



BRIEF REVIEW: GREEN CHEMISTRY APPROACH

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Abstract:

The main aim of current review article is to study the various recent advances in Green Chemistry Approach. "Green chemistry" refers to the use of a set of rules to lessen the use of hazardous compounds in the development, manufacture, and use of chemical products. Microwave synthesis is a major development in synthetic chemistry technology, yet it has long been known to be time-consuming, ineffective and artistically limited. Microwave synthesis allows chemists to spend more time creating new protocols, verifying theories, and using their imagination. Instead of needing as much time to synthesize a single reaction, chemists can now perform the same reaction in a matter of hours or even days. The problem of disposing of solvent waste has been overcome by performing processes without the need of a solvent under microwave radiation provides safe chemical processes without requiring.

Keywords: Green chemistry, dipole polarization, microwave technology, Reproducibility.

Introduction

The US Environmental Protection Agency is credited for coining the term "green chemistry," which is described as applying a set of guidelines to minimise or completely do away with the use of hazardous materials in the creation, production, and usage of chemical goods. The following twelve Green Chemistry concepts can be used to accomplish this goal [1]. Preventing waste is preferable to treating or cleaning it up after it has been produced [2]. The design of synthetic procedures should aim to maximise the amount of each material that is incorporated into the finished product during the process [4].

Large-scale organic synthesis requires the use of catalysts and basic chemical materials from the petrochemical industry. It also entails the separation, purification, storage, packaging, and distribution of the reaction's byproducts. Conventional organic synthesis processes typically need more time for heating and laborious apparatus setup, leading to increased process costs and an overuse of solvents and reagents. In addition to the environmental issues arising from the use and disposal of trash, these operations also pose numerous health and safety risks to the workers. Green Chemistry aims to minimise waste to the greatest

extent feasible while increasing the efficiency of synthetic processes, reducing the number of stages involved, and using less hazardous solvents [5].

Because microwave synthesis is a more environmentally benign method, it is regarded as a significant step towards green chemistry. Microwave irradiation has been utilised to improve several chemical syntheses because of its capacity to couple directly with the reaction molecule and by passing thermal conductivity, which causes a rapid rise in temperature [6-7]. The study of using microwave radiation to accelerate chemical reactions is known as microwave chemistry. A significant advancement in synthetic chemistry technology, microwave synthesis has long been acknowledged to be laborious and inefficient, and it has also been shown to be artistically constrictive. Chemists can devote more time to developing new procedures, testing hypotheses, and exercising their creativity thanks to microwave synthesis. Today, chemists may complete the same reaction in a matter of hours or even days rather than spending that time synthesising a single one. By conducting reactions without a solvent under microwave irradiation, the issue with solvent waste disposal has been resolved. offers clean chemical processes without the need for solvents, with the benefits of increased yields, easier manipulation, improved reaction rates, and increased selectivity. Therefore, microwave synthesis presents itself as a possible green chemistry tool [6,8].

MECHANISM OF MICROWAVE HEATING:

Since different materials react differently to microwave radiation, not all materials can be heated by microwaves. The following broad categories can be applied to materials based on how they react to microwaves:

- (1) Materials that reflect microwaves, like copper
- 2) Materials that are transparent to microwaves, like sulphur
- (3) Substances like water that can absorb microwaves

Three primary mechanisms dipolar polarisation, conduction mechanism, and interfacial polarization are involved in the heating of microwave-absorbing materials, which are crucial for microwave chemistry.

1) Dipole polarisation:

A material needs a dipole moment in order to produce heat when exposed to microwave radiation. When a dipole tries to reorient itself with respect to an alternating electric field, it loses energy in the form of heat due to molecular friction; this is the electric field component of the microwave radiation, not the magnetic field component that is responsible for heating. Heat can be produced by dipolar polarisation through the interaction of polar solute molecules like ammonia and formic acid, or by the interaction of polar solvent molecules like water, methanol, and ethanol. The primary prerequisite for dipolar polarisation is that the oscillating field's frequency range must be suitable to allow for sufficient inter-particle interaction. If the range of frequencies is extremely high, intermolecular polar molecules will not attempt to follow the field because of intermolecular forces, which will lead to insufficient inter-particle interaction. In contrast, the

polar molecule has enough time to align itself in phase with the field if the frequency range is low. The frequency range of microwave radiation (0.3-30 GHz) is suitable for polar particle oscillation and sufficient inter-particle interaction. It is therefore the best option for heating polar solution

2) Conduction mechanism:

When an electric current encounters resistance heat is produced. An electric current is produced when an oscillating electromagnetic field causes an oscillation of electrons or ions in a conductor. The conductor gets heated as a result of internal resistance to this current. Under the influence of an electric field, ions in a solution containing ions, or even a single isolated ion with a hydrogen bonded cluster, will move through the solution, requiring energy to be expended because it is thought that the more polar the solvent, the more easily the microwave radiation is absorbed and the higher the temperature obtained. The charge carriers (electrons, ions, etc.) are moved through the material under the influence of the electric field when the irradiated sample is an electrical conductor, resulting in a polarisation. Because of any electrical resistance in the sample, these induced currents will heat it up. The method's main drawback is that it cannot be used on materials with high conductivity because those materials reflect the majority of incident energy.

3) Interfacial polarization

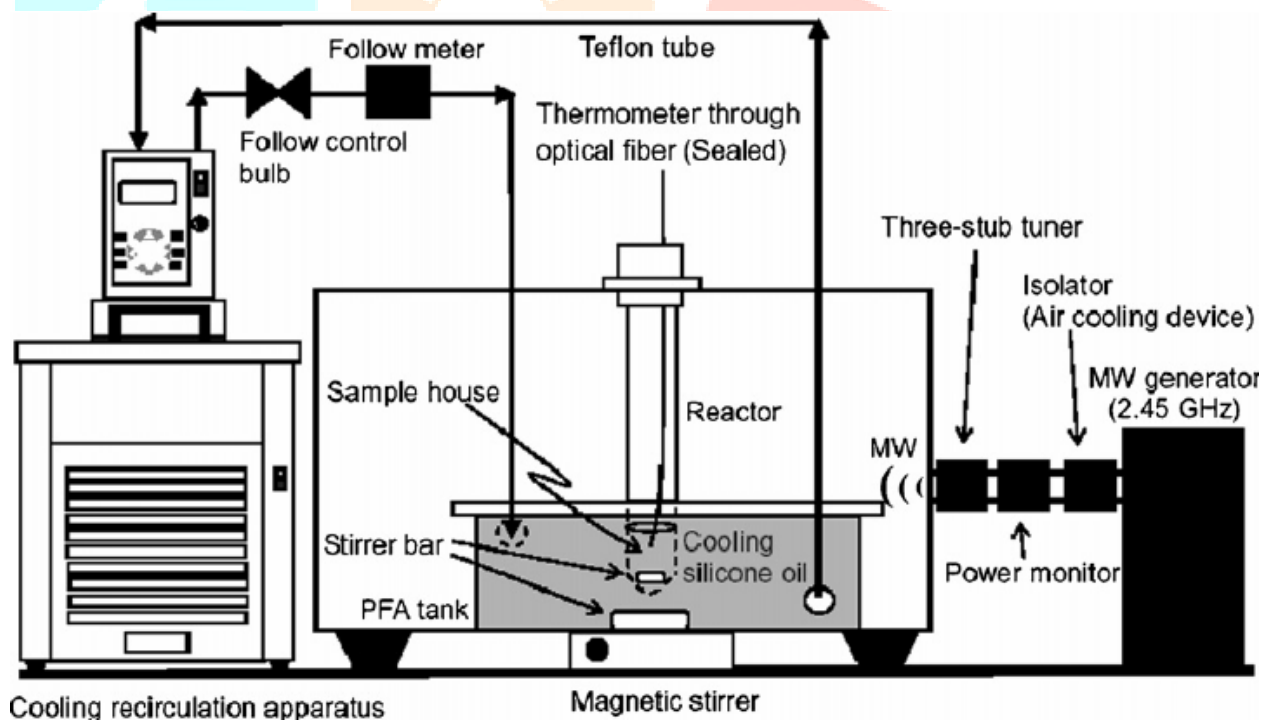
The interfacial polarisation technique can be interpreted as a synthesis of the conduction and dipolar polarisation mechanisms. For heating systems where a conducting material is distributed throughout a nonconducting material, it is crucial. Take into account, for instance, how metal particles disperse in sulphur. Combining the two results in a good material that absorbs microwaves: metals reflect most of the microwave energy they are exposed to, and sulphur does not react to microwaves. But in order for this to happen, metals must be used in powder form. This is due to the fact that metal powder effectively absorbs microwave radiation, in contrast to a metal surface. It heats up through a process akin to dipolar polarisation and absorbs radiation. The metal powder's environment acts as a solvent for polar molecules and uses forces similar to those found in inter-particle interactions in polar solvents to limit the motion of ions. These limiting forces cause an oscillating field to cause a phase lag in the ion's motion, which leads to the ions moving randomly and, eventually, the system heating [9].

Microwave Synthesis Equipment: Single-mode and multimode microwave ovens are examples of the equipment used for microwave assisted synthesis.

1) Single-mode apparatus: In sealed-vessel conditions, these devices can handle volumes of up to 50 ml, and in open-vessel conditions, up to 150 ml. Currently, small-scale drug discovery, automation, and combinatorial chemical applications are served by single-mode microwave ovens. The sample's distance from the magnetron determines how a single-mode apparatus is designed. To guarantee that the sample is positioned at the antinodes of the standing electromagnetic wave pattern, this distance needs to be suitable. The fact that only one vessel can be exposed to radiation at a time is one of the drawbacks of single-mode equipment. The ability to produce a standing wave pattern, which is produced by the interference of fields

with the same amplitude but different oscillating directions, is what distinguishes a single-mode apparatus from others. An array of nodes with zero microwave energy intensity and an array of antinodes with the maximum microwave energy magnitude are produced by this interface

2) Microwave equipment with multiple modes: This type of equipment intentionally avoids creating a standing wave pattern inside of it. The idea is to cause as much chaos as you can within the device. The area inside the apparatus that can effectively heat up increases with increasing chaos because radiation disperses more widely when chaos is higher. Because of this, a multi-mode microwave heating device can heat multiple samples at once, in contrast to a single-mode device that can only heat one sample at a time. This feature makes a multimode heating device useful for bulk heating and performing chemical analysis procedures like extraction, ashing, etc. Several litres of reaction mixture can be processed in both open and closed vessel conditions using a large multi-mode apparatus. The idea is to cause as much chaos as you can within the device. The area inside the apparatus that can effectively heat up increases with increasing chaos because radiation disperses more widely when chaos is higher. Because of this, a multi-mode microwave heating device can heat multiple samples at once, in contrast to a single-mode device that can only heat one sample at a time



The importance of synthesising microwaves

1) Increased purity and improved yield:

When using microwave irradiation, fewer byproducts are observed to form and a higher yield of the product is recovered. As a result, the purification process is also simpler and quicker. For example, the yield of the reaction increases from 85% to 97%¹⁸ when aspirin is synthesised using microwaves.

2) Green synthesis: Compared to traditional heating techniques, microwave-based reactions are more environmentally friendly and cleaner. Solvents can be used less or not at all in chemical reactions since

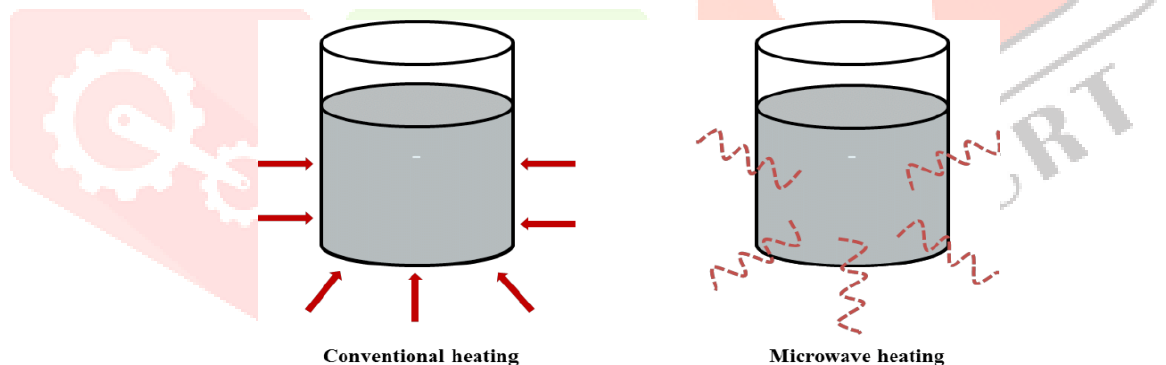
microwaves heat the compounds directly. Reagents are absorbed on mineral supports during solventless synthesis, which has great potential as an environmentally friendly green synthesis protocol. Additionally, the amount of purification needed for the byproducts of chemical reactions involving toxic reagents has decreased due to the use of microwaves [19].

3) Reproducibility: Due to uniform heating and improved process parameter control, microwave heating reactions are more repeatable than conventional heating. Chemical reaction temperatures are also readily observable.

4) Faster reaction: Experimental data has shown that chemical reaction rates accelerated by microwaves can surpass those of traditional heating techniques by a factor of 1,000. Because the microwave can reach higher temperatures than traditional heating systems, reactions can be finished in a matter of minutes rather than hours. For example, fluorescein synthesis, which typically takes several hours to complete using conventional heating methods, can be completed in just 35 minutes when using microwave heating [10].

What distinguishes microwave heating from conventional heating?

Chemical synthesis is traditionally heated using conductive heating from an external source [5]. In this, heat is transferred through the vessel walls into the materials. As a result, the reaction vessel heats up more than the reaction mixture does. Being an inventive method of heating that doesn't rely on the vessel's thermal conductivity, microwave synthesis instantly heats the molecules in the reaction mixture [11]



Applications:

(1) Microwave Application in Material Chemistry: Synthesising inorganic solids using microwaves is a very effective and practical technique in material chemistry. Ceramics have been prepared using microwaves, and Ayappa and Kenkre et al.'s groups have studied the theoretical modelling of microwave interaction with ceramic material. Moreover, Lee et al. According to Rao et al. SiC is produced when powdered Si and C (charcoal) is placed in a silica crucible and microwaved for four to ten minutes at a home microwave oven set to 2.45 GHz. SiC is a large volume ceramic that finds extensive use in industrial applications, including the production of abrasion tools and grinding wheels.

(2) Catalyst preparation under microwave irradiation: Using an aluminate and silicate sodium with a molar ratio of 5 SiO₂: Al₂O₃: 50Na₂O:1000H₂O, a high-performance NaA zeolite, YBa₂Cu₃O_{7-X}

membrane, was synthesised in 15 minutes in a modified home microwave oven operating at 2450 MHz. The permeance of the zeolite membrane produced by microwave heating was found to be four times greater than that of the zeolite membrane produced by conventional heating.

(3) Using Microwave Technology for Nanotechnology: Single-site catalyst synthesis, antimicrobial nanocomposites, fire retardant materials, innovative electro-optical devices, sensors, ultra-soft magnets, and medication delivery systems are just a few of the fields in which nanotechnology is being used today

4) Use of microwaves in polymer synthesis: Polyacrylamide (PAM) synthesis was investigated using microwave radiation. PAM is employed in the treatment of waste water as a flocculating agent. There was discussion of how the power of the microwave radiation affected the acrylamide molecular transformation ratio in relation to the PAM molecular weight, initiation, and dissolve time.

(5) Analytical Chemistry: The field of analytical chemistry makes extensive use of microwave irradiation. Techniques for solvent extraction and sample digestion frequently involve microwave irradiation. They've also been used in gravimetric analysis, moisture determination, and enthalpy of solvent vaporisation calculations.

(6) Digestion: High pressure develops H. Matusiewics describes Asher focused microwave digestion (HPAFM), a novel approach. Focused milliwave operates at 2.45 GHz with 650 W of power in this system. The quartz used to make the pressure vessels allows for the conductivity of temperature and pressure to reach up to 320 C and 130 bar, respectively. This device was used to develop the methodology for the digestion of biological reference material, such as the liver of a cow.

(7) Microwave radiation in waste management: The treatment of nuclear, hazardous, and domestic waste is greatly aided by microwave heating. In situations where human exposure may result in health issues, waste management can benefit from the use of microwave heating. The high frequency and microwave technology required to handle this kind of hazardous waste is available for use. Kasai et al. have filed for patent on a method for using MW heating to carbonise organic waste in order to produce activated carbon. With MW heating, organic wastes like used paper, wood, waste plastic, etc. can be converted into activated carbon with a high carbonization efficiency. Roszel has developed the apparatus and method for both continuous and batch processes in waste treatment. In this process, wastes like sludge, ores, car exhaust, medical waste, and more are treated in an anaerobic environment using MW energy

Types of reactions

Different Types of Organic Reactions Assist by Microwave There are two main categories into which the organic reactions aided by microwaves can be divided: solvent-assisted microwave reactions as well as solvent-free microwave assisted reactions

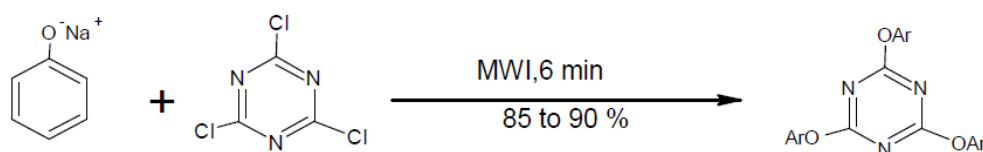
A) Microwave Assisted Reactions using Solvents

There is currently a growing need for solvent-free reactions and effective synthetic processes because of environmental concerns. To reduce and avoid pollution from chemical activities, both new and old methods are being employed. In this regard, microwaves are now a significant energy source for a variety of laboratory processes. Furthermore, because it combines the selectivity associated with most microwave-assisted reactions with solvent- and waste-free processes in which organic solvents are avoided at all stages, microwave-assisted solvent-free organic synthesis, or MASFOS, has been developed as an environmentally friendly process. In Nowadays, with everyone being so concerned about the environment, research and development is focused on creating greener methods. The concept of green chemistry, which involves safe reagents and conditions, has rapidly evolved due to environmental hazards and the ensuing degradations. Three different types of MASFOS reactions exist.

Reactions employing solid mineral supports solid-liquid phase transfer catalysis (PTC) reactions employing neat reactants. At least one of the reactants at the reaction temperature should typically be liquid when conducting neat reactants, or heterogeneous reactions, which do not require the use of a solvent or support. In this configuration, the liquid is adsorbed onto the solid surface and the reaction takes place at the interface, or the solid is partially soluble in the liquid phase. Another possibility is that neither of the reactants is a solid. Typically, they melt during the course of the reaction and go through the previously mentioned reaction. In examples of microwave-assisted reactions with well-organized reactants are shown below.

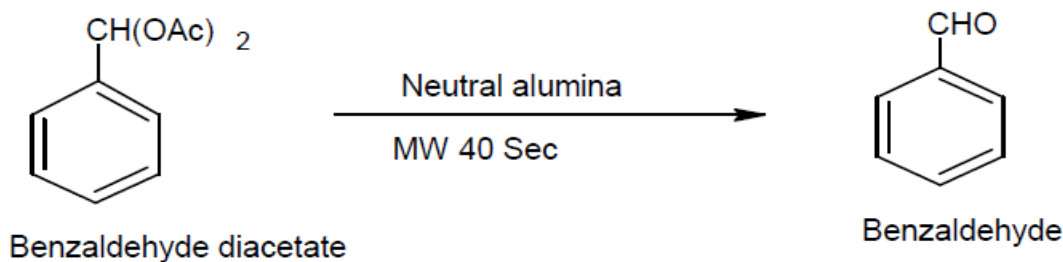
(1) Aromatic Nucleophilic Substitutions

Creation of Triazines That Are Substituted Sodium phenoxide and 1,3,5-trichlorotriazine are used in aromatic nucleophilic substitutions, which are done under microwave radiation (6 min). In 85–90% of cases, the products 1,3,5-triarlyoxytriazines are obtained.



(2) Deacetylation (62)

Acetylation provides protection for alcohols, phenols, and aldehydes. Following the reaction, the product is typically deacetylated in an acidic or basic environment; this process is laborious and produces low yields. The yields are good and the deacetylation time is shortened when microwave irradiation is used.

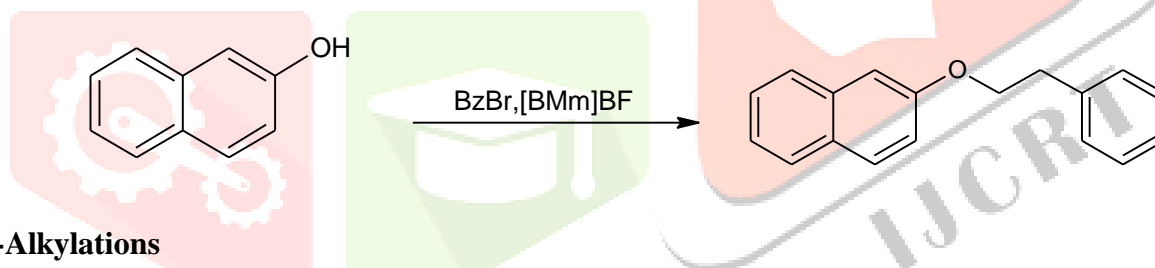


B) Microwave assisted Reactions using Solid Liquid Phase

Solid liquid phase transfer catalysis (PTC) is a technique that is currently being researched and has been characterised as an efficient way to synthesise organic compounds. Due to the anionic activation involved, this method is unique to anionic reactions. The mixture of both pure reactants is mixed with a catalytic amount of either a cat ion complexing agent or a tetralkyl ammonium salt (in equimolar amounts). Only the electrophilic R-X is present in the liquid organic phase, where reactions take place. It is not advantageous to have a second liquid component because it dilutes the reactants and reduces their reactivity. Thus, the reactant and organic phase of the reaction are the electrophile R-X.

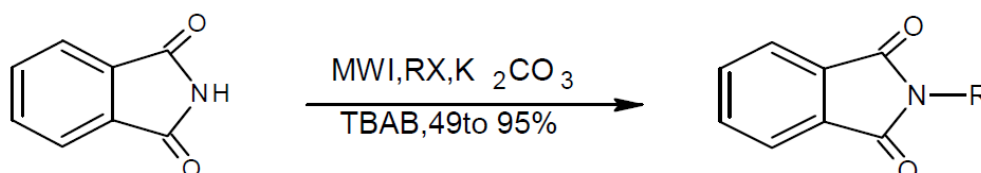
(1) O-Alkylation

Using benzyl bromide and 1-butyl-3-methyl-imidazolium tetrafluoroborate, ethers were prepared from β -naphthol under microwave irradiation (6–12 min). The products were isolated in 75–90% yields.



(2) N-Alkylations

In organic chemistry, N-alkylations performed with phase transfer catalysts under microwave irradiation have a special place. Using phthalimide, alkyl halides, potassium carbonate, and TBAB, Bogdal and colleagues reported synthesising N-alkyl phthalimides, yielding products in 45–98% yields.



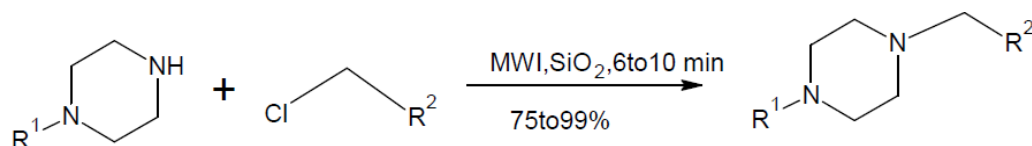
C) Microwave assisted Reactions on Mineral Supports in Dry Media

Solid supports act as highly effective microwave absorbers despite frequently being very poor heat conductors. Consequently, there is a very quick and even heating process. As a result, in comparison to classical heating, they exhibit a very strong specific microwave effect that plays a significant role in

temperature homogeneity and heating rates, enabling faster reactions and less product degradation. The Microwave Activation Example with Supported Reagents is shown below.

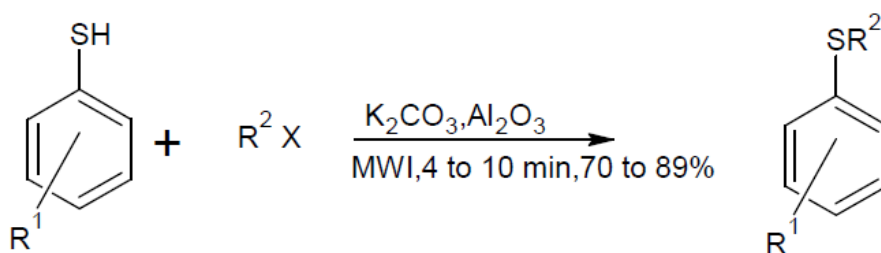
(1) N-Alkylation

Under microwave radiation, N-alkylation was performed between piperidines and chloroalkanes with silica serving as the solid support (6–10 min). 79–99% yields of N-alkyl products were isolated.



2) S-Alkylation

S-Alkylation was investigated and achieved by utilising potassium carbonate and alumina to conduct the reaction between mercaptobenzene and alkyl halides under microwave radiation (4–10 min). Isolated products had yields ranging from 70 to 89%. [12].



Limitations:

- Limited Applicability:** Microwave synthesis works best in certain types of reactions, like those in organic chemistry, and might not be appropriate for other kinds of chemical processes.
- Temperature and Pressure Constraints:** Localised hot spots caused by microwave heating can make it difficult to regulate temperature and pressure in some reactions.
- Reaction Vessel Compatibility:** Certain reaction vessels are not appropriate for microwave synthesis, and specific, potentially costly equipment may be needed.
- Safety Concerns:** If incompatible materials are used, microwaves have the ability to heat some materials quickly, which could result in explosions or fires.
- Limited Scalability:** Since microwave synthesis is frequently employed in laboratories, it might not be simple to scale up for use in large-scale manufacturing [13].

Conclusion:

The phrase "green chemistry," which refers to a set of rules to reduce or eliminate the use of hazardous compounds in the development, manufacture, and use of chemical products, is attributed to the US Environmental Protection Agency. To do this, apply the twelve Green Chemistry concepts. Green chemistry seeks to minimize waste as much as is practical while boosting synthetic process efficiency, cutting down on the number of steps required, and employing fewer potentially dangerous solvents. The heating of materials that absorb microwaves involves three main mechanisms: dipolar polarization, conduction mechanism, and interfacial polarization. These mechanisms are essential for understanding microwave chemistry. There are some limitations of this Green Chemistry that are: Limited Applicability, Temperature and Pressure Constraints, Reaction Vessel Compatibility, Safety Concerns and Limited Scalability. Solid liquid phase transfer catalysis (PTC) is a technology being explored for microwave assisted reactions and has been shown to be an effective means of synthesizing organic molecules.

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