according to Ostwald, are substances that speed up a reaction by permitting an energetically preferred transition state between reactants, but are not

consumed by the reaction and are not included in the net reaction equation. Catalysts are critical components of our contemporary industrial economy, environmental management, and all biological processes. Iron and copper sulphate as catalysts enhanced the process of oxidative degradation of cellulosic wastes using 35 percent hydrogen peroxide, according to Saleh and colleagues. There was a 95.2 percent weight decrease in the presence of copper sulphate and an 87.8 percent weight reduction in the presence of ferrous sulphate. Nano-catalysts of specified size and shape have recently been produced, allowing for easy mobility of materials in the reacting phase and control over nanostructure morphology to adjust physical and chemical characteristics. Rapid and selective chemical transformations with great product yield and ease of catalyst separation and recovery are possible with nano-catalyst systems including a paramagnetic core.

When it comes to catalysis, it's no longer optional to include biocatalysis, which involves the use of enzymes as highly selective and active catalysts created by Mother Nature. Not only do enzymes carry out the required reactions at low temperatures and pressures, which is similar to the energy efficiency concept stated earlier. Furthermore, they are predestined to drive reactions involving renewable materials (similar to the renewable feedstock concept) and, in certain situations, even enable reactions that would otherwise be impossible to achieve with standard catalysts, such as the synthesis of enantiopure products. Furthermore, biocatalysts in free or immobilised form are increasingly being used for bioremediation, resulting in the removal of contaminants from the environment[11].

2.10 Design for degradation

One of the most significant goals of green chemistry is to increase output while reducing undesired by-products. The creation of sustainable mortar composite that could be considered a value-added product suitable for various applications as an inert matrix for immobilisation of some low and intermediate levels of radioactive wastes, decorative tiles, building bricks, and light concrete is reported, as is the design of products and processes that have a reduced impact on humans and the environment. In this situation, extremely reactive hydroxyl radicals combine with the organic moieties of the spinning fibre wastes to produce organic radicals that are easily oxidised by oxygen, either by deleting hydrogen ions or by adding to the unsaturated site. As a result, the degradation process produced just carbon dioxide and water as its final products.

2.11 Real-time analysis for pollution prevention

The creation of several harmful compounds has become a severe concern for the environment as chemistry has progressed. Pollution preventionists are aware with one of the fundamental ideas of green

chemistry. For many years, the need has been made for less hazardous ingredients in chemical formulations and a reduction in waste generation. As a result, green chemistry attempts to eliminate the use and creation of hazardous chemicals by building improved chemical material manufacturing methods with minimal waste production and real-time monitoring of running operations. As a result, an early intervention may be made before waste or toxins are formed.

2.12 Inherently safer chemistry for accident prevention

It's critical to stay away from highly reactive compounds that might result in an accident during the reaction. Chemical mishaps, such as poison releases, explosions, and fire creation, can be avoided if the material and form of the substance utilised in a chemical process are chosen carefully. Water, for example, may accidentally trigger an explosion if it flowed into a tank storing methyl isocyanate gas, releasing a huge volume of methyl isocyanate into the surrounding environment. Alkali metals also contain other well-known elements that undergo interactions with water that are frequently destructive. The risk of explosion, even death, may have been reduced if an alternate reaction had been designed that did not involve this chemical.

Safe chemistry may also be done in flow mode, utilising tubular microreactors with small reaction channels. Such flow chemistry approaches dramatically reduce reaction volume, reaction time, and catalyst requirements, intensifies processes by increasing space/time yield, opens new process windows in terms of the extreme temperature and pressure conditions that can be applied, and even allows for the safe execution of highly dangerous reactions. Furthermore, the use of flow chemistry in microreactors demonstrates an approach for overcoming traditional disadvantages of microwave-driven processes, such as microwave penetration depth into absorbing material.

3. GREEN SOLVENTS

Organic solvents, which are utilised in many syntheses, are extremely toxic to the environment. Because they are utilised in considerably larger quantities than the reagents themselves, volatile organic solvents are discharged into the environment in significant volumes through evaporation or flow. To tackle this difficulty, a new strategy is to carry out chemical reactions in the absence of such media, i.e. without solvents or with non-volatile solvents that are safe for humans and the environment. The ideal "green" solvent would have a high boiling point, be non-toxic, dissolve a wide range of organic molecules, be inexpensive, and, of course, be recyclable. Clearly, such limitations restrict the types of substances or classes of compounds that may be used as green solvents. Supercritical liquids, ionic liquids, low-melting

polymers, perfluorinated (fluorous) solvents, and water have all been developed as good alternatives to typical organic solvents thanks to the efforts of research organisations all around the world.

3.1 Alternative Solvents in Organic Syntheses

• Water

Water is both the source and the bearer of life. Water has been working for millions of years to prepare the world for the evolution of life. Numerous biological organic (and inorganic) processes take happen in the presence of water. All of these reactions have an impact on biological systems and occur in an aqueous medium. Modern organic chemistry, on the other hand, is nearly entirely based on the fact that organic reactions are frequently carried out in organic solvents. People have just recently refocused their attention on carrying out organic reactions in water, roughly in the last two decades.

• Ionic Liquids

The vast number of papers in the literature dedicated to this issue confirms that ionic liquids are the most frequently investigated alternatives to organic solvents. This is a new field of applied organic chemistry and organic chemical technology, in our opinion. The considerable interest in these compounds stems from the fact that they have several appealing qualities, including low vapour pressure, strong chemical and thermal stability, inflammability, high ionic conductivity, a broad electrochemical potential, and the ability to operate as catalysts. Unlike traditional solvents, which are made up of single molecules, ionic liquids are made up of ions and are either liquid at room temperature or have low melting temperatures (typically below 100 degrees Celsius). When compared to ordinary molecular liquids, these materials have unusual characteristics when utilised as solvents due to their ionic composition. Simple combinations of various cations and anions can produce a wide range of ionic liquids. Physical qualities like as hydrophobicity, viscosity, density, and solvating ability can be altered by modifying the anion or alkyl chain of the cation. The use of ionic liquids in organic processes is not limited to the substitution of organic solvents in reaction media. Ionic liquids can be used as reagents, catalysts, or media to immobilise catalysts or produce chirality in particular instances.

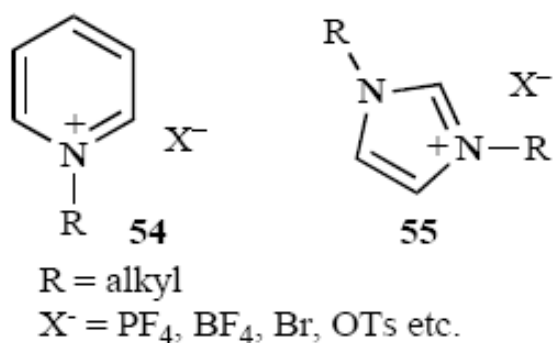


Figure 1: Chemical structures of some widely used ionic liquids

• Poly(ethylene glycol)

Poly(ethylene glycol) (PEG) is a linear polymer made by ethylene oxide polymerization. A polyether having a molecular mass less than 20000 is referred to as a PEG. PEG is well-known as a low-cost, thermally stable, biocompatible, non-toxic, and recyclable substance. PEG and its monomethyl ethers also have low vapour pressures, are inflammable, and can be easily isolated from the reaction media. As a result, PEG is thought to be a green alternative to volatile organic solvents and a useful medium for chemical processes. PEG is employed as a phase transfer catalysis medium and, in certain situations, as a polyether catalyst in phase transfer catalysis reactions.

PEG has recently been employed as a reaction medium for chemical processes; low molecular weight (less than 20000) derivatives are typically chosen since they have low melting points or are liquids at ambient temperature. Despite their less widespread use, PEGs are commercial goods that are significantly less expensive than ionic liquids, but unlike the latter, their characteristics cannot be easily modified. One of the most significant drawbacks of PEGs (which also applies to ionic liquids) is that organic solvents must be employed to remove reaction products, however supercritical carbon dioxide (scCO_2) might be utilised in both circumstances. Although there are few examples of PEG use in the literature, polyethylene glycol-promoted reactions have recently attracted the attention of organic chemists due to their solvating power and ability to act as a phase transfer catalyst, low vapour pressure, easy recyclability, reusability, ease of work-up, eco-friendly nature, and low cost. [12]

• Perfluorinated (Fluorous) Solvents

Horvath and Rabai coined the word "fluorous" as a synonym for "aqueous" or "aqueous medium" for the first time. Gladysz and Curran recently classified fluorine compounds as substances with a high fluorination level that are based on sp^3 -hybridized carbon atoms. Perfluoroalkanes, perfluoroalkyl ethers, and perfluoroalkylamines, for example, are chemically stable and environmentally friendly since they are non-toxic (unlike freons), inflammable, thermally stable, and recyclable. These chemicals have a strong

capacity to dissolve oxygen, which is useful in medicinal applications. Fluorine atoms are substituents on carbon atoms in fluorine fluids or liquids (C–F bond). High density, high stability (owing to the stability of the C–F bond), limited dissolving ability, and extremely low solubility in water and organic solvents characterise fluorine liquids, but they are miscible with the latter at higher temperatures. Low surface tension, poor intermolecular interactions, high densities, and low dielectric constants all contribute to the perfluorinated fluids' low solubility. [13]

• Supercritical Liquids

A material above its critical temperature (T_c) and critical pressure (CP) is referred to as a supercritical liquid (SCL) (P_c). An SCL's characteristics are a mix of those of its liquid and gaseous phases. Variations in temperature and pressure can particularly alter these qualities.

Carbon dioxide is the most often used SCL (scCO_2). CO_2 has a critical point of 73 atm and 31.1°C , which can be easily obtained in the laboratory. Because of the severe conditions necessary to reach the critical point, other supercritical solvents aren't as helpful. Water, for example, has a critical point of 218 atm and 374°C . Recently, instances of reactions in scH_2O have surfaced in the literature.

The following are some of the benefits of employing scCO_2 : CO_2 is inflammable and less toxic than most organic solvents; it is relatively inert toward reactive substances; it is a natural gas found in the atmosphere; it can be easily removed by lowering the pressure, allowing it to be easily removed from reaction products; it has a high gas-dissolving ability, a low solvating ability, a high diffusion rate, and good mass transfer properties; it is a natural gas found in the atmosphere; it is a natural gas found in the atmosphere; When compared to the use of standard organic solvents, the selectivity of a reaction can be substantially altered when done in sc liquids. [14]

4. CONCLUSIONS

Green chemistry is not a brand-new field of study. It's a new philosophical approach that, if implemented and expanded upon, might result in significant advancements in chemistry, the chemical industry, and environmental protection. Green chemistry concepts should be taught to future generations of chemists, and they should have knowledge and habits that can be put into practice. Currently, one can readily discover fairly fascinating instances of the application of Green Chemistry laws in the literature. These concepts might be applied not just to chemical production, but also to their processing and utilisation. Several novel analytical procedures have been established, all of which are carried out in accordance with Green Chemistry guidelines. These methods are especially useful for executing chemical operations and measuring their environmental effect. Green

Chemistry will remain appealing and useful in the future decades. This method is supposed to solve a variety of environmental issues. The development of waste-free technologies and technologies with a lower environmental effect in the research stage does not imply that they will be used on a large scale. More flexible laws, new initiatives to accelerate technical transfer between academics and governments, and, last but not least, tax benefits for enterprises who use cleaner technologies in industry can all help to secure the adoption of such technologies in industry. By utilising the conveniences of contemporary civilisation, we all contribute to environmental damage and owe Mother Nature a debt. Future generations of chemists will benefit from a Green Chemistry education, which will help them solve a variety of environmental challenges on a national, regional, and global scale, as well as make them more competitive in the global economy. By beginning Green Chemistry education today, we will be well on our way to fulfilling our objective and enjoying the fruits of our labours for future generations of chemists and other experts.

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