Synthesis of 14-Aryl-14H-Dibenzo[a,j]xanthene Derivatives Using $Cu(CH_3CN)_4PF_6$ as Catalyst

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Abstract: A simple and expedient method for the synthesis of a series of 14-aryl-14H-dibenzo[a.j]xanthenes and bis **(**14-aryl-14H-dibenzo[a.j]xanthenes**)** is described through a one-pot condensation of β-naphthol with aryl aldehydes catalyzed by $Cu(CH_3CN)_4PF_6$ under solvent-free conditions. The novel synthesis method offers the advantages of high yields, short reaction times, simplicity and easy workup compared to the conventional method of syntheses.

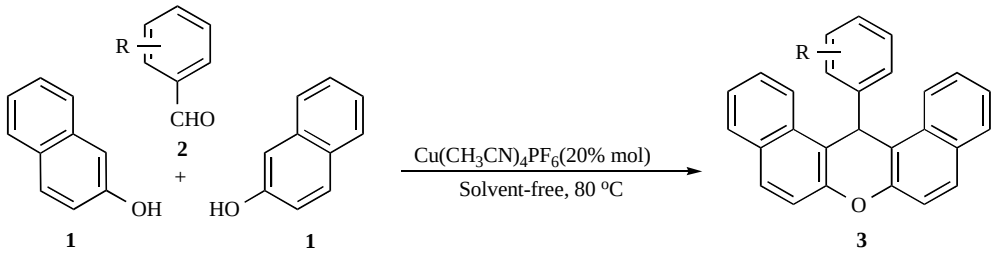
Keywords: 14-aryl-14H-dibenzo[a.j]xanthene, aldehyde, bis-14-aryl-14H-dibenzo[a.j]xanthene, $Cu(CH_3CN)_4PF_6$, solvent-free, β-naphthol.

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, antiviral and anti-inflammatory activities [1], as well as in photodynamic therapy [2] and for antagonism of the paralyzing action of zoxazolamine [3]. Furthermore, due to their useful spectroscopic properties, they are used as dyes [4], in laser technologies [5], and in fluorescent materials for visualization of biomolecules [6].

The synthesis of benzoxanthenes has been achieved by various methods [7]. Recently, the synthesis of benzoxanthenes has been achieved by the condensation of aldehydes with β-naphthol by cyclodehydration in the presence of various catalysts, such as $AcOH–H_2SO_4$ [8], p-TSA [9], $BF_3.SiO_2$ [10], sulfamic acid [11], ionic liquid [12], iodine [13], Dowex-50W [14], silica sulfuric acid [15], Amberlyst-15 [16], cyanuric chloride [17], LiBr [18], $Yb(OTf)_3$ [19], $InCl_3$ [20], and $KAl(SO_4)_2.12H_2O$ [21]. However, many of these existing methodologies suffer from one or more disadvantages such as prolonged reaction times, low yields, use of harmful organic solvents, requirement of excess of catalyst/reagents, and harsh reaction conditions.

In continuation of our work to develop new synthetic methodologies and solvent-free protocols [22], herein we report efficient, convenient and facile method for the synthesis of some benzoxanthenes derivative **3** by the condensation of β-naphthol **1** with various aromatic aldehydes **2** catalyzed by $Cu(CH_3CN)_4PF_6$ under solvent-free conditions at 80 ˚C (Scheme **1**).



Scheme 1.

RESULTS AND DISCUSSION

To study the feasibility of the $Cu(CH_3CN)_4PF_6$ catalyzed in this reaction, the reaction of 4-nitrobenzaldehyde with β-naphthol was selected as a model under solvent-free conditions. We first studied the model reaction catalyzed by $Cu(CH_3CN)_4PF_6$ (20 mol%) at different temperatures. The reaction rate was increased as the reaction temperature was raised. When it was carried out at 80 ˚C, the maximum yield was obtained in a short reaction period. Next, to evaluate the effect of catalyst concentration, the model reaction was carried out in the presence of different amounts of catalyst (5, 10, 15, 20 and 25 mol%) at 80 ˚C. The result showed that 20 mol% of catalyst was sufficient to achieve a fairly high yield (Table **1**).

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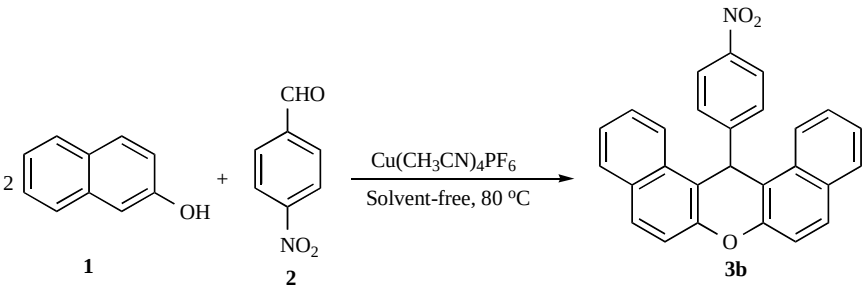
Table 1. Optimization Amount of $Cu(CH_3CN)_4PF_6$ Catalyst



Entry	$Cu(CH_3CN)_4PF_6$ (mol%)	Time (min)	Yield (%)
1	0	180	0
2	5	120	27
3	10	65	50
4	15	50	70
5	20	25	90
6	25	25	91

With the optimized condition established above, we next attempted to extend the process to β-naphthol and various types of aromatic aldehydes. The results have been summarized in Table **2**. In all cases, 14-aryl-14H-dibenzo[a,j] xanthenes were obtained in good yields, whatever the nature of the substituent present on the aldehyde (electron-donating or electron-withdrawing).

We also studied the reaction between terephthaldialdehyde (1 mmol) and excess amount of β-naphthol (4 mmol), we expected that both of the formyl groups on the aromatic ring of terephthaldialdehyde would react with β-naphthol and produced bis-14-aryl-14H-dibenzo[a,j]xanthene. However, we observed that one of the formyl groups was condensed with β-naphthol and another group was intact because of steric effects between o-hydrogen's of terephthaldialdehyde and the xanthene ring and steric interaction between two xanthene ring (Table **2**, entry 8) (Scheme **2**). Reaction between isophthalaldehyde (1 mmol) and excess amount of β-naphthol (4 mmol) was similar reaction between terephthaldialdehyde and β-naphthol (Table **2**, entry 9).

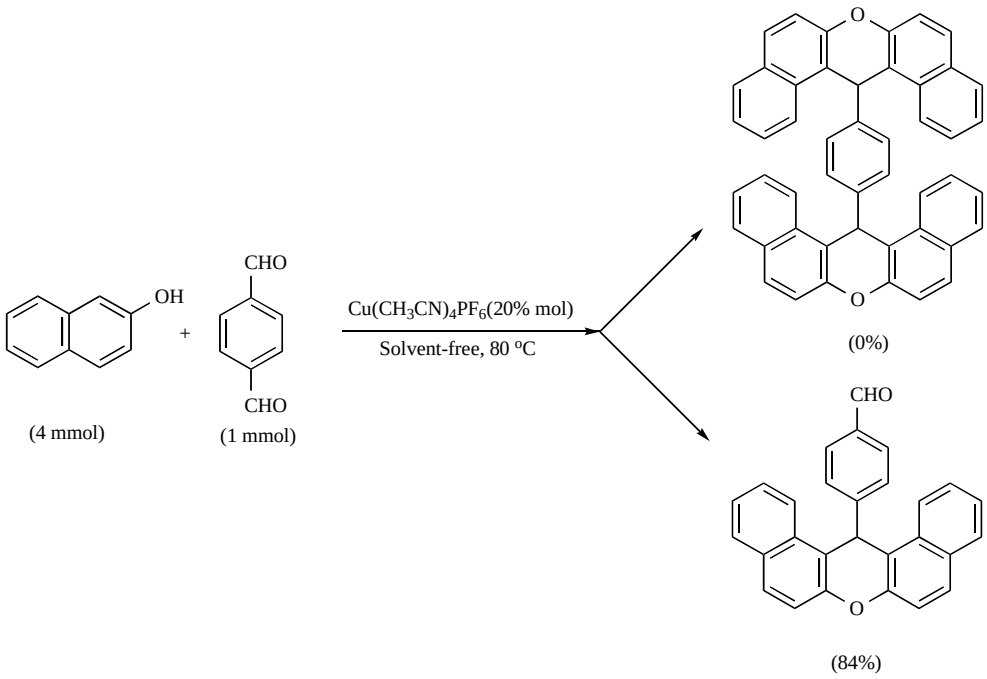
The efficiency of $Cu(CH_3CN)_4PF_6$ (time, yield, reaction conditions) was compared with the efficiencies of other catalysts used in synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes, the results are presented in Table **3**. It is clear that the presented method is simpler, more efficient and less time consuming compared with other methods except for that employing $Cu(CH_3CN)_4PF_6$ having disadvantages already mentioned.

CONCLUSION

In conclusion, we have developed a simple and efficient synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes and bis (14-aryl-14H-dibenzo[a,j]xanthenes) using $Cu(CH_3CN)_4PF_6$ catalyst under solvent-free conditions. This method offers some advantages in terms of simplicity of performance, low reac-

Table 2. Preparation of 14-aryl or alkyl-14H-dibenzo[a,j]xanthenes

Entry	R	Time (min)	Yield (%)	Product	Mp/°C	
					Found	Reported
1	H	120	83	**3a**	182-185	181-183 [23]
2	4-NO_2	25	90	**3b**	312-315	311-312 [23]
3	3-NO_2	40	93	**3c**	211-214	211-212 [23]
4	2-Cl	120	89	**3d**	214-217	215-216 [23]
5	4-Cl	60	92	**3e**	287-289	288-289 [23]
6	4-OH	55	94	**3f**	143-145	141-143 [24]
7	4-Me	50	94	**3g**	225-228	228-229 [23]
8	4-CHO	36	84	**3h**	310-313	310-312 [24]
9	3-CHO	30	86	**3i**	>160(dec)	-



Scheme 2.

Table 3. Comparison of the Efficiencies of Various Catalysts Used in the Synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes

Catalyst	Conditions/T/◦C	Time/h	Yield/%	Reference
Montmorillonite K10	Solvent-free/120	2–4	75–89	26
Selectfluor™	Solvent-free/125	6–12	90–95	25
p-Toluenesulfonic acid	Solvent-free/125	2.5–6	80–96	9
I_2	Solvent-free/90	2–5	85–95	13
Sulfamic acid	Solvent-free/125	6–12	90–95	11
Amberlyst-15	Solvent-free/125	0.5–2	80–94	16
Dowex-50W	Solvent-free/100	1–2	78–91	14
$Cu(CH_3CN)_4PF_6$	Solvent-free/80	0.5-2	83-94	This work

tion times, good yields, solvent-free condition, and it follows along the line of green chemistry. This protocol could serve as a valuable alternative to known reaction systems.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of Bicyclic Phosphonates 4a-i

To a mixture of β-naphthol (2 mmol) and aldehydes (1 mmol), $Cu(CH_3CN)_4PF_6$ (0.074 g, 0.2 mmol) was added and the reaction mixture was heated at 80 ˚C. for the appropriate time (Table **2**). After completion reaction indicated by TLC, the mixture was cooled to 25 ˚C, dichloromethane was added and the mixture stirred for 5 min. Products were filtered and recrystallized from aqueous ethanol.

All the products (except 3i) are known compounds, which were characterized by IR and ^{1}H-NMR spectral data and their mp's compared with literature reports.

3-(14H-Dibenzo[a,j]xanthene-14-yl)benzaldehyde: (3i)

White crystals; yield 0.33 g (86%); M.p. 260>˚C (dec.); IR (KBr, cm^{-1}): 1691, 1590, 1245; MS (70 eV): *m/z* = 386 (M^+), 282, 281, 252, 141; ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 6.22 (1H, s, CH), 6.63-8.00 (14H, m, H-Ar), 8.67 (2H, d, J=8.2 Hz, H-Ar), 9.88 (1H, s, CHO); ^{13}C NMR (50 MHz, DMSO-d_6, δ, ppm): δ = 37.6, 117.1, 118.16, 123.5, 124.7, 125.2, 126.6, 127.9, 128.2, 129.8, 131.0, 132.0, 147.0, 148.4, 153.1, 155.5, 161.8, 195.4.

ACKNOWLEDGMENTS

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DISCLOSURES

It should be noted that the synthesis of 14-alkyl or aryl 14*H*-dibenzo[*a.j*]xanthene derivatives were published by

author from the reaction of β-naphthol, and aldehydes in the presence of catalytic amount of bismuth(III) chloride ($BiCl_3$) under solvent-free conditions at 110 ˚C [27].

REFERENCES

[1] Poupelin, J. P.; Saint-Rut, G.; Fussard-Blanpin, O.; Narcisse, G.; Uchida-Ernouf, G.; Lakroix, R. Synthesis and anti-inflammatory properties of bis (2-hydroxy-1-naphthyl)methane, II. Polysubstituted and polycyclic derivatives. *Eur. J. Med. Chem*., **1978**, *13*, 67-71.

[2] Ion, R. M.; Frackowiak, D.; Planner, A.; Wiktorowicz, K. The incorporation of various porphyrins into blood cells measured *via* flow cytometry, absorption and emission spectroscopy. *Acta. Biochim. Pol*., **1998**, *45*, 833-845.

[3] Saint-Ruf, G.; De, A.; Hieu, H. T. The effect of dibenzoxanthenes on the paralyzing action of zoxazolamine. *Naturwissenschaften*, **1975**, *62*, 584-585.

[4] Kitahara, Y.; Tanaka, K. Synthesis, crystal structure and properties of thiaheterohelicenes containing phenolic hydroxy functions. *Chem. Commun*., **2002**, 932-933.

[5] Ahmad, M.; King, T. A.; Ko, D. K.; Cha, B. H.; Lee, J. Performance and photostability of xanthene and pyrromethene laser dyes in sol-gel phases. *J. Phys. D. Appl. Phys*., **2002**, *35*, 1473-1476.

[6] Knight, C. G.; Stephens, T. Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH. *Biochem. J.*, **1989**, *258*, 683-689.

[7] Jha, A.; Beal, J. Convenient synthesis of 12H-benzo[a]xanthenes from 2-tetralone. *Tetrahedron Lett*., **2004**, *45*, 8999-9001.

[8] Sarma, R. J.; Baruah, J. B One step synthesis of dibenzoxanthenes. *Dyes Pigments*, **2005**, *64*, 91-92.

[9] Khosropour, A. R.; Khodaei, M. M.; Moghhannian, H. A facile, simple and convenient method for the synthesis of 14-alkyl or aryl-14-H-dibenzo [a,j]xanthenes catalyzed by pTSA in solution and solvent-free conditions. *Synlett*, **2005**, 955-958.

[10] Mirjalili, B. B. F.; Bamoniri, A.; Akbari, A. $BF_3{\cdot}SiO_2$: an efficient alternative for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes. *Tetrahedron Lett*., **2008**, *49*, 6454-6456.

[11] Rajitha, B.; Sunil Kumar, B.; Thirupathi Reddy, Y.; Narsimha Reddy, P.; Sreenivasulu, N. Sulfamic acid: A novel and efficient catalyst for the synthesis of aryl-14H-dibenzo[a,j]xan- thenes under conventional heating and microwave irradiation. *Tetrahedron Lett*., **2005**, *46*, 8691-8693.

[12] Gong, K.; Fang, D.; Wang, H. L.; Zhou, X. L.; Liu, Z. L. The one-pot synthesis of 14-alkyl- or aryl-14H-dibenzo[a,j]xanthenes catalyzed by task-specific ionic liquid. *Dyes Pigments*, **2009**, *80*, 30-33.

[13] Das, B.; Ravikanth, B.; Ramu, R.; Laxminarayana, K.; Vittal Rao B. Sulfamic acid: a novel and efficient catalyst for the synthesis of aryl-14H- dibenzo[a,j]xanthenes under conventional heating and microwave irradiation. *J. Mol. Catal. A Chem*., **2006**, *255*, 74-77.

[14] Shakibaei, G. I.; Mirzaei, P.; Bazgir, A. Dowex-50W promoted synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene and 1,8-dioxooctahydroxanthene derivatives under solvent-free conditions. *Appl. Catal. A Gen*., **2007**, *325*, 188-192.

[15] Shaterian, H. R.; Ghashang, M.; Hassankhani, A. One-pot synthesis of aryl 14*H*-dibenzo[*a*,*j*]xanthene leuco-dye derivatives. *Dyes Pigments*, **2008**, *76*, 564-568.

[16] Kumar, C. N. S. S. P.; Srinivas, C.; Sadhu, P. S.; Rao, V. J.; Palaniappan, S. Efficient Synthesis of 14-substituted-14-H-dibenzo[a,j]xanthenes using silica supported sodium hydrogen sulfate or amberlyst-15 catalyst. *J. Heterocycl Chem*., **2009**, *46*, 997-999.

[17] Bigdeli, M. A.; Heravi, M. M.; Mahdavinia, G. Wet cyanuric chloride catalyzed simple and efficient synthesis of 14-aryl or alkyl-14-*H*-dibenzo[*a*,*j*]xanthenes. *Catal. Commun*., **2007**, *8*, 1595-1598.

[18] Saini, A.; Kumar, S.; Sandhu, J. S. A new LiBr catalyzed, facile and efficient method for the synthesis of 14-alkyl or aryl-14H-dibenzo[a,j]xanthenes and tetrahydrobenzo[b]pyrans under solvent-free conventional and microwave heating. *Synlett*, **2006**, 1928-1932.

[19] Su, W.; Yang, D.; Jin, C.; Zhang, B. $Yb(OTf)_3$ catalyzed condensation reaction of β-naphthol and aldehyde in ionic liquids: a green synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes. *Tetrahedron Lett*., **2008**, *49*, 3391-3394.

[20] Kumar, R.; Nandi, G. C.; Verma, R. K.; Singh, M. S. A facile approach for the synthesis of 14-aryl- or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes under solvent-free condition. *Tetrahedron Lett*., **2010**, *51*, 442-445.

[21] Dabiri, M.; Baghbanzadeh, M.; Shakouri Nikcheh, M.; Arzroomchilar, E. Eco-friendly and efficient one-pot synthesis of alkyl- or aryl-14*H*-dibenzo[*a*,*j*]xanthenes in water. *Bioorg. Med. Chem. Lett*., **2008**, *18*, 436-438.

[22] Soleimani, E.; Khodaei, M. M.; Batooie, N.; Samadi, S. An efficient approach to quinolines *via* friedländer synthesis catalyzed by cuprous triflate. *Chem. Pharm. Bull*., **2010**, *58*, 212-213.

[23] Bhattacharya, A. K.; Rana, K. C. Microwave-assisted synthesis of 14-aryl-14*H*-dibenzo[*a*.*j*]xanthenes catalysed by methanesulfonic acid under solvent-free conditions. *Mendeleev. Commun*., **2007**, *17*, 247-248.

[24] Zarei, A.; Hajipour, A. R.; Khazdooz, L. The one-pot synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes catalyzed by P_2O_5/Al_2O_3 under microwave irradiation. *Dyes Pigments*, **2010**, *85*, 133-138.

[25] Kumar, P. S.; Kumar, B.; Rajitha, B. A novel one pot synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes catalyzed by Selectfluor™ under solvent free conditions. *Arkivoc*, **2006**, *12*, 46-50.

[26] Dabiri, M.; Azimi, S. C.; Bazgir, A. One-pot synthesis of xanthene derivatives under solvent-free conditions. *Chem. Papers*, **2008**, *62*, 522-526.