

Quick Chemistry by Microwave

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ABSTRACT; Microwave chemistry is the science of applying microwave radiation to chemical reactions for quick synthesis and better yield.^{1,2,3} Microwaves act as high frequency electric fields and will generally heat any material containing mobile electric charges, such as polar molecules in a solvent or conducting ions in a solid. Polar solvents are heated as their component molecules are forced to rotate with the field and lose energy in collisions. Semiconducting and conducting samples heat when ions or electrons within them form an electric current and energy is lost due to the electrical resistance of the material. Microwave heating in the laboratory began to gain wide acceptance following papers in 1986⁴ although the use of microwave heating in chemical modification can be traced back to the 1950s. Although occasionally known by such acronyms as MAOS (Microwave-Assisted Organic Synthesis)⁵ MEC (Microwave-Enhanced Chemistry) or MORE synthesis (Microwave-organic Reaction Enhancement), these acronyms have had little acceptance outside a small number of groups. MEC (Microwave-Enhanced Chemistry) is also supported and follows green chemistry with its twelve principles would like to see changes in the conventional chemical synthesis and the use of less toxic starting materials, that would like to increase the efficiency of synthetic methods, to use less toxic solvents, reduce the stages of the synthetic routes and minimize waste as far as practically possible which applies across the life cycle of a chemical product, including its design, manufacture, and use. Green chemistry technologies provide a number of benefits, including reduced use of energy and resources, reduced waste, eliminating costly end-of-the-pipe treatments, safer products improved competitiveness of chemical manufacturers and their customers. Looking at the definition of green chemistry, the first thing one sees is the concept of invention and design. In many ways, this is a wonderful time in history to be a chemist or chemical engineer. The challenges that confront the planet are nothing short of the most consequential that humanity has ever faced. Simply put, if we do not meet the challenges of maintaining the viability of the biosphere, humanity will not survive to see any future challenges. Eco-friendly technology is used to produce environment friendly products by using renewable resources. This article is an attempt to provide the basic concept of eco-friendly technology with quick chemistry using microwave. In this way, chemical synthesis will be part of the effort for sustainable development. Microwave assisted synthesis has revolutionized chemical synthesis. Small molecules can be built in a fraction of the time required by conventional methods. Microwave-assisted synthesis is rapidly becoming the method of choice in modern chemical synthesis and drug discovery. The present article will highlight the applications of microwave-assisted synthesis as rapid as clean in organic molecules involved in microwave heating.

KEY WORDS: quick chemistry, microwave chemistry.

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I. INTRODUCTION

A heterogeneous system (comprising different substances or different phases) may be anisotropic if the loss tangents of the components are considered. As a result, it can be expected that the microwave field energy will be converted to heat by different amounts in different parts of the system. This inhomogeneous energy dissipation means selective heating of different parts of the material is possible, and may lead to temperature gradients between them. Nevertheless, the presence of zones with a higher temperature than others (called hot spots) must be subjected to the heat transfer processes between domains. Where the rate of heat conduction is high between system domains, hot spots would have no long-term existence as the components rapidly reach thermal equilibrium. In a system where the heat transfer is slow, it would be possible to have the presence of a steady state hot spot that may enhance the rate of the chemical reaction within that hot zone.

On this basis, many early papers in microwave chemistry postulated the possibility of exciting specific molecules, or functional groups within molecules. However, the time within which thermal energy is repartitioned from such moieties is much shorter than the period of a microwave wave, thus precluding the presence of such 'molecular hot spots' under ordinary laboratory conditions. The oscillations produced by the radiation in these target molecules would be instantaneously transferred by collisions with the adjacent molecules, reaching at the same moment the thermal equilibrium. Processes with solid phases behave somewhat differently. In this case much higher heat transfer resistances are involved, and the possibility of the stationary

presence of hot-spots should be contemplated. A differentiation between two kinds of hot spots has been noted in the literature, although the distinction is considered by many to be arbitrary. Macroscopic hot spots were considered to comprise all large non-isothermal volumes that can be detected and measured by use of optical pyrometers (optical fibre or IR). By these means it is possible to visualise thermal inhomogeneities within solid phases under microwave irradiation. Microscopic hot spots are non-isothermal regions that exist at the micro- or nano scale (e.g. supported metal nanoparticles inside a catalyst pellet) or in the molecular scale (e.g. a polar group on a catalyst structure). The distinction has no serious significance, however, as microscopic hotspots such as those proposed to explain catalyst behavior in several gas-phase catalytic reactions have been demonstrated by post-mortem methods and in-situ methods. Some theoretical and experimental approaches have been published towards the clarification of the hot spot effect in heterogeneous catalysts.



Figure 1- Microwave reactor

A different specific application in synthetic chemistry is in the microwave heating of a binary system comprising a polar solvent and a non-polar solvent obtain different temperatures. Applied in a phase transfer reaction a water phase reaches a temperature of 100 °C while a chloroform phase would retain a temperature of 50 °C, providing the extraction as well of the reactants from one phase to the other. Microwave chemistry is particularly effective in dry media reactions.

Microwave chemistry is not different from traditional chemistry in as much as it embraces the same creativity and innovation that has always been central to classical chemistry. However, there lies a difference in that historically synthetic chemists have not been seen to rank the environment consciousness throughout the world there is a change for chemists to develop new products, processes and services that achieve necessary social, economic and environmental objectives. Dr. B. C. Ranu⁷ and his group have been working on green chemistry using microwave process. The use of microwave irradiation in organic synthesis has become an increasingly popular topic within the pharmaceutical and academic research arenas. It has proven to be a safe and clean means of performing reactions very rapidly, however, has not been fully explored within a teaching environment. Herein, we describe the use of microwave energy to accelerate reactions typically encountered in an undergraduate teaching laboratory, as well as a few that present more interesting challenges and educational opportunities for the undergraduate student. Each of the reactions has proven to be faster, cleaner, and very interesting to students, serving not only to challenge, but also to more fully engage students in the laboratory. The use of emerging microwave (MW)-assisted chemistry techniques is dramatically reducing chemical waste and reaction times in several organic syntheses and chemical transformations (**figure 3**). According to the work carried out by William G Bornmann⁸ and his co-worker including ourselves have made a series of c-Kit compounds using microwave technology as a greener heating tool. Structural or chemical Diversity was first introduced at the beginning of the synthesis with the condensation of 2,6-dichloro nicotinic acid chloride with various zinc halides (e.g., bromide or iodide) in presence of tetrakis(triphenylphosphine)palladium in THF to give first series of starting materials. The second round of structural or chemical diversity was introduced by the condensation of first series compounds with various boronate esters by means of a Suzuki coupling using microwave conditions at 150°C for 10 min produced the next series of compound at a time 24 compound by the help of CEM microwave reactor. The whole Microwave process takes 5 min per each reaction and yield is more than 25 percentages while in normal process the reaction takes three days, with more solvents and yields are less than 15 percentages. So this reaction is much quicker using microwave rather than normal process.

General Synthetic Methods for Preparing Compounds

The following scheme can be used to practice the library of compounds using R₁ and R₂ as diverse aryl groups

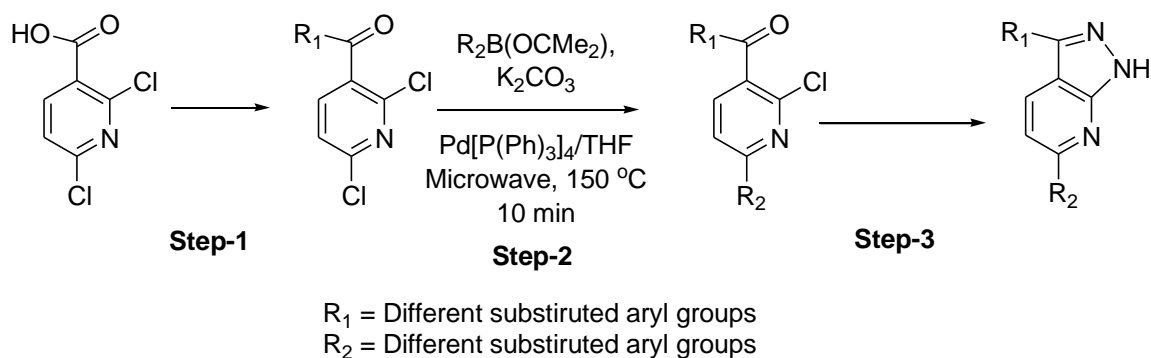


Figure 2 GENERAL SYNTHETIC METHODS FOR PREPARING PYRAZOLO COMPOUNDS

Illustrative of Scheme 1 is the synthesis of 3-[6-chloro-5-{4-ethoxycarbonyl}carbonyl]-2-pyridinyl]acetanilide.

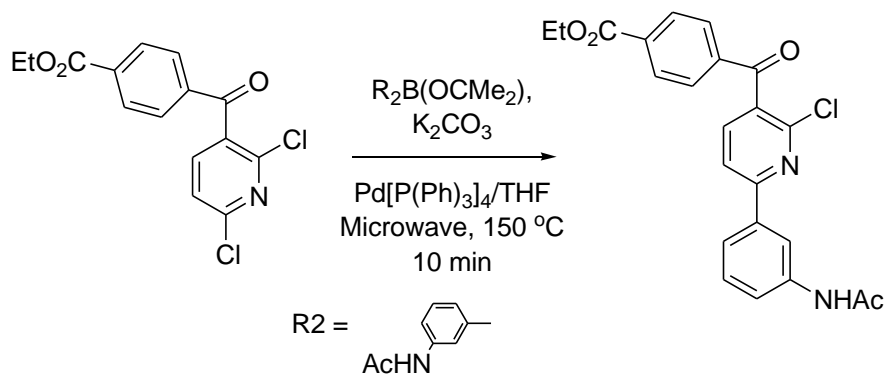


Figure 3: Preparation of PYRAZOLO acetanilide COMPOUND

A mixture of (2,6-dichloro-3-pyridinyl)(4-ethyloxycarbonyl)methanone (300 mg, 0.93 mmol), 3'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acetanilide, potassium carbonate (200 mg), tetrakis(triphenylphosphine)palladium (80 mg) in THF (4 mL) was finished with argon and then subjected to microwave at 155 oC for 10 min. The whole product was adsorbed onto silica, then purified by flash column chromatography over silica gel, using polarity gradient 5-50% EtOAc in hexane to yield acetanilide derivative (200 mg, 49%) as a yellow oil; ^1H NMR (600 MHz DMSO- d_6) δ 10.17 (s, 1H), 8.32 (s, 1H), 7.81(m, 4H), 7.47 (t, 1H, $J = 7.8$ Hz), 7.10 (d, 2H, $J = 9.0$ Hz), 4.36 (q, 2H, $J = 7.2$ Hz), 2.08 (s, 3H), 1.36 (t, 3H, $J = 7.2$ Hz) ^{13}C NMR δ 191.3, 168.5, 164.2, 157.4, 145.9, 140.1, 139.5, 136.8, 133.1, 132.3, 129.5, 128.4, 121.5, 120.8, 119.2, 117.3, 114.5, 60.8, 55.7, 14.2; MS ($\text{C}_{23}\text{H}_{19}\text{Cl}_2\text{N}_2\text{O}_4$) calcd. 422.103 found MH^+ 423.2.

CONCLUSION

Microwave synthesis is a quick technique for facilitating drug discovery, polymer science, chemical and materials research. It reduces reaction times from days to minutes, increases yields, and in many cases, produces cleaner reactions. It allows access to new reaction schemes, which are not possible using conventional heating. It has good advantages towards green chemistry.

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REFERENCES

- [1]. "Microwaves in Organic Synthesis". Organic Chemistry Portal. Retrieved 23 October 2018.
- [2]. Microwaves in organic synthesis. Thermal and non-thermal microwave effects, Antonio de la Hoz, Angel Diaz-Ortiz, Andres Moreno, Chem. Soc. Rev., 2005, 164-178.
- [3]. Developments in Microwave-assisted Organic Chemistry. C. Strauss, R. Trainor. Aust. J. Chem., 48 1665 (1995).
- [4]. The use of microwave ovens for rapid organic synthesis Richard Gedye, Frank Smith, Kenneth Westaway, Humera Ali, Lorraine Baldisera, Lena Laberge and John Rousell Tetrahedron Letters Volume 27, Issue 3, 1986, Pages 279-282.
- [5]. Pizzetti, Marianna (May 2012). "Heterogeneous catalysis under microwave heating", La Chimica & L'Industria. Società Chimica Italiana (4): 78-80.

- [6]. Green Chemistry's Providence and Outlook. Bina Rani, RaazMaheshwari, A K Chauhan, A K Yadav. IAAST Volume 3 [1] March 2012.
- [7]. Transition Metal Free Procedure for the Synthesis of S-Aryl Dithiocarbamates Using Aryl DiazoniumFluoroborate in Water at Room temperature.
- [8]. T. Chatterjee, S. Bhadra, B.C. Ranu, Green Chem. 2011, 13, 1837
- [9]. Inhibitors of C-Kit and the Design, Synthesis, and Uses thereof. William Bornmann, David Maxwell, Ashutosh Pal, ZhenghongPeng, ZeevEstrov, PCT Int. Appl. (2008), 108pp. CODEN: PIXXD2 WO 2008005877 A2 20080110.