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GREEN CHEMISTREE; A SAFER APPROACH TOWARDS CHEMICAL

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ABSTRACT
Green Chemistry also considered as sustainable chemistry as it protects environment from hazardous chemical process and their products. Green chemistry basically approach towards the utilization of techniques or methods that tends to reduce or abolish the use of hazardous substances in the delineation, manufacture and its application. Chemical synthesis involves the utilization of different techniques and methods based on solvent type. Lamentably many of the techniques used in industry, laboratory at study center or hospitals and retails are risking human health, environmental damage through pollution caused by exposed application of organic compound and thus to reduce these we need green chemistry for synthesis. Hence all traditional or modern ongoing synthetic routes lead to harm all living beings by affecting environment. Green and safe approach of chemistry provides passage for different synthetic avenues using non-hazardous and environmental friendly techniques which includes ultra-sonication, microwave irradiation, dry media reaction having enormous advantages of synthesizing chemical compounds without affecting environment and human health.

KEYWORDS: Green Chemistry, avenue, delineation, lamentably.

INTRODUCTION

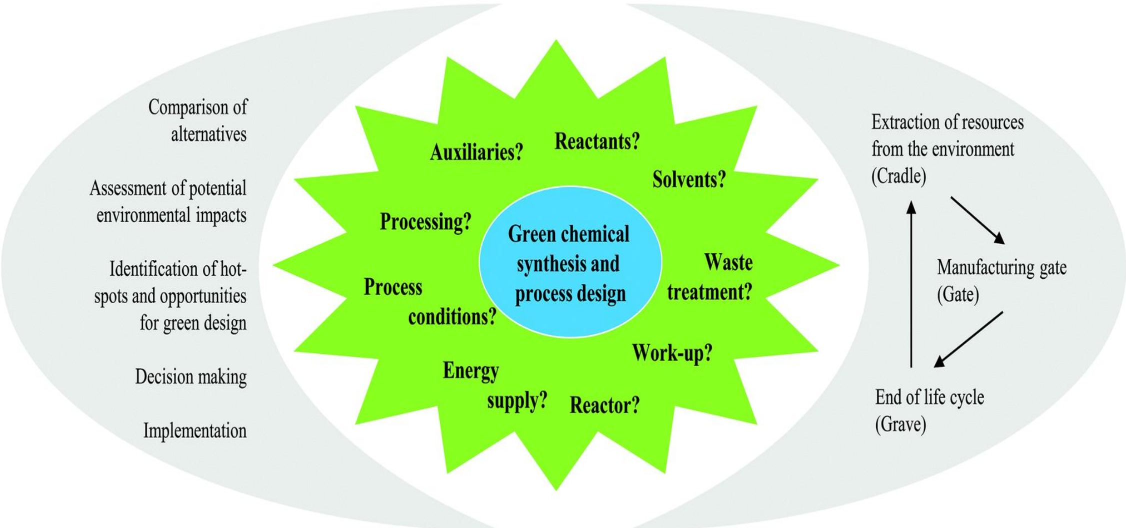

Fig.1.

Green Chemistry furthermore referred as the Environmental Benign chemistry. Despite of the fact that various methods and techniques have been developed till now for the synthesis of the various chemicals and among these, Green chemistry is the only exquisite and unique among them as it is environment friendly and restrain the pollution as well as perilous drawbacks of the chemical reaction. The orientation of green chemistry primarily developed in 1990 as a response to Pollution Prevention Act. The most crucial goal for prevention of pollution source instead of treating pollutants for Environmental Protection Agency (EPA) in 1991 becomes a formal objective of this act.[1] Extensive attention has been gained by Green chemistry in this decade. It is a modern branch of chemical science comprising an interdisciplinary field, having combined knowledge about all the aspect of chemistry i.e. chemical engineering, ecology and toxicology.[2] Green chemistry also promotes determination of certain catalytic processes that lowers the quantity of reagent and also raises eco-friendly reaction media, which almost lead to zero squandering of chemical pollutant by implying the ideal concept of atom economy. Green chemistry also promotes the establishment of certain catalytic processes that lowers the amount of reagent and enhance eco-friendly reaction media, leading to almost zero wastage of chemical pollutant by using concept of atom economy. The most widely accepted definition of Green chemistry was given in 1998, by the Chemist's Dr. Paul Anastas and Dr. John Warner who defined[1] "Green chemistry as the design of chemical products and processes that reduce or eradicate the use and generation of hazardous substances". There are certain techniques that can be used as a prospective of green chemistry and these are.

- Dry Media reaction
- Microwave Irradiation
- Ultra-sonification

These enlisted methods are compiling with the principles given by Dr. Paul Anastas and Dr. John Warner. The principles outlined by them were mainly to demonstrate how chemical production could respect human health and the environment while also being efficient and profitable.[3] The principles that are applied in the green chemistry technique or method are as shown in Fig.2

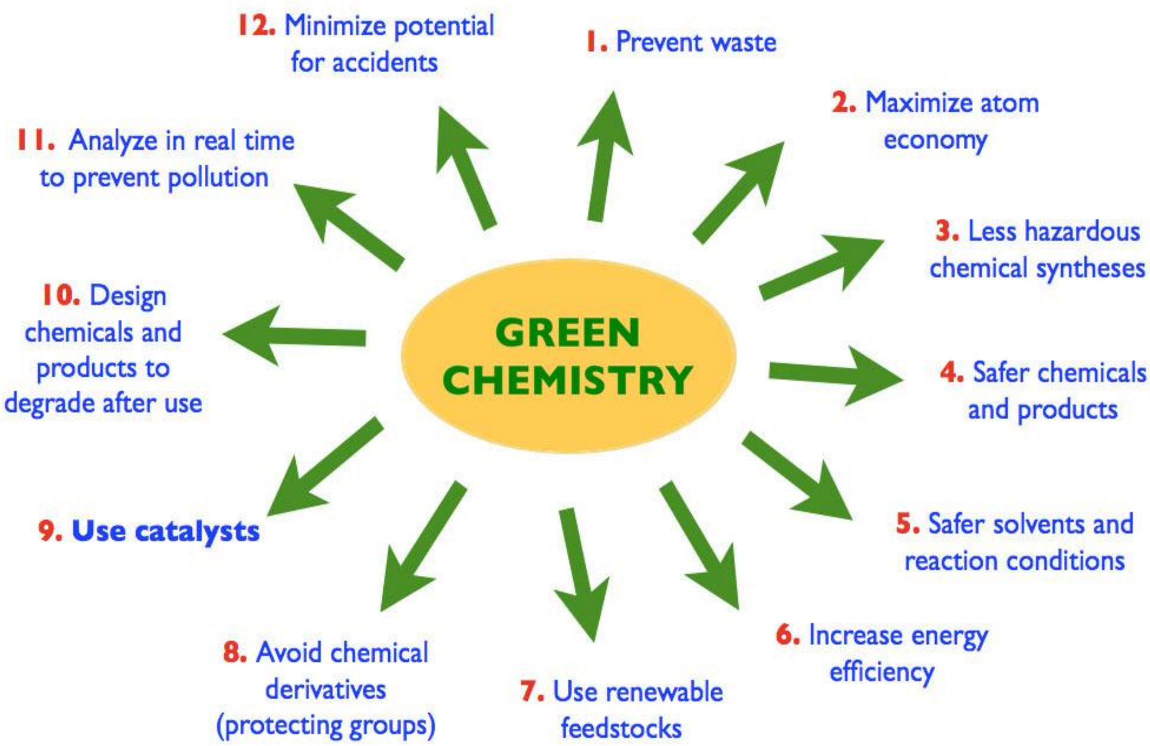

Fig. 2: Principles of green chemistry.

The principles cover such concepts as:

- Design the process in such a manner that it can maximise the consumption of reactants in the formation of product and minimise the waste.
- the use of safe, environment-benign substances, including solvents, whenever possible;
- the design of energy efficient processes;
- Not to create waste in the first place is the best form of waste disposal.

1.1. Dry media reactions

Solid-state reaction or Solvent-free reaction is the another name for the Dry media reaction. The major objective of green chemistry is the advancement of various clean technologies. Earlier, it was believed by the chemist that chemical reaction occurs only if the compounds are dissolved or present in the liquid state. Thus it had made solvents common in chemical synthesis, which leads to the production of perilous waste as some solvents were not environment-friendly. Therefore by performing reactions without a solvent (dry media reactions) under the microwave irradiation(MWI), this problem of waste disposal of solvents has been overcome. Under solvent-free conditions by coupling MWI will provide clean chemical processes with the various advantage such as

- Enhanced reaction rates
- Higher yields
- Greater selectivity and Ease of purification.[4-5]

1.2. Microwave reactions

In chemical synthesis, Microwave irradiation (MWI) has been developed into a recognized tool. To promote synthetic transformation, Microwaves can be used as an energy source. In the recent year, due to high yields, fast reaction rate furthermore improved selectivity, with respect to the conventional reaction conditions, Microwave-assisted organic synthesis (MAOS) has authenticated as a new tool in the synthesis of organic compounds. Synthesis that can be carried out using microwave irradiation follows the principles of Green Chemistry. Polar molecules selectively absorb the microwave energy and due to which it provides an alternate to the other conventional methods introducing energy into the system or for heating.[6] Microwave-assisted reactions are "cleaner" as they last only very few minutes and have high output and produce lessen waste. Due to enormous advantages of MAO's, most of the chemist shift to Microwave assisted chemistry from that of the traditional heating method.[7-8] Some of the advantages are.

- ✓ Simple and clean
- ✓ Uniform heating occurs throughout the reaction.
- ✓ Increased processed speed
- ✓ Cost of operating is low
- ✓ High economy
- ✓ Final product is clear
- ✓ High efficiency in heating
- ✓ Wastage of heating reaction vessel can be reduced
- ✓ Unwanted side reaction reduction

Thereafter it leads to immense development of the microwave irradiation technique from past few years, as a strong tool for fast and effective synthesis of different compounds.

1.3. Ultra-sonification approach

Sonication is the process of applying sound energy to agitate particles in a sample for various purposes. Ultrasonic frequencies are usually used, leading to the process also being known as ultra-sonication.[9] The use of ultrasound in a chemical reaction in solution provides specific activation based on a physical phenomenon called "cavitation". Cavitation is a process in which mechanical activation caused by agitation destroy the attractive forces of molecules in the liquid phase. Ultrasonic frequencies compress and expand the liquid molecules thereby causing sudden pressure drops which form small, oscillating bubbles of gaseous substances. These bubbles expand with each cycle of the applied ultrasonic energy until they reach an unstable size; they can then collide and/or violently collapse. Effective application of the ultrasonic purification process requires consideration of a number of parameters, while time, temperature and chemical nature of the particle. In a laboratory, it is usually applied using an ultrasonic bath or an ultrasonic probe, known as a sonicator.[10]

12 Principles of Green Chemistry

1. Prevention: The formation of waste material ad bi-product can be prevented rather than to clean them after the completion of the process. Synthesis can be carried out in the absence of solvent in case of organic compounds. "Grinding chemistry", process has been stimulated by this process in which the reagents are mixed without solvent, or by simply crushing them in a mortar. Microwaves has been used in developing field of chemistry to irradiate mixtures of neat reagents without solvents

2) Atom economy: The ideology of synthetic efficiency: Atom Economy (AE) also known as Atom Efficiency; was introduced by the Barry Trost in 1990.[11] It refers to the concept of utilizing the use of raw materials so as to ensure that maximum number of atoms from the reactants can be contained by the final product. The ideal reaction would incorporate all the atoms of the reactants. The AE can measured as the ratio of the molecular weight of the desired product over the molecular weights of all reactants that are used in the reaction. It is a theoretical value that help us to determine the efficiency of the reactant. Fig 3 (as an example).

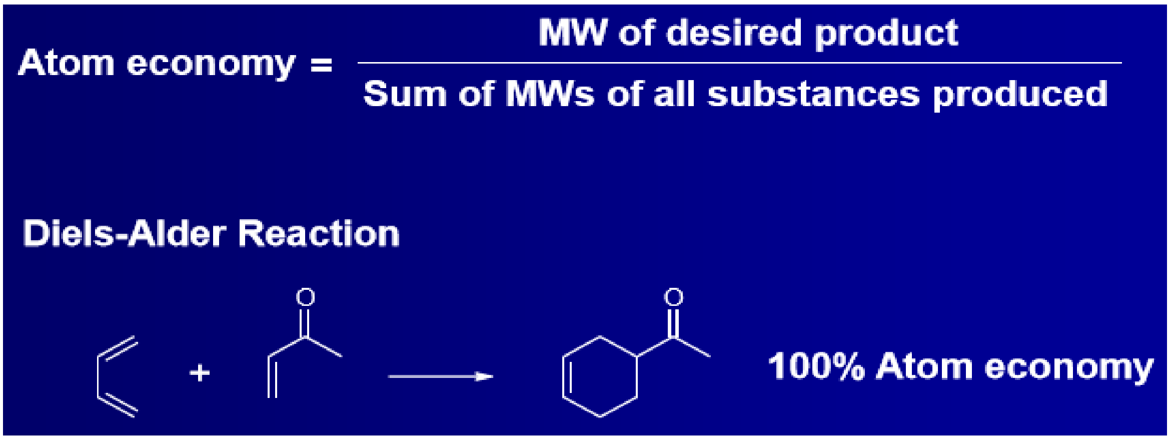

Fig 3: Illustrating the concept of atom economy.

3) Less hazardous chemical Synthesis: The synthetic toolbox of organic chemists has been improved by a significant amount of innovative work. Many of the new reactions that have been developed in the past decade add to the already existing green reactions that were discovered during the past century.

Fig 4(a): Typical example based on rearrangement: The Cope Rearrangement.

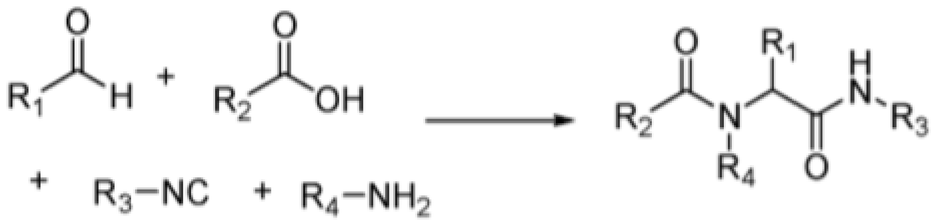

Fig 4(b): Example of Multi-component Coupling Reaction.

Reactions based on rearrangement(Fig 4a), 23 or multi-component coupling reactions (Fig 4b)24 were already known and constitute one category of efficient reactions. Cascade or tandem reactions, C–H activation[12] metathesis, and enzymatic reactions are rather new approaches and illustrate strong examples of cleaner, more efficient synthetic tools available to organic chemists.

It is an essential tool for the construction of larger molecules. C–H activation is another relatively new area of chemistry which holds great promise for the future.[12] In traditional coupling reactions, activated carbon–halogen bonds are usually used because of their high reactivity. Since halogenated molecules are rarely natural, it implies additional steps to produce the precursor. The replacement of traditional coupling reactions with C–H activation eliminates the need for halogenated precursors and therefore the halogenated waste byproduct generated. Two famous examples of C–H activation were published in 1993 by Murai[13] and in 2007 by Fagnou.[14] In the first case, Murai et al. employed a ruthenium catalyst to couple the inactivated substrates acetophenone and 2-methylstyrene. This work was one of the first examples of C–H activation and represents a milestone in the field. In the second case, Fagnou and Stuart coupled two aromatic compounds selectively without the need for any activating or directing groups. Those examples demonstrate the power of C–H activation in advancing Green Chemistry.

4) Safer Chemicals and Products: While there has been significant focus on designing chemicals for various functions ranging from medicines to materials, there has been a surprising lack of interest in taking into consideration hazard in the design process. Understanding the properties of a molecule that have an impact on the environment and the transformations that take place in the biosphere is essential to sustainability. Through a mastery of this understanding, chemistry will be able to genuinely design molecules that are safer for humans and the environment. Work by Arie¨ns[15] in 1984 and by Garrett and Devito in 1996 showed that designing safer chemicals is not only highly needed for the advancement of Green Chemistry, but is also possible.[16] In recent decades, there has been a significant amount of work in the field of toxicology that has moved it from being a descriptive science to one that has a large mechanistic component[17], and even more recently progressively towards the incorporation of an in-silico component.[18] Because of that transition, it has been possible to create correlations, equations, and models that relate structure, properties, and function. These approaches provide the basis for the work being pursued in the development of a comprehensive design strategy. For instance the existing understanding of medicinal chemistry can already help establish some ground rules for designing less toxic chemicals via incorporation of specific design features that block their access into humans and many animal organisms.[19]

5) Safer solvent and reaction conditions: Solvents are perhaps the most active area of Green Chemistry research.[20] They represent an important challenge for Green Chemistry because they often account for the vast majority of mass wasted in syntheses and processes.[21] Moreover, many conventional solvents are toxic, flammable, and/or corrosive. Their volatility and solubility have contributed to air, water and land pollution, have increased the risk of workers' exposure, and have led to serious accidents Green Chemistry and Green Chemical Engineering seeks to utilise benign solvents to develop more efficient synthetic routes. In chemical manufacturing and processes there are solvents used every step of the way. All of these must then be treated before disposal. Although solvents do not participate in liquid phase chemistry, they provide the medium within which the chemical reactions take place. Through the properties of this liquid medium a chemist can manipulate the reactants, heat transfer and separation. Many traditional solvents are volatile petroleum-based substances otherwise known as volatile organic solvents (VOCs). Other types include chlorinated solvents, which, along with the VOCs, pose risks to the environment and are flammable, toxic or carcinogens. These organic solvents are of concern to industry because of the volume used, their toxicity, and the costs of purchase and disposal. While such solvents can be recycled, they often require costly and energy-inefficient purification procedures such as distillation, and use of the recycled products is limited to non-pharmaceutical processes such as the petrochemical and plastics industries. Research into environmentally benign solvents and solvent-less systems has been one of the most active and successful areas of green chemistry research in the last ten years. Work is underway to replace VOCs with non-toxic, non-volatile, recyclable and renewable solvents in a wide variety of chemical processes.[22] Renewable biomass feed-stocks are now being used for solvents for common reactions. There has also been significant research into solvent options such as using high-temperature water and microwave heating, sono-chemistry (chemical reactions activated by sonic waves) and combinations of these and other enabling technologies like liquids that separate easily and which are easier to recover as they don't need an additional extractive processing step.[23] Depending on the physical properties of the reagents used or the desired outcome of the transformation, the approach often requires a new or redesigned chemistry to allow the reaction to proceed without the original solvent. Water is the most abundant molecule on the planet and is sometimes referred to as a benign ''universal solvent.''.[24] Being able to run a reaction in or on water therefore has significant advantages. Water is safe and does not pose any hazards. It can be a useful solvent for large scale process chemistry. The properties of water have even led to improved reaction rates through the hydrophobic effect[25] and easier separation since a lot of organic substances do not dissolve in water.

6) Increase Energy Efficiency: Rising concerns over the depletion of petroleum feedstocks and the increase in energy consumption have pushed the development of more energy efficient processes and for the search for renewable energies; non-depleting resources in a time frame relevant to human scale.[26]

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 reaction energy could be photochemical, microwave or ultrasonic irradiation. A boom is currently occurring in the use of these green energy sources and this is also associated with a marked decrease in the reaction time, to higher yields and, very often, to higher product purity. The design of chemical reactions or systems that do not require intensive energy use is highly desirable. Reducing the energy barrier of a chemical reaction or choosing appropriate reactants so that the transformation may proceed at room temperature is one example of what chemists can do to reduce energetic requirements, with all the direct and indirect benefits associated with it. Increasing the energy efficiency of a chemical system is merely one part of the solution. Alternative energies are also needed. Several of those renewable energies have been identified in biofuels production,[27] solar power (thermal and photovoltaic) wind power, hydro power, geothermal energy, and hydrogen fuel cells.[28] Once again, green chemists have an important role to play in this new challenge as they have the ability to design both energy efficient transformations and materials or chemical systems that can be used to harvest some of those renewable natural energies. Solar energy, the primary sustainable energy source on earth, is one of those alternatives to petroleum. Considerable efforts have been dedicated to understand and design chemical systems that can convert solar radiations into voltaic energy.[29] Organic, inorganic and hybrid solar cells have received interest although more focus has been placed on organic solar cells because of their higher efficiency. The principle of those cells relies on the ability of the material used to absorb photonic energy from solar radiations. The absorption leads to the formation of excited states that can be relayed and generate electronic current. Building materials and polymers that can efficiently transform light into current remain a challenge and are key to the success of this approach. Proton Exchange Membrane (PEM) fuel cells using hydrogen and oxygen gases could also provide another solution to the upcoming increase in energy demand (Fig.5).[29]

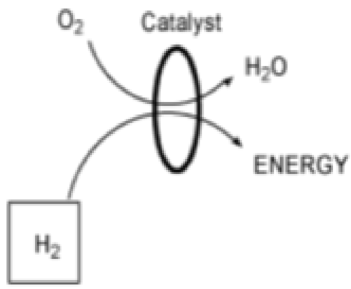

Fig 5: General concept of hydrogen fuel cell.

PEM fuel cells have generated research interest, especially in the past decade with the development of increasingly efficient catalysts such as nanoparticles or even hydrogenase enzymes.[30] An important consideration in this approach is the hazard of handling hydrogen gas, which is highly flammable and explosive.

7) Use Renewable feedstock

It has been estimated that the vast majority of our manufacturing products are derived from petroleum feedstock or natural gas.[20,31] The depletion of those resources will touch many aspects of our consumer life and our economy. Turning towards renewable feedstocks both for material and fuel has now become more urgent. The major renewable feedstock on the planet both for material and energy is bio-mass,[31] the material available from living organisms. This includes wood, crops, agricultural residues, food, etc.[32] Examples of renewable material include cellulose, lignin, suberin and other wood compounds, lactic acid, chitin, starch, glycerol and oil. Reusing this waste of the bio-industries should provide a large amount of raw materials to replace the current petroleum feed-stocks.

Moreover, Biodiesel (fig:6) is a diesel-equivalent biofuel that is usually produced from vegetable oil and/or animal fat by re-esterification with methanol or ethanol and this material can be used in cars and other motors.

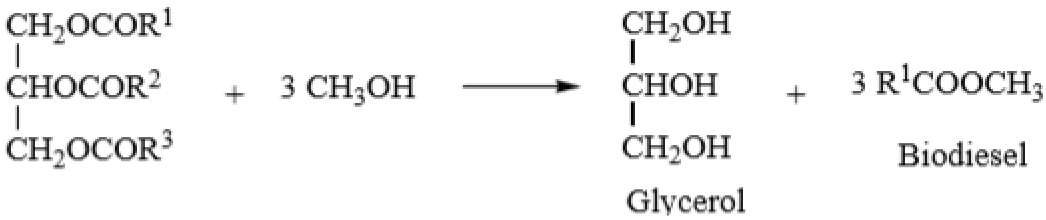

Fig 6: Re-esterification of vegetable or animal fat for biodiesel production.

Interest in biodiesel as an alternative fuel has increased tremendously as a result of recent regulations requiring a substantial decrease in the hazardous emissions from motor vehicles, as well as the high crude oil prices. Biodiesels are biodegradable in water and are not toxic. Upon combustion, much less hazardous emissions are formed (less sulfur is emitted, 80% less carbohydrates and 50% less solid particles) as compared to petro-diesel. Biodiesel can be used in modern diesel motors without the need for alteration of the motor.

8) AVOID CHEMICAL DERIVATIVES

Covalent derivatization is a ubiquitous technique in chemistry whether it is employed for organic synthesis or analytical chemistry.[33] In the early 1990s, an innovative concept surfaced called non-covalent derivatization, a derivatization that does not rely on covalent bonding but rather on intermolecular interactions.[34] 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. For eg. Bromination at the para- or ortho-position of anilines without protection of the amino (fig :7)[35] is a process in which the protection/deprotection steps have been removed.

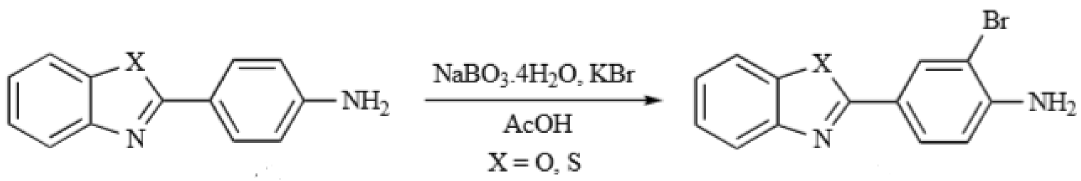

Fig 7: Bromination of anilines without protection of the amino group.

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

It follows that, wherever possible, a catalyst should be used in a chemical process. The advantages of using catalysts include.

- higher yield
- shorter reaction time
- the reaction proceeds in the presence of a catalyst but does not take place in its absence
- increase in selectivity.

  Biocatalysis is yet another example of ‘‘green’’ chemistry as it is a biomimetic approach relying on natural or modified enzymes.

10) 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 pollution. This approach is exemplified by the creation of biodegradable “green” polymers.[36,37] Designing biodegradable materials and chemicals is not a simple task as illustrated by continuing problems of environmental pollution. Trends have emerged following decades of data collection. Certain chemical structures such as halogenated moieties, branched chains, quaternary carbons, tertiary amines, and certain heterocycles may possess enhanced persistence and are avoided. On the other hand, integrating functional groups such as esters or amides which are recognized by ubiquitous enzymes may help the design of environmental degradable products.[38.39]

11) ANALYSE IN REAL TIME TO PREVENT POLLUTION

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

New analytical tools are needed for real-time monitoring of industrial process and to prevent the formation of toxic materials. The growing field of process analytical chemistry is aimed primarily at obtaining the analytical data close to the production operation. A real-time field measurement capability is desired for continuous environmental monitoring and this would replace the common approach of sample collection and transport to a central laboratory.[40] Methods and technologies should be developed so that the prevention or minimization of generation of hazardous waste is achieved. The dramatic downscaling and integration of chemical assays make these analytical microsystems particularly attractive as "green analytical chemistry" screening tools and hold considerable promise for faster and simpler onsite monitoring of priority pollutants.[41] For eg. Automated protein tagging technique helps to tags amino acids commonly found in proteins. It employs non-toxic solutions and generates no hazardous waste and replaces hazardous materials and high temperatures in traditional methods. It has also applications in the food and pet food sectors. Analytical methodologies should be developed in such a way that the process can be monitored in real time.It is necessary to have accurate and reliable reasons, monitors and other analytical methodologies to assess the hazardous that may be present in the process stream. These can prevent any accidents which may occur in chemical plants.

12 MINIMIZE POTENTIAL FOR ACCIDENTS

The reagents used to carry out chemical processes should be chosen with caution in order to avoid accidents, such as the release of poisonous substances into the atmosphere, explosions and fires. Dangerous substances and processes have multiplied in our working environment. According to the ''Chemical accident prevention and the clean air act amendments of 1990,'' preventing accidents starts by identifying and assessing the hazards.[42] All types of hazards whether it is toxicity, physical hazards such as explosive or flammability, and global hazards should be addressed in the design of chemicals and processes in order to prevent accidents such as Bhopal or the Love Canal incident.[43]

CONCLUSION

The term Green chemistry has been considered as an invention of certain chemical processes and techniques in the field of chemistry. With the development of these techniques, one can make a better control over the production of the hazardous chemicals and can also eliminate them. Green chemistry has switched off the use of the other techniques that were being employed earlier. The principles of the green chemistry has ideally put up its application and their utilization can be useful for regulating, cleaning and as well as the protection of the environment. In-fact, it has been developed to that level now-a days, from being at the last sort its being considered as the first choice. There are various methods that are being employed in the Green chemistry which can be put into usage as they are eco-friendly. The need of an hour is to make a switch to the Green chemistry for developing the narratives for the future and to contribute for the environment protection in this era of modern civilization. By doing so, we will be able to travel all long way on this new path to enjoy the outcomes of the efforts of scientists and chemists for this sustainable chemistry.

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