
4-Dodecylbenzenesulfonic acid (DBSA) as an efficient and recyclable catalyst for synthesis of 14-aryl- and 14-alkyl-14-H-dibenzo [a,j]xanthenes under solvent-free conditions

H. Hashemi and A. R. Sardarian*

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 75454, Iran
E-mail: sardarian@susc.ac.ir

Abstract

14-Aryl- and 14-alkyl-14-H-dibenzo [a,j]xanthenes are prepared from the reaction of aromatic- and aliphatic aldehydes with β -naphthol in the presence of catalytic amounts of 4-dodecylbenzenesulfonic acid (DBSA) as a surfactant-type Brønsted acid catalyst in toluene and under solvent-free conditions in excellent yields and short reaction times. The catalyst was recovered and reused for five successive times without considerable loss in its activity.

Keywords: 4-Dodecylbenzenesulfonic acid (DBSA); β -Naphthol; Benzoxanthenes; Solvent-free

1. Introduction

Benzoxanthenes are flat rigid structures which have been used as a linker for peptide synthesis [1] and in unnatural amino acids and related pharmaceutical precursors [2]. Furthermore, due to their useful spectroscopic properties, they are used as dyes [3], in laser technologies [4], and in fluorescent materials for visualization of biomolecules [5]. Upon oxidation, these compounds can be converted to the corresponding xanthylium salts which are also useful as dyes and fluorescent materials [6]. Xanthene based compounds have also been investigated for agricultural bactericide activity [7], photodynamic therapy [8], anti-inflammatory effects [9], and for antagonism of the paralyzing action of zoxazolamine [10].

Several synthetic methods exist for the synthesis of benzoxanthenes, such as the cyclocondensation reaction of 2-hydroxyaromatic aldehydes and 2-tetralone [11], the reaction of benzaldehyde and acetophenone [12] and the condensation of β -naphthol with alkyl or aryl aldehydes. The latter synthetic method can be promoted by many Brønsted acid catalysts such as: H_2SO_4 [13], HCl [14], *p*-toluenesulfonic acid [15], sulfamic acid [16], methanesulfonic acid [17], H_3PO_4 or $HClO_4$ at $0^\circ C$ in acetic acid [18], ionic liquid [19], heteropolyacid [20], silica sulfuric acid [21], cyanuric chloride [22], LiBr [23], $CoPy_2Cl_2$ [24],

$Yb(OTf)_3$ [25], $Sc[N(SO_2C_8F_{17})_2]_3$ [26], $NaHSO_4$ [27], $Al(HSO_4)_3$ [28], bismuth(III)chloride [29], $ZrO(OTf)_2$ [30], ruthenium chloride hydrate [31], silica supported perchloric acid [32], P_2O_5 / Al_2O_3 [33] and silica chloride [34].

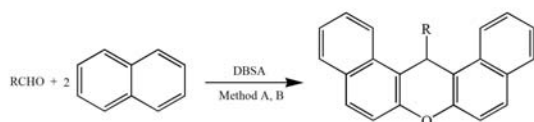
Although many useful and reliable methods for preparation of benzoxanthenes have been reported in the literature, many of these procedures have significant drawbacks such as low yields of the products, long reaction times, and harsh reaction conditions. Thus, the development of simple, convenient, and environmentally benign methods for the synthesis of benzoxanthenes is still required.

Dodecylbenzenesulfonic acid, an anionic surfactant, can act as a combined Brønsted acid-surfactant-catalyst (BASC). It performs the dual role of both an acid catalyst to activate the substrate molecules and a surfactant to increase the concentration of organic reactants by forming micellar aggregates in water [35]. Recently, the potential of DBSA has been described in some acid catalyzed reactions such as esterification [36], synthetic method for bis (indol-3-yl)alkane derivatives [37], *N*-alkylation of aldoximes [38], synthesis of tetrahydrobenzopyrans [39], dehydration reactions in water [40], and thia-Michael addition reactions in water [41].

Herein, we report on the use of dodecylbenzenesulfonic acid which is a mild, non-volatile and non-corrosive organic acid, as an efficient surfactant-type Brønsted acid catalyst for synthesis of benzoxanthenes (Scheme 1).

*Corresponding author

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Scheme 1

2. Experimental

2.1. General

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points, spectral data and CHN analysis with those reported in the literature. NMR spectra were recorded on a Bruker Avance DPX-250 (^1H NMR 250 MHz and ^{13}C NMR 63 MHz) spectrometer in DMSO-*d*₆, using TMS as an internal standard. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instrument at 70 or 20 eV and CHN data were reported on a Flash EA instrument. Melting points were determined in open capillary tubes in a Büchi-545 circulating oil melting point apparatus.

2.2. General procedure for the preparation of benzoxanthenes

Method A: To a solution of β -naphthol (2 mmol) and aldehyde (1 mmol) in toluene (1 mL), DBSA (15 mol %) was added and the reaction mixture was stirred for the appropriate time under reflux condition. The reaction progress was monitored by TLC. After the reaction was completed, ethanol was added to the reaction solution to produce the crude product as a precipitate. The product was recrystallized from ethanol to give the pure corresponding benzoxanthene.

Method B: To a mixture of β -naphthol (2 mmol) and aldehyde (1 mmol), SiO_2 (0.6 g) and DBSA (15 mol %) were added. The mixture was stirred at 85°C for an appropriate time. The reaction progress was followed by TLC. After the reaction was completed ethyl acetate (20 mL) was added and the mixture was stirred for 10 min. The mixture was filtered and SiO_2 was separated. Then 2 mL aqueous solution of NaHCO_3 (5%) was added to remove the catalyst. The organic layer was dried on anhydrous CaCl_2 and the solvent was evaporated. The obtained solid was recrystallized from ethanol to give the pure benzoxanthene.

3. Results and Discussion

Our initial experiments were carried out using benzaldehyde and β -naphthol in the presence of 15

mol% of DBSA in different solvents such as water, acetonitrile, dichloromethane, and toluene.

According to the results of Table 1, in acetonitrile and dichloromethane (Entries 1, 3) the reaction did not proceed at all, even under reflux conditions. In water the corresponding product was produced only in 33% at reflux after 18h [42] (Entry 2). The best isolated yield of the corresponding benzoxanthene was obtained in toluene using a mixture of benzaldehyde, β -naphthol and dodecylbenzenesulfonic acid in 1:2:0.15 molar ratios for 20 min at reflux (Entry 6). A lower amount of DBSA, 10 mol %, led to lower yield but a higher amount, 20 mol %, did not show any improvement in the yield or the reaction time (Entries 5 and 7). The shorter reaction time in toluene could be due to its higher boiling.

The reaction progress was also observed under solvent-free conditions; the stirring of the mixture was somehow difficult. In order to solve this problem, we decided to add 0.06g silica to prevent the magnet from sticking to the reaction mixture.

The reaction progress at different temperatures was examined, and the best result was gained at 85°C (Entry 9).

Table 1. Optimization of conditions for preparation of 14-alkyl- or aryl- 14-*H*-dibenzo-[a, j] xanthenes using dodecylbenzenesulfonic acid as a catalyst.

Entry	Solvent	DBSA (mol%)	Temp.(°C)	Time (h)	Yield (%)
1	Acetonitrile	15	Reflux	2	--
2	H ₂ O	20	Reflux	18	33 [42]
3	Dichloromethane	15	Reflux	2	--
4	Solvent-free	15	100	0.6	60
5	Toluene	20	Reflux	0.3	90
6	Toluene	15	Reflux	0.3	90
7	Toluene	10	Reflux	0.3	70
8	Toluene	15	60	2	50
9	SiO ₂ /Solvent-free	15	85	0.6	85
10	SiO ₂ /Solvent-free	15	60	2	50
11	SiO ₂ /Solvent-free	15	120	0.6	85

Therefore, DBSA was applied as a surfactant-type Brønsted acid catalyst in the synthesis of benzoxanthenes from β -naphthol and various aldehydes in boiling toluene (method A) and under solvent-free conditions at 85°C in the presence of SiO_2 to allow smooth stirring of the mixture (method B). Under these reactions, the corresponding benzoxanthenes were produced in 68–95% yields (Table 2, entries 1–12). As can be seen from Table 2, both aromatic and aliphatic aldehydes were used for synthesis of benzoxanthenes. Aromatic aldehydes including electron-withdrawing groups (Entries 2-6) can be efficiently reacted with β -naphthol in short reaction times with good isolated yields. Under similar conditions, aliphatic aldehydes (Entries 11, 12) were reacted with lower yields. Aromatic aldehydes including electron-donating groups were reacted with high to moderate yields (Entries 7-10).

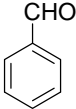
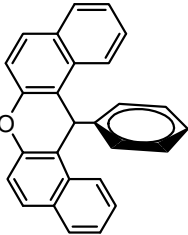
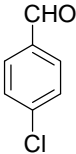
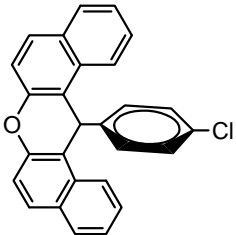
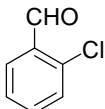
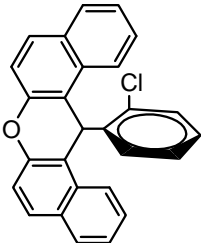
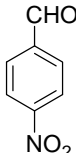
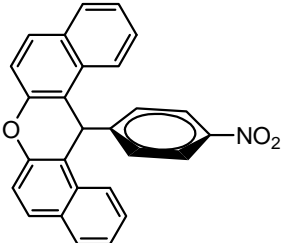
A literature survey showed that there are few

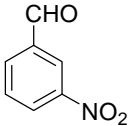
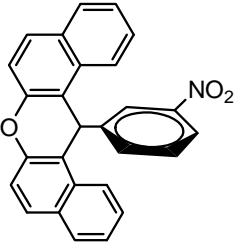
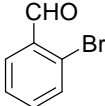
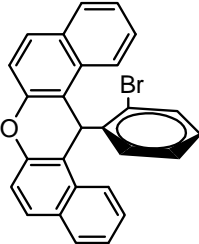
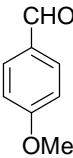
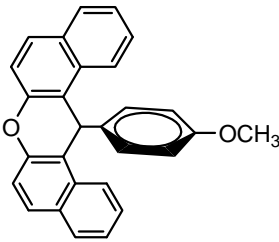
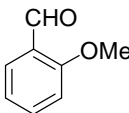
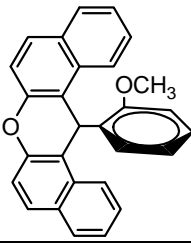
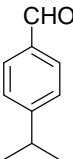
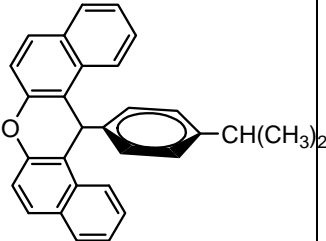
reports on the preparation of benzoxanthenes from the reaction of aliphatic aldehydes with β -naphthol. So, a decision was made to use aliphatic aldehydes for this purpose. Phenylacetaldehyde and 3-phenylpropanal, as aliphatic aldehydes, were investigated for preparation of the related xanthenes under the same conditions. However, a lower yield was obtained compared to aromatic aldehydes (Table 2, entries 11 and 12).

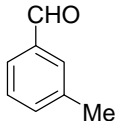
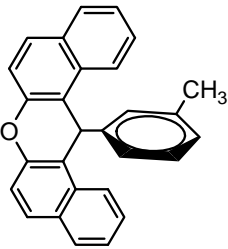
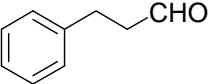
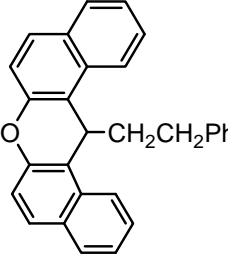
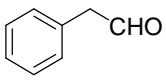
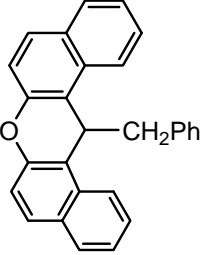
When we looked closely at the reaction mixture

during the progress of the reaction, we observed that some of the aldehydes were evaporated or sublimated out of the reaction mixtures and therefore were not in perfect contact with β -naphthol and dodecylbenzenesulfonic acid. We thought this might be the reason for the lower yields. To overcome this problem, 1.2/2/0.15 (instead of 1/2/0.15) mole ratio of aldehyde/ β -naphthol/ DBSA was used.

Table 2. Synthesis of 14-alkyl- or aryl- 14-*H*-dibenzo [a, j] xanthenes in the presence of a catalytic amount of DBSA

Entry	Aldehyde	Product	Time(min) (A/B) ^a	Yield(% (A/B)	Mp. (°C) (Lit.) [Ref.]
1			20 / 8	90 / 85	184-186 (183) [43]
2			15 / 15	85 / 80	289-291 (287) [44]
3			5 / 12	95 / 85	215-217 (215) [44]
4			5 ^b / 15 ^b	95 / 80	213-215 (212) [44]

5			10 / 10	95 / 85	214-216 (213) [44]
6			5 / 10	88 / 82	203-205 (204-206) [45]
7			50 / 20	85 / 80	205-207 (204) [44]
8			40 / 15	88 / 82	256-258 (258) [44]
9			25 / 25	82 / 74	153-155 (151-153) [16]

10			25 / 25	90 / 85	196-198 (198.5) [45]
11			25 ^b / 25 ^b	78 / 72	162-164 (164) [45]
12			30 / 30	75 / 68	157-159 (159) [45]

a: Isolated yields

b: The mole ratio of aldehyde/ β -naphthol is 1.2 / 2

In order to show the effectiveness of the presented methods in the preparation of benzoxanthenes, the obtained results in the reaction of benzaldehyde with β -naphthol catalyzed by DBSA were compared with some of those reported in the literature (Table 3). The results showed that our methods are superior in terms of the catalyst amount, reaction times or product yields.

Table 3. Comparison among the efficiency of various acid catalysts used in the synthesis of 14-phenyl-14*H*-dibenzo[a,j]xanthenes

Entry	Catalyst (mol%)	Conditions	Time (min)	Yield (%)	Ref.
1	BiCl ₃ (20)	Solvent-free/110°C	7	96	[29]
2	NaHSO ₄ (10)	Solvent-free/ 90°C	40	88	[27]
3	AcOH /H ₂ SO ₄ (4:1)	H ₂ O/ 80°C	73h	60	[13]
4	<i>p</i> -toluenesulfonic acid (10)	Solvent-free/ 125°C	90	90	[15]
5	RuCl ₃ .nH ₂ O(10)	EtOH/100° C	120	90	[31]
6	DBSA (15)	Toluene/ reflux	20	90	Present work
7	DBSA (15)	SiO ₂ /Solvent-free/ 85°C	8	85	Present work

The reusability of a catalyst is important from economical and environmental points of view. Therefore, we decided to develop a work-up procedure for the recovery and reuse of the catalyst. In this manner, the reaction of benzaldehyde and β -naphthol was chosen as the model reaction. At the end of the reaction (method B) ethyl acetate (20 mL) was added and the mixture was stirred for 10 min, filtered and SiO_2 was separated, then 2 mL aqueous solution of NaHCO_3 (5%) was added to remove the catalyst, the aqueous phase was separated and 1 mL of HCl (37%) was added. Then, the catalyst was extracted with diethyl ether (2 \times 2 mL). The catalyst was obtained after evaporation of solvent. The recovered catalyst was reused for five consecutive times without significant loss of its activity (Table 4). All attempts for recovery of the catalyst from method A were unsuccessful.

Table 4. Reusability of DBSA for the synthesis of 14-phenyl-14H-dibenz [a, j] xanthenes from the method B

Entry	No. of recycles	Yield (%)
1	0	85
2	1	85
3	2	75
4	3	70
5	4	70

4. Conclusions

These studies showed that DBSA, as Brønsted acid catalysts, is an efficient catalyst for the fast preparation of a wide range of 14-substituted dibenzoxanthenes with aromatic and aliphatic aldehydes. Furthermore, these methods (A and B) offer several other advantages such as high conversion, short reaction times, simple experimental and work up procedures. Finally, recovery of DBSA is another advantage of these methods.

Acknowledgments

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