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Microwave assistant synthesis of *trans*-4-nitrostilbene derivatives in solvent free condition

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ABSTRACT

A general method for the synthesis of trans-4-nitrostilbenes has been developed. The trans-4-nitrostilbene could be synthesized in good yields under microwave irradiation within 10 min through Perkin reaction by using 4-nitrophenylacetic acid, benzaldehydes and pyrrolidine.

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1. Introduction

The microwave-assisted synthesis in organic chemistry has been receiving great attention as a promising heating technique in recent decades [1]. Compared with conventional heating methods, higher yields, milder reaction conditions and shorter reaction times can be achieved [2,3]. Some reviews have been published on the application of microwaves in chemical synthesis [1,4,5].

Stilbene, which is one kind of very useful material in chemistry, life sciences and materials science, has received great attention in organic synthesis [6]. The conventional syntheses of such derivatives through transition-metal-catalyzed cross-coupling and Mizoroki-Heck reactions or Wittig-type reactions usually need complicated multi-steps and suffer from byproducts [7-13]. Several papers have been published for the synthesis of stilbene derivatives under microwave. Srinivasan group reported the synthesis of dinitrostilbene under microwave, which only a few compounds have been studied [14]; and Sinha *et al.* reported the synthesis of hydroxylated stilbene under microwave [15], which needed to add PEG into the system. It is still necessary to study the general method for the synthesis of stilbene under microwave. In present study, a fast microwave-assisted synthesis of *trans*-4-nitrostilbene derivatives in solvent free condition has been reported.

2. Experimental

2.1. Instrumentation

All the commercial reagents and solvents were used without further purification. Microwave irradiation was performed in XH-100A, Beijing microwave reactor (800 W). The ^{1}H NMR spectra were measured on a Bruker AVANCE 400 (400 MHz) spectrometer using TMS as internal standard and $CDCl_3$ as solvent.

2.2. General procedure for the synthesis of trans-4-nitrostil benes

A mixture of 4-nitrophenylacetic acid (**1**) (0.1 mol) and aldehyde (**2**) (0.1 mol) was irradiated under microwave of 800 W in a microwave reactor in presence of pyrrolidine (0.6 mL) for 10 min. The resultant mixture was recrystallized from ethanol (Scheme 1). The solid product was filtered and dried. The structure of *trans*-4-nitrostilbenes was consistent with their spectral data in references [7,16].

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Table 1. The reaction of aldehydes and 4-nitorphenylacetic acid in presence of pyrrolidine under microwave irradiation.

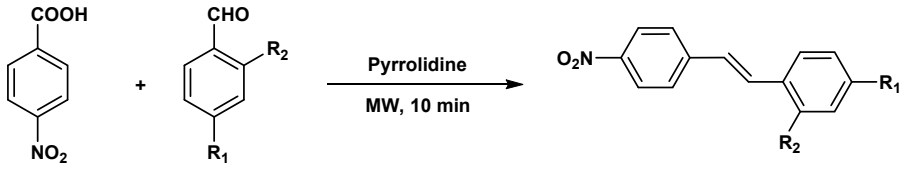
Entry	Time (min)	Pyrrolidine (mL)	Yield (%)
1	5	2.00	62.1
2	10	2.00	90.3
3	20	2.00	90.1
4	10	0.60	90.0
5	10	0.20	78.2
6	120[a]	2.00	85.7

[a] Under refluxed condition.

Table 2. Synthesis of *trans*-4-nitrostilbenes under microwave irradiation.

Entry	Substrates	Isolated yields (%)	Conventional methods yields (%) [a]
1	Benzaldehyde	90.3	85.7
2	4-Bromobenzaldehyde	92.6	87.2
3	2-Bromobenzaldehyde	92.1	88.6
4	4-Chlorobenzaldehyde	91.2	86.3
5	4-Fluorobenzaldehyde	89.6	83.8
6	4-Cyanobenzaldehyde	90.1	89.2
7	4-Nitrobenzaldehyde	92.3	80.2
8	4-Methoxybenzaldehyde	86.2	60.5
9	2-Methoxybenzaldehyde	85.3	65.3
10	4-Methylbenzaldehyde	87.3	70.2
11	4-Dimethylaminobenzaldehyde	85.5	85.3

[a] The yields were obtained under refluxed conditions for 2 h.



Scheme 1

3. Results and discussion

The results were summarized in Tables 1 and 2. As shown in Table 1, the reaction of aldehydes and 4-nitrophenyl acetic acid could be carried out in presence of pyrrolidine to give *trans*-4-nitrostilbene through a Perkin type reaction under microwave irradiation. The *trans*-4-nitrostilbene was previously prepared in 85% yield under refluxed condition in an oil bath [16]; while 4-nitrostilbene was obtained in 90.3% yield under microwave irradiation. We also did experiment in the absence of microwave, the mixture of 4-nitrophenylacetic acid, benzaldehyde and pyrrolidine was refluxed for 2 h to produce *trans*-4-nitrostilbene in 85.7% yield. Obviously, the microwave could accelerate the Perkin type reaction. The effect of irradiation time was studied. The product was obtained in 62.1% under microwave irradiation for 5 min, and if prolonged the irradiation time to 10 or 20 min, higher yields (90.3 or 90.1%, respectively) could be achieved. In addition, the amount of pyrrolidine was also evaluated. Similar yields of product were obtained in presence of 2.0 mL or 0.6 mL pyrrolidine, however, if the amount of pyrrolidine reduced to 0.2 mL, only much lower yield was obtained. Therefore, the synthesis of *trans*-4-nitrostilbene derivatives was carried out in presence 0.6 mL pyrrolidine for 10 min under microwave irradiation.

The reaction of aldehydes and 4-nitrophenylacetic acid under microwave irradiation was summarized in Table 2. According to Table 2, the *trans*-4-nitrostilbene derivatives could be synthesized in very good yield under microwave irradiation within 10 min. Moreover, the aldehydes with electron withdrawing groups could give higher yields for product than the aldehydes with electron donating groups, and the position of substituent had little effect on the yield, which indicated that the yield of this Perkin reaction could be improved with the electron withdrawing group.

4. Conclusion

In summary, a facile synthesis of *trans*-4-nitrostilbene in excellent yields under microwave irradiation has been developed. This method provided a general and very convenient procedure for the synthesis of trans-stilbenes.

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