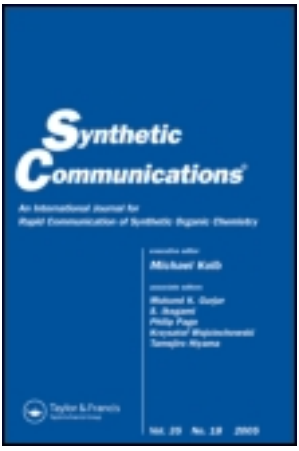

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MICROWAVE-INDUCED SYNTHESIS OF NITROSTILBENES UNDER NEAT CONDITION

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MICROWAVE-INDUCED SYNTHESIS OF NITROSTILBENES UNDER NEAT CONDITION

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ABSTRACT

Nitrostilbenes **3a–e** were synthesized in good yield using microwave under neat conditions, whereas heating at 90°C resulted in poorer yields of products.

During the last decade, microwave methodology[1–5] and solventless[6,7] experiments have been carried out in organic synthesis. They offer shorter reaction times, increased yields, clean, efficient, economical procedures, and safer work-up and are environmentally friendly. In the present investigation, solvent-free microwave technique was employed to synthesize nitrostilbenes. These compounds **3a–d** were synthesized[8] in boiling benzene with piperidine as catalyst. It is our interest to synthesize these nitrostilbenes as precursors for polynitroaromatic compounds as potential high-temperature explosives[9] and for electrochemical studies.[10] Neat condensation of 2,4-dinitrotoluene[11] **1** with various aromatic aldehydes **2a–e** in the presence of pyrrolidine under microwave irradiation of 800 W power gave nitrostilbenes **3a–e** in good yield (60–85%, Scheme 1). Simple heating on a water bath upto 15 min gave the same in comparatively poorer yield (18–68%). A comparison of yields obtained by both methods is shown in the Table.

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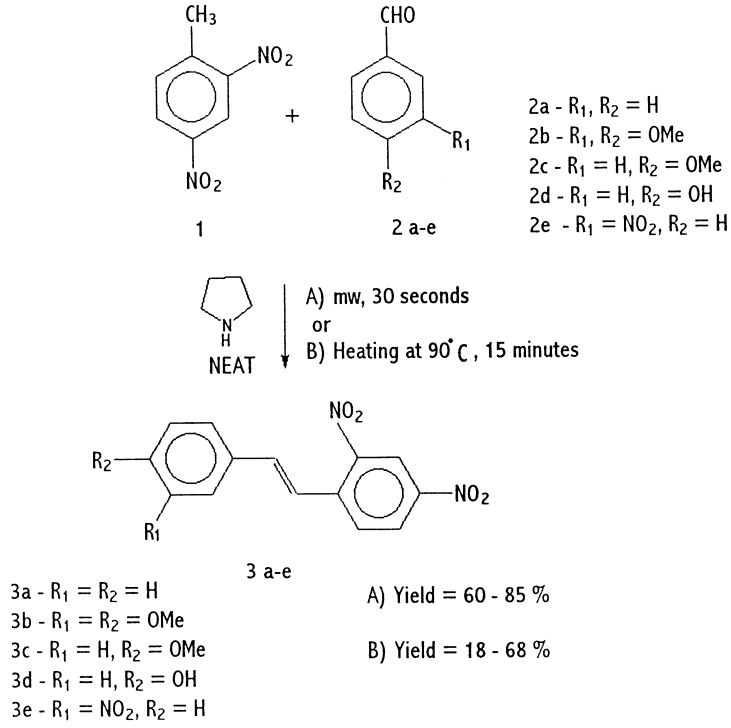

Scheme 1.

Table.

Stilbene	Activation Mode	Time (min)	Yield %	m.p.°C
3a	Microwave	0.5	85	139
	Thermal	15	68	
3b	Microwave	0.5	70	142
	Thermal	15	28	
3c	Microwave	0.5	82	162
	Thermal	15	52	
3d	Microwave	0.5	60	187
	Thermal	15	18	
3e	Microwave	0.5	80	180
	Thermal	15	35	

In summary, a rapid synthesis of nitrostilbenes in good yields under microwave irradiation was developed.

EXPERIMENTAL

General

The nitrostilbenes **3a–d** had the correct melting point as reported in the literature.[8] The structure of **3e** was consistent with its spectral data.

Preparation of 2,4-Dinitrotoluene **1**

4-Nitrotoluene (13.7 g, 100 mmol) was dissolved in con. sulphuric acid (30.6 g, 312 mmol). Fuming nitric acid (15 g, 230 mmol) was added slowly with stirring. The temperature was maintained below 50°C by occasional cooling in water. Then the mixture was heated at 90°C for 30 min, cooled to 25°C, and poured over crushed ice. The crude product was filtered, dried, and recrystallized from methanol. Yield: 95%; m.p. 71°C.

General Procedure for the Synthesis of Stilbenes Under Microwave Irradiation and Conventional Heating

Synthesis of stilbene **3e** is representative for the general procedure followed. A mixture of 2,4-dinitrotoluene **1** (0.93 g, 5 mmol) and aldehyde **2e** (0.63 g, 5 mmol) was irradiated under microwave of 800 W in a domestic-type microwave oven in the presence of pyrrolidine (0.106 g, 1.5 mmol) for 30 sec. The resultant mixture was washed with ethanol. The solid product was filtered and dried. Yield: 80%; m.p. 180°C; IR(KBr) 1600, 1570, 1380 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.9 (d, J = 2.4 Hz, 1H), 8.51 (d, J = 7.8 Hz, 1H), 8.4 (d, J = 2.2 Hz, 1H), 8.25 (d, J = 9.2 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 7.84 Hz, 1H), 7.78 (d, J = 16.1 Hz, 1H), 7.65 (m, 1H), 7.3 (d, J = 15.6 Hz, 1H) MS: m/z 315 (2% M^+), 182 (28%), 165 (100%), 151 (95%).

The above procedure was repeated using heating at 90°C for 15 min in a water bath. Yield **3e**: 35%.

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