

## MICROWAVE-ASSISTED ECO-FRIENDLY METHOD FOR THE SYNTHESIS OF CINNAMIC ACIDS

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### Abstract

In this method we used acylals and malonic acid as substrate and under microwave irradiation for the synthesis of the cinnamic acids in a mild, convenient experimental conditions and green method.

**Keywords:** cinnamic acid, acylal, microwave, green, Knoevenagel-Doebner

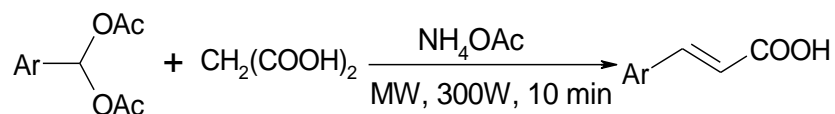
### Introduction

The paramount importance of microwave to high speed synthesis of organic compounds has been established in recent years.<sup>i</sup> More than 2000 articles have been published in the area of microwave assisted organic synthesis (MAOS) since the first reports on the use of microwave heating to accelerates organic chemical transformations by the groups of Gedye and Giguere/Majetich in 1986.<sup>ii,iii</sup> Not only direct microwave heating is able to reduce chemical reaction times from hours to minute, but also it is known to reduce side reactions, increase yields, and improve reproducibility. All of these advantages may encourage all chemists to examine this method. Therefore, this method was used by our research group to synthesis cinnamic acids from acylals. Acylals are interesting compounds because of their stability to basic and neutral media, and also are good starting material for the synthesis of dienes for Diels –Alder reactions.<sup>iv</sup> It is reported that acylals are used as cross linking reagent for cellulose in cotton.<sup>v</sup>

We now report the use of acylals for the synthesis of cinnamic acids which compose a relatively large family of organic compounds which are important reagents in organic synthesis both as intermediates and final products. They also appear to have antibacterial, antifungal, and anti parasite activities. They are used in macromolecular synthesis as very important building blocks for various classes of polymers, having attractive properties, especially a high photo reactivity due to the presence, in the main or side chains, of cinnamoyl group, well-known as a photo responsive unit. Polymers containing cinnamoyl moieties are used in a wide range of application in emerging fields such as advanced microelectronics,<sup>vi</sup> photolithography,<sup>vii</sup> non-linear optical materials,<sup>viii</sup> integrated circuit technology<sup>ix</sup> and photo curable coatings.<sup>x</sup> For their use in perfume production, the food industry, pharmaceuticals, medicine and technical application, therefore cinnamic acids, such important compounds are synthesized on commercial scale. There are various methods for the synthesis of cinnamic acids such as Perkin reaction<sup>xi</sup> Claisen condensation,<sup>xii</sup> Knoevenagel-Doebner condensation<sup>xiii</sup> and Heck reaction.<sup>xiv</sup> But yet there is a

demand for the development of new procedures. In this paper we wish to report an efficient and clean technique for the synthesis of cinnamic acids.

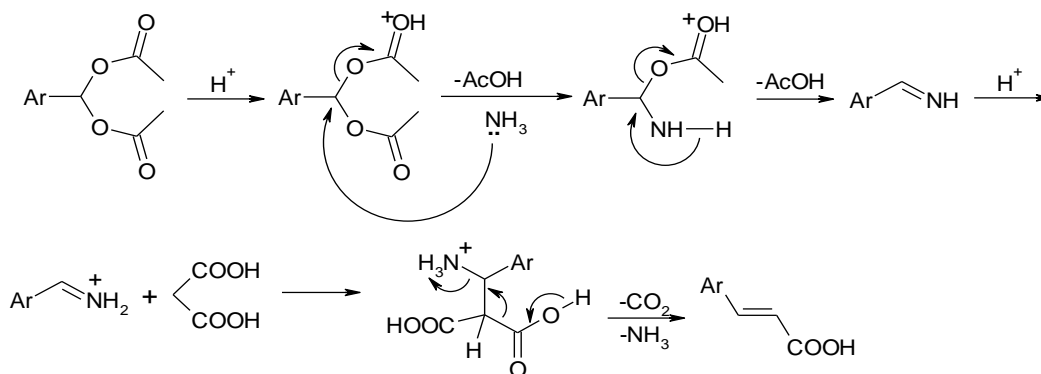
In this method acylals, malonic acid and ammonium acetate as a catalyst were used under microwave irradiation for the synthesis of cinnamic acids. Since malonic acid is highly acidic, therefore weakly basic catalysts are required.



Scheme 1

### Results and Discussion

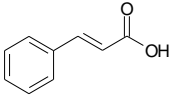
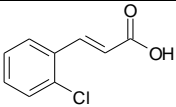
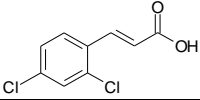
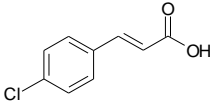
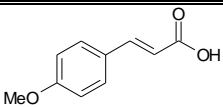
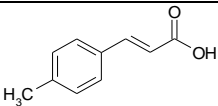
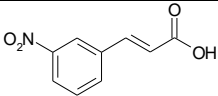
Due to the volatility of aldehydes under high temperature of microwave irradiation condition, our first investigation was replacement of aromatic aldehydes by the corresponding acylals, and also this reaction is of a wide scope and applies to aromatic acylals bearing various substituents. By stepwise investigation, the reaction parameter such as reagent stoichiometry, reaction time and power were examined. The best results were obtained with (3:2:1) mole ratio of malonic acid:ammonium acetate: acylal for 10 min under 300 W microwave irradiation. A plausible mechanism is shown in scheme 2.



Scheme 2

In the first step of this reaction an imine is formed from the reaction of acylal with ammonium acetate. At the second step the reaction of malonic acid with this imine followed by subsequent decarboxylation to give the desired product (table 1). Formation of cinnamic acids confirms the proposed mechanism (scheme 2). All of the products were characterized by their melting points, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectral data and also comparison with authentic samples.

**Table 1. Cinnamic acids obtained by using acylals under microwave irradiation**

Entry	Ar	Product	Yield %
1	C <sub>6</sub> H <sub>5</sub>		90
2	2 - Cl C <sub>6</sub> H <sub>4</sub>		75
3	2, 4 -(Cl) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>		70
4	4 - ClC <sub>6</sub> H <sub>4</sub>		85
5	4 -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		80
6	4- CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		80
7	3 -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		88

### Experimental

All reagents were purchased from Merck Chemical Company and were used without further purification. Acylals were prepared according to the procedure reported in the literature.<sup>xv, xvi</sup> IR spectra were recorded on a Bruker-Tensor FT-IR spectrometer (KBr). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a BRUKER DRX-500 AVANCE spectrometer in DMSO-d<sub>6</sub>.

#### *General procedure for the preparation of cinnamic acid derivatives*

Malonic acid (3 mmol), ammonium acetate (2 mmol), acylal (1 mmol) were mixed in a one neck round bottom flask. This mixture was exposed to microwave irradiations at 300W for 10 min. Then sodium carbonate solution was added to the resulting mixture. After the first filtration of resulting mixture, the filtration solution was acidified by HCl. After the filtration of the acidic solution, the desired product was obtained.

#### *Spectral data for selected compounds*

**Cinnamic acid: (entry 1)**  $\nu_{\max}$  (KBr, cm<sup>-1</sup>): 3230-2485, 1692, 1625; <sup>1</sup>H NMR (DMSO, d<sub>6</sub>):  $\delta$  = 12.41 (s, 1H, OH), 7.69-7.67 (m, 2H, CH<sub>arom</sub>), 7.60 (d, J = 16.0 Hz, 1H, CH), 7.42-7.41 (m, 3H, CH<sub>arom</sub>), 6.54 (d, J = 16.0 Hz, 1H, CH); <sup>13</sup>C NMR (DMSO, d<sub>6</sub>):  $\delta$  = 168.4, 144.7, 135.1, 133.1, 129.7, 129.1, 120.1.

**4-Methoxycinnamic acid: (entry 5)**  $\nu_{\max}$  (KBr, cm<sup>-1</sup>): 3250-2550, 1693, 1637; <sup>1</sup>H NMR (DMSO, d<sub>6</sub>):  $\delta$  = 12.22 (s, 1H, OH), 7.64 (d, J = 8.55 Hz, 2H, CH<sub>arom</sub>), 7.55 (d, J = 15.95 Hz, 1H, CH),

6.97 (d, J = 8.55 Hz, 2H, CH<sub>arom</sub>), 6.38 (d, J = 15.95 Hz, 1H, CH), 3.97 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (DMSO, d<sub>6</sub>): δ = 168.6, 161.8, 144.6, 130.7, 127.7, 117.3, 115.2, 56.1.

### Acknowledgement

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