

INTERNATIONAL JOURNAL OF INSTITUTIONAL PHARMACY AND LIFE SCIENCES

Pharmaceutical Sciences

Review Article.....!!!

Received: 30-10-2015; Revised: 18-11-2015; Accepted: 19-11-2015

A REVIEW ON GREEN CHEMISTRY

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Keywords:

Green chemistry

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ABSTRACT

This review article discusses real-world chemistry, introducing chemical principles as needed. Chemistry has been misused in many respects, such as the release of pollutants and toxic substances and the production of non biodegradable materials, resulting in harm to the environment and living things, including humans. It is now obvious that chemical science must be turned away from emphasis upon the exploitation of limited resources and the production of increasing amounts of products that ultimately end up as waste and toward the application of Chemistry in ways that provide for human needs without damaging the Earth support system upon which all living things depend. Fortunately, the practice of chemical science and industry is moving steadily in the direction of environmental friendliness and resource sustainability. The practice of Chemistry in a manner that maximizes its benefits while eliminating or at least greatly reducing its adverse impacts has come to be known as **Green Chemistry**. The beginning of green chemistry is frequently considered as a response to the need to reduce the damage of the environment by man-made materials and the processes used to produce them. A quick view of green chemistry issues in the past decade demonstrates many methodologies that protect human health and the environment in an economically beneficial manner.

INTRODUCTION

Green chemistry is an approach to the design, manufacture and use of chemical products to intentionally reduce or eliminate chemical hazards. The goal of green chemistry is to create better, safer chemicals while choosing the safest, most efficient ways to synthesize size them and to reduce wastes.

Green chemistry is an innovative way to reduce or eliminate the use of hazardous and toxic chemicals. Green chemistry is a fundamentally new approach to environmental protection, transitioning away from managing materials containing toxic chemicals at the end of a product's life cycle, to reducing or eliminating the use of toxic chemicals altogether. Green chemistry encourages cleaner and less-polluting industrial processes and products, and ensures that manufacturers take greater responsibility for the products they produce.

A central goal of green chemistry is to avoid hazard in the design of new chemicals. This objective is best achieved when information about a chemical's potential hazardous effects is obtained as early in the design process as feasible.

THE IDEAS OF GREEN CHEMISTRY:

Green chemistry incorporates a new approach to the synthesis, processing and application of chemical substances in such a manner as to reduce threats to health and the environment. This new approach is also known as:

- Environmentally benign chemistry
- Clean chemistry
- Atom economy
- Benign-by-design chemistry

Green chemistry is commonly presented as a set of twelve principles proposed by Anastas and Warner. The principles comprise instructions for professional chemists to implement new chemical compounds, new syntheses and new technological processes.

The first principle describes the basic idea of green chemistry — protecting the environment from pollution. The remaining principles are focused on such issues as atom economy, toxicity, solvent and other media using consumption of energy, application of raw materials from renewable sources and degradation of chemical products to simple, nontoxic substances that are friendly for the environment.¹

THE BENEFITS OF GREEN CHEMISTRY

1. Economical
2. Energy efficient

3. Lowers cost of production and regulation
4. Less wastes
5. Fewer accidents
6. Safer products
7. Healthier workplaces and communities
8. Protects human health and the environment
9. Competitive Advantage

DEFINATION OF GREEN CHEMISTRY

The term “**Green Chemistry**” is defined as “the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances”. Green chemistry can diminish the need for other approaches to environmental protection. Ideally, the application of green chemistry principles and practice renders regulation, control, clean-up, and remediation unnecessary, and the resultant environmental benefit can be expressed in terms of economic impact.

THE TWELVE PRINCIPLES OF GREEN CHEMISTRY

1. Prevention:

It is better to prevent than to clean or to treat afterwards (waste or pollution). This is a fundamental principle. The preventative action can change dramatically many attitudes among scientists developed in the last decades. Most of the chemical processes and synthetic routes produce waste and toxic secondary substances. Green Chemistry can prevent waste and toxic byproducts by designing the feed stocks and the chemical processes in advance and with innovative changes.

2. Maximize synthetic methods, Atom Economy:

All synthetic methods until now were wasteful and their yields between 70-90%. Green Chemistry supports that synthetic methods can be designed in advance to maximize the incorporation of all reagents used in the chemical process into the final product, eliminating the need to recycling the byproducts. The concept of **Atom Economy** was developed by Barry Trost of Stanford University (USA), for which he received the Presidential Green Chemistry Challenge Award in 1998. It is a method of expressing how efficiently a particular reaction makes use of the reactant atoms.

3. Less hazardous chemical syntheses:

Green Chemistry must strive, wherever practical, to design safer synthetic methods by using less toxic substances as well as the products of the synthesis. Less toxic materials mean lower hazards to workers in industry and research laboratories and less pollution to the environment.

4. Designing safer chemicals:

Designing must become a fundamental aim of Green chemists to effect the desired function and properties of the chemical product while minimizing their toxicity to human and the environment. At present, there are around 100.000 chemical substances and materials in the market. Most of these substances have been characterized as to their physiochemical properties And toxicities, but there is lack of eco toxicological data for most of them. From the 1980s there are more stringent regulation and new chemicals are monitored more effectively.

5. Safer solvents and auxiliary substances:

Solvents, separation agents and auxiliary chemicals used in synthetic chemistry must be replaced or reduced with less toxic chemicals. Green Chemistry initiated big changes in chemical laboratories and in the last decade there are less toxic solvents in chemical laboratories and alternative techniques.

6. Design for energy efficiency:

Chemists must recognize that until now there was very little thought to energy requirements in chemical synthetic chemical processes Designing more efficient methods is a necessity and if possible synthetic methods should be conducted at room temperature and pressure to reduce energy requirements.

7. Use of renewable raw materials and feed stocks:

Starting raw material for synthetic processes are mostly petrochemical substances and products of refining. Raw materials must have very low toxicity and if possible to be renewable, rather than depleting. We know that there are many practical problems in finding renewable raw materials. Green chemists must change the manufacturing process by discovering renewable chemicals. Development with depleting natural resources is a negative aspect of economic growth.

8. Reduce intermediate derivatives:

Chemists must aim for reducing unnecessary derivatization (use of blocking groups, protection/deprotection techniques and temporary modification of physical and chemical processes) in the synthetic routes. These derivatizations use additional reagents, are wasteful and produce large amounts of by-products and waste. The principle reminds chemists to change their old ways of producing chemicals with more chemical steps and additional materials. Designing new chemical synthetic routes are desirable.

9. Catalysis, catalytic reagents:

The use of catalysts is well known that can change dramatically the efficiency of chemical reactions and the yield of products. Catalytic reagents with great selectivity can be superior to stoichiometric reagents. New catalysts and more emphasis on catalytic processes is the future of green chemistry techniques.

10. Design products which degrade easily:

Most chemical products and consumer items do not degrade very easily, thus causing environmental problems... Green Chemistry aims at designing products so that at the end of their useful life to break down into innocuous materials. Persistence into the environment is a negative aspect of many consumer products (e.g. plastic products) and this can be reversed by designing products which degrade in a short time.

11. Real- time analysis for pollution prevention:

Analytical methodologies need to be further developed to allow for real time, in-process monitoring and control prior to the formation of hazardous substances

12. Inherently safer chemistry for accident prevention.

Raw materials and chemical substances used in chemical process should be inherently safe, i.e. their properties and their degradation products to be nontoxic and not dangerous (e.g. to explode, to be flammable, allergic to humans, cause burns to skin, etc). Green Chemistry aims to stop the use of dangerous materials for the health and safety of workers and the consumer. Many chemical processes. After twenty years of Green Chemistry initiatives and industrial applications it is amazing to see many creative innovations at various scientific and industrial processes. The cooperation of chemists, engineers, material scientists, bioscientists and technologists has achieved interesting results. The interdisciplinary approach has expanded the fields of green chemistry and produced some excellent non-toxic materials and feedstock savings in chemical industries.



Fig.1: Principles of green chemistry

GREEN GUIDELINES FOR TEACHERS AND STUDENTS IN LABORATORY

1. Experiments should involve the use of alternative reagents which are not only eco-friendly but also be easily available anywhere in the country in bulk quantities at very cheap price. They should not preferably involve the use of organic solvents (like ether, petroleum ether or ethyl acetate); ethanol and methanol are mostly preferred.
2. Modified Experiments, if possible should not involve sophisticated instrumentation techniques like high-pressure system, evacuated system, inert atmosphere using argon, etc. This is in view of the stringent situations in many of the laboratories in most of the institutions of our country, specially, in rural areas.
3. Experiments should avoid tedious experimental procedure like longer reaction time, reaction at high temperature etc.
4. All organic chemistry experiments (preparation, separation of mixture of compounds, identification of functional groups etc.) should preferably be conducted in semi-micro or micro-scale. Thin-layer chromatography (TLC), spectroscopic techniques (UV, IR and wherever available NMR) should be methods of choice for determining purity, functional groups and structure elucidation.
5. One can use ethyl chloroformate as a substitute for PCl_5 , PCl_3 , POCl_3 or SOCl_2 . The acid is converted to anhydride which can be used for the same purpose
6. Dimethyl carbonate may be used as a suitable substitute for dimethyl sulfate and methyl halides for methylation as the end product is only carbon dioxide
7. Preparation of derivatives on large scale and assessing them could be dispensed with. Instead the student may be asked to report TLC behavior of the compounds prepared.

SUGGESTION FOR IMPROVEMENT OF LABORATORY ATMOSPHERE:

1. Direct use of H_2S gas generated from Kipp's apparatus must be avoided.
2. H_2S may be generated from the Kipp's apparatus in a fume cupboard (or, in absence of it, in open air) and be dissolved in water. Saturated solution of H_2S is to be prepared and kept in air-tight bottles. This H_2S water is to be supplied in dropping bottles and be used when required.
3. A better alternative for H_2S in inorganic group analysis is highly desirable and efforts should continue to find one.
4. Laboratory remains filled up with acid fumes. Rampant use of conc. acids like HNO_3 , HCl must be avoided. Ammonia bottles must always remain tightly corked. Chemical tests using conc. acids or ammonia must be carried out in fume-cupboard. The gases from

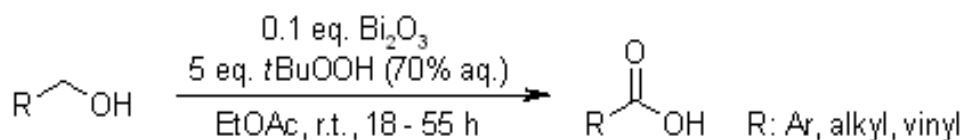
the exhaust may be passed through alkali solution (preferably lime water) for absorption. The nitrite or nitrate salts of calcium may be used as fertilizer. The laboratory must be provided with sufficient number of exhaust fans.

5. Dissolution of ores/alloys for making solution for quantitative analyses must be carried out in the modified fume cupboard.
6. Fire extinguisher, first aid kit, eye shower should be kept ready in a particular common place. Hand gloves, safety glasses, and aprons must be made compulsory during lab work.
7. 'SPOT TESTS' must be introduced for the detection of basic as well as acid radicals (Inorganic Analysis).
8. Preliminary experiments leading to the detection of NO₂-, NO₃ -, Br-, Cl- should be carried out in test tubes fitted with an outlet (bent tube). Gases issuing out of the tube must pass through alkali solution.
9. Tests with Hg, As, Cd, Pb, Bi, Cr - salts, which are toxic, must be excluded from syllabus meant for the undergraduate general stream students. But these tests may be kept for Honors. Students for demonstration only. For these metal ions 'spot-tests' are only recommended. The waste, after the tests, may be dumped in pits specially designed for waste disposal. Plants that absorb the heavy metals are seeded or transplanted into metal-polluted soil and are cultivated using established phytoremediation practices, if possible. As they become saturated with the metal contaminants, roots or whole plants are harvested for disposal. The plants include water hyacinth, penny wort ("Thankuni" - *Hydrocotyle Umbellata* L.) duduweed ("Pana" - *Lenna Minor* L). The roots of Indian mustard are effective in the removal of Cd, Cr, Cu, Ni, Pb, Zn, and sunflower removes Pb, U, ¹³⁷Cs and ⁹⁰Sr from hydroponic solutions.

RECENT RESEARCH PAPERS ON GREEN CHEMISTRY SYNTHETIC ORGANIC ROUTES

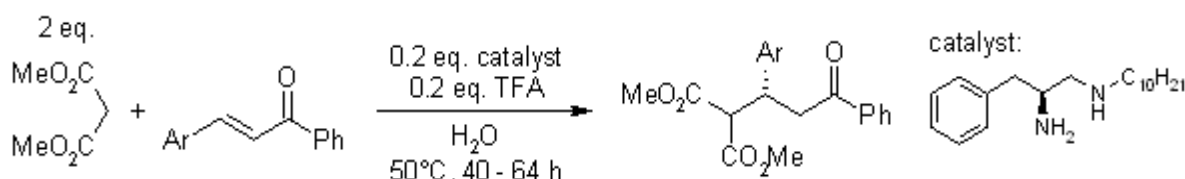
1. Transformation of aromatic and aliphatic alcohols in the equivalent carboxylic acids and ketones. Green synthetic method

Various aromatic, aliphatic and conjugated alcohols were transformed into the corresponding carboxylic acids and ketones in good yields with aq 70% *t*-BuOOH in the presence of catalytic amounts of bismuth(III) oxide. This method possesses does not involve cumbersome work-up, exhibits chemoselectivity and proceeds under ambient conditions. is The overall method green.. Bismuth (III) oxide catalyzed oxidation of alcohols with tert-butyl hydroperoxide.



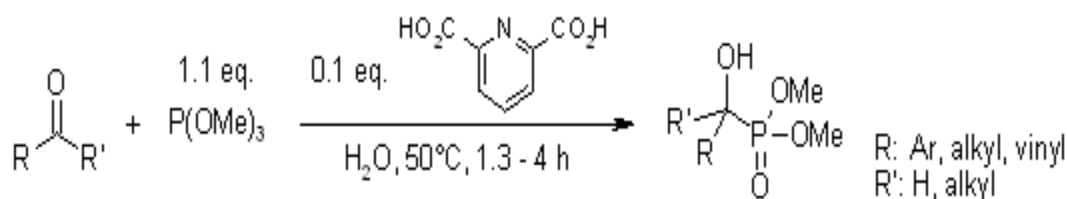
2. Enantioselective Michael addition

A highly enantioselective Michael addition of malonates to α,β -unsaturated ketones in water is catalyzed by a primary-secondary diamine catalyst containing a long alkyl chain. This asymmetric Michael addition process allows the conversion of various α,β -unsaturated ketones.



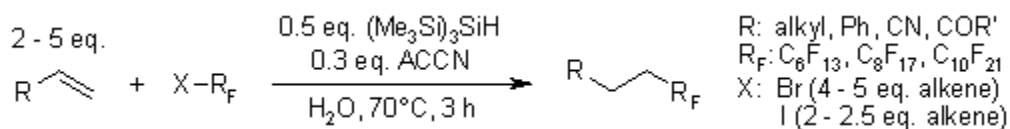
3. Organocatalytic direct α -hydroxy phosphonate of aldehydes and ketones

An organocatalytic, direct synthesis of α -hydroxy phosphonates via reaction of aldehydes and ketones with trimethylphosphite in the presence of catalytic amounts of pyridine 2,6-dicarboxylic acid in water is simple, cost-effective and environmentally benign.



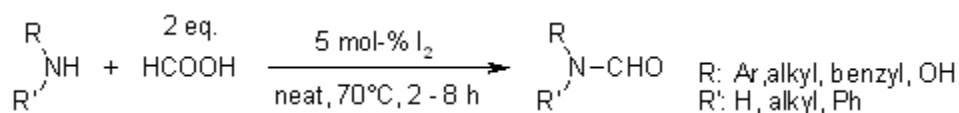
4. Intermolecular addition of perfluoroalkyl radicals

Intermolecular addition of perfluoroalkyl radicals on electron rich alkenes and alkenes with electron withdrawing groups in water, mediated by silyl radicals gives perfluoroalkyl-substituted compounds in good yields. The radical triggering events employed consist of thermal decomposition of 1,1'-azobis(cyclohexanecarbonitrile) (ACCN) or dioxygen initiation.



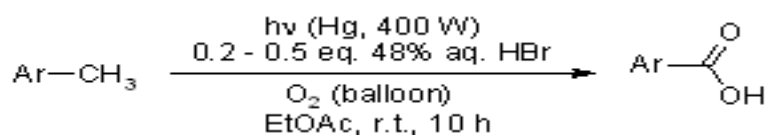
5. Practical catalytic method for N-formylation

A simple, practical, and catalytic method for the N-formylation in the presence of molecular iodine as a catalyst under solvent-free conditions is applicable to a wide variety of amines. α -Amino acid esters can be converted without epimerization.



6. Direct oxidation of methyl group in aromatic nucleus

A methyl group at an aromatic nucleus is oxidized directly to the corresponding carboxylic acid in the presence of molecular oxygen and catalytic hydrobromic acid under photoirradiation.



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