REVIEW ARTICLE

Green Chemistry for Chemical Synthesis

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ABSTRACT

In the environmental conscious era, the role of chemistry and chemist is to develop processes and design products, which can either eliminate or minimize the generation of toxic by-products and other pollutants. Any new synthesis of chemical approach must consider and an element of environmental awareness. As per saying that, “preventing pollution and minimizing waste generation will gradually clean up our sins of the past”. After almost one and half century, a new kind of chemical revolution has come up i.e. “Green Chemistry”. Green chemistry is also termed as clean chemistry benign by design chemistry, sustainable chemistry, eco-friendly chemistry and environmentally benign chemistry.

Keywords: Atom Economy, Green Chemistry, Chemical Syntheses, Green Solvents, Green Catalysts.

INTRODUCTION

The term Green Chemistry was coined in 1991 by Anastas (1998). Anastas and Warner developed the twelve principles of Green Chemistry Anastas (1999) that serve as guidelines for preventing chemists in developing and assessing how green synthesis, compound, process technology is. These principles addresses some basic aspects such as use of various solvents, the amount waste produced, the use of catalyst and reagents, energy efficiency, atom economy and use of safer chemicals and reaction conditions.

Green chemistry approach is holistic in nature and encompasses almost all branches of chemical sciences like synthesis, catalysis, bio-inorganic, nano-chemistry, material science, drug discovery, pharmaceuticals etc. Ametha (2012).

The processes on industrial scale involve many chemical reactions using huge quantities and wider varieties of smaller molecules, reagents, solvents, acids, alkali etc. These processes do not produce the required products but also large quantities of undesired and harmful substances in the form solids, liquids and gases and hence become the biggest challenge that chemistry has to face. So, the pressing need for synthetic chemist is to minimize chemical pollution (Badami, 2008). Commercial applications of Green Chemistry have lead to novel academic research to examine alternatives to existing synthetic methods. Keeping view of twelve principles of Green Chemistry, a short review of Green chemical synthesis is taken in this paper.

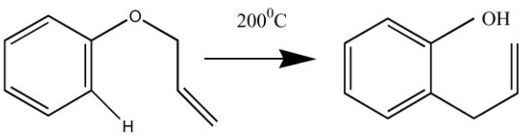
Atom Economy

The concept of atom economy as developed by Barry Tost considers how much of reactants in chemical reaction ends up in the final useful product/s. The goal of atom economy is to create syntheses in which most of the atoms of the reactants becomes incorporated in to desired final products leading to lower percentage of waste by-products (Kidwai and Thankur, 2005). Atom economy is a concept that evaluates the efficiency of chemical transformation, and is calculated as a ratio of total mass of atoms in the desired products to the total mass of atoms in the reactants.

$$\text{\% Atom Economy} = \frac{\text{No. of Atoms in the reactant}}{\text{No. of Atoms incorporated}} \times 100$$

It is observed that rearrangement and addition reaction are most economical.

Claisen Rearrangement:



I

Atom Economy % = (134.18/ 134.18) x 100 = 100 %

Addition Reaction:

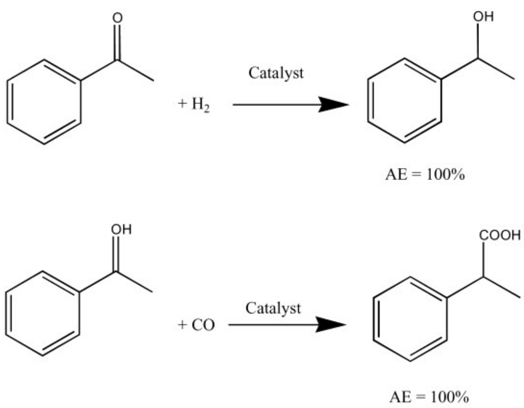
$$H_3C\text{-}CH{=}CH_2 + H_2 \xrightarrow{Ni} H_3C\text{-}CH_2\text{-}CH_3$$

II

Atom Economy % = (44.09/ 44.09) x 100 = 100 %

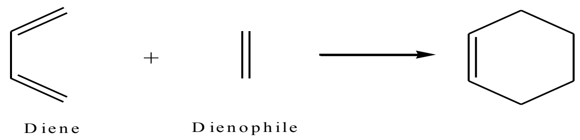
Many atom economical reactions using various transition metal catalysts have been developed (Trost, 1983; 1998-2000; Trost et al., 2000).

Atom Economy of Catalytic Processes:



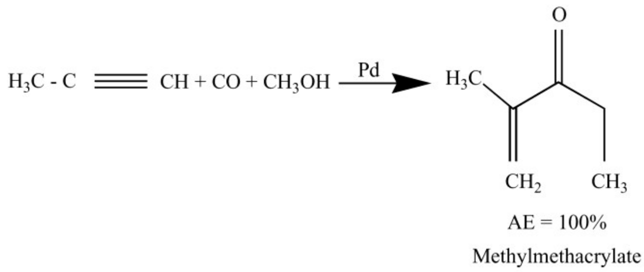
III

Diels Alder reaction is 100 % atom economy reaction as all the atoms of the reactants are incorporated in the cyclo adduct.



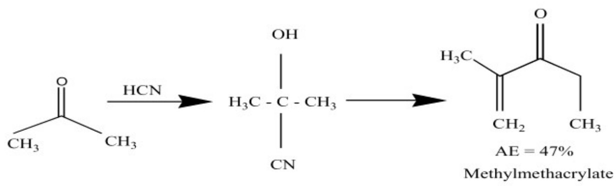
IV

Palladium catalyzed synthesis of methyl methylacrylate has 100% atom economy via green synthesis.



V

The old method of synthesis has only 47% atom economy.



VI

Recently many classical roots for chemical synthesis are being replaced by catalytic processes.

Prevention of Waste:

It is better to prevent waste than to treat up waste after its formation. For this it is necessary to redesign chemical transformation so as to minimize hazardous waste to prevent pollution. Many sources of waste are stochiometric reagents (acids, bases, oxidants and reductants), solvent losses, and multistep syntheses. For this atom and step economic processes in alternative reaction media can be solution.

Less Hazardous Chemical Syntheses:

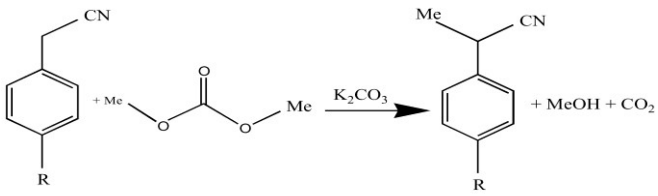
It is essential to design new synthetic methods so as to use and generate substances that are not toxic to human health. E.g. In manufacture of polystyrene foam sheet, chlorofluorocarbons responsible for O_2 depletion, global warming, has now been replaced by CO_2 as blooming agent.

Monasto Company has developed a method of synthesizing polyurethanes that totally eliminates the use of phosgene(Walden and Riley, 1994).

$$RNH_2 + CO_2 \longrightarrow RNCO + H_2O \xrightarrow[R'OH]{} RNHCOOR'$$

VII

Di-methyl Carbonate (DMC) is good chemical alternative as methylating reagent for toxic methyl halide or methyl sulphate. The reactions of DMC with reactive methylene compounds produce monomethylated derivatives with selectivity (Tundo et al., 1987; 1989).

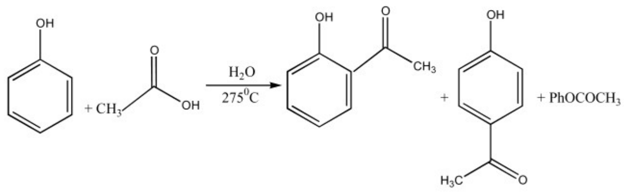


VIII

Use of Green Solvents:

Organic solvents are toxic and volatile which are harmful to human health and creates pollution in environment. Therefore, it is necessary to replace these solvents by safer solvents like ionic liquids, supercritical CO_2 or supercritical water and also solvent free systems that utilizes the surfaces or interiors of clay, zeolites, silica and alumina. Superficial CO_2 fluid is now becoming an important commercial and industrial solvent for chemical separation because of low toxicity and non inflammability. Ionic liquids (Welton, 1999; Holbery and Seddon, 1999; Seddon, 1997) are substances composed of cations and anions. Ionic liquids have emerged as green solvents because they have no measurable vapor pressure and that wide range of chemical reactions can be performed in them. Commonly used ionic liquids are those with alkyl ammonium, alkyl phophonium, N-alkyl pyridium cations and Cl^-, Br^-, I^-, BF_4^- anions. Ionic liquids find their useful and important application from hydrogenation to biocatalytic reactions.

Near critical water offers outstanding performance as benign solvents for both organic and ionic compounds (Eckert et al., 1999). Friedal-Craft's acylation requires Lewis acids but in near critical water, phenol could be converted with acetic acid to produce 2'-hydroxy acetophenone, 4'-hydroxy acetophenone and phenyl acetate without addition of an acid catalyst.



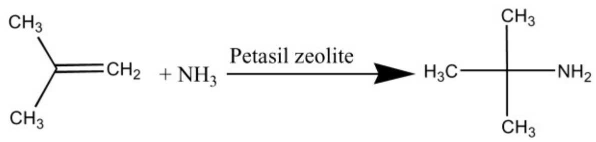
IX

Liquid polymers, flourous solvents, eutectic mixtures etc have potential to be used as green solvents (Kenton, 2009).

Green Catalysts:

Conventional catalysts are hazardous, corrosive and toxic in nature, therefore, it is pertinent to use green catalyst, which is environmentally benign and has maximum selectivity for product formation. Now a days, conventional catalysts are replaced by silica alumina catalysts for production of alkyl benzene. Zeolites, clayzic, titanium silicate are few examples among other green catalysts.

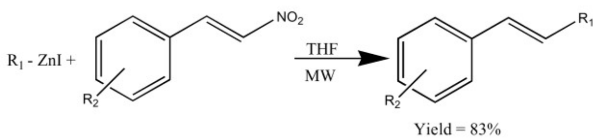
Bio-catalytic transformations represent an immense potential in organic synthesis. Enzymes occupy a prominent place among bio-catalysts. Zeolites themselves account for more than 40% of acid based catalysts.



X

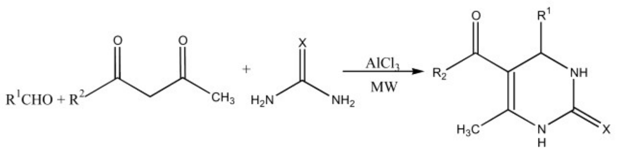
Microwave-assisted Organic Synthesis:

Microwave-assisted eco-friendly organic synthesis trend with many applications in synthesizing organic materials. Organic reactions under the microwave irradiation have many advantages compared to conventional reactions which need very high temperature. Microwave-assisted reactions are 'cleaner', last only few minutes, have high yield and produce minimum waste (Lindstrom and Wathey, 2001). Microwave-assisted synthesis can be achieved by solvent assisted or solvent free methods.



XI

$AlCl_3$ has been used as catalyst for microwave enhanced and solvent free green protocol for production of dihydropyrimidine-2-(1H)-ones (Suresh and Sandhu, 2010).

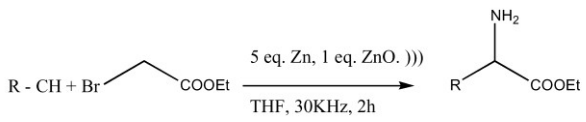


XII

Beckman rearrangement of oximes in the solid state with microwave irradiation gave quantitative yields of the product without use of catalysts.

Ultra-sound assisted organic synthesis is another 'green' methodology which applied in many organic synthetic routes with great advantages for high efficiency, low waste, low energy requirements. Sono-chemical processes are most widely developed for heterogenous reactions.

β-Amino-α,β-unsaturated esters were produced by sono-chemical Blaise reaction of nitriles, zinc powder, zinc oxide and ethyl bromo acetate in THF in commercial ultra-sonic cleaning bath (Ylee and Cheng, 1997).



XIII

It is need to design chemicals and their forms to minimize the chemical accidents including explosion, fires and releases to environment. Earlier manufacturers of gold atom nano particles used diborane (highly toxic and bursts in to flames near room temperature) and cancer causing benzene. But now diborane is replaced by $NaBH_4$ which is environmentally benign. Nano science and nano technology is another important contribution to green chemistry.

Thus there is a need to develop the methods of green synthesis which will minimize the use of chemicals and there will be growth towards sustainable development.

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