



Exploring Recent Trends in Green Chemistry towards Organic Transformations.

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Abstract:

One of the foremost active areas of research and development in green chemistry is that the development of analytical methodologies, giving rise to the so-called green analytical chemistry. The impacts of green chemistry on pharmaceutical analyzes, environmental, population, analyst and company are described during this review and that they are multidimensional. Green chemistry and environmental chemistry is interrelated subjects, green chemistry approach accustomed design new chemical moiety by minimizing chemical waste which effect on human health in addition as green chemistry approach step up towards pollution less environment. Now a day's desire of worldwide scientist's makes chemical that are effective, which might be synthesized in limited recourses.

Keywords: Phase Transfer Catalyst, Biodegradable, Hazardous Products.

1. Introduction:

Green chemistry is additionally called as sustainable chemistry. Over the past two centuries, fundamental theories and reactivity in chemistry are soundly established.¹ Such theories and reactivity have provided the foundations for the chemical enterprise that generates critical living needs like food for the world's population, achieves various medical wonders that save lots of lives and improve people's health, and produces materials essential to this and future needs of mankind. Any synthesis, whether performed in laboratories or industries scale should create minimum amount of by-products which pollute the environment.² In line with the work applied by Paul T. Anastas, the following basic principles of green chemistry are formulated.

- Prevention of waste/by-products.
- Maximum incorporation of the reactants (starting materials and reagents) into the ultimate product.
- Prevention or minimization of hazardous products.
- Designing of safer chemicals.
- Energy requirement for any synthesis should be minimum.
- Selecting the foremost appropriate solvent.
- Selecting the appropriate starting materials.
- Use of the protecting group should be avoided whenever possible.



- Use of catalysts should be preferred wherever possible.

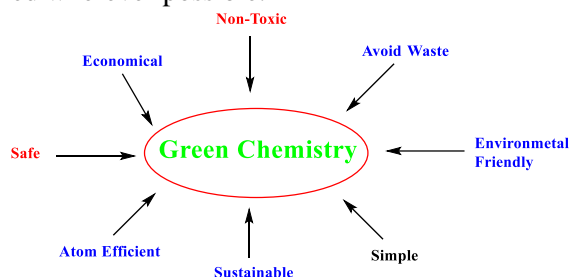


Fig 1. Graphical Representation of Principals of Green Chemistry.

- Products obtained should be biodegradable.
- The manufacturing plants should be so designed as to eliminate the possibility of accidents during operations.
- Strengthening of analytical techniques to control hazardous compounds.

Implementing these Green Chemical Principles requires a particular investment, since this, very inexpensive chemical processes must be redesigned. However, in times when certain raw materials become dearer (for example, because the availability of transition metals becomes limited) and also the prices for energy increase, such an investment should be paid back because the optimized processes quieten down expensive than the optimized ones. The event of greener procedures can therefore be seen as an investment for the long run, which also helps to confirm that the assembly complies with possible upcoming future legal regulations. A typical natural action generates products and wastes from raw materials like substrates, solvents and reagents. If most of the reagents and also the solvent will be recycled, the mass flow looks quite different

In any synthesis of target molecules the starting materials that are made to react with a reagent under appropriate conditions. Before coming to a judgement, consider all the possible methods which will give the specified product. The identical product can even be obtained by modifying the conditions. The tactic of choice shouldn't use toxic starting materials and will eliminate by-products and wastes, following are the some important considerations which improve the synthesis without byproducts.³

- Choice of starting material,
- Choice of reagents,
- Choice of Solvents
- Choice of catalyst.

The first goal of green chemistry is to provide a primary solid solution to the requirement for an ex novo design of this and necessary chemical processes by primarily considering safety, pollution prevention, waste minimization and energy optimization. To appreciate such goals, the requirement of chemists from different areas is apparent. Also important is how this novel approach to research has led to a special and hopefully more practical paradigm within the collaboration between industry and academia.

Herein we are discussing recent trends in Green Chemistry which motivate to synthesis environmentally benign chemicals, various catalyst and reactions has been developed. Improving the speed and then the selectivity of a reaction affects importantly its sustainability since it's visiting allow shorter amount, lower temperature, lower catalytic loadings, better yields and easier purification. In fact, the emergence of the utilization of water as a solvent for organic reactions was probably impulsed by the work of Breslow within

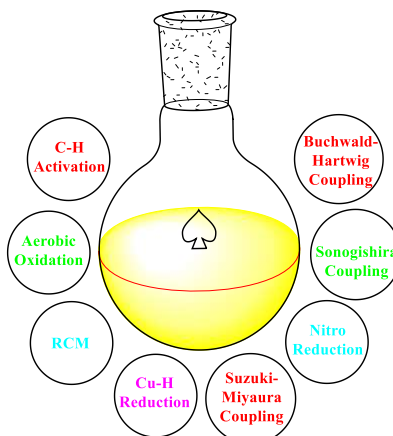
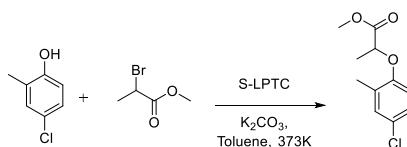


Fig 2. Explored Reaction by Green Chemistry.

the 1980s on the substantial rate enhancement of Diels–Alder reactions conducted in water compared to in other organic solvents.

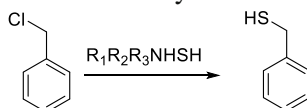
Phase transfer catalysed synthesis:

This method is specific for anionic reactions as it involves “anionic activation.” A catalytic amount of a tetraalkylammonium salt or a cation complexing agent is added to the mixture of both pure reactants. Reactions occur in the liquid organic phase which consists only of the electrophile R-X. The presence of a solvent is prejudicial as it induces a dilution of reactants and, consequently, a decrease in reactivity. The electrophile RX, acts as both the reactant and the organic phase for the reaction. Synthesis of Mecoprop ester using solid-Liquid Phase transfer catalyst in presence of K_2CO_3 base give liquid as product and two solid co-products.⁴



Scheme 1. Synthesis of Mecoprop ester from 4-chloro-2-methyl phenol.

H_2S utilization is difficult task in organic transformation, petroleum refinery industries. Recent report explore Phase Transfer Catalysed sulphidation of benzyl chloride with excellent yields.⁵



Scheme 2.Phase Transfer Catalysed Sulphidation of benzyl chloride.

Phase Transfer Catalyst (PTC) such as tetrabutylammonium bromide (TBAB) have been used for the sulphidation of benzyl chloride.

Water as green solvent in organic synthesis:

In taking stock of this instance, it's instructive to review the numerous roles that solvents play in reactions. Perhaps the foremost obvious is to bring the educts together during a standard phase, with the thought that rates are visiting be faster than once they're largely localized in separate phases. Water is that

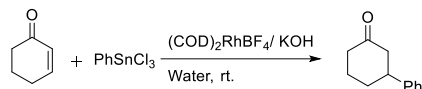


the perfect green chemistry solvent: it's benign, non-toxic, and non-flammable, features an awfully low odour, features a high heat capacity to take in energy from reactions, is on the market at a coffee cost, and is sustainable. The growing environmental pollution because of exponential use of volatile and harmful organic solvents in chemical industries has forced chemists to specialize in alternative green solvents. The concept of "green" solvent implies to scale back the environmental impact resulting from its use in chemical processes. During this sense, water may be considered as a potentially green solvent since is non-toxic to health and therefore the environment. Moreover, it's the safest and least expensive solvent. the very fact that water is one among the few "green" solvents capable of tunable their properties by changing the temperature has contributed to a rise within the number of publications using water as extraction solvent.

Organic functional group transformation reaction in water as solvent: Narayan et al has used water as greenest solvent in many reactions and proved importance of water as solvent in organic functional group transformation. All water insensitive reaction can be performed successfully in water and gives good yield. Mostly all reaction in water as solvent finished in less time duration, it proves that water is ultimate solvent for many organic transformations.

Narayan et al. has reported (**Scheme 3**) Diels-Alder reaction (4+2 cycloaddition) at room temperature and in water as solvent with 100% yield.⁶ Narayan et al. also were presented Cleisen rearrangement (3,3-Sigmatropic reaction) in water as solvent with 100% yield but the same reaction taken more time (120 h) at 23 °C (**Scheme 3**).⁶ The above same scientist has published enantioselective trans epoxide opening reaction with amine to afford α -Hydroamine in water as solvent at 50 °C, 88% yield in 12 h. ⁶ Thermal Ene (1,5 hydride transfer) reaction usually work in high temperature or at low temperature in presence of metal catalyst but Narayan et al. has reported Ene reaction at 50 °C in water as solvent with 91% yield (**Scheme 3**).⁶ Narayan et al. has presented Cycloaddition reaction in water as solvent and it proved that organic transformations works smoothly in water.⁶

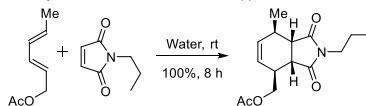
Water as solvent in conjugate addition of unsaturated carbonyl: Narayan et al. have reported Rhodium catalysed Michael addition of phenyl in water at room temperature. Rhodium catalyst coordinate with



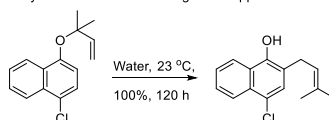
Scheme 4. Rhodium catalysed Michael addition.

carbonyl oxygen to make Beta carbon more electrophilic and increase the rate of addition of phenyl at beta-carbon.⁶

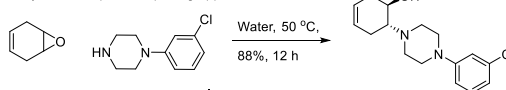
1. Narayan et al. Diels-Alder Reaction approach :



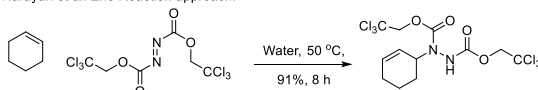
2. Narayan et al. Claisen rearrangement approach:



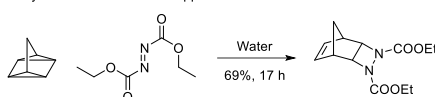
3. Narayan et al. Epoxide Opening approach:



4. Narayan et al. Ene Reaction approach:



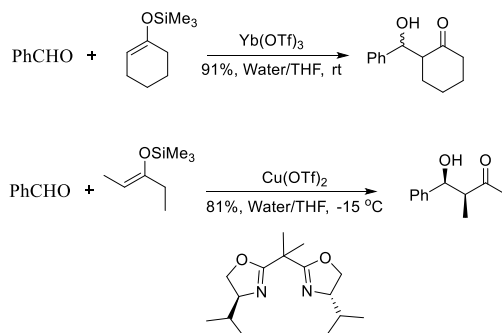
5. Narayan et al. Ene Reaction approach:



Scheme 3. Water as solvent in Diels-Alder reaction.

Water as solvent in Aldol Reaction: Normally in Mukaiyama aldol reaction, enolate nucleophilic attack on electrophile needs dry condition, but when benzaldehyde reacts with silyl enol ether in presence of Yb(OTf)₃ in water/THF solvent mixture gives beta hydroxyl ketone with 91% yield. In second equation of scheme 5. Silyl enol ether reacts with benzaldehyde in presence of copper catalyst in water as solvent.⁷

1. Mukaiyama Aldol Reaction in Water as solvent:



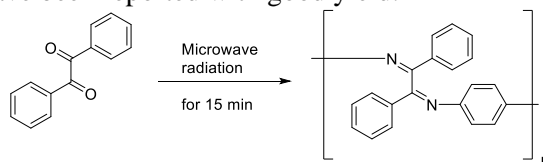
Scheme 5. Mukaiyama Aldol reaction in water.

Solvent free organic synthesis using microwave:

The emerging area of green chemistry envisages minimum hazard as the performance criteria while designing new chemical processes. New strategies have recently been developed aimed at working without solvent. Furthermore, it is also possible to activate processes by physical means such as ultrasound, pressure or microwaves. Among these new nonconventional methods in organic synthesis,

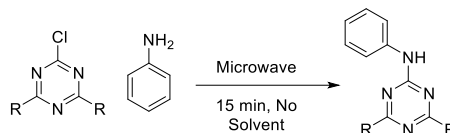


microwave irradiation takes a particular place as it induces specific interactions between materials and waves of electromagnetic nature assimilated to dielectric heating. Microwave (MW) irradiation, as an unconventional energy source has been used for a variety of applications including organic synthesis. Wherein chemical reactions are accelerated because of selective absorption of MW energy by polar molecules, non-polar molecules being inert to the MW dielectric loss. The combination of solvent-free procedures and microwave irradiation can be used to carry out a wide range of reactions within short reaction time and with high conversions and selectivity. Also, the yields and purity of the products are greatly improved compared to those obtained by conventional heating. This approach is efficient, easy to perform, economic and less polluting. Some major advantages of the organic synthesis under microwaves are very rapid reactions, requiring few minutes, brought about by high and homogenous temperatures and combined with pressure effects (if conducted in closed vessels). Higher degree of purity achieved due to short residence time at high temperatures, no local overheating, minor decomposition and minor Occurrence of secondary reactions. Synthesis of Polyimine using solvent free organic transformations with microwave assistance have been reported with good yield.⁸



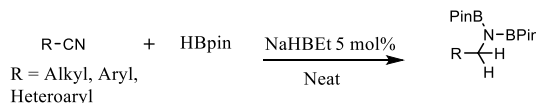
Scheme 6. Solvent free and Microwave assisted polyimine synthesis.

Aromatic Substitution reaction were reported using microwave radiation without any solvents with good 80% yields.⁹



Scheme 7. Solvent free and Microwave assisted aromatic substitution.

Synthesis of thioketones, thiolactones, thioamides, thionoesters, and thioflavonoids, Oxidation reactions, Reduction reactions, Multicomponent synthesis has been reported by solvent free microwave assistance. A highly efficient, room temperature, and Transition metal free and solvent free double hydroboration of nitrile also were reported. Sodium triethylborohydride is used as a catalyst and yields up to 99% are disclosed.¹⁰



Scheme 8. Solvent free and Microwave assisted double hydroboration of nitrile.

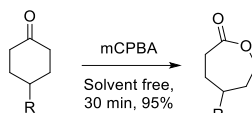
Solvent free organic synthesis or dry reaction techniques:

Among the most promising procedures for Green Chemistry, solvent free techniques hold a strategic position as solvents are very often toxic, expensive and problematic to use and to remove. The concept of solvent free reactions is not a new one and chemistry texts of the late 19th and 20th century contain numerous examples of reactions carried out using neat reactants. Many excellent examples exist of solvent free reactions in single crystals including photochemical reactions. In fact, solvent-free reactions and the reactions carried out in a homogenous phase where all reactants are dissolved in a mutual solvent can be considered as one of the big breakthrough in modern chemistry. Solvent-free reaction makes it possible to reduce consumption of environmentally unfriendly solvents and utilize



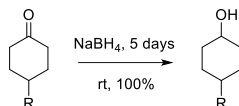
scaled down reaction vessels. Moreover, the use of a catalyst for solvent-free reaction can achieve energy savings. Several techniques for the efficient use of solvent-free reaction have been developed.

Baeyer-Villiger Oxidations of the ketone in presence of m-chloroperbenzoic acids gives ester, this reaction is faster in solid state than the solution state. In solid state gives 95% yield and in solution state it gives 94% yield.¹¹



Scheme 9. Solvent free Baeyer-Villiger Oxidation.

Many Solvent free Reduction reactions of ketone were also reported, ketone reacts with NaBH₄ in solid state given 100% yields. The same reaction mixture was crushed at room Temperature in mortar and pestle for 5 days.¹¹



Scheme 10. Solvent free reduction in presence of NaBH₄.

Various Organic Functional group transformations were performed without solvents such as Halogenations, Hydro halogenations, Michael addition, Aldol reactions, Cycloaddition reactions, elimination reactions, condensation reactions, coupling reactions, Substitution reactions, Hydrolysis, Rearrangement or Isomerisation reactions, Photoreactions. Enantioselective reacts also reported without solvents.

Conclusion:

In conclusion, this eco-friendly solvent-free microwave, phase transfer catalysed approach opens up numerous possibilities for conducting rapid organic synthesis and functional group transformations more efficiently. Additionally, there are distinct advantages of these green chemistry protocols since they provide reduction or elimination of solvents thereby preventing pollution in organic synthesis “at source”. The chemo-, Regio- or stereo-selective of high value chemical entities and parallel synthesis to generate a library of small molecules will add to the growth of microwave-enhanced reactions in the near future.

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