

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

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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.

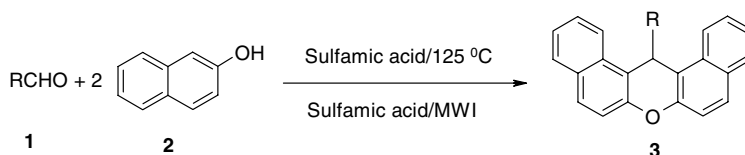
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1. Introduction

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 antiviral² and anti-inflammatory activities,³ as well as in photodynamic therapy⁴ 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 benzyne 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*]xanth-

enes and related products are prepared by reaction of β -naphthol with formamide,¹⁴ 2-naphthol-1-methanol¹⁵ 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 deprotections¹⁷ and the synthesis of isoamyl acetate¹⁸ and polymeric ethers.¹⁹ Moreover, some important organic transformations, including the Beckmann rearrangement,²⁰ and Pechmann²¹ and Big-nelli 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).

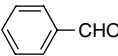
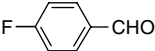
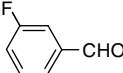
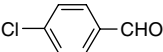
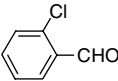
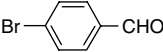
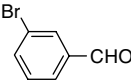
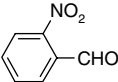
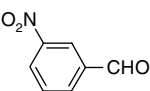
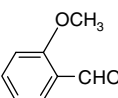
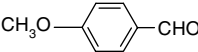


Scheme 1.

Keywords: Xanthene; One-pot reaction; Condensation; Aldehyde; β -Naphthol; Sulfamic acid; Solvent free; Microwave irradiation.

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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 ¹H 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 microwave 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): δ = 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 ($J_{\text{C-F}}$ 21.5 Hz), 115.6 and 115.9 ($J_{\text{C-F}}$ 21.5 Hz), 117.1, 118.2, 122.9, 124.31 and 124.34 ($J_{\text{C-F}}$ 2.8 Hz), 124.8, 127.4, 129.3, 129.5, 130.1 and 130.2 ($J_{\text{C-F}}$ 8.3 Hz), 131.5, 131.7 ($J_{\text{C-F}}$ 19.4 Hz), 147.8, 147.9 ($J_{\text{C-F}}$ 6.2 Hz), 149.2, 161.7, 165.0; EIMS, 70 eV, m/z : 376 (M^+), 281, 268; Anal. Calcd for $\text{C}_{27}\text{H}_{17}\text{FO}$: 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): δ = 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 $\text{C}_{27}\text{H}_{17}\text{NO}_3$: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.25; H, 4.24, N, 3.57.

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