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Guanidinium Chloride: A Novel and Efficient Organocatalyst for the Synthesis of 14-Aryl-14H-dibenzo[*a,j*]xanthenes under Solvent-Free Conditions

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ABSTRACT

A facile, efficient and environment-friendly protocol for the synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthenes has been developed by one-pot condensation of 2-naphthol with aromatic aldehydes in the presence of guanidinium chloride as a novel organocatalyst under solvent-free conditions. The present approach offers the advantages such as clean reaction, shorter reaction times, excellent product yields, simple reaction and work-up procedure, economic availability of the organocatalyst and purification of products by non-chromatographic methods.
KEYWORDS*:* Xanthene; guanidinium chloride; naphthol; aldehyde.

1. INTRODUCTION

The synthesis of xanthenes and benzoxanthenes is important in organic synthesis because of their wide range of biological and pharmaceutical properties, such as agricultural bactericide activity[1], anti-inflammatory [2] and antiviral activity [3]. They have also been used as dyes [4] and fluorescent material for visualization of biomolecules [5] and in laser technologies [6].

The synthesis of benzoxanthenes has been achieved by various methods. Among them, condensation of 2-naphthol with aldehydes has been explored using different catalysts such as sulfamic acid [7], p-TSA [8], selectfluor TM [9], I_2 [10], silica sulfuric acid [11], $Yb(OTf)_3$ [12], acidic ionic liquid [13], oxalic acid [14], $H_4[SiW_{12}O_{40}]$ [15], $Sc[N(SO_2C_8F_{17})_2]_3$ [16], $Fe(HSO_4)_3$ [17], P_2O_5/Al_2O_3 [18], $BiCl_3$ [19], Amberlyst-15 [20], HBF_4-SiO_2 [21], cyanuric chloride [22], LiBr [23] and $CoPy_2Cl_2$ [24]. Although some of these methods have convenient protocols with good to high yields, the majority of these methods suffer at least from one of the following disadvantages: harsh reaction conditions, long reaction time, tedious experimental procedures, the use of toxic solvents, special apparatus and catalysts. Hence, a practical and more efficient method for the synthesis of dibenzoxanthene derivatives would still be of interest. The search for milder and more environmentally benign conditions is, therefore, highly demanding for the synthesis of these compounds.

Recently, guanidinium salts have been successfully employed as novel chiral phase-transfer catalyst in the conjugate addition of nitroalkanes with enones [25]. Moreover, these organocatalysts provide an environment to the process activating the nucleophile, the electrophile or both reagents through weak interactions, such as hydrogen bonding or ion pairing or much stronger interactions such as covalent bonding.

In a continuation of our interest in developing green multi-component reactions [26-28], we report herein the synthesis of xanthene derivatives via 2-naphthol and aromatic aldehydes in the presence of guanidinium chloride as a organocatalyst under solvent-free conditions. To the best of our knowledge in the open literature, one-pot synthesis of benzoxanthene derivatives catalyzed by guanidinium chloride has not previously been reported.

2. RESULT AND DISCUSSION

In our initial experiments, the reaction of 2-naphthol (2 mmol) and benzaldehyde (1 mmol) was selected as a model reaction, and its behavior was studied in the presence of 10 mol% of guanidinium chloride under solvent-free conditions. Moreover, to optimize the temperature in the mentioned reaction, we have carried out a model study with benzaldehyde and 2-naphthol using 10 mol% of catalyst at various temperatures under solvent-free conditions. Our investigation demonstrated that 140 °C is an effective temperature in terms of reaction time and yield obtained. Then, we screened the catalyst concentration on model reaction at this temperature. We have varied the concentration of catalyst to 2, 5, 7, 10 and 15 mol %. The results indicated that when the reaction was carried out in the presence of 10 mol % of catalyst it gave excellent of product. Even after increasing the catalyst concentration at 15 mol % the yields of the product were found to be constant. So, the use of 10 mol % of catalyst appears to be optimal.

To show the generality of this method the optimized system was used for the synthesis of other 14-aryl-14H-dibenzo[*a,j*]xanthenes from the condensation of 2-naphthol with a wide range of aromatic aldehydes utilizing guanidinium chloride as organocatalyst under solvent-free conditions at 140 °C (Scheme 1). All reactions were complete with in 30-90 min, as indicated in Table 1; The reaction proceeds via condensation of 1 mol of aldehyde with 2 mol of 2-naphthol followed by intramolecular elimination of water from two hydroxyl groups to form the corresponding dibenzoxanthene in high yields.

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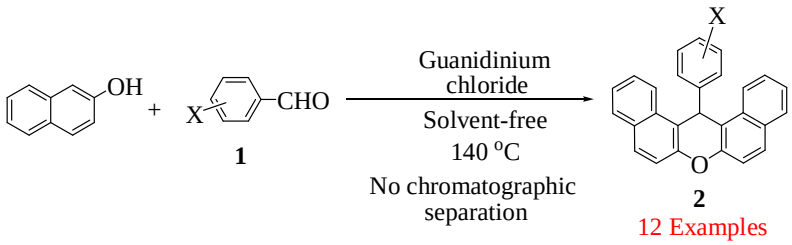
Table 1. Guanidinium chloride catalyzed one-pot synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes

Entry	Aldehyde	2	Time (min)	Yield (%)
1	benzaldehyde	2a	60	89
2	4-methoxybenzaldehyde	2b	75	85
3	4-methylbenzaldehyde	2c	75	87
4	4-fluorobenzaldehyde	2d	60	92
5	2-chlorobenzaldehyde	7h	30	87
6	4-chlorobenzaldehyde	2f	60	89
7	2,6-dichlorobenzaldehyde	2g	45	88
8	3-nitrobenzaldehyde	2h	90	90
9	4-nitrobenzaldehyde	2i	30	92
10	4-bromobenzaldehyde	2j	60	89
11	formaldehyde	2k	75	85
12	2,4-dichlorobenzaldehyde	2l	75	88



Scheme 1. Guanidinium chloride promoted one-pot synthesis of xanthenes.

Most substituted benzaldehydes reacted with 2-naphthol completely and afforded the corresponding products (**2**) in high yields. Since electron-donating group can stabilize the carbocation formed in the reaction, the reaction is mild and the yield is high. In contrast, aldehydes with electron-withdrawing group were more reactive and the reaction with 2-naphthol was faster. Thus, the aromatic aldehydes bearing both electron-donating and electron withdrawing groups are desirable substrates for this reaction.

Concerning the reaction mechanism, we proposed that guanidinium chloride initially acts as a hydrogen-bond donor to activate aldehyde by formation of six-membered ring with aldehyde oxygen. Subsequent, the reaction proceeds through the in situ formation of ortho-quinone methide intermediate by the nucleophilic addition of 2-naphthol to aldehyde, which is further attacked by second molecule of 2-naphthol followed aryl-methanebisnaphthols are formed, which then undergo dehydration in the presence of guanidinium chloride to give the final product.

All the products are known compounds, which were characterized by IR and ^{1}H and ^{13}C NMR spectral data and their mp's compared with literature reports.

3.Experimental

General Procedure for the Synthesis of 14-aryl-14H-dibenzo[a,j]xanthene (**2**): To a mixture of aldehyde (1 mmol), and 2-naphthol (2 mmol), guanidinium chloride (10 mol %) was added and heated at 140 ^{o}C for the appropriate amount of time as indicated in Table 1. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion, the reaction mixture was cooled to room temperature and EtOH (5 mL) was added until white solid products precipitated. The precipitate was filtered, washed with cold ethanol and dried. The obtained products **2** were found to be pure upon TLC examination.

14-Phenyl-14H-dibenzo[*a,j*]xanthene (2a)

IR (KBr): 3019, 1587, 1509, 1397, 1247 (C–O–C), 958 cm^{-1}; ^{1}H NMR (400 MHZ, DMSO-d$_6$) δ: 6.72 (s, 1H, *methine-H*), 6.98-8.69 (m, 17H, *Ar-H*).

14-(4-Methoxyphenyl)-14H-dibenzo[*a,j*]xanthene (2b)

IR (KBr): 3005, 1592, 1508, 1397, 1244 (C–O–C), 958 cm^{-1}; ^{1}H NMR (400 MHZ, DMSO-d$_6$) δ: 3.55 (s, 3H, *CH$_3$*), 6.66 (s, 1H, *methine-H*), 6.69-8.67 (m, 16H, *Ar-H*).

14-(4-Methylphenyl)-14H-dibenzo[*a,j*]xanthene (2c)

IR (KBr): 3021, 1588, 1509, 1395, 1242 (C–O–C), 958, 809 cm^{-1}; ^{1}H NMR (400 MHZ, DMSO-d$_6$) δ: 2.05 (s, 3H, *CH$_3$*), 6.66 (s, 1H, *methine-H*), 6.92-8.66 (m, 16H, *Ar-H*).

14-(4-Fluorophenyl)-14H-dibenzo[*a,j*]xanthene (2d)

IR (KBr): 3032, 1590, 1502, 1395, 1240 (C–O–C), 953, 803 cm^{-1}; ^{1}H NMR (400 MHZ, DMSO-d$_6$) δ: 6.75 (s, 1H, *methine-H*), 6.96-8.69 (m, 16H, *Ar-H*).

14-(2-Chlorophenyl)-14H-dibenzo[*a,j*]xanthene (2e)

IR (KBr): 3052, 1590, 1509, 1399, 1240 (C–O–C), 955, 810, 744 cm^{-1}; ^{1}H NMR (400 MHZ, DMSO-d$_6$) δ: 6.75 (s, 1H, *methane-H*), 7.02-8.61 (m, 16H, *Ar-H*).

14-(4-Chlorophenyl)-14H-dibenzo[*a,j*]xanthene (2f)

IR (KBr): 3066, 1588, 1509, 1482, 1397, 1242 (C–O–C), 959, 814 cm^{-1}; ^{1}H NMR (400 MHZ, DMSO-d$_6$) δ : 6.75 (s, 1H, *methine-H*), 7.20-8.67 (m, 16H, *Ar-H*).

14-(2,6-Dichlorophenyl)-14H-dibenzo[*a,j*]xanthene (2g)

IR (KBr): 3050, 1592, 1432, 1245 (C–O–C), 794, 774, 739 cm^{-1}; ^1H NMR (400 MHZ, DMSO-d_6) δ: 6.92 (s, 1H, *methine-H*), 7.07- 8.42 (m, 15H, *Ar-H*).

14-(3-Nitrophenyl)-14H-dibenzo[*a,j*]xanthene (2h)

IR (KBr): 3021, 1624, 1588, 1395, 1242 (C–O–C), 958, 809, 740 cm^{-1}; ^1H NMR (400 MHZ, DMSO-d_6) δ: 6.97 (s, 1H, *methine-H*), 7.47-8.76 (m, 16H, *Ar-H*).

14-(4-Nitrophenyl)-14H-dibenzo[*a,j*]xanthene (2i)

IR (KBr): 3062, 1593, 1514, 1341, 1242 (C–O–C), 822, 744 cm^{-1}; ^1H NMR (400 MHZ, DMSO-d_6) δ: 6.93 (s, 1H, *methine-H*), 7.47-8.70 (m, 16H, *Ar-H*).

14-(4-Bromophenyl)-14H-dibenzo[*a,j*]xanthene (2j)

IR (KBr): 3072, 1588, 1523, 1343, 1248 (C–O–C), 958 cm^{-1}; ^1H NMR (400 MHZ, DMSO-d_6) δ: 6.75 (s, 1H, *methine-H*), 7.34 – 8.68 (m, 16H, Ar-H).

14H-14H-dibenzo[*a,j*]xanthene (2k)

IR (KBr): 3049, 1599, 1569, 1394, 1236 (C–O–C), 1177, 1078, 997, 805, 741 cm^{-1}; ^1H NMR (400 MHZ, DMSO-d_6) δ: 4.50 (s, 2H, CH_2), 7.44-8.33 (m, 12H, *Ar-H*).

14-(2,4-Dichlorophenyl)-14H-dibenzo[*a,j*]xanthene (2l)

IR (KBr): 3056, 1593, 1529, 1350, 1248 (C–O–C), 1048, 804, 742 cm^{-1}; ^1H NMR (400 MHZ, DMSO-d_6) δ: 6.90 (s, 1H, *methine-H*), 7.49-8.70 (m, 15H, *Ar-H*).

4.Conclusions

In summary, a novel and highly efficient method for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes by condensation reaction of 2-naphthol with aromatic aldehydes catalyzed by guanidinium chloride has been described. The attractive features of this protocol are simple experimental procedure, solvent-free reaction conditions, utilization of an inexpensive and readily available organocatalyst, short reaction time and its adaptability for synthesis of a diverse set of benzoxanthene derivatives. To the best of our knowledge this is the first report on synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthene derivatives with guanidinium chloride.

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