MICROWAVES IN ORGANIC SYNTHESIS :

Green chemistry also known as sustainable chemistry is defined by the EPA (www.Epa.Gov/Gcc) as 'the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

Paul Anastas, of the United States Environmental Protection Agency, and John C. Warner developed 12 principles of green chemistry, which help to explain what the definition means in practice. The 12 principles are :

1) It is better to prevent waste than to treat or clean up waste after it is formed.
2) Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3) Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and environment.

4) Chemical products should be designed to preserve efficacy of function while reducing toxicity.

5) The use of auxiliary substances (e.g. solvents, separation agents etc.) should be made unnecessary wherever possible and innocuous when used.

6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7) A raw material or feedstock should be renewable rather than depleting, wherever technically and economically practicable.

8) Reduce derivatives–unnecessary derivatization (blocking group, protection /deprotection, temporary modification) should be avoided whenever possible.

9) Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10) Chemical products should be designed so that at the end of their function, they do not persist in the environment and break down into innocuous degradation products.

11) Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.

12) Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions and fires.

The use of microwave irradiation leads to acceleration of synthetic processes due to shortening of the reaction time.

The growth of chemistry has been closely associated with the discovery of new reagents and new modes of introducing energy in to chemical reactions. The first reliable device for generating fixed frequency microwave radiation was designed by Randall and Booth at the University of Birmingham during World War II. It formed the basis of radar transmitters, particularly in aircraft and anti aircraft batteries. The first patent for microwave dielectric heating was filed by the Raytheon Company in 1946 and a prototype oven was installed in Boston Restaurant. In the food processing industries, the advantages of Microwave dielectric heating for drying was recognized in 1950's and 1960's.

DuPont built large scale facilities for drying nylon, based on Microwave technology.The advantages of microwave dielectric heating for analytical processes were also recognized. These applications utilized the interactions between microwave energy with a frequency of 2.45 GHz and water, either on the surface of analytical samples or in the acidic solutions. During the 1970s, microwave dielectric heating was being used for inorganic reactions, for example, in ceramic processing and calcining etc. During this time, the application of microwave dielectric heating in chemical laboratories remained very limited.

In 1986, R. Gedye[72-76] G. Majetich and coworkers observed that, a range of organic reactions could be accelerated under microwave conditions, and then the use of microwave dielectric heating in organic, inorganic and organometallic chemistry has expanded very rapidly and now there are more than 2000 papers that describe the applications of this technique for the synthesis of new compounds.

Advantages and disadvantages of Solvent-free methods :

The following benefits have been reported for microwave heated reactions under solvent-free conditions :-

1) Avoidance of large volume of solvent reduces emissions and the need for redistribution.
2) Work-up is simple, by extraction, distillation or sublimation.
3) Recyclable solid supports can be used instead of polluting mineral acids and oxidants.
4) Reactions are quite cleaner, faster and higher yielding than conventional synthesis.

The disadvantages include a low ratio of organic reactants to solid support and a lack of facilities for mixing reactants and for measuring temperature. If the reaction temperature is not known and not uniform throughout the sample, reaction may not be reproducible in microwave systems.

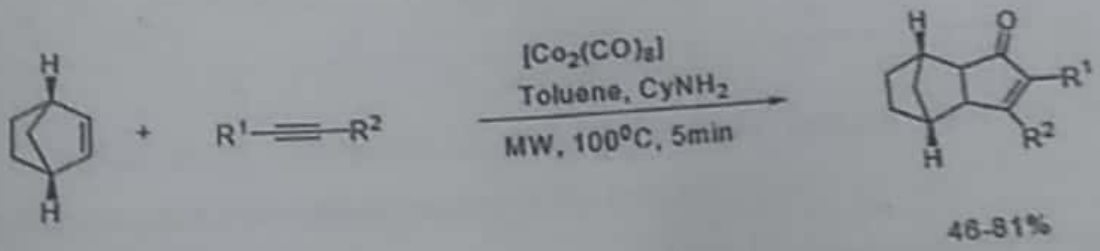
Advantages of utilizing solvents :

Solvent based methods have the following advantages:

1) The reaction conditions can be measured and reproduced.
2) Solvents moderate the reaction and minimize the risk of pyrolysis.
3) Reactions are cleaner, faster and high yielding.
4) Microwave energy is absorbed directly by the sample and not via the vessel or a solid support.
5) Thermally unstable products can be cooled rapidly, after the heating step.

Microwave Assisted Organic Synthesis (M A O S) is considered as a green technology and therefore a huge number of research papers have appeared over the last decades on the application of microwave technology in organic synthesis.

Fischer and co-workers have studied the ***Pauson Khand*** *Cycloaddition Reaction* under microwave conditions and obtained the product in 5 min.



46-81%

Petasis Olefination :

C.O. Kappe reported that the treatment of ketones with Petasis reagent in toluene at 120°C for 180 min. generated an alkene in 71% yield. The reaction was much more efficient when carried out under microwace heating for 10 min. to form 82% yield.

In 2008, the rapid and efficient oxidation of organic compounds in microwave conditions with new phase transfer oxidative agent i.e. Cetyl trimethy ammonium bromochromate (CTMABC) has also been reported.