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E: ISSN NO.: 2455-0817 *Remarking An Analisation*

Green Chemistry for Controlling Environmental Pollution and Chemical Hazards

Abstract

Chemistry is undeniably a prominent part of our day to day lives. With the discovery of a number of drugs ,fertilizers, insecticides ,pesticides, herbicides chemistry brought revolution in our lives. Development of chemicals also bring new environmental problems and unexpectedly harmful side effects which results in the need for greener chemical products. Utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products is the principle aim of green chemistry .Green chemistry is also defined as environmentally benign chemistry. With the proper utilisation of green chemistry such pesticides that affect target organisms and degrade to innocuous by products may be developed. Green chemistry tasks at the prevention of pollution on the molecular levels and is extremely important area of chemistry due to the importance of chemistry in our world today. Some of the important developments of green chemistry include use of ionic liquids, Carrying out the synthetic reactions in water, solvent free reactions in microwave to reduce carbon footprint etc. In this paper we have discussed implementation of green chemistry principles to reduce environmental pollution and avoid chemical hazards in everyday life

Keywords: Green Chemistry, Chemical Hazards, Environmental Pollution.

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Introduction

Throughout the world and particularly in developing countries there is an increasing concern about environmental pollution and a desire to secure a healthy earth for our future generation .To ensure progress and sustainable development it is essential to reduce the toxic and hazardous effect of chemicals on earth. Pollution due to the use and production of chemicals has become a major challenge for human life. Green chemistry is a pro-active approach to pollution prevention. It targets pollution at the initial stage, before it even begins. Designing of chemical products and processes that reduce or eliminate the use and/or the generation of hazardous substances is the only purpose of Green chemistry. In Traditional technologies a lot of focus is on limiting the exposure of a hazardous material. Sometimes unfortunately exposure precautions can and will fail (i.e., gloves can tear, goggles can break, releases of harmful chemicals can occur). Green chemistry reduces pollution at the source by minimizing or eliminating the hazards of chemical feedstocks, reagents, solvents, and products and thats how it aims to eliminate the hazard itself. Green Chemistry is the only science that reduces or eliminates the intrinsic hazard of a chemical or chemical process. Environmental chemistry is the chemistry of natural environment and of pollutant chemicals in nature, whereas Green chemistry particularly tends to reduce and prevent pollution at source (1).Term Green chemistry was coined by Paul Anastas in 1991.Green chemistry refers to the field of chemistry that deals with

1. Synthesis of environment friendly chemicals
2. Processing for a safer path of synthesis
3. Use of chemicals that reduces risk to human life and harmful impact on the environment.

The twelve principles of green chemistry given in 1998 by Paul Anatas and John Warner ask chemists (2) to

1. Minimisation of waste
2. Atom economy- Synthehetic methods should be designed to maximize the incorporation of all materials thatt are used in process into the end product.

3. Less hazardous chemical syntheses
4. Designing the safer chemicals
5. Use of safer chemicals and auxillaries
6. Design for energy efficiency
7. Use of renewable sources
8. Reduce derivatives
9. use of catalyst in place of reagent
10. Design for degradation
11. Real time analysis for Prevention of Pollution
12. Inherently safer chemicals for prevention of accidents.

Chemical Hazard

A hazardous chemical is a chemical that has potential to cause personal injury or ill health due to over exposure .eg Benzene may cause damage to the environment like fire or explosion if not handled safely or in a workshop fire may be caused by CNG .We may get affected by the over exposure of chemicals simply due to inhalation of contaminated air ,passing of chemical through the skin , by swallowing workplace chemicals accidently by contaminated hands or food or due to the injection of chemicals into blood stream . Many type of risks are there that are caused by the over exposure to chemicals in the workplace. Exposure to the chemicals may cause long time detrimental health effects on almost all parts of body. Almost all type of workplaces use chemicals hence a broad range of workers are exposed to these hazardous chemicals. Exposure for a long time to chemicals such as silica dust, engine exhausts, smoke of tobacco, and heavy metals like lead (among others) increases the risk of heart disease, stroke, Cancer and high blood pressure (3).The best method to avoid the Hazards caused by these chemicals is to eliminate the use of these chemicals or if elimination is not possible then substitute these harmful chemicals with the safer ones. Green chemistry methods reduce the use and production of these hazardous chemicals .

*** Green Chemistry controls environmental pollution and chemical hazards by using a variety of green alternatives to conventional methods-**

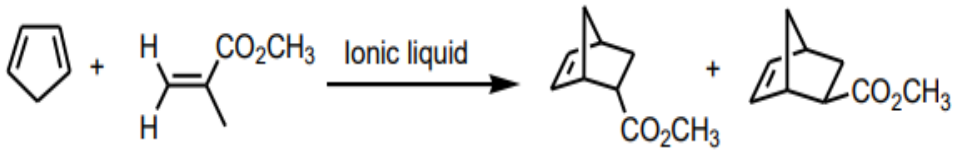
Ionic liquids:

Ionic liquids are the salts with their melting points below 100 degree celcius (4)and sometimes it is below room temperature(5).Ionic liquids are a material that is a fluid at ambient temperature, can be easily handled ,has low viscosity ,is colourless i.e a material that can be used as a suitable solvent for many reactions .Ionic liquids are formed from organic cations eg 1,3-dialkylimidazolium ,tetraalkylphosphonium, tetraalkyl ammonium, N-alkylpyridinium and trialkyl sulphonium cations .Ionic liquids have high chemical stability large liquid ranges ,easily recyclable little or no vapour pressure ,thermal stability and changeable properties by making suitable choice of cations and anions .Therefore they are considered a suitable medium for chemical syntheses. Ionic liquids are divided into many types eg .room temperature ionic liquids(RTLs) task specific ionic liquids(TSILs) ,polyionic liquids(PILs) and supported IL membranes (SILMs) that include composites of ILs supported on metal organic framework(MOFs).

Ionic liquids can be prepared in two steps . first step involves direct quaternisation of appropriate amine or phosphine and in second step Introduction of different anions by anion exchange takes place(6,7).

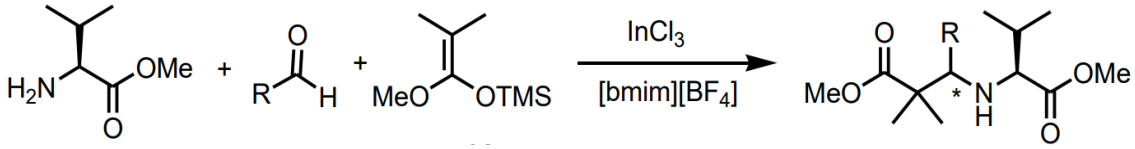
The first use of ionic liquid was (8) in the reaction of cyclopentadiene with methyl acrylate(Diels Alder reaction). These reactions lead to endo and exo products

Diels-Alder reaction in ionic liquid

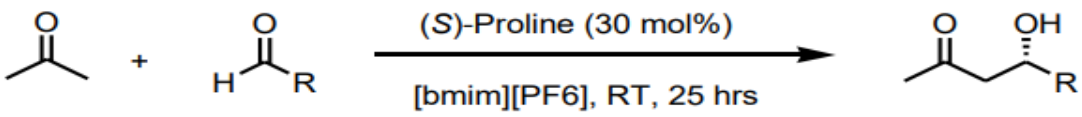


Besides the above ionic liquids have been successfully applied for a number of organic reactions like Mannich type reaction, Knovengeal reaction, 1,3 - cycloaddition,synthesis of thiazolidinones etc. Some of the examples are

Mannich reaction in ionic liquid



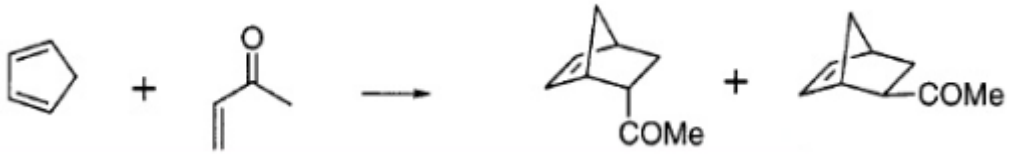
Aldol reaction in [bmim] [PF6] ionic liquid



Using Water in Organic Synthesis to replace Organic Solvents

Although water is used as a solvent in most of the inorganic reactions yet due to the poor solubility of most of the organic compounds in water it is not preferred as a solvent in organic reactions. Organic solvents like benzene and toluene are not only highly carcinogenic but they pollute the environment as they are highly volatile. Many physicochemical properties of water make it a unique solvent and such characterstics can be modified as per the requirement of the reaction by using various catalysts and

additives like surfactant. Unique properties of water include extensive hydrogen bonding, high heat capacity and large dielectric constant. In the past years most of the important organic synthesis have been tried to be carried out using water as solvent or as one of the components in the solvent mixture with some modifications in the traditional techniques.



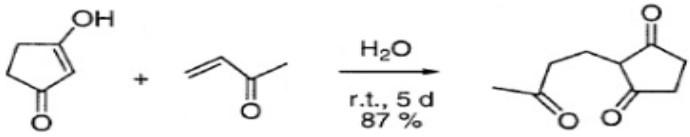
Diels Alder Reaction: Cycloaddition between cyclopentadiene and methyl vinyl ketone

One of the most powerful reaction for carbon -carbon bond formation is nucleophilic Michael type addition onto α ,β unsaturated ketones which is

Breslow et al. showed that rate of Diels Alder reaction increases 700 times when carried out in water(9) and suggested that the hydrophobic packing(10) of reactants is responsible for the increase of rate of Diels -Alder reaction.

promoted under pressure(11).This reaction is highly accelerated with water due to the hydrophobic effect of water.

Michael addition of 1,2 cyclopentadione



Solvent Free Reactions

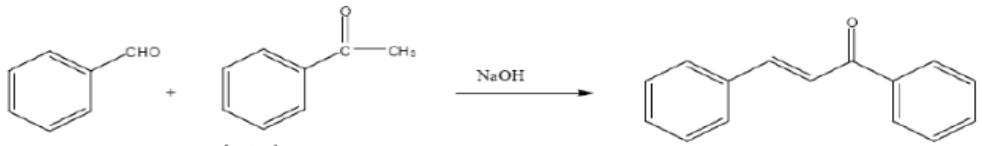
Earlier it was believed that it is not possible to carry out any reaction without solvent. In most of the synthetic organic reactions liquid solvents that are generally used are hydrocarbons, chlorinated hydrocarbons, a few ethers, esters, alcohols, amide derivatives, sulphoxides, etc. liquid ammonia and carbon disulfide. However A number of commonly used solvents are restricted as These solvents are highly volatile and toxic in nature and their wide use in a huge amount has posed a serious threat to environment. The logic behind using a solvent medium for synthesis is that the reactants effectively interacts in a homogeneous solution. However in organic reactions role of solvent is much complex as a solvent has the power to increase or decrease the rate of a reaction.

Now it has been established that a large number of reactions can be carried out in solid state without using any solvent (12,13).Such reactions occur more efficiently and with more selectivity .It is found that solvent free organic synthesis and transformations are useful industrial purpose and are environment friendly.

Advantages of solvent free reactions are that these reactions

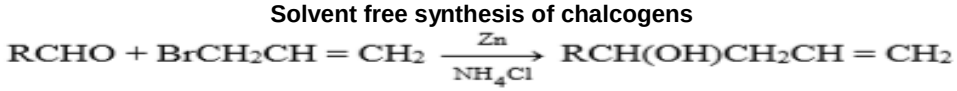
1. Tends to Reduce pollution and brings down handling costs due to simple experimental procedure.
2. Solid state or solvent free reaction may be carried out using the reactants alone or mixing them in clays, zeolites, silica, alumina. Thermal process or irradiation with UV, microwave or ultrasound can be employed to bring about the reaction.
3. Products of solid states reactions are different from solution phase reactions because of the specific orientation of reacting molecules in crystalline state and this has made it possible to synthesize chiral molecules from prochiral ones either by the formation of intermediates with chiral partners or by complexation with chiral hosts

Some of solvent free reactions like Solvent free synthesis of Chalcones (14), Luche reaction (15) Tishchenko reaction(16) etc. are given below.

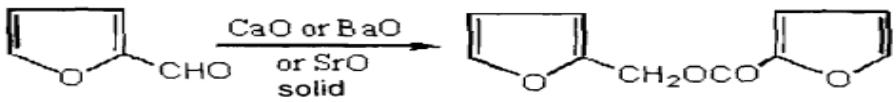


Benzaldehyde Acetophenone Benzalidineacetophenone

Solvent free synthesis of chalcogens



Luche reaction



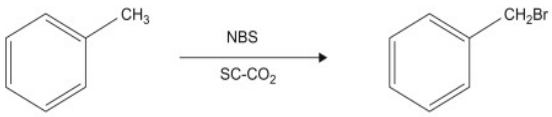
Tishchenko reaction

The reactions take place in half an hour when heating of the contents is done on water bath. The same reaction occurs only in one minute by heating in microwave at 540 watt.

Supercritical Carbon-Dioxide and Super-Critical Water

When a compound is subjected to a pressure and a temperature higher than its critical point, the fluid is said to be " supercritical " . In supercritical region a fluid shows some particular properties and its behaviour is intermediate between liquid and gas . Supercritical fluids (SCFs) possess liquid-like densities, gas-like viscosities and diffusivities intermediate to that of a liquid and a gas. Any fluid is said to be "supercritical" when it is heated above its critical temperature and compressed above its critical pressure. Carbon dioxide and water are the most widely used supercritical fluids. Unlike many organic solvents, supercritical Carbon dioxide is non-flammable. It is not only inert but also non-toxic and has a relatively low cost and has moderate critical constants. Its strength of solvation can be changed by adjusting the density of the fluid. Carbon dioxide leaves a lower amount of residue in products as compared to conventional solvents, and it is available in relatively pure form and in large quantities.

Supercritical carbon dioxide is good solvent for many non polar and a few polar compounds . Supercritical carbon dioxide has been tested in various industrially important reactions, such as alkylations, hydroformylations and hydrogenation(17) as an alternative reaction medium. e.g Supercritical – Carbon dioxide is, effective alternative to carbon tetra chloride for use in the classic Ziegler bromination reaction with the brominating reagent, N-bromosuccinimide, as is shown in the following reaction

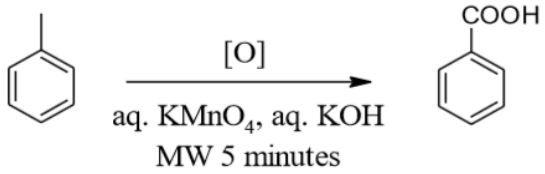


Microwave Assisted Solvent Free Reaction

Microwave assisted organic synthesis reactions are considered to be a most promising green chemical approach because it reduces time of reaction from days or hours to minutes or even seconds, and has many other advantage like .

1. Uniform heating throughout the material
2. Process speed is increased
3. High efficiency of heating
4. Reduction in unwanted side reaction hence preventing waste and increase yields in comparision to the classical techniques(18)
5. Purity in final product
6. Improve reproducibility
7. Environmental heat loss can be avoided

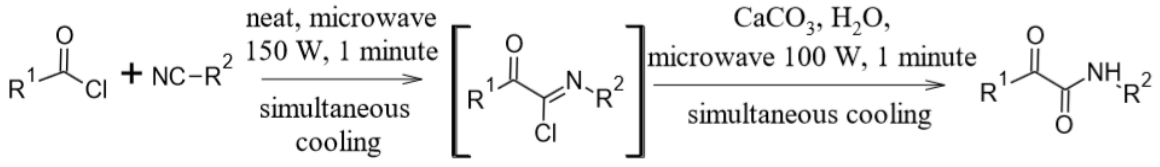
Microwave-assisted organic synthesis can be most conveniently conducted at atmospheric pressure in reflux conditions, for example, oxidation of toluene to benzoic acid with KMnO4 under normal conditions of refluxing takes 10-12 hours compared to reaction in microwave conditions, which takes only 5 minutes.



Oxidation of toluene to benzoic acid with KMnO4

By externally cooling the reaction vessel with compressed air and simultaneously administering microwave irradiation, more energy can be directly applied to the reaction mixture. This Enhanced microwave synthesis ensures that a high, constant level of microwave energy is applied.Cooling enables a greater amount of microwave energy to be introduced into a reaction, while keeping the reaction temperature low. This results in significantly greater yields and cleaner chemistries e.g synthesis of a variety of α-keto amides(19,20)

Improved Synthesis of α-keto Amides by Enhanced Microwave Synthesis



Green Organic Analysis

Conventionally in laboratories for performing lassaigne test the fusion of organic compound is done with Sodium metal which is highly hazardous when comes in contact with moisture and water as it may cause explosion. Sometimes the explosion is so violent that it may strike to the eyes of students causing damage. Alternatively using Zinc dust and sodium carbonate instead of using sodium metal may reduce the risk of such violent reactions. In this alternative method the sample is mixed with Zinc Dust and sodium carbonate in a fusion tube first gently and then strongly till it become red hot and kept for two minutes in this red hot condition.The bottom part of the fusion tube is plunged into distilled water and ground well and then filtered .With the filtrate the tests for Nitrogen ,Halogens and Sulphur are carried out as usual as in case of laissaigne test.

Green Qualitative Inorganic Analysis

H_2S is generated in the laboratory by the reaction of FeS and H_2SO_4 using Kipps apparatus .Some of the H_2S escapes to atmosphere causing air pollution ,while rest contaminates the water.To eliminate the use of toxic H_2S , increase the efficiency and ensure the certainity of analytical results a green scheme was developed. The Analysis of mercury and

arsenic was not done because they are highly toxic but they can be successfully analyzed by this scheme.The present scheme ensures seperation on the basis of common chemical properties and requires fewer steps as the number of groups is reduced from six to four(21,22).The solution is very dilute and these cations are difficult to detect and frequently missed.

Group	Cation	Precipitated as
Zero First Second Third A Third B Fourth	NH_4^+,K+ Pb^{2+}, Ag^+ Ba^{2+},Sr^{2+},Ca^{2+} Pb^{2+} Fe^{3+},Mn^{2+},Mg^{2+} Cu^{2+},Cd^{2+},Ni^{2+},Co^{2+} Cr^{3+},Al^{3+},Zn^{2+},Sn^{2+}	Directly detected in water extract Chlorides Sulphates Hydroxides Soluble amine Complexes Present as soluble hydroxo complexes(Cr^{3+}as CrO_4^{2-})

This scheme of analysis has been carried out in a mixture in which interfering radicals such as borate, oxalate ,Phosphate and fluoride are present. Hazards: there are very few hazards associated with this experiment as the corrosive Sulphuric acid used earlier has been replaced by Sodium sulphate .Con Nitric acid used to oxidize Ferrous to Ferric has been replaced by 6% H_2O_2, which is less corrisive .Heating is considerably reduced thereby lowering cases of spurting .Due to the toxic nature a very dilute solution of Nessler s reagent is used. The concentratin may be further reduced by using it as a spot reagent.

Green Quantitative Analysis using flower petal extracts as Indicators

The artificialy made indicators like methyl orange and phenolphthalein etc are not only hazardous tohuman health but are also prominent pollutants. The Green Chemistry has proved that these unsafe chemicals can be substituted by the petal extract as an indicator for acid base titration. The accuracy of the observed results has been examined by performing titration between different acids and bases of varying normality using petal extracts which are neither harmful to the environment nor it causes any health hazards e.g. Delonix regia flower petals, Urena lobata, Hibiscus rosa sinensis, Dahlia pinnata etc.(23)

Chemists are trying to find some more environment friendly methods to be used in daily life like making

1. Biodegradable plastic by using corn starch,
2. Eco friendly paints by using mixture of soya oil and sugar in place of petroleum petrochemicals derived paints resins and solvents which reduced the hazardous volatiles by 50%.
3. Green bleaching agents
4. Conventionally during manufacturing of good quality white paper, lignin from wood used for it, is removed by placing small pieces of wood into a bath of sodium hydroxide and sodium sulphide followed by its reaction with chlorine. During this process chlorine reacts with the aromatic rings of the lignin to form chlorinated dioxins and chlorinated furans. Being carcinogenic these compounds may cause severe health problems. Terrence Collins of cambegie mellon university developed a green bleaching agent where hydrogen peroxide is used as a bleaching agent in the presence of some activators such as Tetra-amido macrocyclic ligands which catalyses the fast conversion of hydrogen peroxide into hydroxyl radicals that cause bleaching. This bleaching agent breaks down lignin in a shorter time and at much lower temperature .It can be used in laundry and results in lesser use of water.
5. During the preparation of computer chips use of supercritical CO_2 is one of the important step that significantly reduces the quantities of water, chemicals and energy that are needed to produce chips.

Conclusion

The ultimate aim of green chemistry is to cut down the use of harmful chemicals and pouring them into the environment. With the development of new processes of green chemistry to reduce the pollutions new challenges are coming in front of scientists at a greater rate .Though many efforts are being made for designing pollution free starting materials and to make products that are safer and are without side products yet the aim seems unattainable in the present scenario. India is one of the major producer of pesticides and pharmaceuticals and because of that it has led an over stress on our environment ,therefore along with the use of traditional techniques of chemistry Indian scientists needs to emphasize more on developing greener methods and as such there is great potential of research on green chemical methods in India. Moreover a bitter fact is that in comparison to the developed countries where there is much emphasis on instrumentation developing countries are still relying more on classical methods at the grass root level .Therefore the greatest challenge before developing countries is to incorporate green chemistry in Industrial as well as laboratory and in daily life processes not only to control the pollution of the environment but also to check the hazardous incidences.

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