

A DABCO Derived Ionic Liquid Based on Tetrafluoroborate Anion: Preparation, Characterization and Evaluation of its Catalytic Activity in the Synthesis of 14-Aryl-14*H*-dibenzo[*a,j*]xanthenes

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A room-temperature ionic liquid (RTIL) derived from 1,4-diazabicyclo[2.2.2]octane (DABCO) consisting of tetrafluoroborate anion, 1-butyl-4-(4-sulfonylbutyl)-1,4-diazoniabicyclo[2.2.2]octane hydrogen sulfate tetrafluoroborate ([C₄DABCO₄SO₃H][BF₄][HSO₄]) was synthesized and catalytically evaluated in the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes by cyclocondensation reaction of β -naphthol and aryl aldehydes. This novel RTIL with an acidic SO₃H group showed high catalytic activity with good to excellent yields of the desired products in short reaction times. Moreover, the catalyst could be recovered and reused at least three times with only slight reduction in its catalytic activity.

Key Words : Ionic liquid, DABCO, Tetrafluoroborate anion, 14-Aryl-14*H*-dibenzo[*a,j*]xanthenes

Introduction

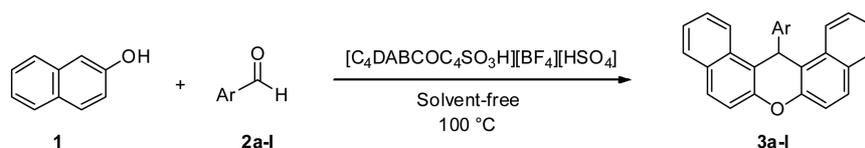
The synthesis of xanthenes and dibenzoxanthenes' derivatives have received significant attention in recent years because of their wide range of biological and pharmaceutical properties such as agricultural bactericide,¹ anti-viral,² anti-bacterial,³ and anti-inflammatory⁴ activities. Also, a number of these compounds have been considered as dyes and fluorescent visualization materials for biomolecules and laser technologies.⁵ There are several methods reported for the synthesis of xanthenes and dibenzoxanthenes, such as palladium catalyzed cyclization of polycyclic aryltriflate esters,⁶ and intramolecular trapping of benzyne by phenols.⁷ Furthermore, 14-aryl-14*H*-dibenzo[*a,j*]xanthenes are generally synthesized by cyclocondensation of β -naphthol with aldehydes in the presence of various catalysts such as silica sulfuric acid,^{8,9} AcOH-H₂SO₄,¹⁰ *p*-TSA,¹¹ MeSO₃H,¹² sulfamic acid,¹³ cyanuric chloride,¹⁴ LiBr,¹⁵ Yb(OTf)₃,¹⁶ and Sc[N(SO₂C₈F₁₇)₂]₃.¹⁷ However, these methods show varying degrees of success as well as limitations such as unsatisfactory yields, expensive catalysts, prolonged reaction times, toxic organic solvents, and harsh reaction conditions. Thus, the development of an alternate milder and clean procedure is highly demanding for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes, which surpasses those limitations.

Ionic liquids (ILs), specially room temperature ILs (RTILs), are known as environmentally benign catalysts or media and much attention has currently been focused on organic reactions in the presence of these compounds as catalysts or as dual catalyst-solvent.¹⁸⁻²⁰ Functionalized ILs are often designed for a particular use, and referred to as "task specific ILs". The introduction of Brønsted-acidic functional groups into cations or anions of the ILs, especially the SO₃H-functional group, obviously enhanced their acidities and water solubilities.²¹⁻²³ Therefore, these ILs can be used as highly

efficient acid catalysts and have been receiving extensive interest as green substitute for H₂SO₄, HF and AlCl₃ catalysts in chemical processes.²⁴ In fact, use of Brønsted-acidic ILs is an area of ongoing activity.

Very recently, the formation of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes in the presence of acidic ionic liquids containing SO₃H-functional group, has been reported in the literature.²⁵⁻²⁷ For example, Hajipour and co-workers²⁵ have reported that synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes can be catalyzed by 15 mol % of *N*-(4-sulfonic acid) butyl triethyl ammonium hydrogen sulfate ([TEBSA][HSO₄]) at 120 °C. Also, some Brønsted-acidic task-specific ILs based on 1-methyl-3-propane sulfonic-imidazolium cation, [MIMPS], with various anions containing HSO₄, H₂PO₄ and BF₄ have been used as catalyst for the synthesis of these compounds by Liu and co-workers.²⁶ The best results have been obtained using 5 mol % of IL containing HSO₄ anion, [MIMPS]-HSO₄, at 100 °C, while use of ILs containing BF₄ and H₂PO₄ anions, [MIMPS]BF₄ and [MIMPS]H₂PO₄, gave the target compound in lower yield and longer time. On the other hand, there are several reports that show ILs containing BF₄ anion play a role as promotor or reaction media and accelerate the organic reaction rates.²⁸

These finding prompted us towards further investigation in search for a new SO₃H-functionalized IL containing BF₄ anion, which will carry out the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes under simple experimental set up and eco-friendly conditions. Therefore, as part of our current studies on the development of new routes for the synthesis of organic compounds using ILs,²⁹ herein firstly we report the synthesis of a RTIL derived from 1,4-diazabicyclo[2.2.2]octane (DABCO) consisting of BF₄ anion, 1-butyl-4-(4-sulfonylbutyl)-1,4-diazoniabicyclo[2.2.2]octane hydrogen sulfate tetrafluoroborate ([C₄DABCO₄SO₃H][BF₄][HSO₄]) (Figure 1) and then investigate its catalytic activity in the



Scheme 1. Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes catalyzed by [C₄DABCOC₄SO₃H][BF₄][HSO₄].

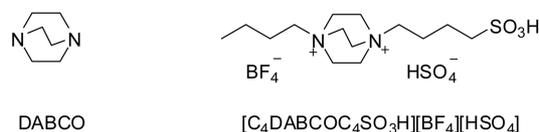


Figure 1. DABCO and DABCO based SO₃H-functionalized IL structure.

synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes by cyclocondensation reaction of β -naphthol and aryl aldehydes (Scheme 1).

Experimental

All chemicals were available commercially and used without additional purification. Melting points were recorded on a Stuart SMP3 melting point apparatus. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. The ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded with a Bruker DRX500 spectrometer. Mass spectra were also obtained using a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV.

Preparation of the Catalyst [C₄DABCOC₄SO₃H][BF₄][HSO₄]. A mixture of [C₄DABCO][BF₄]^{30a} (3 mmol) and 1,4-butane sultone (3 mmol) in toluene (10 mL) was heated under reflux for 1 h until it turned into solid. The obtained solid was washed repeatedly with ethyl acetate, filtrated to remove non-ionic residues and dried in a vacuum oven to give the white solid zwitterion, [C₄DABCOC₄SO₃][BF₄], in 92 % yield. The structure of the zwitterion was confirmed by ¹H NMR, ¹³C NMR, MASS, and FT-IR spectral data.

[C₄DABCOC₄SO₃][BF₄]: mp 314-316 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 0.93 (t, 3H, *J* = 6.8 Hz, CH₃), 1.31 (sex, 2H, *J* = 6.9 Hz, CH₂), 1.55-1.75 (m, 4H, CH₂), 1.77-1.90 (m, 2H, CH₂), 2.54 (t, 2H, *J* = 6.8 Hz, CH₂), 3.40-3.60 (m, 4H, N-CH₂), 3.84 (s, 12H, N-CH₂); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 14.27, 19.85, 21.09, 22.69, 24.09, 25.20, 50.96, 51.26, 63.99, 64.30; MS, *m/z* 392 (M⁺); IR (KBr disc): ν 3018, 2960, 2879, 1627, 1474, 1419, 1236, 1170, 1038.

Then, a stoichiometric amount of concentrated sulfuric acid (98%) was added dropwise to [C₄DABCOC₄SO₃][BF₄], and the mixture was heated in the oil bath at 80 °C for 6 h. The produced liquid was washed with diethyl ether and dried *in vacuo* to get the viscous clear light yellow IL, [C₄DABCOC₄SO₃H][BF₄][HSO₄]. The structure of the IL was confirmed by ¹H NMR, ¹³C NMR, MASS, and FT-IR spectral data.

[C₄DABCOC₄SO₃H][BF₄][HSO₄]: ¹H NMR (500 MHz, DMSO-*d*₆) δ 0.87 (t, 3H, *J* = 7.3 Hz, CH₃), 1.25 (sex, 2H, *J*

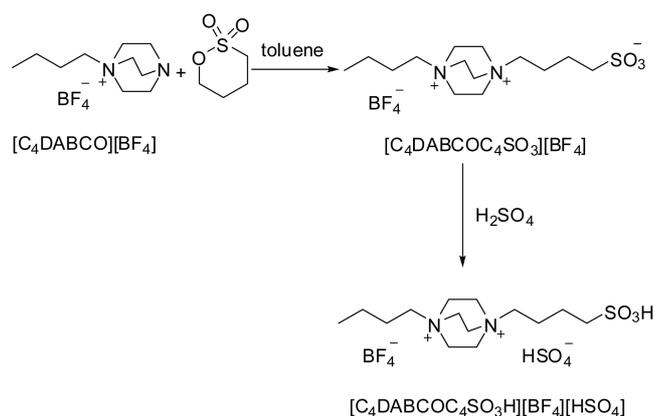
= 7.3 Hz, CH₂), 1.55-1.68 (m, 4H, CH₂), 1.77 (quin, 2H, *J* = 7.5 Hz, CH₂), 2.61 (t, 2H, *J* = 7.4 Hz, CH₂), 3.40-3.55 (m, 4H, N-CH₂), 3.85 (s, 12H, N-CH₂), 9.89 (s, 2H, OH); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 13.79, 19.33, 20.66, 21.89, 23.25, 23.58, 50.54, 50.76, 63.54, 63.81; MS, *m/z* 490 (M⁺); IR (KBr disc): ν 3346, 2968, 1719, 1606, 1470, 1235, 1054, 853, 580.

General Procedure for the Synthesis of 14-Aryl-14*H*-dibenzo[*a,j*]xanthenes 3a-I Using [C₄DABCOC₄SO₃H][BF₄][HSO₄] as Catalyst. A mixture of β -naphthol **1** (4 mmol), aromatic aldehyde **2a-I** (2 mmol), and [C₄DABCOC₄SO₃H][BF₄][HSO₄] (0.06 mmol, 3 mol % based on aromatic aldehyde) was heated in the oil bath at 100 °C for 10-20 min. During the procedure, the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature, the obtained solid was washed with water, and recrystallized from ethanol to give pure products **3a-I** in high yields.

Recycling and Reusing of the Catalyst. The catalyst [C₄DABCOC₄SO₃H][BF₄][HSO₄] is soluble in water and could therefore be recycled as the filtrate. The catalyst was recovered by evaporation of the water, washed with diethyl ether, dried at 50 °C under vacuum for 1 h, and reused in another reaction with only slight reduction in the catalytic activity.

Results and Discussion

There are few reports in the literature on the synthesis of DABCO-based ILs and their application in organic reactions.³⁰ Hence, we decided to synthesize a new DABCO based SO₃H-functionalized IL containing BF₄ anion and investigate its catalytic performance in the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes. For this purpose, firstly, the IL [C₄DABCO][BF₄]^{30a} was reacted with 1,4-butane sultone in refluxing toluene to form a white solid zwitterion [C₄DABCOC₄SO₃][BF₄]. The structure of this zwitterion was characterized by ¹H NMR, ¹³C NMR, MASS, and FT-IR spectral data. The ¹H NMR spectrum in *d*₆-DMSO shows 7 signals at δ 0.93 (t, 3H), 1.31 (sex, 2H), 1.55-1.75 (m, 4H), 1.77-1.90 (m, 2H), 2.54 (t, 2H), 3.40-3.60 (m, 4H), 3.84 (s, 12H) ppm. Also, ¹³C NMR spectrum with 10 signals at δ 14.27, 19.85, 21.09, 22.69, 24.09, 25.20, 50.96, 51.26, 63.99, and 64.30 ppm confirms the structure of this compound. Furthermore, the molecular ion of this compound was observed at *m/z* 392 (M⁺) corresponding to the molecular formula C₁₄H₂₉BF₄N₂O₃S. The significant absorption bands in FT-IR spectrum has been reported in experimental section. The zwitterion acidification was then accomplished



Scheme 2. Synthesis of $[C_4DABCOC_4SO_3H][BF_4][HSO_4]$.

by mixing of zwitterion with a stoichiometric amount of concentrated sulfuric acid to give the viscous clear IL identified as $[C_4DABCOC_4SO_3H][BF_4][HSO_4]$ (Scheme 2). Characterization of this new acidic IL was also performed by 1H NMR, ^{13}C NMR, MASS, and FT-IR spectral data. The 1H NMR spectrum in d_6 -DMSO showed the signals at δ 0.87 (t, 3H), 1.25 (sex, 2H), 1.55-1.68 (m, 4H), 1.77 (quin, 2H), 2.61 (t, 2H), 3.40-3.55 (m, 4H), 3.85 (s, 12H) and 9.89 (s, 2H) ppm that is in accordance with the structure of $[C_4DABCOC_4SO_3H][BF_4][HSO_4]$. Further proof came from ^{13}C NMR spectrum which showed 10 signals at δ 13.79, 19.33, 20.66, 21.89, 23.25, 23.58, 50.54, 50.76, 63.54 and 63.81 ppm. Also, the molecular ion of this compound was observed as a weak peak at m/z 490 (M^+) corresponding to the molecular formula $C_{14}H_{31}BF_4N_2O_7S_2$. The significant absorption bands in FT-IR spectrum has been reported in experimental section.

Finally, in order to evaluate the catalytic activity of $[C_4DABCOC_4SO_3H][BF_4][HSO_4]$ in the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes, at first, the synthesis of compound **3e** was selected as a model reaction to determine suitable reaction conditions. The reaction was carried out by heating a mixture of β -naphthol (**1**) (4 mmol) and 4-chlorobenzaldehyde (**2e**) (2 mmol) in the presence of $[C_4DABCOC_4SO_3H][BF_4][HSO_4]$ in different solvents and under solvent-free conditions (Table 1). As can be seen from Table 1, the shortest time and best yield was achieved in solvent-free conditions (entry 9). It was also found that the yield of compound **3e** was strongly affected by the catalyst amount and reaction temperature in solvent-free conditions. No product was obtained in the absence of the catalyst (entry 1) and only a trace amount of the product was obtained in the presence of the catalyst at room temperature (entry 5) indicating that the catalyst and temperature are necessary for the reaction. Increasing the amount of the catalyst and reaction temperature up to 3 mol % (based on 4-chlorobenzaldehyde) and 100 °C, respectively, increased the yield of the product **3e**, whereas further increase in both catalyst amount and temperature was found to have an inhibitory effect on the formation of the product (entries 10-14).

Table 1. Effect of $[C_4DABCOC_4SO_3H][BF_4][HSO_4]$ amount, solvent and temperature on the model reaction^a

Entry	Catalyst (mol %)	Solvent	T (°C)	Time (min)	Yield (%) ^b
1	None	Solvent-free	100	100	None
2	1	Solvent-free	90	20	70
3	1	Solvent-free	100	20	77
4	1	Solvent-free	120	20	77
5	3	Solvent-free	rt	60	14
6	3	Solvent-free	50	60	31
7	3	Solvent-free	70	30	55
8	3	Solvent-free	90	20	80
9	3	Solvent-free	100	10	95
10	3	Solvent-free	120	10	89
11	6	Solvent-free	100	10	90
12	6	Solvent-free	120	10	84
13	12	Solvent-free	100	10	85
14	12	Solvent-free	120	10	80
15	3	H ₂ O	Reflux	30	15
16	3	MeOH	Reflux	30	30
17	3	EtOH	Reflux	30	38
18	3	CH ₃ CN	Reflux	30	40
19	3	CHCl ₃	Reflux	30	80

^a4 mmol β -naphthol and 2 mmol 4-chlorobenzaldehyde. ^bThe yields were calculated based on 4-chlorobenzaldehyde and refer to the pure isolated product.

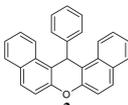
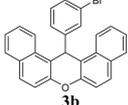
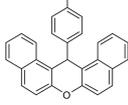
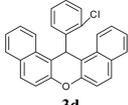
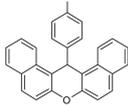
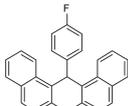
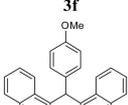
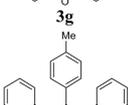
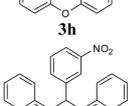
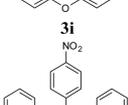
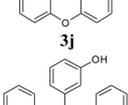
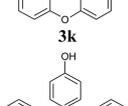
In order to evaluate the general character of this model reaction, we extended the reaction of **1** with other aromatic aldehydes under the optimized reaction conditions. The results are given in Table 2. In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the expected products in high yields and short reaction times.

Reusability of the catalyst $[C_4DABCOC_4SO_3H][BF_4][HSO_4]$ was also investigated. For this purpose, the same model reaction was again studied under optimized conditions. After the completion of the reaction, the catalyst was recovered according to the procedure mentioned in experimental section and reused for a similar reaction. The catalyst could be used at least three times with only slight reduction in the catalytic activity (95% for 1st use; 94% for 2nd use; 91% for 3rd use).

Conclusion

In conclusion, a DABCO based SO_3H -functionalized IL containing BF_4^- anion, $[C_4DABCOC_4SO_3H][BF_4][HSO_4]$, was synthesized and characterized by 1H NMR, ^{13}C NMR, MASS and FT-IR spectral data. The performance of this IL, as catalyst or reaction media, in the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes was also evaluated. It was found that the synthesized IL is very efficient catalyst and media obtaining high yields of the desired products in short reaction times. Moreover, the catalyst could be recovered

Table 2. [C₄DABCO][C₄SO₃H][BF₄][HSO₄] catalyzed synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes **3a-l**^a

Entry	Ar	Products ^b	Time (min)	Yields (%) ^c	mp (°C)	
					Found	Reported
1	C ₆ H ₅	 3a	15	90	195-196	182-183 ^{20b}
2	3-BrC ₆ H ₄	 3b	10	90	197-200	190-192 ^{20c}
3	4-BrC ₆ H ₄	 3c	10	95	296-298	295-296 ^{20b}
4	2-ClC ₆ H ₄	 3d	10	90	217-220	214-215 ^{20b}
5	4-ClC ₆ H ₄	 3e	10	95	293-295	289-290 ^{20c}
6	4-FC ₆ H ₄	 3f	10	89	250-253	239-240 ^{20b}
7	4-MeOC ₆ H ₄	 3g	20	85	208-211	202-203 ^{20b}
8	4-MeC ₆ H ₄	 3h	15	87	235-237	227-229 ^{20c}
9	3-O ₂ NC ₆ H ₄	 3i	10	93	227-229	210-211 ^{20b}
10	4-O ₂ NC ₆ H ₄	 3j	10	88	320-322	310-311 ^{20b}
11	3-HOC ₆ H ₄	 3k	15	78	250-252	242-243 ^{20b}
12	4-HOC ₆ H ₄	 3l	15	80	147-150	139-140 ^{20b}

^a4 mmol β-naphthol, 2 mmol aryl aldehyde, and 3 mol % (based on aryl aldehyde) [C₄DABCO][C₄SO₃H][BF₄][HSO₄] at 100 °C under solvent-free conditions. ^bAll the products were characterized by IR spectral data and comparison of their melting points with those of authentic samples. Also, the structures of some products were confirmed by ¹H NMR spectral data. ^cThe yields were calculated based on aryl aldehyde and refer to the pure isolated product.

and reused at least three times with only slight reduction in its catalytic activity. Further applications of this IL for other reaction systems are currently under investigation.

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