Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (5): 2213-2216

(International Peer Reviewed Journal)

Microwave Assisted Synthesis of 14- aryl- 14*H*-dibenzo [a, j] xanthenes Catalyzed by Oxalic acid

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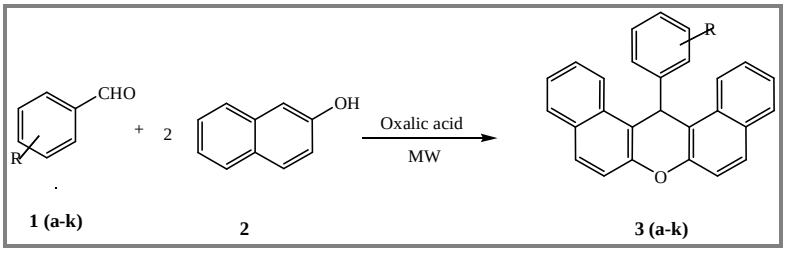
Accepted on 10th September, 2019

ABSTRACT

An eco-friendly and efficient protocol was developed for the one-pot synthesis of 14- aryl-14H-dibenzo [a, j] xanthenes from the condensation of various substituted aldehydes and 2-naphthol under microwave irradiation using inexpensive oxalic acid as catalyst. The method is general with wide substrate scope giving products in excellent yields and short reaction time.

Graphical Abstract



14- aryl- 14H-dibenzo [a, j] xanthenes.

Keywords: Oxalic acid, Dibenzoxanthene, Aldehydes, Microwave activation.

INTRODUCTION

Benzoxanthenes has attracted the attention of organic chemists due to their wide range of biological and therapeutic properties such as antibacterial [**1**], antiviral activities [**2**] and also as a candidate in photodynamic therapy (PDT) [**3, 4**]. Furthermore, benzoxanthenes are used as dyes [**5**], in laser technologies [**6**], and in fluorescent materials [**7**]. The synthesis of 14H-dibenzo [a, j] xanthene is generally achieved by a) dehydration of bis(2-hydroxy-1-naphthyl) methane using $POCl_3$ [**8**]or by boiling acetic acid diester of bis(2-hydroxy-1-naphthyl) methane [**9**], b) condensation of 2-naphthol with aliphatic and aromatic aldehydes in the presence of hydrochloric acid or phosphoric acid [**10**] and also sulfuric acid [**11**] in acetic acid as solvent. All these methods suffer from harsh reaction conditions, long reaction times, unsatisfactory yields and tedious experimental procedures. Recently,

the synthesis of 14*H*-dibenzo [a, j] xanthene has been reported by condensation of 2-naphthol and aldehydes in the presence of Selectfluor [12], molecular iodine[13], sulfamic acid [14], Amberlyst-15 [15], Nanocatalytic MCM-41-SO_3H [16] and thiamine hydrochloride [17] as catalyst. However, these methods typically involve strong acids and bases, harsh reaction conditions, and longer reaction time, among other considerations. Considering the limitations of the reported methods, the development of new methods for the synthesis of benzoxanthene is desirable.

The application of microwave irradiation to the combinatorial chemistry becomes a powerful tool in accelerating the pace of library synthesis [18]. Our results show that the effect of microwave irradiation on the reaction studied was a shortening of the reaction times and a smooth increase in the yields. Major aim of this integrated technology is to exploit high degree of molecular diversity and high-throughput organic synthesis to rapid access greatly expanded drug-like compound collection without tedious or time-consuming processes [19].

MATERIALS AND METHODS

Reagents and analysis: All the reagents and aromatic aldehydes were obtained from commercial suppliers and were not purified. Melting points were determined in open capillaries apparatus and are uncorrected. The reactions were monitored by TLC. IR spectra were recorded on a matrix of KBr with Perkin-Elmer 1430 spectrometer.^{1}HNMR spectra were recorded on Varian NMR spectrometer, Model Mercury Plus (400MHz) and the chemical shifts are given in ppm relative to signal for TMS as an internal standard. For the microwave irradiation experiments described below, a conventional (unmodified) household microwave oven equipped with a turntable was used (LG Smart Chef MS-255R operating at 2450 MHz having maximum output of 900 W).

General Procedure: To a mixture of aromatic aldehydes (1 mmol), 2-naphthol (2 mmol) and a catalytic amount (10 mol%) of oxalic acid was added in a borosil beaker. The reaction mixture was mixed properly with the help of a glass rod and irradiated in a microwave oven at 720 W for an appropriate time (Table 1). The reactions were monitored by TLC. Then crude reaction mixture was cooled to room temperature and treated with ice- cool water. The product was filtered, dried, recrystallized from ethanol, and identified by comparison of physical data, ^{1}HNMR and IR spectra with those described in the literature.

Table 1. One pot synthesis of 14-aryl 14*H*-dibenzo [*a,j*]xanthene derivatives

[a]Product	R	Time (min)	Yield (%)	M.P.(^{0}C)
3a	H	2	96	182
3b	2-Cl	4	90	118
3c	3-Cl	4	91	174
3d	4-Cl	4	92	288
3e	4-OH	5	85	140
3f	4-Me	5	90	224
3g	3-NO_2	3	92	214
3h	4-NO_2	3	92	312
3i	4-OMe	5	89	200
3j	3-Cl, 4-Cl	5	87	228
3k	2-OMe-4-OH	5	85	170

[a]Yields refer to pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of IR and NMR spectra with authentic samples [11-15].

Spectral data:

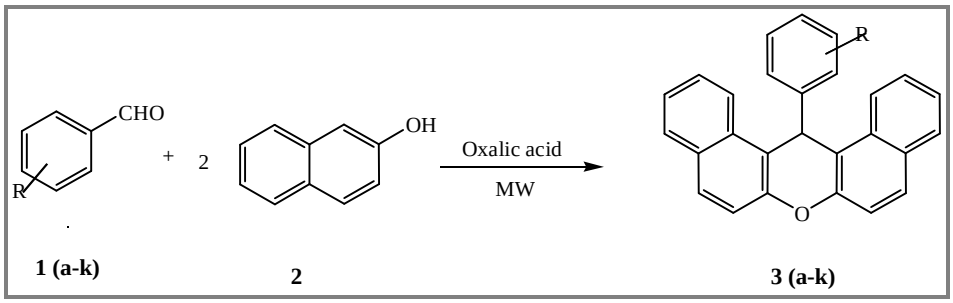
14-(4-Nitrophenyl)-14Hdibenzo [a, j] xanthene (3h): Yellow solid: MP 312°C. IR (KBr, cm^{-1}): 3402, 3055, 1590, 1520, 1352, 1245, 1140, 812, 750; ^{1}H NMR (300 MHz, $CDCl_3$): d = 7.55 (s, 1H) 7.12–8.58 (m, 16H).

14-(4-methylphenyl)-14H-dibenzo [a, j] xanthene (3f): Yellow Solid; MP. 224°C; IR (KBr Cm^{-1}): 3074, 1623, 1515, 1258, 1123, 1086, 966, 841, 744; m/z (%) = 372 (M.+).^{1}HNMR (400 MHz, $CDCl_3$): δ = 2.13 (s, 3H), 6.44 (s, 1H), 6.96 (d, *J* =8.0 Hz, 2H), 7.39 -7.43 (m, 4H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.54-7.58 (m, 2H), 7.78–8.39 (m, 6H).

RESULTS AND DISCUSSION

As a part of our plan to discover improved synthetic routes for the preparation of organic compounds [**20**], in this study, we report our investigation into an environmentally friendly and highly efficient procedure for the synthesis of 14- aryl-14*H*-dibenzo [a, j] xanthenes. The compounds were synthesized in good yield from aldehydes and 2-naphthol under microwave using oxalic acid as the catalyst (Scheme 1). To determine the optimum reaction conditions, we considered the synthesis of (**3a**) as a model reaction and we studied the effect of the catalyst. The effect of catalyst loading on the product yield is also investigated (Table 2). We performed the reaction for compound (**3a**) and used oxalic acid at various loads, such as 25 mol%, 20 mol%, 15 mol%, 10 mol% and 5 mol%. The results revealed that the use of 10 mol% oxalic acid is the most functional, yielding up to 98% of product.

Under the optimum conditions, we extended the study to explore the applicability of the oxalic acid catalyst for the synthesis of 14- aryl-14*H*-dibenzo [a, j] xanthenes **3(a–k)**. The reaction proceeded smoothly under microwave irradiation and accommodated a wide range of xanthenes bearing an electron-donating and an electron-withdrawing substituent. Note that the products **3(a–k)** were obtained simply by filtration from the reaction medium. In this methodology, condensation reactions were completed in a shorter reaction time (2-5min) and with excellent yields (85-96%). Thus, this is an excellent method for the synthesis of various benzoxanthenes.



Scheme 1. 14- aryl- 14H-dibenzo [a, j] xanthenes.

Table 2. Effect of catalyst loading on the yield of 14-Phenyl-14*H*-dibenzo [a,j] xanthene

S. No.	Catalyst	Quantity (mol%)	Yield (%)
1	Oxalic acid	5	78
2	Oxalic acid	10	96
3	Oxalic acid	15	96
4	Oxalic acid	20	96
5	Oxalic acid	25	96

APPLICATION

Microwave irradiation on the reaction studied was a shortening of the reaction times and a smooth increase in the yields.

CONCLUSION

Developed a simple, safe and efficient general method for the synthesis of 14-aryl 14*H*-dibenzo [a, j] xanthene by using inexpensive and easily commercial available oxalic acid as a catalyst under microwave irradiation. There are few advantages of this procedure such as good yields, short reaction time, easy work-up and low catalyst loading,

REFERENCES

[1]. T. Hideo, Jpn. Tokkyo Koho, *Chem. Abstr*. **1981**, 95 80922b, JP 56005480.
[2]. R. W. Lambert, J. A.Martin, H. J. Merrett,. K. E. B Parkes, G. J. Thomas, *Chem. Abstr*. **1997**, 126 p212377y.
[3]. R. M. Ion, *Prog. Catal.*, **1997**, *2*, 55.
[4]. R. M.Ion, D.Frackowiak, A.Planner, K. Wiktorowicz,. *Acta Biochim. Pol*. 45,**1998**, 833.
[5]. A. Banerjee, A. K.Mukherjee, *Stain Technol.* **1981**, 56, 83.
[6]. M. Ahmad, T. A.King, Ko, K. Do B. H Cha, J. J. Lee, *Phys. D: Appl. Phys.* **2002**, 35 1473.
[7]. C. G. Knight, T.Stephens, *Biochem. J.* **1989**, 258, 683.
[8]. W. Wolf, *Chem. Ber*. **1893**, 26, 83.
[9]. I. K.Rosebush, *Das Leder* **1955**, 6, 58.
[10]. A. Khorramabadizad, Z.Kazemi, H. Amini Rudbari, *J. Kor. Chem. Soc*. **2002**, 46, 541.
[11]. R. J.Sarma, J. B.Baruah, *Dyes Pigm.* **2005**, 64, 91.
[12]. P. S. Kumara, B. S.Kumara, B.Rajithaa, P. N. Reddya, N. Sreenivasulua, Y. T. Reddy, *Arkivoc* **2006**, 46.
[13]. B. Das, B. Ravikanth, R. Ramu, K. Laxminarayana, B. Vittal Rao, *J. Mol. Catal. A: Chem.,* **2006**,255, 74.
[14]. B. Rajitha, B. Sunil Kumar, Y. Thirupathi Reddy, P. Narsimha Reddy, N. Sreenivasulu, *Tetrahedron Lett.*, **2005**, 46, 8691.
[15]. S. Ko, C. Yao, *Tetrahedron Lett.*, **2006**, 47, 8827.
[16]. M. Fathollahi, S. Rostamizadeh, A.M. Amani, *Comb Chem High Throughput Screen*, **2018**, 21(1), 5.
[17]. U. Kusampally, R. Soma, C. R. Kamatala, *Rasayan J. Chem.*, **2019**,12(1),152.
[18]. A. Lew, P. O. Krutzik, M. E. Hart, R. A Hamberlin, *J.Comb. Chem.,* **2002**, 495. (a) F. Al-Obeidi, R. E. Austin, J. F.Okonya, D. R. S.Bond, *Med.Chem.*, **2003**,3, 459.
[19]. M. R. Ezhilarasi, B. Prabha, S. Prabakaran, *J. Applicable Chem.*, **2014**, 3(5), 1929. (d) R. Gupta, Y. Madan, E. Menghani, *J. Applicable Chem.*, **2014**, 3(5), 1955.
[20]. (a) K. F., Shelke, R. E. Khadse, *J. Applicable Chem*, **2015**, 4(6), 1804. (b) K. F Shelke,. S. S. Idhole, A. D. Badar, J. B. Devhade, *Der Pharmacia Lett.*, **2016**, 8(5), 72. (c) K. F. Shelke, Badar, A. D. Devhade, *J. B. Chem and Bio. Interface*, **2016**, 6(3), 157. (d) K. F. Shelke, A. D. Badar, J. B. Devhade *Int. J. Scientific Res in Sci. & Tech.*, **2018**, 4(1), 146. (e) K. F. Shelke, A. D. Badar, J. B. Devhade, *Review of Research*, **2019**, 1(3), 54.