Microwave Irradiation

Way to Eco-friendly, Green Chemistry

Rashmi Sanghi

This article highlights with examples, the usefulness of microwaves for carrying out a variety of organic transformations

Rashmi Sanghi is currently working as a Scientist at the Facility for Ecological and Analytical Testing, IIT Kanpur. She got her PhD degree in natural products from Allahabad University in 1994 and then carried out postdoctoral work both at IIT Kanpur and at Rutgers University.

Introduction and Background

The rapid heating of food in the kitchen using microwave ovens prompted a number of scientists engaged in different disciplines to explore the potential of microwave technology in a number of useful processes. These include the preparation of samples for analysis; application to waste treatment; polymer technology; drug release or targeting; ceramics; alkane decomposition; hydrolysis of proteins and peptides, etc.

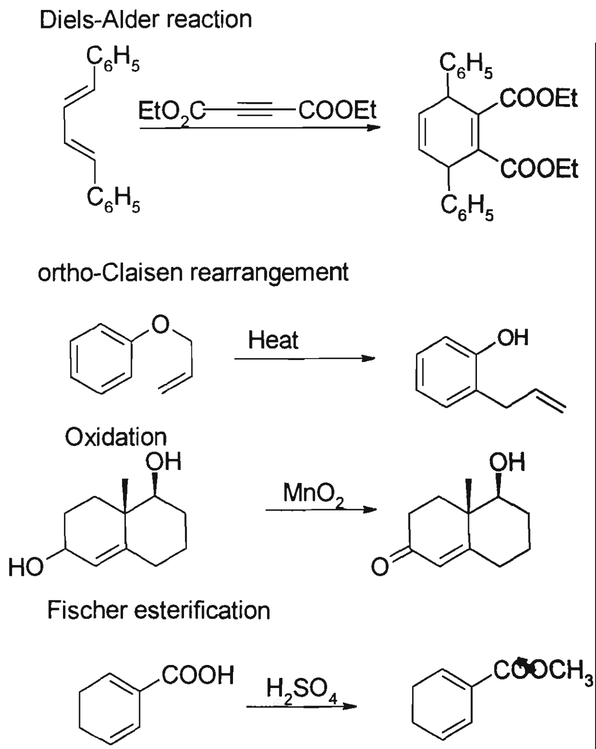
Microwaves form a part of the electromagnetic spectrum with the wavelength lying between 1 cm and 1 m. In order to avoid interference with radar and telecommunication activities, which also operate in this region, most commercial and domestic microwave ovens operate at 2450 MHz (12.25cm). The difference between microwave energy and other forms of radiation, such as X- and γ-rays, is that microwave energy is non-ionizing and therefore does not alter the molecular structure of the compounds being heated – it provides only thermal activation. The heating effect utilized in microwave assisted organic transformations is mainly due to dielectric polarization. When a molecule is irradiated with microwaves, it aligns itself with the applied field. The rapidly changing electric field (2.45×10^9 Hz) affects the molecule and consequently the molecule continually attempts to align itself with the changing field and energy is absorbed. The ability of a material to convert electromagnetic energy into thermal energy is dependent on the dielectric constant. The larger the dielectric constant the greater is the coupling with microwaves. Thus, solvents such as water, methanol, DMF, ethyl acetate, acetone, acetic acid, etc. are all heated rapidly when irradiated with microwaves. However, solvents with low dielectric constants such as hexane, toluene, carbon tetrachloride, etc. do not couple and therefore do not heat that rapidly under microwave irradiation.

Microwave heating has thus been found to be a very convenient thermal source not only in the kitchen but also in a chemical laboratory. Chemists have explored the possibility of the application of a conventional microwave oven to carry out chemical reactions. It has been found that many reactions progress much faster upon microwave irradiation than with traditional heating techniques. The application of microwave irradiation to activate and accelerate organic reactions has taken a new dimension and has experienced exponential growth in the last eight years. Microwave chemistry is becoming increasingly popular both in industry and in academia. The future for the application of microwave technology looks bright because of its efficiency and its potential to contribute to clean products. Microwaves are revolutionizing the way we do our chemical cookery, even though how they work is sometimes more of a mystery.

Microwaves and Organic Synthesis

In the past few years there has been growing attention on the use of microwave heating in organic synthesis since the first contributions by Gedye and Giguere in 1986. It has several advantages over conventional technology: remarkable decrease in the time necessary to carry out reactions; improved isolated yields of products; and sometimes remarkable effects on chemo-, regio- and stereoselectivity (*Table* 1). It also appears that microwaves have a specific 'microwave effect' that lowers the activation energy of a reaction. Thus, microwave mediated organic reactions take place more rapidly, safely, environmentally friendly and with high yields.

As discussed earlier, a dipolar solvent with relatively low mo-



Reaction		Conventional	Microwave
Diels-Alder reaction	solvent	DMF	DMF
	reaction temp	153	198
	yield	34%	80%
	reaction time	5 h	5 min
ortho-Claisen rearrangement	solvent	DMF	DMF
	reaction temp	153	195
	yield	72%	97%
	reaction time	36 h	5 min
Oxidation	Solvent	diethyl ether	diethylether
	reaction temp	36	103
	yield	33%	79%
	reaction time	90 min	7 min
Fischer esterification	solvent	methanol	methanol
	reaction temp	65	120
	yield	92%	92%
	reaction time	80 min	1 min

Table 1.

lecular weight will heat under microwave irradiation. Indeed, many solvents are not just heated, but they superheat up to 20°C above their normal boiling points! Superheating is widely believed to be responsible for the increase in the rates and yields of chemical transformations. Water for example reaches 105°C (5 degrees above the boiling point) and acetonitrile reaches 120°C, an amazing 38°C higher then its usual boiling point. In many cases microwave mediated reactions can also be done in the complete absence of solvents! Therefore, toxic and expensive organic solvents can be avoided for carrying out many organic reactions. Such reactions not only reduce the amount of waste solvent generated, but the products often need very little purification. These processes will hopefully be adapted by big industries and will therefore reduce the pollution of the environment.

Microwave Synthesis on Solid Supports

Microwave heating for carrying out reactions on solids has also attracted considerable attention in recent years. For such 'dry media' reactions, solid supports such as alumina, silica and bentonite, montmorillonite clays and zeolites have been investigated. Although this technique seems best suited to transformations involving a single organic species, condensation reactions have also been reported. The practical feasibility of microwave assisted solvent-free protocols has been demonstrated in useful transformations like protection, deprotection, condensation, oxidation, reduction, rearrangement reactions and in the synthesis of various heterocyclic systems on solid supports. A wide variety of industrially important compounds and intermediates such as enones, imines, enamines and nitroalkenes have been prepared by this environmentally friendly solvent-free approach (*Table* 2). In these reactions, the organic compounds adsorbed on the surface of inorganic oxides, such as alumina, silica and clay or 'doped' supports absorb microwaves whereas the solid support does not absorb or restrict their transmission. The bulk temperature is relatively low in such solvent free reactions

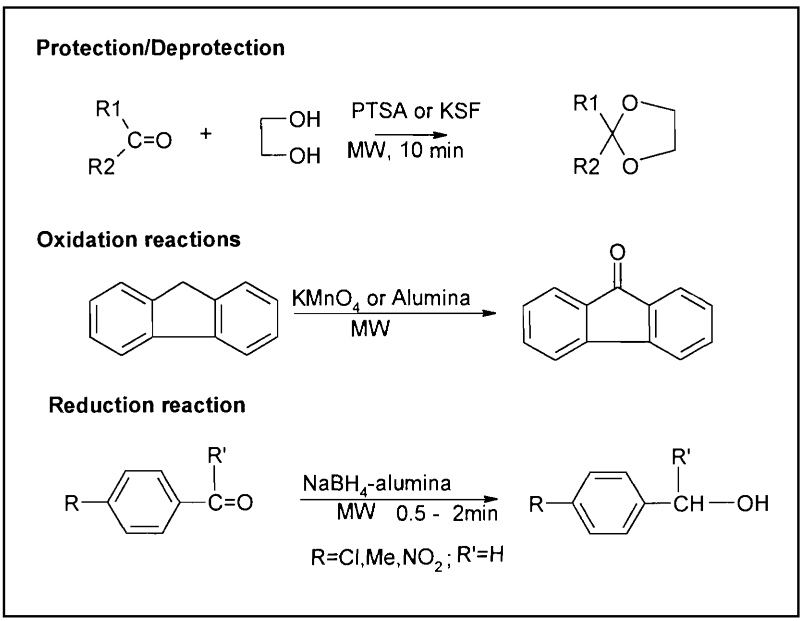


Table 2.

although highly localized temperatures may be reached during microwave irradiation. In recent years, 'dry media' other than supports have been used to drive reactions; *p*-toluenesulphonic acid (PTSA) in particular is commonly used as a homogeneous acid. When used as a co-reactant in the dry medium synthesis of esters, PTSA invariably showed yields 10-20% higher than the best reactions on supports under identical conditions. These solvent free MW-assisted reactions provide an opportunity to work with open vessels as opposed to the specialized teflon vessels and sealed containers used for solution phase reactions, thereby avoiding the risk of pressure build up in large-scale reactions.

Other Applications

The rapid heating effect has also been exploited to create better crystallinity in intercalation compounds such as ceramics and synthetic zeolites. Polymer curing too has benefited from microwave heating. Certain organometallic compounds of second row transition metals which are often impossible to produce by conventional means can be quickly made with microwave heating. The major industrial applications of MW-enhanced clean chemistry also includes the preparation of hydrogen cyanide, a chlorination plant, drying of pharmaceutical powders and pasteurization of food products.

Conclusions

The entry of microwave ovens in the chemistry laboratory has made it possible to carry out many transformations with greater efficiency and ease of workup. We believe that in the future many more microwave-assisted reactions will be developed which will simplify time consuming conventional procedures. It is also hoped that appropriate technology will develop so that some of these fascinating microwave-assisted transformations could be done on industrial scales thereby increasing the overall efficiency of the processes and reducing pollution of the environment through the use of solvent free reaction protocols.

Address for Correspondence
Rashmi Sanghi
302, Southern Laboratories,
Facility for Ecological and
Analytical Testing
Indian Institute of Technology,
Kanpur 208 016, India.