Microwave radiation as a catalyst for chemical reactions

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Up to the middle of 1980s, microwave oven was used only for defrosting frozen food and cooking. Microwave oven has now found an important utility value for carrying out chemical reactions in organic synthesis of compounds. Commercial microwave oven has found its way into India only recently. Microwave irradiation catalyses various chemical reactions efficiently. The main reason for this acceleration in the rate of chemical reactions is the rapid superheating of solvents. Many of the reactions which are conventionally run by thermal process; except for the reactions which require necessary precautions such as the use of dry nitrogen atmosphere, lachrymatric and fuming substances or the substances which may corrode the interior of the oven; can be conducted inside a microwave oven at a much faster rate. Commercial microwave ovens are sufficient for carrying out these reactions. Nevertheless, for carrying out certain reactions specially designed microwave ovens at the laboratory have to be used.

TILL the middle 1980s, microwave oven was used only for thawing and cooking food. The usual modes for conducting chemical reactions were the thermal, photo-chemical, sonochemical, electrochemical and high pressure techniques till the late 1980s. Since 1986, however, the microwave oven has become a source for accelerating chemical reactions[1,2], extraction techniques, etc. This acceleration of chemical reactions is a catalytic process and is entirely different from the process using catalysts which are generally chemical reagents. This rate enhancement in microwave oven is due to its high heating efficiency in a short time.

Microwave oven emits microwave radiation – a part of the electromagnetic spectrum consisting of cosmic, gamma, X-rays, UV, visible, IR, microwave, radar, television, radio and alternating current (Table 1). During the second world war, Randall and Booth at the University of Birmingham were concentrating on the development of RADAR. At that time they designed a device called magnetron[3] for generating fixed frequency microwaves. Microwaves were known, even at that time, to heat up water rapidly, and domestic and commercial appliances for heating and cooking foodstuffs began to appear in the US in the 1950s. In the 1970s there was an upsurge of microwave ovens elsewhere in the world, but it was only recently that microwave ovens have found their way in India. Commercial microwave ovens operate at a frequency of 2450 MHz and the power output can be varied anywhere up to 900 W (Box 1).

Microwave heating essentially follows the principle of microwave dielectric loss[4,5,6a]. Polar molecules absorb

Table 1. The electromagnetic spectrum, with wavelengths λ and frequency v

	λ/m	v/Hz
Cosmic rays	10^{-14}	10^{22}
Gamma rays	10^{-11}	10^{19}
X-rays	10^{-9}	10^{17}
Far ultraviolet	10^{-7}	10^{15}
Ultraviolet	10^{-7}	10^{15}
Visible	10^{-6}	10^{14}
Infrared	10^{-5}	10^{13}
Far infrared	10^{-4}	10^{12}
Microwave	10^{-3}	10^{11}
Radar	10^{-2}	10^{10}
Television	10^{0}	10^{8}
Nuclear magnetic resonance	10	10^{7}
Radio	10^{2}	10^{6}

Box 1.

Microwave heating is routinely used for rapid cooking of food stuffs. There are also other potential applications for this method of heating in a number of disciplines in science. It is having a great impact in the field of chemical analysis[37]. Biologists began using microwaves in the 1970s as a quick way of decomposing sample of tissue in concentrated acids. The best containers for chemical analysis of trace elements such as copper, zinc and nickel are sealed teflon bottles. Geological specimens have also been analysed by microwaves. Apart from chemical analysis, the microwave heating finds applications in polymer technology[38], drug release/targeting[39], ceramics[40] and alkane decomposition[41]. It has also found use in a range of decomposition processes including hydrolysis of proteins and peptides[42]. Applications to inorganic and solid state synthesis have also been shown to have significant advantages.

microwave energy through dipole rotations and thus get heated up whereas nonpolar molecules do not absorb because of lower dielectric constants. The polar molecules align themselves along the external applied field. The electric field of the irradiation frequency in commercial microwave oven (2450 MHz) changes sign 2.45×10^9 times per sec and the tortional effect in dipolar molecules rotating back and forth causes heating by absorbing energy, since the molecular rotation is slower than the changes in the electric field. Although the dielectric constant is the guiding factor behind absorption of energy, there are several other factors which are involved in microwave heating. Even if a solvent has a much lower dielectric constant, the solvent can get heated up rapidly due to its lower heat capacity. For example, 1-propanol ($\varepsilon = 20.1$) having a lower dielectric constant than water ($\varepsilon = 78.54$) heats up 1.7 times faster than water mainly because propanol has a lower heat capacity (2.45 J/gK) compared with water (4.18 J/gK)[6b]. Similarly, porcelain has a higher dielectric constant (6.0–8.0) than acetic acid (6.15 at 20°C) but the latter heats up rapidly since ceramic molecules cannot rotate in the alternating microwave field[6b]. Teflon, polystyrene, glass and ice are nearly transparent to microwaves (Box 2).

So far, there are atleast three ways of carrying out chemical reactions in the domestic microwave oven apart from using the modified form of the equipment. These are (i) sealed vessels[1,2], (ii) open vessels[7] and (iii) dry reactions[8] without solvents. Initially, sealed vessels were used and there were reports of explosion in the oven. This led to the use of open long-necked Erlenmeyer flasks wherein the solvent condenses from the top of the container since the glass vessel does not heat up. To avoid building up of pressure, in the reaction, a new type of reaction was carried out which involved only certain types of solids, e.g. clay with the reagents. Several reviews have appeared in the literature[9] and in the following section we will discuss a selected set of reactions that have been carried out in the microwave oven from 1986 till the present.

Catalysis of organic reactions by a microwave oven

The reports from Gedye et al.[1] and Giguere et al.[2] were the seminal papers in the utilization of microwave oven for accelerating organic reactions. Gedye et al.[1] found rate acceleration up to 240-fold in a variety of reactions in sealed teflon vessels. In the following section, a selected set of reactions conducted in microwave oven will be described:

Diels–Alder reaction is one of the key transformations in organic synthesis for producing cyclic systems in a single step. This reaction has been conducted in a microwave oven with great success. Thus Diels–Alder reaction of anthracene and dimethyl fumarate proceeds in 10 min in xylene (87% yield)[2] whereas under thermal conditions the reaction proceeds in 4 h (67%). The disadvantages of the above process are the use of xylene, which has a lower dielectric constant, and conducting the reaction in a sealed vessel. Hence, Bose[7] has modified this process by conducting the reaction in a long-necked

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Box 2.

Microwave irradiation superheats certain solvents rapidly depending upon the dielectric constants of the solvents. What is meant by dielectric constant of a solvent? The magnitude of the force acting between two given electric charges, placed at a definite distance apart in a uniform medium, is determined by a property of the medium and is known as the dielectric constant. If e_1 and e_2 are the values of two electric charges placed at a distance r apart in a uniform medium, then the force F acting between them is given by Coulombs law as $F = e_1 e_2 / \varepsilon r^2$, where ε is the dielectric constant of the medium. Qualitatively, the larger the dielectric constant, the greater the coupling with microwaves and thus faster the rate of heating. Of course this is not always true as shown in the text. A comprehensive list of dielectric constants of solvents[43] is given below (solvent, dielectric constant, T/K):
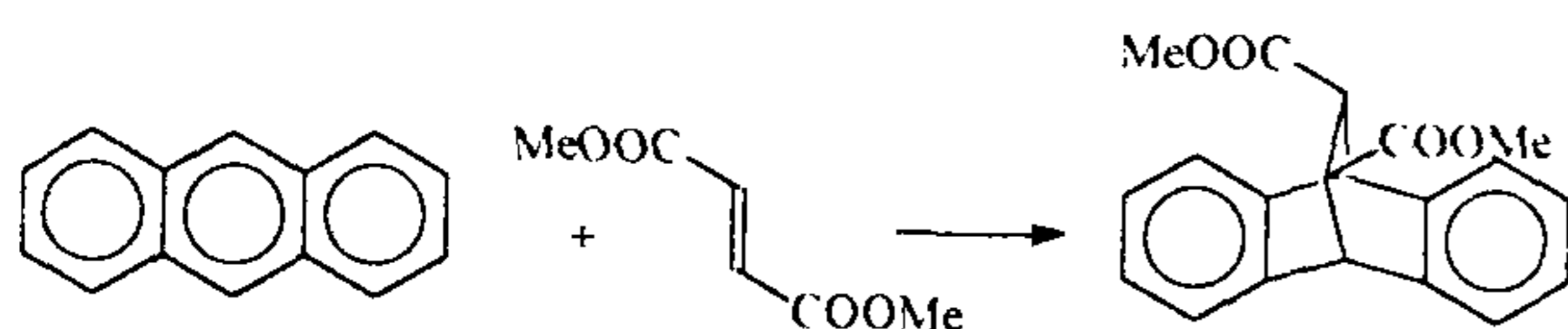
Water	80.0 (293.2)	Chlorobenzene	5.69 (293.2)
Formic acid	51.1 (298)	Chloroform	4.807(293.2)
Dimethylformamide	38.25 (293.2)	Trichloroacetic acid	4.34 (333.2)
Acetonitrile	36.64 (293.2)	Diethyl ether	4.26 (293.2)
Methanol	33.0 (293.2)	Propanoic acid	3.44 (298.2)
Ethanol	25.3 (293.2)	Xylene	2.5 (293.2)
Acetone	21.01 (293.2)	Toluene	2.38 (296.4)
Dichloromethane	8.93 (298)	Benzene	2.285 (293.2)
Tetrahydrofuran	7.52 (295.2)	Tetrachloroethylene	2.26 (303.2)
Dimethoxy ethane	7.30 (296.7)	Carbon tetrachloride	2.24 (293.2)
Acetic acid	6.20 (293.2)	1,4-Dioxane	2.22 (293.2)
Ethyl acetate	6.08 (293.2)	Hexane	1.88 (293.2)

Erlenmeyer flask using 1,2,4-trichlorobenzene which has a higher dielectric constant (Scheme 1). Although the duration of reaction is almost similar, it certainly avoids the untoward explosion due to sealed vessel.

N,N-dimethyl formamide was found to be ideal for conducting Claisen rearrangement[2] inside a microwave oven. The reaction of allyl ether (Scheme 2) proceeds in 5 min compared to 45 min under usual thermal conditions. The reaction proceeds much faster in NMF in 90 sec with 87% yield.

Fischer indole cyclization reaction has been conducted in three different ways in a microwave oven. The Abramovitch group[10] has found irradiation of preformed hydrazone in formic acid in a Parr bomb producing indoles in excellent yields. The Villemin group[11] utilizes montmorrilonite as the absorption medium for phenyl hydrazine and ketone and then it was irradiated for 5 min at 160 W. There is another report[12] wherein acetic acid is used as the medium and the reaction proceeds in 28 sec with 385-fold rate acceleration with excellent yields (Scheme 3).

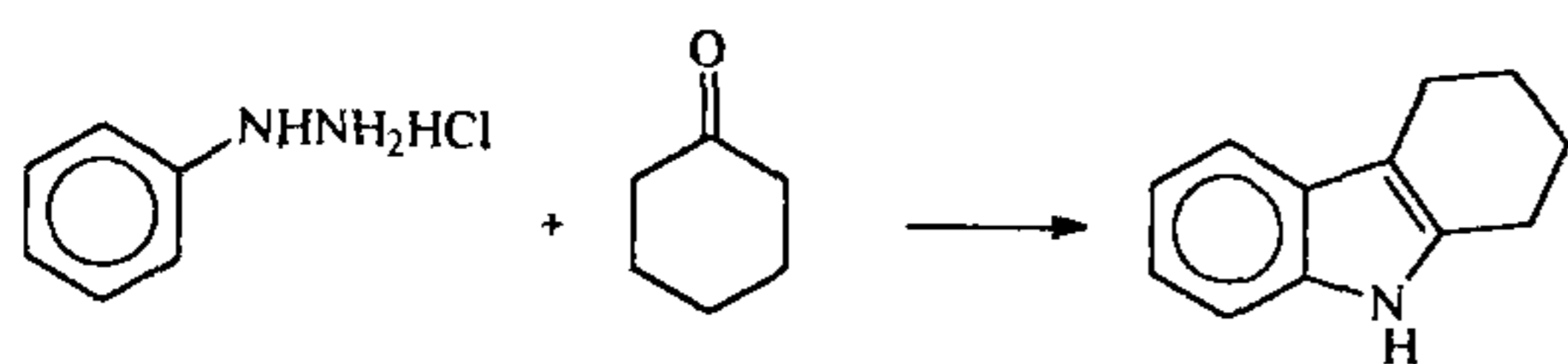Srikrishna and Nagaraju[13] have shown that the ortho-ester Claisen rearrangement, a three-step transformation, which proceeds in 48 h in a sealed tube under thermal conditions takes only 10 min with microwave irradiation (Scheme 4) in an open vessel showing a rate acceleration of 288-fold.
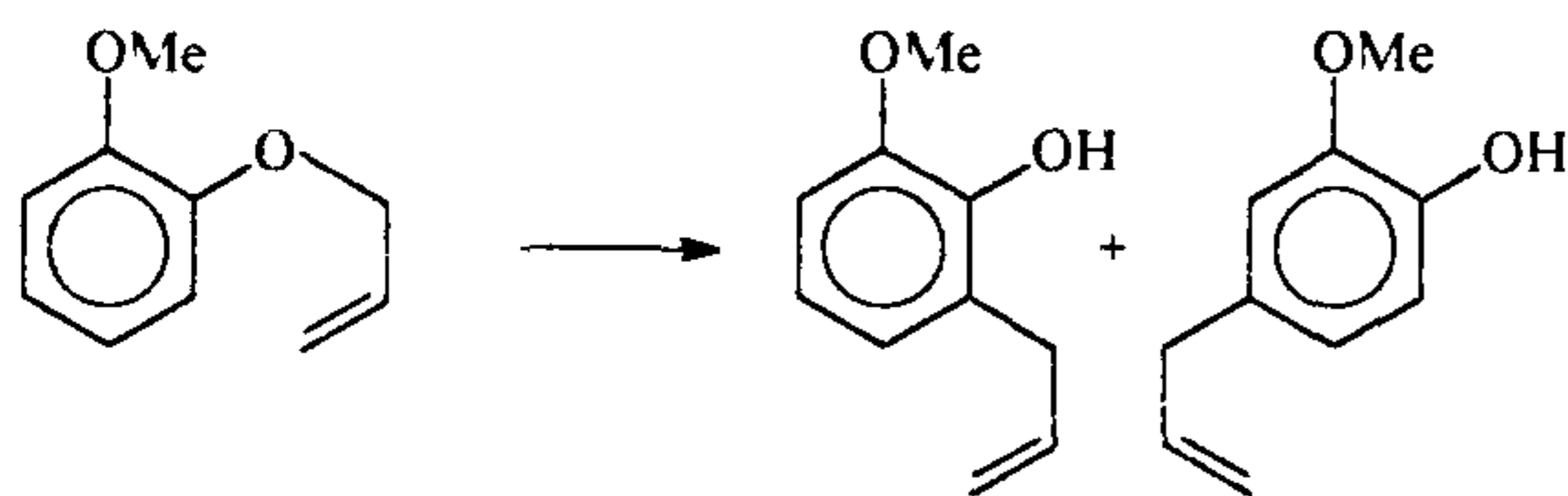
Even change of course of reaction by microwave irradiation from thermal process has been observed by the same group[14]. Heating the ketone 1 for 48 h at 250°C produces the ketone 2 whereas under microwave conditions the dry reaction follows a different path to produce substituted naphthalenes (Scheme 5). This is probably due to the high temperatures attained in a microwave oven.

Sandhu et al.[15] have carried out Michael addition of 1,3-dicarbonyl compounds to α,β-unsaturated ketones under microwave irradiation with $BiCl_3$ or CdI_2 as the catalyst (Scheme 6). The advantage of the reaction is that it proceeds without solvent in 15 min in excellent yields.

Villemin group et al.[16] have observed that the condensation involving piperonal and benzenesulfonylace-tonitrile can be carried out under dry conditions on KF/Al_2O_3 in a microwave oven, resulting in the condensation product in 55% yield (Scheme 7). Under the same conditions without microwave irradiation only a poor yield is obtained.
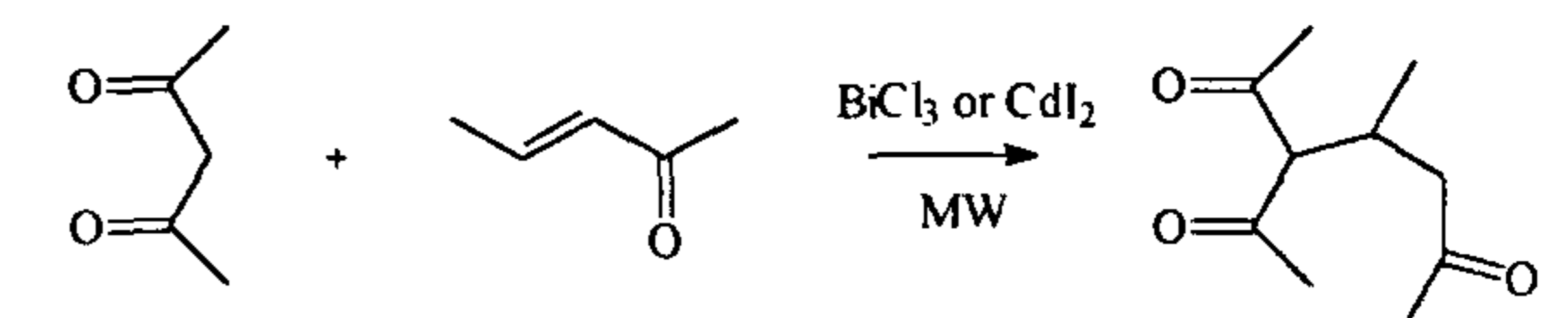
Varma et al.[17–19] have utilized microwave oven for several deprotection strategies (Scheme 8) which are encountered in a major way in total synthesis of natural products.
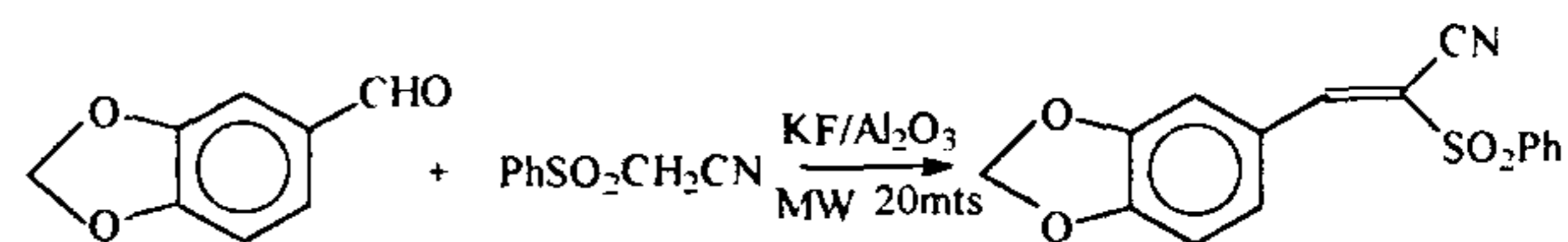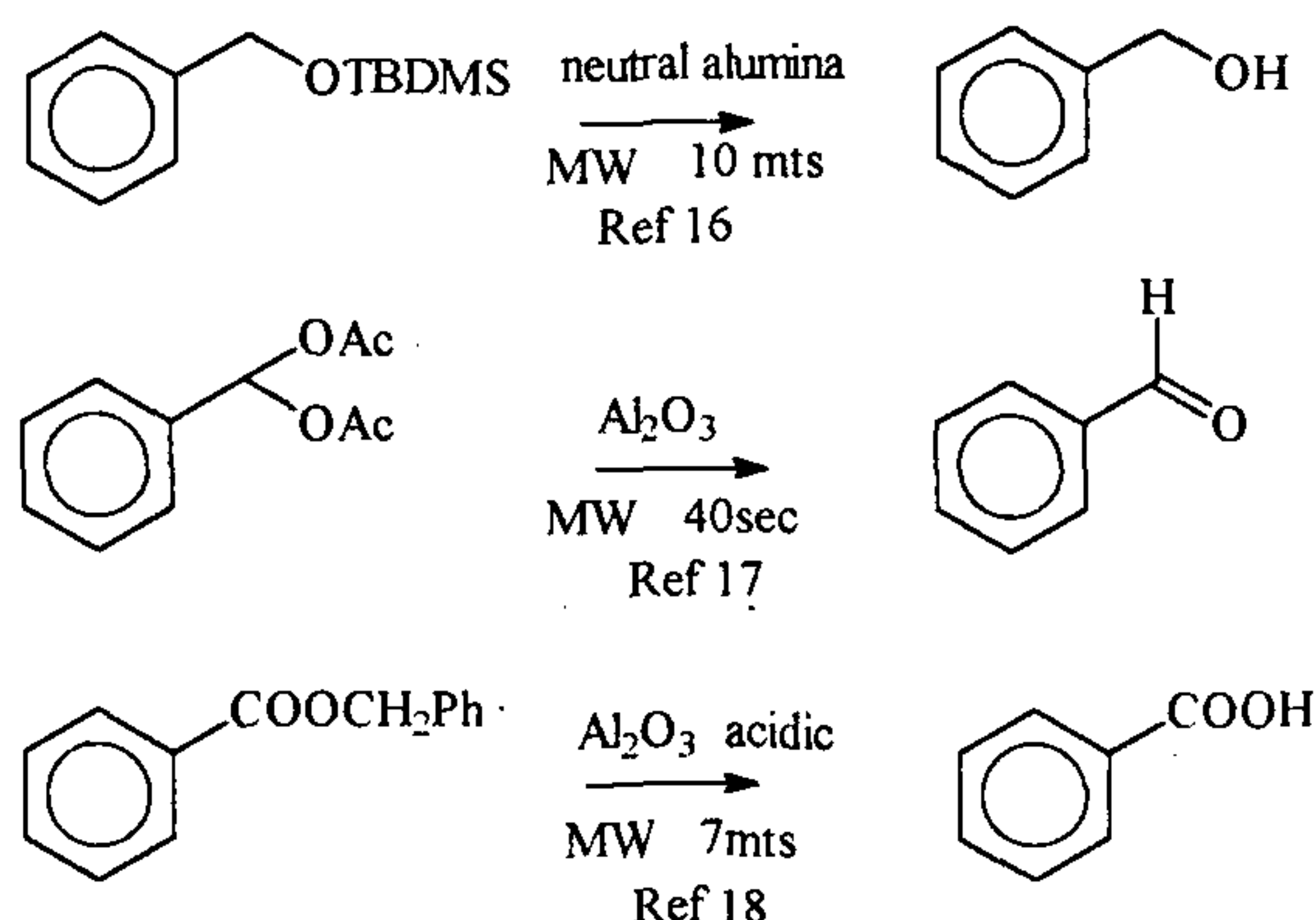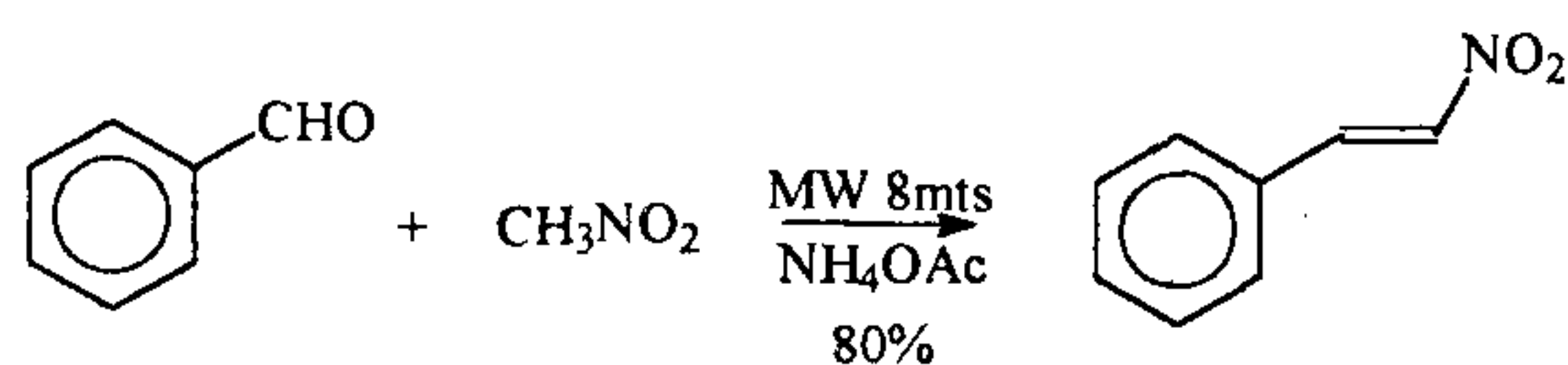

Scheme 1.

Scheme 2.
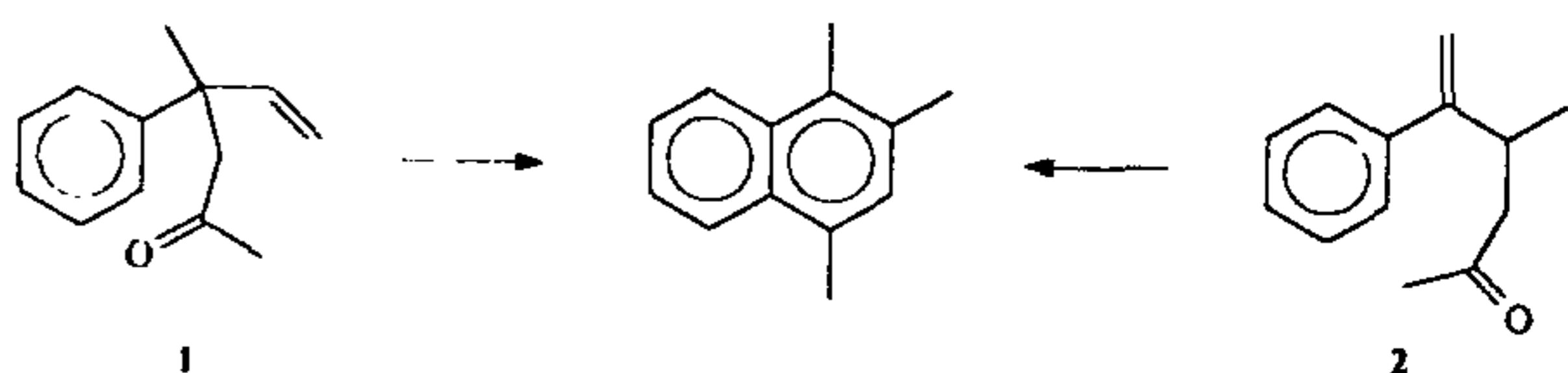
Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Scheme 7.

Scheme 8.

Varma et al.[20] have shown that in a solventless system and under microwave irradiation, nitroalkenes react with arylaldehydes in the presence of a catalytic amount of ammonium acetate to afford conjugated nitralkenes (Scheme 9) without the isolation of intermediary β-nitroalcohols and the rate acceleration is about 140-fold.

Scheme 9.

Conclusion

This review has given a general account of the current utilization of microwave oven only for selected organic reactions since there are already two review articles on this which were published in 1995. There are a variety of other processes which have been conducted in a microwave oven such as ene reactions[21], hetero DA reactions[22], hydrosilylation of alkenes[23], Bischler–Naperialski reactions[7,24], Fries rearrangement[25], intramolecular Diels–Alder reactions[26], oxime formation reactions[27], S_N2 substitution to form esters[28], β-lactam synthesis[29], various cyclization reactions[30], oxidative processes[31], catalytic transfer hydrogenation[7], alkylation reactions[32], decarboxylation reactions[33], Ferrier rearrangement[34], radical reactions[7], porphyrin synthesis[35], di-hydropyridine synthesis[36], etc. Thus, the application of microwave oven as a catalyst in accelerating reactions is being extended to a variety of reactions in organic synthesis and its potential use in the industry is yet to be realized.

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