Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Dyes and Pigments 62 (2004) 21–25
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Microwave-assisted solvent-free synthesis of some hemicyanine dyes

Lan-Ying Wang*, Xiao-Gang Zhang, Ya-Peng Shi, Zu-Xun Zhang

Department of Chemistry, Northwest University, Xi'an 710069, China

Received 12 July 2003; received in revised form 22 August 2003; accepted 24 October 2003

Abstract

A series of hemicyanine dyes: 1,3-dimethyl-2-substituted styryl benzimidazolium salts and 1-methyl-4-substituted styryl pyridinium salts were synthesized in a fast, efficient and high yield by the condensation of 1,2,3-trimethyl benzimidazole salts or 1,4-dimethyl pyridine salts with aromatic aldehydes in the present of piperidine under solvent-free microwave irradiation. The products were identified by ^{1}H NMR, MS, IR, UV–vis and elemental analysis. The approach provides an attractive and environmentally friendly pathway to several useful hemicyanine dyes.

Keywords: Hemicyanine dye; Microwave irradiation; Synthesis; Aromatic aldehydes

1. Introduction

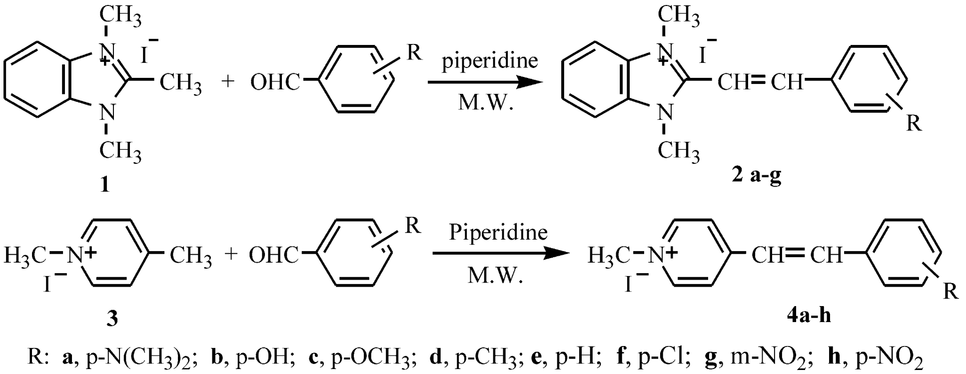
Hemicyanine dyes are widely used as sensitizers and other additives in the photographic industry [1–3] as optical recording medium in laser disks [4], laser dyes [5], and as optical sensitizers in various other fields [6]. Our previous efforts have been devoted to develop the synthesis and applications of cyanine, hemicyanine dyes [7–10]. Classical synthesis of hemicyanine dyes with benzimidazole nucleus or with 4-linked pyridine nucleus is often carried out by refluxing the mixture of aromatic aldehyde, a quaternary salt of benzimidazole or pyridine having reactive methyl group and catalyst in organic medium [2,11,12]. This preparation has substantial drawbacks, such as relatively strenuous reaction conditions namely refluxing reactants for several hours in organic solvents, a lot of organic solvents to be not friendly to environment and complexity of isolation of the products. Microwave irradiation technique has been used for the rapid synthesis of a variety of compounds, and microwave-accelerated solvent-free organic reactions have received special attention in recent years [13,14]. 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 hemicyanine dyes *via* condensation of quaternary salts of a heterocyclic 2- or 4-methyl compound and a variety of aromatic aldehydes without solvent is described in high yield (Scheme 1). The approach provides an attractive and environmentally

---

* Corresponding author. Tel.: +86-29-8303403; fax: +86-29-8303798.

E-mail address: wanglany@nwu.edu.cn (L.-Y. Wang).

0143-7208/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2003.10.019



Scheme 1.

friendly pathway to several synthetically useful hemicyanine dyes.

2. Experimental

Melting points were taken on a XT-4 micro-melting apparatus and uncorrected. Elemental analyses were performed with Vario EL-III instrument. IR spectra in cm^{-1} were recorded on a Brucker Equiox-55 spectrometer. MS were taken on a HP5989B instrument. ^1H NMR spectra were recorded at 400 M Hz on a Varian Inova-400 spectrometer and chemical shifts were reported relative to internal Me_4Si. The UV absorption spectra were recorded on a General TU-1201 UV-vis spectrometer.

2.1. Preparation of the quaternary salt having reactive methyl group

1,2,3-Trimethyl benzimidazolium iodide **1** and 1-methyl-4-picolinium iodide **3** were prepared according to the literatures [15,16].

2.2. General procedure for the synthesis of dyes

The condensation of quaternary salts of benzimidazole or pyridine having reactive methyl group with various aromatic aldehydes is carried out in a Galanz microwave oven. 10 mmol 1,2,3-trimethyl benzimidazole salts or 1,4-dimethyl pyridine salts, 12 mmol aromatic aldehydes and a few drops of piperidine were mixed together at ambient temperature in a glass conical flask (100 ml). The mixture was subjected to microwave irradiation for an optimized time and power. After cooling, the reaction mixture was recrystallized from EtOH-H_2O for elemental analysis. The details of reaction conditions and yields are provided in Table 1.

3. Results and discussion

In all cases investigated, we found that the hemicyanine dyes with benzimidazole nucleus or with 4-linked pyridine nucleus formation reactions proceeded efficiently with high to excellent in short reaction time (Table 1) and reactions proceeded well even when both the starting reactants were solids and the reaction temperature was maintained below the melting points of both components. Hemicyanine dyes with benzimidazole nucleus **2a**–**g** were isolated in 82–93% yield within 1–2 min when a mixture of 10 mmol 1,2,3-trimethyl benzimidazolium iodide, 12 mmol aromatic aldehydes and a few drops of piperidine was subjected to microwave irradiation at 252–324 W under solvent-free conditions. Similarly, hemicyanine dyes with 4-linked pyridine nucleus **4a**–**h** were also synthesized in good yield (73–99%) under the present reaction conditions. In the experiment, the products could be easily purified by recrystallization from the diluted ethyl alcohol. Besides, the waste disposal of solvents and excess chemicals in classical synthesis of hemicyanine dyes was avoided or minimized.

The structure and purity of the prepared hemicyanine dyes **2a**–**g**, **4a**–**h** were confirmed by elemental analysis, UV–vis absorption spectra, IR, ^{1}H NMR, MS data and thin layer chromatography. The structural analysis of the dyes is presented in Tables 2 and 3. When changing substituents R, UV–vis absorption spectra showed bathochromic shift for the same series of hemicyanine dyes. The order of bathochromic shift was as follows:

$$N(CH_3)_2 > OH > OCH_3 > CH_3 > H \sim Cl > NO_2$$

The IR spectra showed typical aromatic absorption ($\upsilon_{=C\text{-}H}$, 3100–2997cm^{-1}, $\upsilon_{C=C}$, 1650–1400 (s) cm^{-1}, $\delta_{=CH}$, 700–1000 cm^{-1}) and resonance conjugated unsaturated stretching modes in the chromophore (C=C, C=N, 1380–1480 cm^{-1}). The ^{1}H NMR chemical shift data and the MS *m*/*z* values was in accordance with the dye structures.

4. Conclusions

We have described a rapid and highly efficient method for the synthesis of hemicyanine dyes with

Table 1
The reaction conditions and yields for the synthesis of dyes

Dye	Time (min)	Power (W)	Yield (%)	Dye	Time (min)	Power (W)	Yield (%)
2a	1	252	87	**4a**	1.5	163	99
2b	2	252	91	**4b**	2.0	163	85
2c	2	324	93	**4c**	2.5	163	98
2d	1	252	89	**4d**	2.5	163	80
2e	2	252	86	**4e**	3.0	163	87
2f	1	324	83	**4f**	3.5	163	75
2g	2	252	82	**4g**	4.0	163	95
				4h	5.0	163	73

Table 2
Melting points, elemental analysis and UV-vis data of dyes

Dye	Mp (°C)	Empirical formula	E. A. (%)			λ_{nax} (nm) (MeOH)
			C (calc.)	H (calc.)	N (calc.)	
2a	>300	$C_{19}H_{22}N_3I$	54.30 (54.42)	5.18 (5.25)	9.98 (10.02)	412
2b	>300	$C_{17}H_{17}N_2OI$	52.18 (52.07)	4.40 (4.34)	7.11 (7.14)	352
2c	291–292	$C_{18}H_{19}N_2OI$	53.05 (53.21)	4.75 (4.71)	6.93 (6.90)	348
2d	>300	$C_{18}H_{19}N_2I$	55.64 (55.41)	4.78 (4.80)	7.09 (7.12)	331
2e	293–294	$C_{17}H_{17}N_2I$	54.43 (54.29)	4.73 (4.52)	7.34 (7.45)	322
2f	290–291	$C_{17}H_{16}N_2ICl$	49.68 (49.72)	3.97 (3.93)	6.88 (6.82)	324
2g	295–297	$C_{17}H_{16}N_3O_2I$	48.28 (48.45)	3.79 (3.80)	10.30 (10.00)	316
4a	262–263	$C_{16}H_{19}N_2I$	52.77 (52.47)	5.09 (5.23)	7.58 (7.65)	476
4b	265–266	$C_{14}H_{14}NOI$	49.47 (49.57)	4.14 (4.16)	4.11 (4.13)	392
4c	218–219	$C_{15}H_{16}NOI$	50.94 (51.01)	4.49 (4.56)	3.95 (3.96)	387
4d	233–234	$C_{15}H_{16}NI$	53.31 (53.43)	4.63 (4.78)	4.08 (4.16)	359
4e	219–220	$C_{14}H_{14}NI$	52.00 (52.02)	4.17 (4.36)	4.23 (4.33)	347
4f	260–261	$C_{14}H_{13}NICl$	46.96 (47.02)	3.56 (3.66)	3.90 (3.92)	349
4g	>290	$C_{14}H_{13}N_2O_2I$	45.87 (45.67)	3.66 (3.56)	7.63 (7.61)	329
4h	229–230	$C_{14}H_{13}N_2O_2I$	45.80 (45.67)	3.62 (3.56)	7.62 (7.61)	342

Table 3
^{1}H NMR, IR and MS data of dyes

Dye	^{1}HNMR δ	IR (υ/cm^{-1})	MS
2a	($CDCl_3$): 3.06 (s, 6H, $N(CH_3)_2$), 3.92 (s, 6H, NCH_3), 6.65 (m, 2H, CH=CH), 7.0–7.73 (m, 8H, Ar–H)	3016, 2923, 1592, 1536, 1506, 1477, 1377, 1288, 999, 850, 755	276 (M–HI–CH_3, 100), 277 (55), 261(10), 232 (4), 142 (11), 127 (6), 77 (3)
2b	(DMSO-d_6): 4.12 (s, 6H, NCH_3), 6.92 (d, $J = 8.4$ Hz, 2H, Ar–H), 7.31 (d, $J = 17.6$ Hz, 1H, CH=CH), 7.67–7.68 (m, 2H, Ar–H), 7.74 (d, $J = 16.4$ Hz, 1H, CH=CH), 7.81 (d, $J = 9.2$ Hz, 2H, Ar–H), 8.01–8.04 (m, 2H, Ar–H), 10.24 (s, 1H, OH)	3021, 1597, 1522, 1473, 1264, 1164, 980, 820, 761	249 (M–HI–CH_3, 100), 250 (30), 234 (13), 142 (21), 127 (11), 77 (8)
2c	(DMSO-d_6): 3.86 (s, 3H, OCH_3), 4.13 (s, 6H, NCH_3), 7.12 (d, $J = 8.4$ Hz, 2H, Ar–H), 7.42 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.67–7.69 (m, 2H, Ar–H), 7.80 (d, $J = 17.2$ Hz, 1H, CH=CH), 7.92 (d, $J = 8.4$ Hz, 2H, Ar–H), 8.03–8.05 (m, 2H, Ar–H)	3022, 1633, 1518, 1474, 1250, 1022, 963, 818, 756	263 (M–HI–CH_3, 100), 220 (16), 142 (26), 127 (13), 77 (15), 15 (9)
2d	($CDCl_3$): 2.42 (s, 3H, CH_3), 4.13 (s, 6H, NCH_3), 7.00-7.77 (m, 10H, Ar–H, CH=CH)	3021, 1629, 1601, 1566, 1515, 1476, 1348, 992, 805, 753	247 (M–HI–CH_3, 100), 248 (36), 232 (16), 218 (4), 142 (7), 127 (7), 77 (6)
2e	(D_2O): 3.95 (s, 6H, NCH_3), 7.17 (d, $J = 16.8$ Hz, 1H, CH=CH), 7.40–7.42 (m, 3H, Ar–H), 7.51 (d, $J = 18.0$ Hz, 1H, CH=CH), 7.54–7.56 (m, 2H, Ar–H), 7.66–7.71 (m, 4H, Ar–H)	3024, 1624, 1514, 1476, 972, 763, 691	233 (M–HI–CH_3, 100), 234 (55), 218 (29), 142 (23), 127 (11), 116 (11), 77 (10)
2f	(DMSO-d_6): 4.16 (s, 6H, NCH_3), 7.62 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.65 (d, $J = 8.8$ Hz, 2H, Ar–H), 7.70–7.72 (m, 2H, Ar–H), 7.84 (d, $J = 16.8$ Hz, 1H, CH=CH), 7.99 (d, $J = 8.0$ Hz, 2H, Ar–H), 8.06–8.08 (m, 2H, Ar–H)	3019, 1628, 1515, 1475, 1083, 958, 799, 749	267 (M–HI–CH_3, 100), 269 (33), 268 (35), 270 (12), 252 (12), 254 (4), 217 (6), 142 (20), 127 (11), 116 (11), 77 (8)
2g	(DMSO-d_6): 4.19 (s, 6H, NCH_3), 7.72–7.74 (m, 2H, Ar–H), 8.07–8.09 (m, 2H, Ar–H), 7.84 (d, 1H, $J = 16.0$ Hz, CH=CH), 7.99 (d, 1H, $J = 16.0$ Hz, CH=CH), 7.88–7.82 (m, 1H, Ar–H), 8.43 (d, 1H, $J = 8.0$ Hz, Ar–H), 8.36–8.38 (m, 1H, Ar–H), 8.85 (s, 1H, Ar–H)	3008, 1638, 1611, 1572, 1530, 1476, 1348, 982, 806, 761	278 (M–HI–CH_3, 100), 279 (52), 232 (57), 216 (10), 142 (19), 127 (6), 77 (4)
4a	(DMSO-d_6): 3.02 (s, 6H, $N(CH_3)_2$), 4.17 (s, 3H,–N^+–CH_3), 6.79 (d, $J = 8.8$ Hz, 2H, PhH), 7.18 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.60 (d, $J = 8.4$ Hz, 2H, PhH), 7.91 (d, $J = 16.4$ Hz, 1H, CH=CH), 8.05 (d,$J = 6.0$ Hz, 2H, pyridinio-H), 8.69 (d, $J = 6.4$ Hz, 2H, pyridinio-H)	2997, 2914, 1642, 1576, 1529, 1463, 1430, 1259, 1150, 976, 869, 821, 529	224 (M–I–CH_3, 100), 223 (68), 209 (28), 180 (12), 142 (14), 127 (6)
4b	(DMSO-d_6): 4.08 (s, 3H,–N^+–CH_3), 6.51 (d, $J = 8.8$ Hz, 2H, PhH), 6.90 (d, $J = 15.6$ Hz, 1H, CH=CH), 7.45 (d, $J = 8.4$ Hz, 2H, PhH), 7.81 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.85 (d, $J = 6.8$ Hz, 2H, pyridinio-H), 8.49 (d, $J = 6.8$ Hz, 2H, pyridinio-H), 9.42 (s, 1H,-OH)	3424, 3010, 1644, 1569, 1511, 1470, 972, 843, 534	197 (M–I–CH_3, 100), 212 (74), 196 (59), 180 (10), 168 (30), 93 (46), 77 (10), 39 (10)
4c	(DMSO-d_6): 3.83 (s, 3H, OCH_3), 4.24 (s, 3H,–N^+–CH_3), 7.07 (d, $J = 8.0$ Hz, 2H, PhH), 7.37 (d, $J = 16.0$ Hz, 1H, CH=CH), 7.73 (d, $J = 8.0$ Hz, 2H, PhH), 7.98 (d, $J = 16.4$ Hz, 1H, CH=CH), 8.16 (d, $J = 6.0$ Hz, 2H, pyridinio-H), 8.81 (d, $J = 6.0$ Hz, 2H, pyridinio-H)	3023, 2929, 1644, 1595, 1515, 1465, 1421, 1259, 1025, 975, 879, 832, 534	211 (M–I–CH_3, 100), 210 (25), 196 (10), 180 (11), 142 (16)
4d	(DMSO-d_6): 2.37 (s, 3H, CH_3), 4.25 (s, 3H,–N^+–CH_3), 7.32 (d, $J = 7.2$ Hz, 2H, PhH), 7.47 (d, $J = 16.4$ Hz, 1H, CH=CH), 7.66 (d, $J = 7.2$ Hz, 2H, PhH), 7.99 (d, $J = 16.8$ Hz, 1H, CH=CH), 8.21 (d, $J = 6.4$ Hz, 2H, pyridinio-H), 8.85 (d, $J = 6.4$ Hz, 2H, pyridinio-H)	2998, 2930, 1619, 1596, 1562, 1515, 1470, 1335, 972, 880, 829, 532	195 (M–I–CH_3, 100), 194 (65), 180 (90), 154 (8), 142 (26), 127 (17)

Table 3 (*continued*)

Dye	^{1}HNMR δ	IR (υ/cm^{-1})	MS
4e	(DMSO-d_6): 4.26 (s, 3H,–N$^+$–CH$_3$), 7.47–7.52 (m, 3H, PhH), 7.54 (d, J = 16.4 Hz, 1H, CH=CH), 7.76 (d, J = 6.8 Hz, 2H, PhH), 8.02 (d, J = 16.4 Hz, 1H, CH=CH), 8.24 (d, J = 6.4 Hz, 2H, pyridinio-H), 8.87 (d, J = 6.8 Hz, 2H, pyridinio-H)	3015, 1619, 1568, 1513, 1471, 970, 877, 817, 761, 687, 528	180 (M–HI–CH$_3$, 100), 181 (82), 154 (8), 142 (20), 127 (8)
4f	(DMSO-d_6): 4.27 (s, 3H,–N$^+$–CH$_3$), 7.57 (d, J = 16.4 Hz, 1H, CH=CH), 7.58 (d, J = 8.0 Hz, 2H, PhH), 7.79 (d, J = 8.4 Hz, 2H, PhH), 8.02 (d, J = 16.4 Hz, 1H, CH=CH), 8.23 (d, J = 6.4 Hz, 2H, pyridinio-H), 8.90 (d, J = 6.4 Hz, 2H, pyridinio-H)	3008, 1619, 1514, 1470, 1079, 968, 831, 527	215 (M–I–CH$_3$, 100), 217 (32), 214 (46), 180 (82), 179 (12), 142 (28), 127 (10)
4g	(DMSO-d_6): 4.29 (s, 3H,–N$^+$–CH$_3$), 7.78 (d, J = 16.4 Hz, 1H, CH=CH), 7.82 (d, J = 8.0 Hz, 2H, PhH), 8.16 (d, J = 16.4 Hz, 1H, CH=CH), 8.19 (d, J = 8.0 Hz, 2H, PhH), 8.27 (d, J = 6.4 Hz, 2H, pyridinio-H), 8.60 (s, 1H, PhH), 8.94 (d, J = 6.4 Hz, 2H, pyridinio-H)	3005, 1621, 1564, 1521, 1473, 1346, 976, 877, 816, 737, 645, 537	226 (M–I–CH$_3$, 100), 225 (10), 180 (20), 179 (25), 142 (20), 127 (8)
4h	(DMSO-d_6): 4.29 (s, 3H,–N$^+$–CH$_3$), 7.76 (d, J = 16.4 Hz, 1H, CH=CH), 8.00 (d, J = 8.8 Hz, 2H, PhH), 8.12 (d, J = 16.8 Hz, 1H, CH=CH), 8.29 (d, J = 6.4 Hz, 2H, pyridinio-H), 8.36 (d, J = 8.8 Hz, 2H, PhH), 8.95 (d, J = 6.8 Hz, 2H, pyridinio-H)	3033, 1628, 1594, 1514, 1466, 1342, 982, 854, 528	226 (M–I–CH$_3$, 100), 225 (12), 196 (4), 180 (24), 179 (28), 154 (7), 142 (23), 127 (11)

benzimidazole nucleus and with 4-linked pyridine nucleus through the condensation of quaternary salts of benzimidazole or pyridine having reactive methyl group with aromatic aldehydes in the presence of piperidine under solvent-free microwave irradiation conditions. The procedure offers several advantages including short reaction times, cleaner reaction profiles and simple experimental/product isolation procedures.

Acknowledgements

We appreciate the financial support for this research by a grant from the Special Science Research Foundation of Education Committee of Shaanxi Province (No. 02JK060).

References

[1] Mees CEK, James T. The theory of the photographic process, part 1, trans. Tao H. Beijing: Science Press; 1979.
[2] Hamer FM. The cyanine dyes and related compound. New York: Interscience; 1964.
[3] Li Q, Lin GL, Peng BX, Li ZX. Dyes and Pigments 1997; 38:211.
[4] Li Q, Peng BX. Photographic Science and Photochemistry 1994;12:150.
[5] Ying JL, Zhu ZH, Yao ZG, Chem J. Chinese Universities 1990;11:286.
[6] He GS, Bhawalker JD, Shao CF. Appl Phys Lett 1995; 65:2433.
[7] Guo ZX, Hao JX, Zhang ZX, Cao ZX. Science in China (Series B) 1993;36:1416.
[8] Zhang ZJ, Hao JX, Wu BY, Yuan HA. Journal of Imaging Science and Technology 1995;39:373.
[9] Zhang ZX, Zhang YJ, Hao JX, Zhang ZJ, Li CE. Science in China (Series B) 1995;38:1173.
[10] Zhang CL, Wang LY, Zhang XH, Zhang ZX, Cao ZX. Journal of Functional Material 2001;32:546.
[11] Phillips AP. J Org Chem 1949;14:302.
[12] Abdel MO, Khairy MH, Zarif HK, Vlademir DT. J Appl Chem Biotechnol 1976;26:71.
[13] Lidström P, Tierney J, Wathey B, Westman J. Tetrahedron 2001;57:9225.
[14] Yadav JS, Reddy BVS. Tetrahedron Lett 2002;43:1905.
[15] Zakharova NA, Porai-Koshits BA, Efros LS. Zhur Obshchei Khim 1953;23:1225.
[16] Bergmann ED. J Am Chem Soc 1952;74:5979.