Introduction

Various Industries are using hazardous and toxic chemicals which are harmful on environment. These harmful substances cause bad impact on human health. Past two decades ago, the chemistry community has been developed a new branch of chemistry that are not harmful to human health and the environment. This new approach is known as Green Chemistry which is the use of chemical engineering and methodologies that eliminate or reduce to generation or the use of chemical products, by-products, reagent, solvents, etc., that are harmful to human health or the environment. Green Chemistry is also an approach to the synthesis, processing and use of chemicals that reduces or eliminates the risks of humans and the environment. Green Chemistry that possesses the spirit of sustainable development was booming in the 1990s\(^1\), and has attracted more and more interest in the 21st century. In recent year there has been growing interest in the development of green synthesis of organic compound using green solvents like water, supercritical fluids, and ionic liquids or on a solid support in which no solvent or using microwave radiation or using specific catalyst.

Principles of Green Chemistry

Twelve principles of Green Chemistry are given below:

Prevent waste: It is better to prevent waste than to treat or clean up waste after it has been produced.

Maximize atom economy: The design of synthetic methods should be such that in which maximum starting materials and regents are incorporated to give final product. There is no waste (by product) visible in the above calculation if the yield of the reaction is 100%. The synthesis will be green if all the starting materials reagents used in the process into the final product. The percentage of atom utilization can be calculated by the following equation.

Less hazardous chemical syntheses: The design of synthetic methodologies should be such that in which no toxic materials for human health or environment has been used or generated.

Designing safer chemicals and products: The design of chemical products should be such that which has no toxicity or less toxicity to human health or environment.

Use of safer solvents and auxiliaries: The use separating agents, solvents like CCl\(_4\), CHCl\(_3\), CH\(_2\)Cl\(_2\), benzene etc. should be avoided where necessary or should used which is no toxicity to human health or environment.

Increase energy efficiency: Energy requirements should be minimize for environmental and economic impacts.

Use of renewable feedstock: The use of raw materials should be renewable.
Avoid unnecessary chemical derivatives: Unnecessary derivatization (protection, deportation, blocking group etc.) should be avoided whenever possible.

Use of catalytic reagents rather than stoichiometric: Catalytic reagents should be used for the synthesis of chemicals. The use stoichiometric regents should be avoided where necessary.

Design chemicals products for degradation: The design of chemical products should be degradable. After end their functions, they cannot be persist in the environment and break down into degradation products which are not harmful to human health or environment.

Analyze in real time to prevent pollution: Analytical methodologies need to be further developed to allow for real time, in process monitoring and control prior to the formation of hazardous substances.

Safer chemicals for accident prevention: The use of substances in a chemical process should such that which have minimum the potential for chemical accidents, including releases, explosions and fires.

Results and discussion

Biosynthesis of 4-hydroxybenzoic acid from toluene: 4-Hydroxybenzoic acid (4) is synthesized from p-cresol using an enzyme, methylhydroxylase (PCMH) in presence of water\(^2\).

Michael addition reactions using microwave irradiation: Microwave assisted solvent-free without organic solvents Michael addition reactions on CdI\(_2\), BiCl\(_3\), CeCl\(_3\).5H\(_2\)O, EuCl\(_3\), and Al\(_2\)O\(_3\) surfaces using microwave have been reported\(^3\)-\(^6\).

The reaction of active methylene (6) compounds with Michael acceptor on K\(_2\)CO\(_3\) surface in presence of microwave radiation have been reported by Rao et al. (Scheme 2)\(^7\).

Cannizaro reaction of aromatic aldehydes: The Cannizaro reaction of differene aldehyde having no \(\alpha\)-hydrogen in presence of Et\(_3\)N at room temperature in a solvent free environment have reported by Mojtahed et al. (Scheme 3)\(^8\). These reactions are catalyzed by lithium bromide (LiBr). As there is no use of organic solvents, the reactions are considered green reaction.

Scheme 1. Synthesis of 4-hydroxybenzoic acid from p-cresol.

Scheme 2. Michael addition reactions using microwave irradiation.
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\begin{align*}
\text{Ar-CH} &= \text{LiBr (0.5 equiv), Et}_3\text{N (1.5 equiv), rt} \\
8 &\quad \rightarrow \\
\text{H}_2\text{O} &\quad \text{Ar-COOH} + \text{Ar CH}_2\text{OH} \\
\text{Ar} &= \text{Ph}, \text{p-MeOC}_6\text{H}_4, \text{p-O}_2\text{NC}_6\text{H}_4
\end{align*}
\]

Scheme 3. Cannizaro reaction of aromatic aldehydes.

Directed Aldol reactions: Environmental friendly directed Aldol reactions of ketene silyl acetylts (12) with different aldehydes (11) in presence of a catalytic amount of DBU have been reported by Loh et al. (Scheme 4)\(^9\).

There reactions were carried out at room temperature under solvent free condition. This can consider as green synthesis \(\beta\)-hydroxy carbonyl compounds.

Aromatic nucleophelic substitution reactions: The microwave assisted coupling reaction of phenols (14) having electron withdrawing group (-NO\(_2\), -Cl, -CF\(_3\) etc.) with aryl halides (15) in presence of K\(_2\)CO\(_3\) as base have been reported by Li et al. (Scheme 5)\(^10\). The product diaryl ethers (16) with high yields was obtained within very short time (5–10 min).

Hoffmann elimination reaction: Quatertary ammonium salts (17) undergo E2 elimination reaction results in the formation less substituted alkene. These reactions require a high temperature and yield are generally poor. In 1995, C. R. Strauss reported microwave assisted Hoffmann elimination reaction of compound (17) in CHCl\(_3\) and water mixture as a solvent. In this reaction, aryl vinyl ketone (18) derivative is obtained as good yield. When the compound (50) was heated at 105ºC in only water medium, polymerization product was isolated through the formation of aryl vinyl ketone derivatine (18) as intermediate compound\(^11\) (Scheme 6).

Wittig reaction: Wittig reaction of aldehydes (19, 22) with stabilized ylides (20) in water medium yields desired products with high yield\(^12\) (Scheme 7). The reaction of ketone (24) with CH\(_2\)=Zn in presence of Ultrasound, the expected product will be ketone derivative greater number of carbon atom. For this reaction, interestingly, olefin (25) is obtained

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\begin{align*}
\text{R-CHO} &\quad + \\
\text{R}_2 &\quad \rightarrow \\
\text{OTMS} &\quad \text{1. DBU/neat, rt, 24} \\
\text{OMe} &\quad \text{2. 1M HCl/THF} \\
\text{R} &= 2-\text{NO}_2\text{C}_6\text{H}_4, \text{R}_2 = \text{CH}_3 \\
&\quad \text{R} = 2-\text{NO}_2\text{C}_6\text{H}_4, \text{R}_2 = \text{H} \\
&\quad \text{R} = 4-\text{ClC}_6\text{H}_4, \text{R}_2 = \text{H} \\
&\quad \text{R} = \text{C}_6\text{H}_5, \text{R}_2 = \text{H}
\end{align*}
\]

Scheme 4. Directed Aldol reactions.

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\begin{align*}
\text{R} &\quad + \\
\text{X} &\quad \rightarrow \\
\text{K}_2\text{CO}_3/\text{DMSO} &\quad \text{MW, 5-10 min} \\
\text{R}_2 &\quad \text{X} = \text{F, Cl, Br}
\end{align*}
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Scheme 5. Aromatic nucleophelic substitution reactions.
instead of ketone derivative. Generally phosphonium ylide is formed by the treatment of strong base like PhLi or nBuLi or LDA in dry ether medium. It is also reported that the both stabilized and non-stablized ylides are formed using weaker base like K$_2$CO$_3$ under solvent less condition$^{13}$. Under conversational process of Wittig reaction gives kinetically favorable cis olefins but here stable trans product is obtained.

*Benzoin condensation:* Generally aromatic aldehydes (30) react with NaCN or KCN in ethanol-water medium yields benzoin derivative (31) (Scheme 8). Breslo reported the benzoin condensation reaction in water medium in presence of inorganic salts. It has been found the rate of reaction is 200 times faster than in ethanol medium. This reaction is also more favorable in presence of $\gamma$-cyclodextrine due to size match selective$^{14}$. It was also reported that the benzoin condensation reaction occur in presence of co-enzyme, thiamine hydrochloride instead of poisonous cyanide ion.
Maity et al.: Green Chemistry: Synthesis of organic compounds through green approach

Simon smith reaction: It was reported that the reaction of alkene (32) with CH$_2$I$_2$/Zn in presence of Ultrasound yield cyclopropane derivative (33) with high yield (91%) (Scheme 9). This reaction is not exothermic and the formation of iodine is absent. The absence of ultrasound, the yield (51%) of this reaction is comparatively low, reaction is highly exothermic and iodine is formed as one of the products\textsuperscript{15}.

Heck reaction: Ultrasound-initiated Heck reaction has been reported by using Pd-C catalyst in N-methylpyrrolidone (NMP) solvent at room temperature. Without ultrasound the above reaction cannot take place\textsuperscript{16} (Scheme 10).

The rate and stereo selectivity of Heck reaction is enhanced in ionic liquid under sonication. Under heating and stirring conditions a mixture of E- and Z-isomers were obtained but under sonication in ionic liquid only stable E-isomer was obtained\textsuperscript{17}. In some cases no reaction occurred in ionic liquid without sonication. Therefore ultrasound has a specific effect for occurrence of reaction. Solvent free Heck reaction has been reported by ball-milling process using Pd(OAc)$_2$ as catalyst and reducing agent (HCOONa)\textsuperscript{18}. The addition of sodium formate enhances the rate of reaction and improves the yield. It also act as reducing agent for the conversion of Pd(OAc)$_2$ to Pd(0).

Suzuki coupling reaction: Solvent free Suzuki coupling reaction has been reported by ball-Milling process in presence Pd(Ph$_3$P)$_4$ as catalyst, base (K$_2$CO$_3$) and grinding

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**Scheme 8.** Benzoin condensation.

**Scheme 9.** Simon smith reaction.

**Scheme 10.** Heck reaction.
medium (NaCl). KF supported on \( \text{Al}_2\text{O}_3 \) can be used instead of the mixture of \( \text{K}_2\text{CO}_3 \) and NaCl. The rate of reaction depends on nature of halogens\(^{19}\) (Scheme 11).

**Ullmann reaction:** The reaction of \( \text{o}-\text{iodonitrobenzene} \) with Cu-powder in DMF solvent at 60ºC for 48 h yield 2,2'-dinitrobiphenyl derivative\(^{20}\). When the same reaction is ultrasound, the reaction was completed within 1.5 h (Scheme 12).

**Conclusions**

In this era, with the increasing concerns about the protection of human health and environment synthesis of organic compounds from raw materials through a Green Chemistry approach is desirable. Therefore the design of methodology, design of product, use of chemicals, and use of solvent etc. will be such that which are not is harmful to human health or environment. The use of water as green solvent in organic synthesis or solvent free reaction is most leading research areas of Green Chemistry. The above reactions are carried out in green solvents like water, or in absence of solvent, or using microwave radiation. However, Green Chemistry is not a solution to all the problems but most fundamental approach to prevent the problems of pollution.

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**References**