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SYNTHETIC COMMUNICATIONS
Vol. 32, No. 22, pp. 3481–3486, 2002

THE RAPID SYNTHESIS OF β-NITROSTYRENES UNDER MICROWAVE IRRADIATION WITHOUT SOLVENT

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ABSTRACT

The β-nitrostyrenes (**3a–l**) were prepared by condensation of benzaldehydes with nitromethane in the presence of K_2CO_3/Al_2O_3 under microwave irradiation without solvent. They were characterized by IR, ^{1}H-NMR, and elemental analysis.

Many reports dealing with the biological activity of β-nitrostyrene stated that it had a detrimental effect on sects and on the growth of fungi and that it could be used for the protective treatment of textiles, leather, and other organic materials. Generally, β-nitrostyrenes were synthesized by condensation with benzaldehydes and nitromethane. And the condensation was usually been catalyzed by (a) bases such as alcoholic potassium hydroxide, aqueous sodium hydroxide or alcoholic methylamine[1]; (b) buffer solutions containing a conjugate acid–base pair such as ammonium acetate in

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DOI: 10.1081/SCC-120014781 0039-7911 (Print); 1532-2432 (Online)

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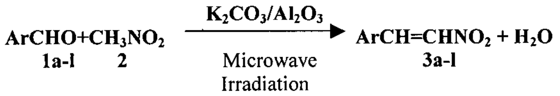
acetic acid[2]; (c) salts such as zinc chloride or potassium fluoride in the presence of dimethylammonium chloride in refluxing toluene solution.[3] Recently many studies have shown that some organic reactions are faster and more efficient under microwave irradiation in the solid state than in solution.[4,5] To develop a more reliable procedure for β-nitrostyrenes, we have found that β-nitrostyrenes were conveniently obtained under mild conditions by the reaction between benzaldehydes and nitromethane in the presence of potassium carbonate under microwave irradiation without solvent (Sch. 1). The optimum proportions of the reagents involved



$$\underset{\textbf{1a-l}}{ArCHO}+\underset{\textbf{2}}{CH_3NO_2} \xrightarrow[\text{Microwave Irradiation}]{K_2CO_3/Al_2O_3} \underset{\textbf{3a-l}}{ArCH{=}CHNO_2} + H_2O$$

1a: Ar = C_6H_5;
1b: Ar = p-HOC_6H_4;
1c: Ar = 2,4 -$Cl_2C_6H_3$;
1d: Ar = p-$O_2NC_6H_4$;
1e: Ar = 3,4 -$CH_2O_2C_6H_3$;
1f: Ar = p-ClC_6H_4;
1g: Ar = 3 -CH_3O-4-HOC_6H_3 ;
1h: Ar = o-HOC_6H_4;
1i: Ar = p –$(CH_3)_2NC_6H_4$;
1j: Ar = p -$CH_3OC_6H_4$;
1k: Ar = 3 -C_6H_5 CH_2O-2-$O_2NC_6H_3$;
1l: Ar = 2 -CH_3CO_2- 3 -C_6H_5 CH_2O-6-$O_2NC_6H_2$;

Scheme 1.

Table 1. Preparation of Compounds **3**

Compound	Formula	Microwave Power (W)	Irrad. Time (min)	Yield[a] (%)	M.P. (°C) [Lit. °C]
3a	$C_8H_7NO_2$	175	5	86	57–58 (59–59)[2]
3b	$C_8H_7NO_3$	200	5	91	167–169 (168–169)[2]
3c	$C_8H_5NO_2Cl_2$	200	4	95	109–110 (110)[1,6]
3d	$C_8H_6N_2O_4$	225	4	94	94–96
3e	$C_9H_7NO_4$	225	4	90	165–166
3f	$C_8H_6NO_2Cl$	200	5	92	113–114 (113–114)[7]
3g	$C_9H_9NO_4$	225	5	94	167–168 (167–168)[4]
3h	$C_8H_7NO_3$	225	4	89	133–134 (134.5–135)[3]
3i	$C_{10}H_{12}N_2O_2$	175	6	90	186–188 (187–188)[8]
3j	$C_9H_9NO_3$	225	5	91	85–87 (86–87)[2]
3k	$C_{15}H_{12}N_2O_5$	175	6	74	140–141 (141)[9]
3l	$C_{17}H_{14}N_2O_7$	175	6	71	144–146 (144–147)[10]

[a] Isolated yield.

Table 2. Elemental Analyses and Spectral Data of Compounds **3**

	Anal. (%)			
Compound	Calcd.	Found	^{1}H-NMR ($CDCl_3$, ppm)	IR (KBr cm^{-1})
3a	C 64.40 H 4.73 N 9.39	64.41 4.70 9.36	6.90–8.10 (m, 7H)	1660, 1630, 1530, 965, 770, 710
3b	C 58.18 H 4.27 N 8.48	58.10 4.25 8.45	6.81–8.18 (m, 6H), 10.0–11.5 (bs, 1H)	3500–3200, 1630, 1530, 1510, 1350, 970, 830
3c	C 44.06 H 2.31 N 6.42	44.01 2.30 6.29	6.80–8.18 (m, 5H)	1640, 1590, 1510, 1350, 870, 810
3d	C 49.49 H 3.12 N 14.43	49.46 3.08 14.40	7.40–8.10 (m, 6H)	1630, 1610, 1570, 1335, 980, 820
3e	C 55.96 H 3.65 N 7.25	55.88 3.61 7.10	6.90–8.00 (m, 5H), 6.12 (s, 2H)	1635, 1600, 1510, 1380, 880, 810
3f	C 52.33 H 3.29 N 7.63	52.10 3.27 7.68	7.10–7.80 (m, 6H)	1630, 1620, 1530, 1360, 965, 820

(*continued*)

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Table 2. Continued

	Anal. (%)			
Compound	Calcd.	Found	^{1}H-NMR ($CDCl_3$, ppm)	IR (KBr cm^{-1})
3g	C 55.39 H 4.65 N 7.18	55.34 4.60 7.20	6.60–8.20 (m, 5H), 3.74 (s, 3H), 9.80–11.5 (bs, 1H)	3500–3200, 1630, 1610, 1535, 1350, 880, 810
3h	C 58.18 H 4.27 N 4.48	55.00 4.23 4.50	6.88–8.20 (m, 6H), 10.3–11.0 (bs, 1H)	3500–3200, 1630, 1605, 1530, 1350, 980, 830
3i	C 62.49 H 6.30 N 14.58	62.22 6.40 14.20	6.72–7.96 (m, 6H), 3.09 (s, 6H)	1620, 1610, 1530, 1380, 980, 830
3j	C 60.34 H 5.06 N 7.82	60.10 4.88 7.86	6.80–8.18 (m, 6H), 3.68 (s, 3H)	1620, 1530, 1460, 1380, 990, 830
3k	C 60.00 H 4.00 N 9.33	59.87 3.90 9.20	7.10–8.20 (m, 10H), 5.22 (s, 2H)	1630, 1610, 1535, 1350, 880, 810
3l	C 56.98 H 3.91 N 7.82	56.90 3.87 7.80	7.15–8.20 (m, 9H), 5.20 (s, 2H), 2.25 (s, 3H)	1760, 1700, 1630, 1580, 1530, 1350, 980, 830

have been experimentally determined. The best reaction time and microwave power have been selected also under microwave irradiation without solvent (Table 1). All the products have been fully characterized on the basis of their microanalytical and spectral data (Table 2).

In conclusion, we developed a procedure for the efficient preparation of β-nitrostyrenes (**3**) from benzaldehydes and nitromethane with excellent yields (71–95%). The final products were easily isolated and purified directly by silica gel chromatography. The simplicity of the experimental procedure, direct conversion of benzaldehydes to β-nitrostyrenes (**3**) in the presence of the catalyst K_2CO_3/Al_2O_3, quick reaction times (4–6 min) and lower power (175–225 W) made this method more attractive than others known in literature.

EXPERIMENTAL

Melting points were uncorrected, elemental analytical data were obtained using a model 240 elementary instrument. IR spectra were measured using a model 408 infrared spectrometer, ^{1}H NMR spectra were recorded on a JNM-90Q spectrometer using TMS as internal standard ($CDCl_3$ solutions).

General Procedure for the Preparation of β-Nitrostyrenes (3a–l)

A mixture of 5 mmol benzaldehyde, 1.53 g (25 mmol) nitromethane and 0.35 g potassium carbonate was finely ground by agate mortar and pestle and was mixed with 5 g aluminum oxide (150 mesh). The mixture was then put in a 25 mL beaker and introduced into a Galan WP750A domestic microwave oven. Microwave irradiation was carried out for the appropriate time and at the power indicated (see Table 1). The mixture was cooled to ambient temperature, then water and nitromethane were removed by reduced pressure. The residue was purified by silica gel chromatography (petroleum ether [60–90°C]/ethyl acetate/dichloromethane, 1 : 1 : 0.3) to give the product (**3a–l**). The structures of all products were identified on the basis of elemental analytical data, IR, and ^{1}H NMR data (see Table 2).

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Received in Japan July 10, 2001