

## Research Article

# Microwave-Assisted Synthesis of Arylidene Acetophenones

Sheauly Khatun,<sup>1</sup> M. Z. H. Khan,<sup>1</sup> Khodeza Khatun,<sup>2</sup> and M. A. Sattar<sup>1</sup>

<sup>1</sup> Department of Chemical Engineering, Jessore Science and Technology University, Jessore 7408, Bangladesh

<sup>2</sup> Department of Applied Chemistry and Chemical Technology, Islamic University, Kushtia 7003, Bangladesh

Correspondence should be addressed to Sheauly Khatun; sheauly.jstu@gmail.com

Received 31 March 2013; Revised 10 June 2013; Accepted 10 June 2013

Academic Editor: Dmitry Murzin

Copyright © 2013 Sheauly Khatun et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

An efficient synthesis of arylidene acetophenones have been achieved by using the microwave heating in comparison to the conventional heating. In this work compound 1-phenyle-3-(4-droxyphenyle)-2-propen-1-one, 1-(4-chlorophenyle)-3-phenyle-2-propen-1-one, and 1-(4-chlorophenyle)-3-(4-hydroxyphenyle)-2-propen-1-one have been synthesized by the condensation reaction between aromatic aldehydes and substituted acetophenones under microwave irradiation. The compounds of aldehydes and acetophenones were used as benzaldehyde, parahydroxybenzaldehyde, acetophenone, and parachloroacetophenone. The result shows that the time taken for the reaction was reduced from the conventional 1-2 hours to 60–120 seconds. The yield of the compounds in the conventional heating was moderate while the highest yield of 90–98% was observed in MWI method. The structure of the compounds was characterized by their IR, <sup>1</sup>H-NMR spectral data.

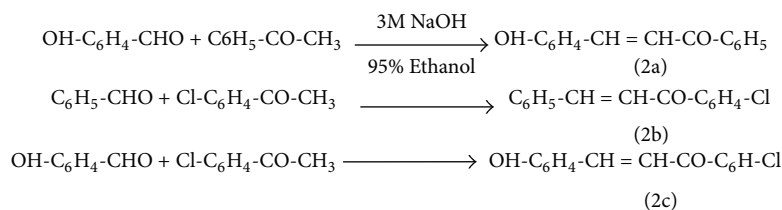
## 1. Introduction

High-speed synthesis with microwave has attracted a considerable amount of attention in recent years [1]. The use of microwave heating to accelerate organic chemical transformations was first reported by the groups of Gedye et al. and Giguere et al. [2, 3], although it can be traced back to the 1950s. While most of the early pioneering experiments in the area of microwave-assisted organic synthesis (MAOS) were performed in domestic, sometimes modified, kitchen microwave ovens, the current trend is to use dedicated instruments which have only become available in the last few years for chemical synthesis. The aim of this work was to highlight the comparative synthesis of organic compound in microwave heating and conventional heating.

Microwaves are a form of electromagnetic energy that can be transferred to the subject compound by the interaction of the electric-field component of the wave with charged particles in the compound. Microwave energy absorbed by the compound will be converted into heat; however, not all materials can be heated by microwaves. The compounds, which absorb the microwave radiations, are termed dielectrics and characterized by possessing very few free charge carriers and exhibiting a dipole movement [4]. When the microwaves are

applied to dielectric compounds with an oscillating electric field, the dipoles within the material attempt to realign themselves and flip around the applied field. Under microwave irradiation at 2.45 GHz, the dipoles realign themselves approximately 2.5 billion times per second due to the alternating electromagnetic field [5]. The dipole movement generates friction inside dielectric compounds and the internal energy is dissipated as heat. The dielectric constant is a measure of the compound's capability to retard microwave energy as it passes through, while the loss factor is a measure of the material's capability to dissipate the energy [6]. The dielectric properties of a compound are related to temperature, moisture content, density, and material geometry.

Microwave irradiation is well known to promote the synthesis of a variety of organic compounds, where chemical reactions are accelerated because of selective absorption of microwave by polar molecules [7]. As a part of our program towards the nontraditional approach to the experimental setup of organic reactions, the concept of "microwave-induced organic reaction enhancement" (MORE) chemistry has been utilized for rapid, sustainable, and efficient synthesis. Microwave-assisted organic synthesis [8–12] has attracted attention in recent years due to enhanced reaction rates, high yields, improved purity, ease of workup after the reaction,



SCHEME 1: Synthesis of arylidene acetophenones (2a–2c).

and ecofriendly reaction conditions compared to the conventional methods.

The present work reveals the comparative aspects of condensation of benzaldehyde with acetophenone by conventional [13] and microwave and their characterization. Arylidene acetophenones are used as starting materials in barbituric acid derivatives, organic intermediates for bulk drugs. Due to their pharmaceutical importance, therefore, it is felt necessary to develop a method for the synthesis of this compound relatively in good yields.

## 2. Materials and Methods

**2.1. Apparatus.** The microwave oven used for this study was classic white ProLine Micro Chef ST44 (650 W, 2450 MHz) which measures 38.2 cm (Height) × 52.6 cm (Width) × 34.5 cm (Depth), with nine power settings. Melting point was uncorrected and was measured with electric-melting point apparatus.

**2.2. Product Analysis.** An IR spectrum (KBr) was obtained on a Fourier transform spectrometer (FTIR-8300). The <sup>1</sup>H-NMR spectra was obtained at room temperature using chloroform-d with a JEOL EX 270 spectrophotometer at 270 MHz. The product was characterized by <sup>1</sup>H NMR spectra and compared their melting point with the literature value. All other chemicals used were of commercial grade without further purification.

**2.3. Rate Enhancements.** The rate enhancement for comparable microwave and conventionally heated reactions, using identical concentration of the following manner:

$$\text{Rate enhancement} = \left( \frac{\text{conventional reaction time}}{\text{microwave reaction time}} \right), \quad (1)$$

where the conventional reaction time and microwave reaction time are for the reactions taken to the same extent of completion. The reactions described in the present paper were carried out following a general procedure [13].

**2.4. General Procedure for the Synthesis of Arylidene Acetophenone (2a–2c).** All of these reactions were carried out under two conditions, namely, (a) the reflux condition (conventional method) and (b) the microwave condition. In both

conditions, the arylidene acetophenones (2a–2c) were synthesized by condensing in equimolar mixture of aromatic aldehydes with substituted acetophenones by adding 15 mL of 3 M NaOH and 25 mL of 95% ethanol.

Under reflux condition, the equimolar mixture of aromatic aldehydes with substituted acetophenones were dissolved in 3 mol NaOH (15 mL) and 95% ethanol (25 mL) in a round-bottomed flask equipped with a refluxing condenser and placed on a magnetic stirrer. The reaction mixture was refluxed at 120°C for 1–2 hours, and the course of the reaction was followed by TLC on silica gel plates (eluting solvent; EtOAc). The flask of the reaction mixture was then poured into the ice-cold water resulting in the formation of crystals. The crystals were filtered and washed with cold water and subsequently with a little ice-cold 95% ethanol.

Under the microwave condition, the arylidene acetophenones (2a–2c) were synthesized (Scheme 1) by condensing in equimolar mixture of aromatic aldehydes with substituted acetophenones by adding 15 mL of 3 mol NaOH and 25 mL of 95% ethanol in a 50 mL beaker, and then the beaker was kept inside a microwave oven and irradiated at different power levels at different time intervals. After irradiation, the beaker of the reaction mixture was removed from the oven and cooled in ice-cold water resulting in the formation of crystals. The crystals were filtered and washed with cold water and subsequently with a little ice-cold 95% ethanol. The reaction was confirmed by thin layer chromatography.

These products were analyzed by IR and proton NMR. The physical and spectroscopic data for each reaction are given as follows.

### 2.5. Reaction of 4-Hydroxy Benzaldehyde with Acetophenone in Ethanol

(a) *Under Conventional Heating Condition.* The product is crystalline solid, color: light yellow; melting point: 69–70°C; IR  $\nu$ : 3100, 1773, 1660, 1446, 1398, 850, 785 3030 (KBr)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.4–7.67 (m, 9H, Ar-H), 4.32–4.21 (s, 1H, Ar-OH), 7.56 (s, 1H, CO-CH), 7.58 (s, 1H, Ar-CH).

(b) *Under Microwave Condition.* This reaction was carried out in a 50 mL beaker for different time at different power levels. The highest yield was obtained at 60 sec at power level 4 (320 W). The physical and spectroscopic data of this product were identical to those found for the reflux reaction.

TABLE 1: Comparative study for synthesis of arylidene acetophenones.

Name of compounds	Conventional method			Microwave method			
	Molar ratio	Time (hr)	Yield (%)	Molar ratio	Time (sec)	Power (W)	Yield (%)
2a	1:1	2	68	1:1	60	320	93.05
2b	1:1	1.30	65.08	1:1	90	240	97.06
2c	1:1	2	70.02	1:1	120	320	98.03

### 2.6. Reaction of Benzaldehyde with 4-Chloroacetophenone in Ethanol

- (a) *Under Conventional Heating Condition.* The product is solid, color: yellowish; melting point: 75–77°C; IR  $\nu$ : 3100, 1776, 1446, 785 (KBr)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 7.35–7.39 (m, 9H, Ar-H), 7.56 (s, 1H, CO-CH), 7.58 (s, 1H, Ar-CH).
- (b) *Under Microwave Condition.* This reaction was carried out in a 50 mL beaker for different times at different power levels. The highest yield was obtained at 90 sec at power level 3 (240 W). The physical and spectroscopic data of this product were identical to those in the reflux reaction.

### 2.7. Reaction of 4-Hydroxy Benzaldehyde with 4-Chloroacetophenone in Ethanol

- (a) *Under Conventional Heating Condition.* The product is powder solid, color: whitish; melting point: 89–90°C; IR  $\nu$ : 3050, 1774, 1724, 1446, 785 (KBr)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 7.4 (m, 9H, Ar-H), 4.5 (s, 1H, Ar-OH), 7.56–7.63 (s, 1H, CO-CH), 7.83–7.82 (s, 1H, Ar-CH).
- (b) *Under Microwave Condition.* This reaction was carried out in a 50 mL beaker for different times at different power levels. The highest yield was obtained at 120 sec at power level 4 (320 W). The physical and spectroscopic data of this product were identical to those in the reflux reaction.

All the experiments in this study were replicated at least three times, and the average value was taken in consideration.

## 3. Result and Discussions

Arylidene acetophenones were prepared by condensing aromatic aldehydes and substituted acetophenones in basic medium. In view of long reaction time, moderate yields, tedious workup after the reaction in conventional method, a relatively more versatile yet simplified procedure was perceived, in microwave irradiation. Microwave synthesis has received attention as a new strategy for organic synthesis due to the fact that many reactions seem to proceed with much alacrity under such conditions as opposed to the corresponding thermal-assisted reactions. The strategy worked well affording the desired product in improved yields in significantly lower reaction time. To ensure the

contribution of specific microwave effect, the results obtained under microwave irradiation are extrapolated to conventional heating. Reactions mentioned in Table 1 are examined by simply heating under the same conditions as mentioned in the typical procedure with microwave irradiation. The rate enhancement under microwave irradiation may be attributed to the absorption of more microwave energy by the polar substrates, which generates sufficient heat energy to promote the reaction. Under microwave irradiation enhanced dipole-dipole interaction and ionic interaction with microwave caused the instantaneous condensation of reactant to afford arylidene acetophenones in a very short time. We have examined the optimum power level and time to find out the highest yield.

*3.1. Synthesis of 1-Phenyle-3-(4-droxyphenyle)-2-propen-1-one (2a).* This condensation reaction has been investigated at the same molar ratio of parahydroxybenzaldehyde and acetophenone at the various powers of microwave irradiation and the different reaction times. The results are shown in Figure 1. The yield increases with the increase of power level. This may be due to the fact that the increase of power level increases the heating rate. In this case more molecules absorb microwave energy to interact with each other and this absorption rate enhances the ionic compound present in reaction through ionic conductance [14]; the better results are obtained as microwave irradiation intensity increases.

We have not been able to isolate the compound when power levels are 240 W and 320 W at 90 s and power level 400 W at 30 s and 60 s, respectively. Probably the compound was decomposed at this level. As indicated, the temperature increased with power level. Since microwave heating significantly increases the reaction temperature [15], it is possible that microwave reaction temperature can exceed the temperature (activation energy) required for a new reaction that is not possible for a lower temperature. If this is the case, different products can be obtained in the microwave reactions. However, in these instances, the amount of the desired product should be small or decomposed. This observation confirmed that power level 320 W showed the highest yield, that is, 93.05%, and required time was only 60 s. Therefore, it can be recommended that for condensation of 4-hydroxybenzaldehyde with acetophenone suitable power level is 320 W and required time is 60 s.

*3.2. Synthesis of 1-(4-Chlorophenyle)-3-phenyle-2-propen-1-one (2b).* Solution of equimolar amounts of benzaldehyde with 4-chloroacetophenone in ethanol, at microwave heating

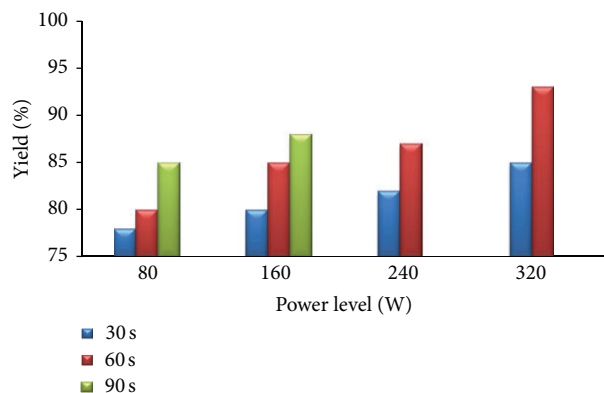


FIGURE 1: Power level versus % yield for the preparation of the compound (2a) under MWI method.

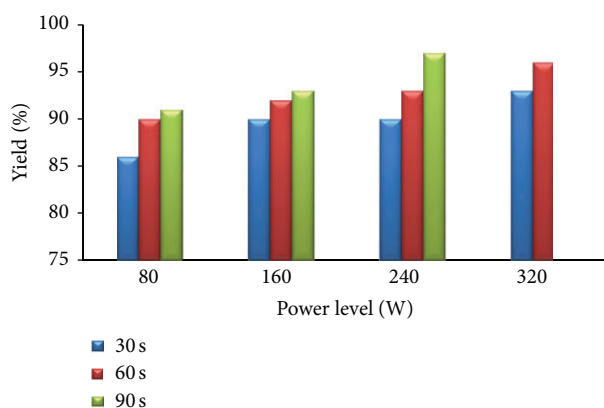


FIGURE 2: Power level versus yield (%) for the preparation of the compound (2b) under MWI method.

in the presence of sodium hydroxide at different time intervals with various power levels.

The rate increases (% yield) with the increase of power level at a definite time, and the reaction rate increases with the increase of time. This increased yield with increasing reaction time is consistent with the heating rate observed because more ions are present in solution. Since ion increases the heating rate by ionic conduction with time, the greatest heating rate and fastest reaction were observed. From Figure 2 the highest yield of the compound (2b) was observed at 90 s of power level at 240 W, but at the same time increased power level is not able to isolate the product from solution.

**3.3. Synthesis of 1-(4-Chlorophenyle)-3-(4-hydroxyphenyle)-2-propen-1-one (2c).** The above two synthesis similar trend was observed for the compound 2c (Figure 3). The workup of the reaction accomplished by equimolar mixture of 4-hydroxybenzaldehyde and 4-chloroacetophenone under the microwave heating in an open vessel in ethanol. Figure 3 shows the result obtained of the series of reactions at different power levels at different time intervals. The highest yield was obtained at 120 s of power level at 320 W.

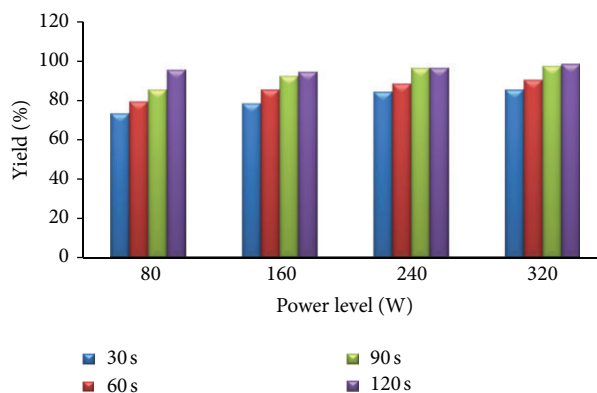


FIGURE 3: Power level versus yield (%) for the preparation of the compound (2c) under MWI method.

The results of these three reactions investigated that the microwave provides a much faster and more efficient method of carrying out organic reaction which is not possible in conventional method. The structures of the compounds 2a–2c are confirmed from physical and spectroscopic data (IR,  $^1\text{H}$  NMR, spectral data). Selected spectroscopic data have been given by experimental section. All data are comparable with the literature value [16–18].

## 4. Conclusion

This study has shown that microwave heating greatly enhanced the percentage yield. Some of the advantages of the present method include easy workup, good isolated products, easy handling of the volatile organic compound. We have observed very efficient microwave-assisted protocol for the synthesis of arylidene acetophenones which can be a viable alternative to the conventional synthesis. In all cases, a comparison of the reactions using conventional and microwave heating was under the same conditions. It can be concluded that MWI method is the rate enhancement method for the condensation of aromatic aldehydes with substitute acetophenones than any other methods.

## References

- [1] D. Adam, "Out of the kitchen," *Nature*, vol. 421, no. 6923, pp. 571–572, 2003.
- [2] R. Gedye, F. Smith, K. Westaway et al., "The use of microwave ovens for rapid organic synthesis," *Tetrahedron Letters*, vol. 27, no. 3, pp. 279–282, 1986.
- [3] R. J. Giguere, T. L. Bray, S. M. Duncan, and G. Majetich, "Application of commercial microwave ovens to organic synthesis," *Tetrahedron Letters*, vol. 27, no. 41, pp. 4945–4948, 1986.
- [4] J. M. Oespchuck, "A history of microwave heating applications," *IEEE Transactions on Microwave Theory and Techniques*, vol. 32, no. 9, pp. 1200–1224, 1984.
- [5] W. Vorster, N. A. Rowson, and S. W. Kingman, "The effect of microwave radiation upon the processing of Neves Corvo copper ore," *International Journal of Mineral Processing*, vol. 63, no. 1, pp. 29–44, 2001.

- [6] K. E. Haque, "Microwave energy for mineral treatment processes—a brief review," *International Journal of Mineral Processing*, vol. 57, no. 1, pp. 1–24, 1999.
- [7] S. P. Hermken, H. Ottenheijm, and D. Ress, "Solid-phase organic reactions II: a review of the literature Nov 95–Nov 96," *Tetrahedron*, vol. 53, no. 16, pp. 5643–5678, 1997.
- [8] P. Kriplani, P. Swarnkar, R. Maheshwari, and K. G. Ojha, "Microwave assisted synthesis of some biologically active benzothiazolotriazine derivatives," *E-Journal of Chemistry*, vol. 3, no. 4, pp. 307–312, 2006.
- [9] E. Rajanarendar and E. Karunakar, "Microwave assisted rapid and efficient synthesis of 2,1-benzisoxazoles," *Indian Journal of Chemistry*, vol. 45, pp. 805–807, 2006.
- [10] S. Caddick, "Microwave assisted organic reactions," *Tetrahedron*, vol. 51, no. 38, pp. 10403–10432, 1995.
- [11] N. Kuhnert, "Microwave-assisted reactions in organic synthesis—are there any nonthermal microwave effects?" *Angewandte Chemie—International Edition*, vol. 41, no. 11, pp. 1863–1866, 2002.
- [12] R. A. Abramovitch, "Applications of microwave energy in organic chemistry. A review," *Organic Preparations and Procedures International*, vol. 23, no. 6, pp. 683–711, 1991.
- [13] A. I. Vogel, *A Text Book of Practical Organic Chemistry*, Longman, New York, NY, USA, 4th edition.
- [14] E. D. Neas and M. J. Collins, *Introduction to Microwave Sample Preparation*, American Chemical Society, 1998.
- [15] R. N. Gedye, W. Rank, and K. C. Westaway, "The rapid synthesis of organic compounds in microwave ovens. II," *Canadian Journal of Chemistry*, vol. 69, no. 4, pp. 706–711, 1991.
- [16] R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, New York, NY, USA, 5th edition, 1963.
- [17] R. N. Jones and C. Sandorfy, *The application of infrared and Raman spectrometry on the elucidation of molecular structure*, Weissbergers Technique of Organic Chemistry vol. 9, pp. 247–580, Interscience, New York, NY, USA, 1995.
- [18] J. A. Elvidge, "Some recent developments in NMR spectroscopy," in *An Introduction to Spectroscopic Methods for the Identification of Organic Compounds*, F. Scheinmann, Ed., vol. 2, p. 211, Pergamon Press, New York, NY, USA, 1974.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

