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Green Chemistry, Green Solvents and Alternative Techniques in Organic Synthesis

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Abstract

Green Chemistry aims for less toxic solvents but in recent years new methods have been developed where organic synthesis can be performed without solvents, mild conditions and low energy consumption. New conferences and symposia have promoted the use of alternative methods or "green" solvents. The new field of "green" solvents in organic synthesis has been extended by research papers and publications. In this article some of these methods are presented with a brief explanation of how they work and some references. Discussion of article gives small idea about green solvent, green catalyst, and green techniques for green synthesis.

Organic Solvents

Ionic Liquids in Organic Synthesis

Ionic liquids are mixtures of anions and cations, molten salts, with melting point around 100^{o}C, which can be used as alternative solvents in organic synthesis. Although the ionic liquids do not comptly full with green chemistry principles, they are very promising as alternatives to organic solvent In the scientific literature there are a large number of research papers for the use of ionic liquids in synthetic routes and various applications.

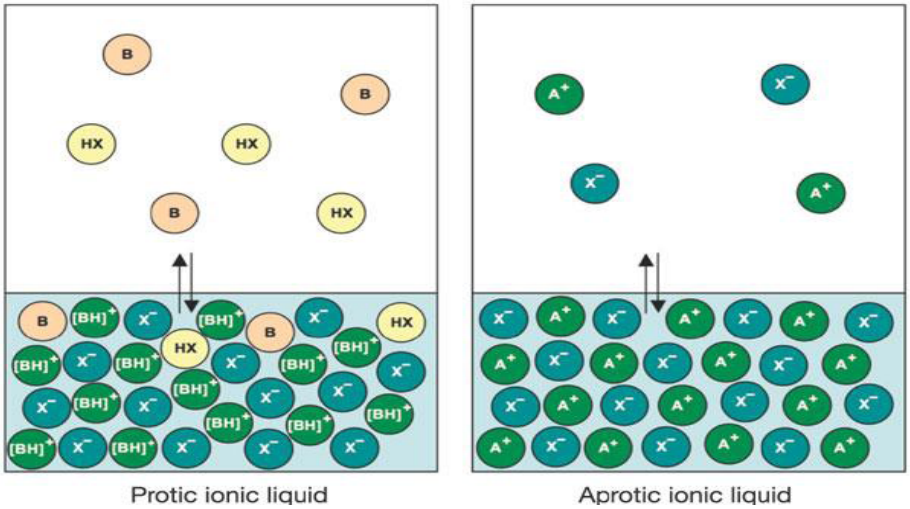

Figure 1. Schematic diagram of protic and aprotic ionic liquids in the liquid and gaseous phase.
[For the protic ionic liquids there is a dynamic balance between the ionic form and the dissociated form [BH]+X-(***l***)B(***l***) + HX(***l***)B(***g***) + HX(***g***). The green circles represent cations, the blue circles anions and the other colours neutral molecules. l=liquid phase, g=gaseous phase]

Organic Synthesis in Water

Although water is considered a problem for organic synthesis and the purification processes and drying in final products is very cumbersome, in recent years water is considered a good solvent for organic reactions. A good example is the synthetic routes of the Diels-Alder reactions in which the hydrophobic properties of some reagents makes water an ideal solvent. Water as a solvent accelerates some reactions because some reagent are not soluble and provides selectivity. The low solubility of Oxygen is also an advantage for some reactions where metal catalysts are used. In the last years water is used in many methods for organic reactions and the scientific literature has a large number of papers.

Supercritical carbon dioxide and supercritical water

A supercritical liquid is at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. The supercritical liquid can effuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned". Supercritical liquids are suiTable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon dioxide and water are the most commonly used supercritical fluids. Supercritical CO2 and water are considered “green” solvents in many industrial processes, providing high yields in many reactions, and there are many examples of their use in the scientific literature.

Organic Synthesis with Carbonic esters

Carbonic esters, such as DMC, dimethyl carbonate (CH3OCOOCH3) are considered a new class of “green” solvents in many organic reaction processes. They can replace methychlorides and dimethyl sulphate esters which are toxic and hazardous.30 DMC can be used in methylation reactions of phenols, anilines and carboxylic acids. DBU is an alternative solvent that can be used for methylation reactions of phenols, indoles and benzimidazoles.

Catalyst

“Green” Catalysis under the Green Chemistry Principles

It is not only the “green” solvents that will change the face of synthetic organic reactions, but also the use of “green catalysts” will improve substantially the efficiency of many industrial processes. The use of catalysts is one of the principles of Green Chemistry. Catalysis is considered a cornerstone for innovative changes in chemical processes. Catalysts will affect energy use and reaction time, will increase yield, reduce use of solvents, and lower production of by-products and waste. Catalysis with “green” catalysts (which can be recycled) is considered a very important step in the direction of Green Chemistry for many industrial processes.

Techniques

Replacement of Toxic Solvents with Less Toxic Ones

The replacement of toxic or hazardous organic solvents in industrial processes and systems has been initiated long time ago. Examples, like replacement of benzene with toluene, cyclohexane instead of carbon tetrachloride, dichloromethane instead of chloroform etc. The scientific literature contains many examples and practices with replacement of the most toxic and hazardous solvents.

Microwaves in Organic Synthesis, without Solvents

We examined in the previous chapters the use of microwave furnaces for organic reactions. These techniques do not require solvents and are considered "greener" than the conventional methods. The wide range of applications of microwave chemistry has been extended recently to many aspects of organic synthesis.Catalysis under the Principles of Green Chemistry and Eco-friendly Synthesis are new innovative trends with substantial applications.

Sonochemistry in Organic Synthesis, without Solvents

Sonochemistry is also considered a methodology of organic reactions without solvents. Their use has been described before and it is obvious that their applications in organic chemistry will be extended further. High yields, low energy requirements, low waste, no use of solvents are some of the fundamental advantages of these sonochemical techniques.

Other "Greener" Techniques

In addition to the above methodologies which do not require solvents or use less solvents than the conventional methods, there are are techniques of biocatalysis, self-thermo-regulated systems, soluble polymers, etc which are considered "green methodologies". Green Chemistry covers all these aspects of eco-friendly methods and promotes their use in research laboratories and in industrial organic synthesis processes.

"Green solvents" from plants

Plants are considered a renewable sources of energy but also a resource for various materials. Plant oils or vegeTable oils derive from plant sources. Unlike petroleum which is the main source of chemicals in the petrochemical industry they are renewable sources. There are three primary types of plant oil, differing both by the means of extraction and by the nature of the resulting oil: VegeTable oils can replace petroleum derived organic solvents, with better properties and more eco-friendly conditions as waste.

Chemists have advanced recently techniques so that some vegeTable oils to become solvents and replace hazardous organic solvents. As an example of plant-based oils we selected the research project by Spear et al. on soybean oils and their esters.

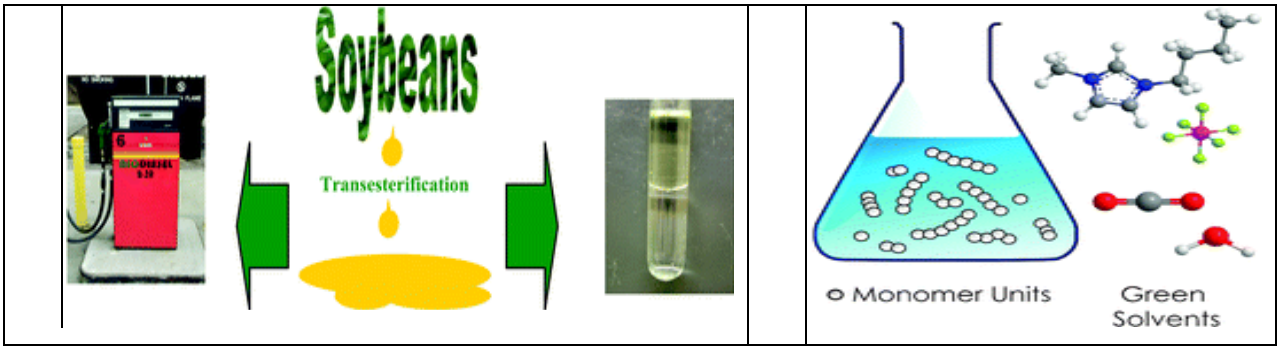

Figure 2 & 3

VegeTable oils can become a starting material for the production of eco-friendly solvents which are less toxic than the petrochemical industry's organic solvents In the last decade, scientists are researching the use of "green" solvents in polymerization methods, since the polymer and plastics industries are using vast amounts of solvents. There have been some successful uses of alternative solvents in polymerization under the principles of Green Chemistry. Polymers can be prepared under industrial scale production with the use of eco-friendly solvents. All these techniques aim at replacing toxic and hazardous solvents in many chemical processes in the synthetic laboratory and in the chemical industry.

Conclusion

Application of any single techniques for any synthesis are not possible. But each organic synthesis have a alternative and green method. Main aim of this article is to understand different types of availability of green solution for organic synthesis and need of green synthesis in present era. All mentioned techniques aim at replacing toxic and hazardous solvents in many chemical processes in the synthetic laboratory and in the chemical industry. Also there have been some successful uses of alternative solvents in polymerization under the principles of Green Chemistry.

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