

Solvent-free Rapid Synthesis of Styryl Dyes with Benzimidazole Nucleus Using Microwave Irradiation

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Abstract: The reactions of 2-methylbenzimidazole or 2-methylbenzimidazolium iodide with aromatic aldehydes are accelerated under microwave irradiation by using Ac_2O or piperidine as dehydrant or catalyst in the absence of any solvent. The approach provides an attractive and environmentally friendly pathway to several useful styryl dyes with benzimidazole nucleus.

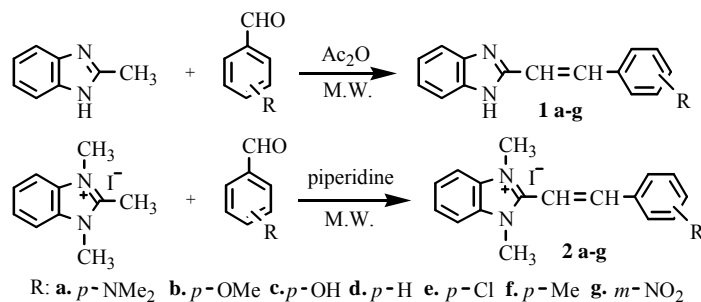
Keywords: Microwave irradiation, styryl dyes, benzimidazole nucleus, aromatic aldehydes.

Styryl cyanine dyes and styryl dyes are widely used as sensitizers and other additives in the photographic industry¹ as optical recording medium in laser disks², laser dyes³, and optical sensitizers in various other fields⁴. Our previous efforts have been devoted to develop the synthesis and applications of cyanine, styryl cyanine and styryl dyes⁵. Microwave irradiation technique has been used for the rapid synthesis of a variety of compounds⁶, and microwave-accelerated solvent-free organic reactions have received special attention in recent years⁷. Many reactions can proceed fast with the assistance of microwave irradiation in high yield. In this paper a microwave-assisted preparation of a series of styryl dyes with benzimidazole nucleus *via* condensation of 2-methylbenzimidazole or 2-methylbenzimidazole methiodide salt and a variety of aromatic aldehydes without solvent is described in high yield (**Scheme 1**). The approach provides an attractive and environmentally friendly pathway to several synthetically useful styryl dyes with benzimidazole nucleus.

Classical synthesis of styryl cyanine and styryl dyes with benzimidazole nucleus is often carried out by refluxing the mixture of aromatic aldehyde, a quaternary salt or base of benzimidazole with reactive methyl group and catalyst in organic medium⁸. However, with the assistance of microwave irradiation, the condensation reactions of 2-methylbenzimidazole or 2-methylbenzimidazole methiodide salt with a variety of aromatic aldehydes using Ac_2O or piperidine as dehydrant or catalyst could proceed rapidly without solvent. The products could be purified by recrystallization from the diluted ethyl alcohol. The yields of products were high. Besides, the waste disposal of solvents and excess chemicals in classical synthesis of styryl cyanine dyes and styryl dyes were avoided or minimized.

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Scheme 1



General Procedure

The condensation of 2-methylbenzimidazole or 2-methylbenzimidazolium iodide with various aromatic aldehydes is carried out in a household Galanz microwave oven. 1 mmol 2-methylbenzimidazole or 2-methylbenzimidazolium iodide, 1.2-1.5 mmol aromatic aldehydes, and a few drops of Ac₂O or piperidine were mixed together at ambient temperature in a glass beaker (25 mL). The mixture was subjected to microwave irradiation for an optimized time and power. After the reaction mixture was cooled to room temperature, 10 mL of 2% potassium hydroxide solution or water was added and the crude product was recrystallized from EtOH-H₂O. The results are shown in **Table 1**.

Table 1 The reaction conditions for the synthesis of compounds **1**_{a-g}, **2**_{a-g}

Compounds	Time (min)	Power (W)	Yield (%)	Compounds	Time (min)	Power (W)	Yield (%)
1a	8	522	93	2a	1	252	87
1b	2	324	89	2b	2	324	93
1c	3	324	87	2c	2	252	91
1d	2	324	97	2d	2	252	86
1e	2	162	91	2e	1	324	83
1f	3	324	92	2f	1	252	89
1g	1	324	95	2g	2	252	82

In order to get optimized experiment conditions, we have examined the effect of microwave power and irradiation time on yield. The results are listed in **Table 1**. From **Table 1**, we can see the condensation of 2-methylbenzimidazole and aromatic aldehydes bearing electron withdrawing group is easier than that bearing electron donating group, and the reactions of 2-methylbenzimidazole methiodide salt and aromatic aldehydes with various substituted groups are all easy. 2-Methylbenzimidazole can react well with aromatic aldehydes with electron withdrawing group because the nucleophilicity of its 2-methyl carbon is not strong. 2-Methylbenzimidazole methiodide salt can react well with aromatic aldehydes with different substituted group because the nucleophilicity of its 2-methyl carbon is strong. In the experiment, we also found that the condensation reactions of 2-methylbenzimidazole proceeded at the melting state, but the condensation reactions of 2-methylbenzimidazole methiodide salt could

proceed well at solid state.

Fourteen styryl dyes were synthesized with the above method. Among them **1a**, **1c** to **1f** and **2a** to **2e** were synthesized previously by classical styryl dyes method^{8, 9}. With the best of our knowledge, the compounds **1b**, **1g**, **2f**, **2g** were unknown and their structures were confirmed by IR, ¹HNMR, Ms, UV and elemental analysis¹⁰. Further investigation of the synthesis of cyanine, styryl cyanine and styryl dyes with other heterocyclic nucleus is in progressing.

Acknowledgments

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10. Data for **1b**: mp 206-207°C; IR (KBr, cm⁻¹) 2500~3100, 3061.4, 2992.0, 1640.4, 1601.0, 1514.1, 1419.6, 1248.0, 1027.6, 964.0, 814.7, 744.4; ¹H NMR (CDCl₃, δ ppm) 3.81 (s, 3H, OCH₃), 6.84 (d, 2H, J=8.0Hz, ArH), 7.42 (d, 2H, J=8.0Hz, ArH), 6.98 (d, 1H, J=16.0Hz, CH=CH), 7.67 (d, 1H, J=16.0Hz, CH=CH), 7.61-7.59 (m, 2H, ArH), 7.26-7.24 (m, 2H, ArH); MS *m/z* (%): 250 (M⁺, 32), 249 (100), 235 (76), 236 (21), 219 (4), 206 (32), 103 (6), 77 (4), 63 (4), 51 (2), 39 (2); UV-VIS (MeOH) λ_{max}: 343 nm; Anal. Calcd. for C₁₆H₁₄N₂O: C, 76.78%; H, 5.59%; N, 11.19%; Found: C, 76.69%; H, 5.57%; N, 11.06%. For **1g**: mp 226-228°C; IR (KBr, cm⁻¹) 2500~3100, 3072.8, 1646.2, 1582.7, 1525.7, 1425.1, 1351.3, 963.9, 857.2, 800.4, 739.5; ¹H NMR (CDCl₃, δ ppm) 8.39 (s, 1H, ArH), 8.18 (d, 1H, J=8.0Hz, ArH), 7.83 (d, 1H, J=8.0Hz, ArH), 7.72-7.23 (m, 7H, CH=CH and ArH); MS *m/z* (%): 265 (M⁺, 46), 264 (100), 266 (6), 218 (67), 217 (28), 128 (2), 109 (6), 77 (4), 63 (6), 51 (4), 39 (3); UV-VIS (MeOH) λ_{max}: 332 nm; Anal. Calcd. for C₁₅H₁₁N₃O₂: C, 67.92%; H, 4.15%; N, 15.20%; Found: C, 67.89%; H, 4.15%; N, 15.07%. For **2f**: mp >300°C; IR (KBr, cm⁻¹) 3021.0, 1628.6, 1601.1, 1566.0, 1515.2, 1475.9, 1348.0, 992.4, 805.3, 753.2; ¹H NMR (CDCl₃, δ ppm) 2.42 (s, 3H, CH₃), 4.13 (s, 6H, NCH₃), 7.00-7.77 (m, 10H, CH=CH and ArH); UV-VIS (MeOH) λ_{max}: 319 nm; Anal. Calcd. for C₁₈H₁₉N₂I: C, 55.41%; H, 4.80%; N, 7.12%; Found: C, 55.64%; H, 4.78%; N, 7.09%. For **2g**: mp 295-297°C; IR (KBr, cm⁻¹) 3008.0, 1638.4, 1610.9, 1571.7, 1529.7, 1476.0, 1347.9, 981.6, 805.5, 761.3; ¹H NMR (DMSO-d₆, δ ppm) 4.19 (s, 6H, NCH₃), 7.74-7.72 (m, 2H, ArH), 8.09-8.07 (m, 2H, ArH), 7.84 (d, 1H, J=16.0Hz, CH=CH), 7.99 (d, 1H, J=16.0Hz, CH=CH), 7.88-7.82 (m, 1H, ArH), 8.43 (d, 1H, J=8.0Hz, ArH), 8.38-8.36 (m, 1H, ArH), 8.85 (s, 1H, ArH). UV-VIS (MeOH) λ_{max}: 316 nm; Anal. Calcd. for C₁₇H₁₆N₃O₂I: C, 48.45%; H, 3.80%; N, 10.00%; Found: C, 48.28%; H, 3.79%; N, 10.30%.

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