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Microwave Assisted Condensation of Aromatic Methyl Groups with Aromatic Aldehydes

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ABSTRACT

Aromatic aldehydes are condensed with 2,4-dinitro-1,5-dimethylbenzene in a Siegrist type coupling. The reported method features microwave irradiation, solvent-free conditions, and a catalytic amount of piperidine to give a high yield of the corresponding 1,3-bisstyryl-4,6dinitrobenzenes within a few minutes.

Key Words: Microwave irradiation; Solvent-free conditions; Distyryl benzenes.

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INTRODUCTION

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Conjugated aryl alkenes have over the last decade proven their usefulness as new materials for molecular electronics and non-linear optics.^[1-4] In connection with an ongoing project, a number of substituted bisstyryl dinitrobenzenes were needed. The *p*-methoxystyryl member of this series was a known compound. The classical synthesis proceeds under solvent-free conditions by heating a mixture of anisaldehyde **2a** and dinitroxylene **1** in the presence of a catalytic amount of piperidine.^[5] However, the long reaction times and the somewhat low yields made a more efficient synthesis desirable.

Microwave-assisted organic synthesis is a technique, which has been shown to be highly useful for thermal reactions.^[6–8] The homogenous nature of microwave heating allows a fast heating of a reaction mixture without local overheating at the walls of the reaction flask. This can be a problem especially in the case of a viscous reaction mixture. There is, however, still an ongoing debate in the literature concerning whether a specific, non-thermal "microwave effect" exists or not.^[9]

RESULTS AND DISCUSSION

The use of microwave heating on the neat reaction mixture of 1,5 dinitro*m*-xylene **1** and a number of aldehydes (**2a**-**h**) afforded the corresponding bisstyryl benzenes (**3a**-**h**) in good to acceptable yields (36–90%) (Sch. 1). Typically, the reaction were heated at 350 W for 3 min and then allowed to cool for 15 min, the heating was repeated 1–3 times. The crude reaction mixture was purified by dry column chromatography.^[10] This procedure gave (*E*,*E*)-1,3-*bis*(4-methoxystyryl)-4,6-dinitrobenzene, **3a** in 90% yield (the use of conventional heating as reported by Ruggli Zimmermann,^[5] afforded typically 40%). The condensation of aldehydes **2b**-**h** afforded the new bisstyryl benzenes **3b**-**h** in 32–82% yield (Table 1). The condensation of aldehyde **2h** yielded additional 27% of the mono adduct (*E*)-1-(dimethylaminostyryl)-3-methyl-4,6-dinitrobenzene **3i** (Sch. 2).



Scheme 1.



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Table 1. Chemical yields of dinitro bisstyryl benzenes upon reaction of 1,5 dinitro-mxylene with different aldehydes (2a-h).

Entry	Aldehyde	Dinitro bisstyryl benzene	Irradiation time (min) ^a	Yield (%)
a		O ₂ N NO ₂	3 × 3	90
b			2	82
c			2 × 3	54
d			3 × 3	75
e		O C2N NO2 O	3 × 3	54
f		O ₂ N HO ₂	3 × 3	82
g		O ₂ N NO ₂	3 × 3	73
h	N	NO2 N	3 × 3	32 ^b

^aThe reaction mixture was typically heated for 3×3 min and allowed to cool for

15 min between each heating. ^bThe condensation of aldehyde **2h** yielded additional 27% of the mono adduct (*E*)-1-(dimethylaminostyryl)-3-methyl-4,6-dinitrobenzene 3i (Sch. 2).

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CONCLUSION

A general method for the condensation of nitroxylenes with aromatic carbonyl compounds by microwave irradiation has been developed. The reaction times are considerably shorter than under the classical conditions and the yields are satisfactory.

EXPERIMENTAL

Melting points were recorded on a hot stage calibrated using a set of Reichert calibration substances. NMR spectra were recorded on a Bruker AM250 or a Varian Unity 400 spectrometer. Mass spectra were recorded on a 4 sector Jeol HX110/HX110. CHN analysis was recorded on a Carlo Elba FLASH 1112 apparatus. The microwave irradiation was carried out using a converted domestic microwave oven (OBH type 7510) operated at 350 W (2450 MHz). The reaction flask was linked to an outside refluxing column as described by Baghurst and Mingos.^[7]

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General Procedure

A 2 mmol (0.392 g) of 1,5-dinitro-*m*-xylene (1), 4 mmol of aldehyde **2a-h** (all commercially available except **2f**, which were prepared according to published procedure^[11]) and three drops of piperidine were typically heated for 3×3 min at 350 W (allowed to cool for 15 min between each heating). The resulting material was purified using dry column chromatography. The resulting product was recrystallised from toluene.

(*E,E*)-1,3-*bis*(4-Methoxystyryl)-4,6-dinitrobenzene (3a). Yield: 90%. Solid, m.p. 179.6–180.6°C (litt.^[5] 179°C); ¹H NMR (CDCl₃, 250 MHz) δ : 3.8 (s, 6H), 6.9 (d, *J* = 8.3 Hz, 4H), 7.2 (d, *J* = 16.6 Hz, 2H), 7.5 (d, *J* = 8.3 Hz, 4H), 7.55 (d, *J* = 16.6 Hz, 2H), 8.0 (s, 1H), 8.64 (s, 1H); ¹³C NMR (CDCl₃, 62.9 MHz) δ : 55.3, 114.4, 119.7, 122.8, 127.0, 128.5, 129.0, 136.7, 137.9, 144.6, 160.8.

EIMS: (*m*/*z*, relative intensity): 432 (M⁺, 98), 279 (40), 160 (50), 135 (64), 121 (100). UV-VIS (acetonitrile): $\varepsilon_{387} = 3.1 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$.





Microwave Assisted Condensation of Aromatic Methyl Groups

(*E,E*)-1,3-*bis*(2,4-Dimethoxystyryl)-4,6-dinitrobenzene (3b). Yield: 82%. Solid, m.p. 207.1–208.7°C; ¹H NMR (CDCl₃, 250 MHz) δ : 3.79 (s, 6H), 3.84 (s, 6H), 6.43 (d, J = 2.4 Hz, 2H), 6.5 (dd, $J_1 = 2.4$ Hz, $J_2 = 9.0$ Hz, 2H), 7.48 (d, J = 16.2 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 16.2 Hz, 2H), 8.02 (s, 1H), 8.61 (s, 1H). ¹³C NMR (CDCl₃, 62.9 MHz) δ : 55.4, 55.5, 98.4, 105.3, 118.1, 120.1, 122.7, 127.1, 128.9, 132.0, 138.5, 144.3, 158.9, 162.0. EIMS m/z (relative intensity): 492 (M⁺, 100), 309 (20), 165 (30). HRMS (M⁺) calcd. 492.1533. Found 492.1544. Anal. calcd. for C₂₆H₂₄N₂O₈: C 63.41; H 4.91; N 5.69. Found C 63.32; H 4.83; N 5.73. UV-VIS (acetonitrile): $\varepsilon_{403} = 2.7 \times 10^4$ mol⁻¹ cm⁻¹.

(*E,E*)-1,3-*bis*(3,5-Dimethoxystyryl)-4,6-dinitrobenzene (3c). Yield: 54%. Solid, m.p. 197.0–199.3°C; ¹H NMR (CDCl₃, 250 MHz) δ : 3.78 (s, 12H), 6.43 (t, *J* = 2.3 Hz, 2H), 6.67 (d, *J* = 2.3 Hz, 4H), 7.17 (d, *J* = 16.0 Hz, 2H), 7.60 (d, *J* = 16.1 Hz, 2H), 7.98 (s, 1H), 8.66 (s, 1H). ¹³C NMR (CDCl₃, 62.9 MHz) δ : 55.4, 101.7, 105.4, 122.5, 122.6, 128.0, 137.2, 137.5, 145.1, 161.1. FAB⁺MS (*m*/*z*, relative intensity): 493 (MH⁺, 4), 460 (3), 307 (20), 154 (100). HRMS (MH⁺) calcd. 493.1611, found 493.1613. UV-VIS (acetonitrile): $\varepsilon_{341} = 2.7 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$.

(*E,E*)-1,3-*bis*(3,4,5-Trimethoxystyryl)-4,6-dinitrobenzene (3d). Yield: 75%. Solid, m.p. 122–123°C. ¹H NMR (CDCl₃, 250 MHz) δ : 3.68 (s, 6H), 3.70 (s, 12H), 6.72 (s, 4H), 8.54 (d, *J* = 8 Hz, 2H), 8.56 (s, 1H), 8.67 (d, *J* = 8 Hz, 2H,), 9.80 (s, 1H). ¹³C NMR (CDCl₃, 62.9 MHz) δ : 39.4, 56.1, 56.3, 104.7, 105.0, 105.3, 120.5, 122.3, 131.0, 132.6, 137.2, 138.1, 139.4, 153.4.

Anal. calcd. for $C_{28}H_{28}N_2O_{10}$: C 60.87; H 5.11; N 5.07, found C 60.91; H 5.16; N 4.99. UV-VIS (acetonitrile): $\varepsilon_{381} = 1.4 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$.

(*E,E*)-1,3-*bis*(2,4,6-Trimethoxystyryl)-4,6-dinitrobenzene (3e). Yield: 56%. Solid, m.p. 189–190°C. ¹H NMR (CDCl₃, 250 MHz) & 3.82 (s, 6H), 3.84 (s, 12H), 6.08 (s, 4H), 7.66 (d, J = 16 Hz, 2H), 7.92 (s, 1H), 7.97 (d, J = 16 Hz, 2H), 8.57 (s, 1H). ¹³C NMR (CDCl₃, 62.9 MHz) & 21.1, 55.3, 55.7, 90.5, 107.0, 121.4, 122.2, 128.7, 131.2, 138.4, 139.8, 145.4, 160.4, 162.1. Anal. calcd. for C₂₈H₂₈N₂O₁₀: C 60.87; H 5.11; N 5.07. Found: C 60.93; H 5.05; N 5.06. UV-VIS (acetonitrile): $\varepsilon_{417} = 2.8 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$.

(*E,E*)-1,3-*bis*(2,5-Dimethoxy-4-methyl-styryl)-4,6-dinitrobenzene (3f). Yield: 82%. Solid, m.p. 161–163°C. ¹H NMR (CDCl₃, 250 MHz) δ : 2.10 (s, 6H), 3.80 (s, 12H), 6.65 (s, 2H), 7.0 (s, 2H), 7.50 (d, *J* = 16 Hz, 2H), 7.60 (d, *J* = 16 Hz, 2H), 8.00 (s, 1H), 8.60(s, 1H). ¹³C NMR (CDCl₃, 62.9 MHz) δ : 16.6, 55.8, 56.1, 108.6, 114.4, 121.2, 121.6, 122.4, 122.6, 127.6, 128.9, 130.1, 132.2, 138.3, 144.5, 151.7, 152.0. HRMS (M⁺) calcd. 520.1846, found 520.1842. UV-VIS (acetonitrile): $\varepsilon_{413} = 1.7 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$.

(E,E)-1,3-bis(2,3,4,5,6-Pentamethylstyryl)-4,6-dinitrobenzene (3g). Yield: 73% Solid. m.p. 152–153°C. ¹H NMR (CDCl₃, 250 MHz) δ : 2.10

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(m, 30H), 6.9 (d, 2H J = 8 Hz), 7.3 (s, J = 8 Hz, 2H), 8.1 (s, 1H) 8.7 (s, 1H). ¹³C NMR (CDCl₃, 62.9 MHz) & 15.1, 15.6, 15.9, 16.6, 17.0, 121.3, 127.3, 127.7, 130.5, 131.9, 132.6, 134.1, 137.3, 144.1. HRMS (M⁺) calcd. 512.2675, found 512.2675. UV-VIS (acetonitrile): $\varepsilon_{338} = 1.5 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$.

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(*E,E*)-1,3-*bis*(-Dimethylaminostyryl)-4,6-dinitrobenzene (3h). Yield 32%. Solid, m.p. 170–173°C. ¹H NMR (CDCl₃, 400 MHz) δ : 2.98 (s, 12H), 6.64 (d, *J* = 9.2 Hz, 4H), 7.17 (d, *J* = 15.3 Hz 2H), 7.42 (d, *J* = 9.2 Hz, 4H), 7.46 (d, *J* = 15.3 Hz, 2H), 7.97 (s, 1H), 8.59 (s, 1H). ¹³C NMR (CDCl₃, 62.9 MHz) δ : 40.1, 111.9, 116.9, 123.1, 123.9, 125.7, 129.0, 137.4, 138.2, 143.5, 151.2. FAB⁺MS (*m*/*z*, relative intensity): 458 (M⁺, 10), 307 (30). Anal. calcd. for C₂₆H₂₆N₄O₄: C 68.11; H 5.72; N 12.22, found C 68.15; H 5.62 N 12.13. UV-VIS (acetonitrile): $\varepsilon_{467} = 3.6 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$.

(*E*)-1-(Dimethylaminostyryl)-3-methyl-4,6-dinitrobenzene (3i). Yield 27% (byproduct). Solid, m.p. 185.0–185.6°C. ¹H NMR (CDCl₃, 400 MHz) δ : 2.74 (s, 3H), 3.05 (s, 6H), 7.21 (d, J = 16.1 Hz, 1H), 7.47 (d, J = 7.88 Hz, 2H), 7.48, (d, J = 16.1 Hz, 1H), 7.72 (s, 1H), 8.69 (s, 1H). ¹³C NMR (CDCl₃, 62.9 MHz) δ : 21.2, 40.1, 111.9, 115.7, 122.5, 123.6, 129.1, 131.0, 138.1, 138.6, 144.5, 145.4, 151.3 (13 of 14 expected signals after 19,100 scans). FAB⁺MS (m/z, relative intensity): 327 (M⁺, 25). Anal. calcd. for C₁₇H₁₇N₃O₄: C 62.38; H 5.23; N 12.84, found C 62.25; H 5.12, N 12.70. UV-VIS (acetonitrile): $\varepsilon_{459} = 2.2 \times 10^4$ mol⁻¹ cm⁻¹.

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