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Sulfamic acid: a novel and efficient catalyst for the synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes under conventional heating and microwave irradiation

B. Rajitha,* B. Sunil Kumar, Y. Thirupathi Reddy, P. Narsimha Reddy and N. Sreenivasulu

Department of Chemistry, National Institute of Technology, Warangal, India

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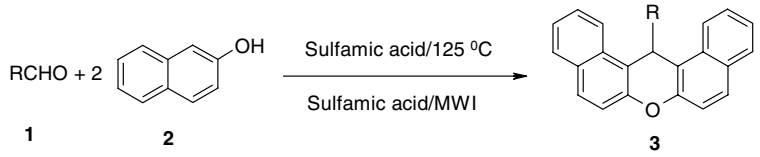
Abstract—A simple and convenient procedure for the synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes is described through a one-pot condensation of β-naphthol with aryl aldehydes in the presence of sulfamic acid as the catalyst in a solvent-free media using both conventional heating and microwave irradiation.

1. Introduction

The synthesis of xanthenes, especially benzoxanthenes, has emerged as a powerful tool in organic synthesis due to their wide range of biological and therapeutic properties such as antibacterial,[1] antiviral[2] and anti-inflammatory activities,[3] as well as in photodynamic therapy[4] and for antagonism of the paralyzing action of zoxazolamine.[5] Furthermore, due to their useful spectroscopic properties, they are used as dyes,[6] in laser technologies,[7] and in fluorescent materials for visualization of biomolecules.[8] Many procedures describe the synthesis of xanthenes and benzoxanthenes including cyclodehydrations,[9] alkylations γ to the heteroatoms,[10] trapping of benzynes by phenols,[11] cyclocondensation between 2-hydroxyaromatic aldehydes and 2-tetralone,[12] the reaction of β-naphthol with aldehydes or acetals under acidic conditions and intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones.[13] In addition, 14*H*-dibenzo[*a*,*j*]xanthenes and related products are prepared by reaction of β-naphthol with formamide,[14] 2-naphthol-1-methanol[15] and carbon monoxide.[16]

Even though various procedures are reported, disadvantages including low yields, prolonged reaction times, use of an excess of reagents/catalysts and use of toxic organic solvents necessitate the development of an alternative route for the synthesis of xanthene derivatives. Recently, sulfamic acid has emerged as a promising solid acid catalyst for acid catalyzed reactions, such as functional group protections and deprotections[17] and the synthesis of isoamyl acetate[18] and polymeric ethers.[19] Moreover, some important organic transformations, including the Beckmann rearrangement,[20] and Pechmann[21] and Bignelli condensations,[22] have been performed successfully in the presence of sulfamic acid. The reported route is an efficient, convenient and novel method for condensation of aldehydes with β-naphthol in the presence of sulfamic acid as catalyst (Scheme 1).



Scheme 1.

Keywords: Xanthene; One-pot reaction; Condensation; Aldehyde; β-Naphthol; Sulfamic acid; Solvent free; Microwave irradiation.
* Corresponding author. Tel.: +91 08702459445; fax: +91 0870245 9547; e-mail: rajitabhargavi@yahoo.com

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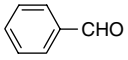
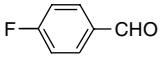
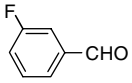
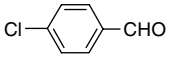
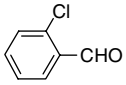
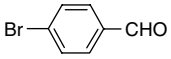
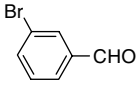
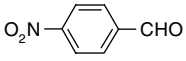
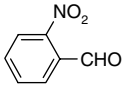
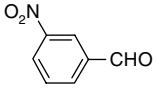
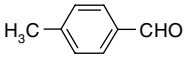
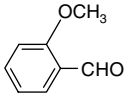
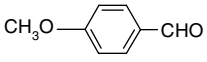
Table 1. Sulfamic acid catalyzed synthesis of aryl-14*H*-dibenzo[*a.j*]xanthenes

Entry	Aldehyde	Method A		Method B		Mp (°C)
		Time (h)	Yield (%)[a]	Time (min)	Yield (%)[a]	
1		8	93	2.5	95	183[9b]
2		6	93	2.0	94	238[9c]
3		7	93	2.5	95	259
4		7	95	3.0	96	287[9c]
5		8	90	3.5	92	215[9c]
6		10	95	2.0	95	296[9b]
7		9	92	4.0	93	190[9c]
8		11	94	3.5	96	312[9b]
9		12	93	4.0	95	293
10		12	91	4.0	93	213[9c]
11		11	92	3.0	95	228[9b]
12		12	93	4.0	94	258[9c]
13		10	92	3.5	94	205[9c]

[a] Yields refer to pure products and all products were characterized by comparison of their physical data and in ^{1}H NMR, IR, mass spectral data with those of authentic samples.

In the conventional method (Method A), β-naphthol was heated with different aromatic aldehydes at 125 °C to afford the products in 6–12 h. As part of our ongoing work with microwave irradiation,[23] β-naphthol was heated under solvent-free conditions with different aromatic aldehydes in the presence of sulfamic acid in a micrcowave oven (Method B) for the appropriate time (Table 1) to yield the desired products.

2. Experimental procedure

2.1. Conventional method (method A)

A mixture of the aldehyde (1 mmol), β-naphthol (2 mmol) and sulfamic acid (0.1 mmol) was stirred at 125 °C for the appropriate time according to Table 1. Completion of the reaction was indicated by TLC. The reaction was cooled to 25 °C, water was added and the mixture stirred for 5 min. The solid obtained was removed by filtration and recrystallized from ethyl alcohol.

2.2. Microwave irradiation method (method B)

To a mixture of aldehyde (1 mmol) and β-naphthol (2 mmol), sulfamic acid (0.04 mmol) was added and the mixture was inserted in a microwave oven (BPL, 800T model) on a silica gel solid support and heated at 300 W for the appropriate time (Table 1). Completion of the reaction was indicated by TLC. After completion, the reaction mass was cooled to 25 °C, water

was added and the mixture stirred for 5 min. The solid so obtained was filtered and recrystallized from ethyl alcohol.

2.3. Selected data

14-(3-Fluorophenyl)-14H-dibenzo[a.j]xanthene (*Table 1, entry 3*): Brown solid: mp 259 °C. IR (KBr, cm^{-1}): 3154, 1594, 1403, 1240, 1207, 1069, 817, 747; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.51$ (s, 1H) 6.72–8.38 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 38.1, 113.8 and 114.0 (J_{C-F} 21.5 Hz), 115.6 and 115.9 (J_{C-F} 21.5 Hz), 117.1, 118.2, 122.9, 124.31 and 124.34 (J_{C-F} 2.8 Hz), 124.8, 127.4, 129.3, 129.5, 130.1 and 130.2 (J_{C-F} 8.3 Hz), 131.5, 131.7 (J_{C-F} 19.4 Hz), 147.8, 147.9 (J_{C-F} 6.2 Hz), 149.2, 161.7, 165.0; EIMS, 70 eV, *m/z*: 376 (M^+), 281, 268; Anal. Calcd for $C_{27}H_{17}FO$: C, 86.15; H, 4.55; F, 5.05. Found: C, 86.11; H, 4.54, F, 5.07.

14-(2-Nitrophenyl)-14H-dibenzo[a.j]xanthene (*Table 1, entry 9*): Yellow solid: mp 293 °C. IR (KBr, cm^{-1}): 3400, 3058, 1593, 1523, 1350, 1240, 1142, 810, 748; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.52$ (s, 1H) 7.10–8.56 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.9, 118.0, 118.4, 123.0, 124.6, 125.0, 125.3, 127.8, 128.0, 129.4, 129.5, 129.9, 130.8, 132.1, 132.6, 134.5, 141.3, 147.5, 149.8; EIMS, 70 eV, *m/z*: 403 (M^+), 281, 268; Anal. Calcd for $C_{27}H_{17}NO_3$: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.25; H, 4.24, N, 3.57.

References and notes

1. Hideo, T. *Chem. Abstr.* **1981**, *95*, 80922b, Jpn. Tokkyo Koho JP 56005480, 1981.
2. Lambert, R. W.; Martin, J. A.; Merrett, J. H.; Parkes, K. E. B.; Thomas, G. J. *Chem. Abstr.* **1997**, *126*, p212377y, PCT Int. Appl. WO 9706178, 1997.
3. Poupelin, J. P.; Saint- Rut, G.; Foussard-Blanpin, O.; Narcisse, G.; Uchida-Ernouf, G.; Lacroix, R. *Eur. J. Med. Chem.* **1978**, *13*, 67.
4. (a) Ion, R. M. *Prog. Catal.* **1997**, *2*, 55; (b) Ion, R. M.; Frackowiak, D.; Planner, A.; Wiktorowicz, K. *Acta Biochim. Pol.* **1998**, *45*, 833.
5. (a) Saint-Ruf, G.; De, A.; Hieu, H. T. *Bull. Chim. Ther.* **1972**, *7*, 83; (b) Saint-Ruf, G.; Hieu, H. T.; Poupelin, J. P. *Naturwissenschaften* **1975**, *62*, 584.
6. (a) Menchen, S. M.; Benson, S. C.; Lam, J. Y. L.; Zhen, W.; Sun, D.; Rosenblum, B. B.; Khan, S. H.; Taing, M. *Chem. Abstr.* **2003**, *139*, p54287f, U.S. Patent, US6583168, 2003; (b) Banerjee, A.; Mukherjee, A. K. *Stain Technol.* **1981**, *56*, 83–85; (c) Reynolds, G. A.; Tuccio, S. A.; Peterson, O. G.; Specht, D. P. *Chem. Abstr.* **1971**, *71*, p81334c, Ger. Offen. DE2109040, 1971.
7. (a) Sirkeeioglu, O.; Talinli, N.; Akar, A. *J. Chem. Res. (S)* **1995**, 502; (b) Ahmad, M.; King, T. A.; Ko, Do-K.; Cha, B. H.; Lee, J. *J. Phys. D: Appl. Phys.* **2002**, *35*, 1473.
8. Knight, C. G.; Stephens, T. *Biochem. J.* **1989**, *258*, 683.
9. (a) Bekaert, A.; Andrieux, J.; Plat, M. *Tetrahedron Lett.* **1992**, *33*, 2805; (b) Sarma, R. J.; Baruah, J. B. *Dyes Pigm.* **2005**, *64*, 91; (c) Khosropour, A. R.; Khodaei, M. M.; Moghannian, H. *Synlett* **2005**, 955; (d) Buehler, C. A.; Cooper, D. E.; Scrudder, E. O. *J. Org. Chem.* **1943**, *8*, 316.
10. (a) Vazquez, R.; de la Fuente, M. C.; Castedo, L.; Domínguez, D. *Synlett* **1994**, 433; (b) Ishibashi, H.; Takagaki, K.; Imada, N.; Ikeda, M. *Synlett* **1994**, 49.
11. (a) Knight, D. W.; Little, P. B. *Synlett* **1998**, 1141; (b) Knight, D. W.; Little, P. B. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1771.
12. Jha, A.; Beal, J. *Tetrahedron Lett.* **2004**, *45*, 8999–9001.
13. Kuo, C.-W.; Fang, J.-M. *Synth. Commun.* **2001**, *31*, 877.
14. Papini, P.; Cimmarusti, R. *Gazz. Chim. Ital.* **1947**, *77*, 142.
15. Sen, R. N.; Sarkar, N. *J. Am. Chem. Soc.* **1925**, *47*, 1079.
16. Ota, K.; Kito, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1167.
17. (a) Jin, T. S.; Sun, G.; Li, Y. W.; Li, T. S. *Green Chem.* **2002**, *4*, 255; (b) Jin, T. S.; Sun, G.; Li, Y. W.; Li, T. S. *J. Chem. Res. (S)* **2003**, 30; (c) Jin, T. S.; Ma, Y. R.; Zhang, Z. H.; Li, T. S. *Synth. Commun.* **1998**, *28*, 3173.
18. Chen, J.; Wu, J. Y. *Specialty Petrochem.* **2001**, *3*, 35.
19. Rhoad, M. J.; Hory, P. J. *J. Am. Chem. Soc.* **1950**, *72*, 2216.
20. Wang, B.; Gu, Y. L.; Luo, G. Y.; Yang, T.; Yang, L. M.; Suo, J. S. *Tetrahedron Lett.* **2004**, *45*, 3369.
21. Singh, P. R.; Singh, D. U.; Samant, S. D. *Synlett* **2004**, 1909.
22. (a) Li, J. T.; Han, J. F.; Yang, J. H.; Li, T. S. *Ultrason. Sonochem.* **2003**, *10*, 119; (b) Jin, T. S.; Zhang, S. L.; Zhang, S. Y.; Guo, J. J.; Li, T. S. *J. Chem. Res. (S)*. **2002**, 37.
23. (a) Rao, G. V. P.; Narsimha Reddy, P.; Thirupathi Reddy, Y.; Naveen Kumar, V.; Rajitha, B. *Ind. J. Chem.* **2005**, *44B*, 1109–1111; (b) Narsimha Reddy, P.; Thirupathi Reddy, Y.; Kanakalingeswara Rao, M.; Rajitha, B. *Heterocycl. Commun.* **2003**, *9*, 647–652; (c) Narsimha Reddy, P.; Kanakalingeswara Rao, M.; Rajitha, B. *Ind. J. Chem.* **2004**, *43B*, 417–419.