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NOVEL IONIC LIQUID [Et_3N-SO_3H][$MeSO_3$]: SYNTHESIS, CHARACTERIZATION AND CATALYTIC PERFORMANCE FOR THE SYNTHESIS OF 14-ARYL-14*H*-DIBENZO[*A,J*]XANTHENES

Masoud Sadeghi-Takallo and Abdolkarim Zare*

Department of Chemistry, Payame Noor University, PO BOX 19395-3697, Tehran, Iran

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ABSTRACT. The main aim of this work is introducing a novel protic acidic ionic-liquid catalyst for organic synthesis. Thus, *N*,*N*-diethyl-*N*-sulfoethanaminium methanesulfonate ([Et_3N-SO_3H][$MeSO_3$]) was synthesized by the reaction of triethylamine with chlorosulfonic acid, and then with methanesulfonic acid. The structure of this novel protic acidic ionic liquid was identified by FT-IR, ^1H NMR, ^{13}C NMR and mass spectral data. Its catalytic activity was examined for the solvent-free reaction of 2-naphthol with arylaldehydes to provide 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes. [Et_3N-SO_3H][$MeSO_3$] efficiently catalyzed the reaction, and the products were obtained in high to excellent yields and in short reaction times.

KEY WORDS: Protic acidic ionic liquid, *N*,*N*-Diethyl-*N*-sulfoethanaminium methanesulfonate ([Et_3N-SO_3H][$MeSO_3$]), 2-Naphthol, Arylaldehyde, 14-Aryl-14*H*-dibenzo[*a*,*j*]xanthene

INTRODUCTION

Ionic liquids (ILs) are an attractive group of organic compounds which have ionic structure (contain cation and anion), and have been extensively utilized as eco-friendly solvents, reagents and catalysts in organic synthesis. Non-flammability, non-volatility, structural designability, thermal and chemical stability, ability to dissolve a wide range of chemicals and wide liquid range are some of ILs benefits [1-8]. Among the subgroups of ILs (neutral, basic and acidic), protic acidic ones have been especially applied as catalysts to promote organic transformations [3-8].

A useful and practical technique, which is in accordance with green chemistry protocols, is solvent-free conditions. This technique has several advantages with respect to the classical synthetic procedures, which consist of: (i) higher yield of product, (ii) shorter reaction time, (iii) safer reaction profile, (iv) easier workup, (v) higher selectivity in many reactions, (vi) fewer energy requirement to promote reaction, (vii) maximum incorporation of the starting materials into the aim product, (viii) prevention or minimization of waste/by-products, and (ix) avoidance of using harmful and volatile organic solvents [9-11].

Xanthene derivatives, as a significant group of oxygen-containing heterocyclic compounds, have attracted much interest in chemistry, medicinal chemistry and industry. These compounds have different pharmacological properties; e.g. antiviral [12], antitumor [13], and anti-inflammatory [14] activities. Xanthenes possess various applications in industry; e.g. they have been used as luminescent sensors [15], as dyes [16], and in laser technology [17]. Consequently, introducing efficient methods for production of this class of heterocycles using novel and attractive catalysts is practically important. An important subgroup of xanthene derivatives is 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes which produce by the reaction of 2-napthol with arylaldehydes using a catalyst [18-27].

In this research, we wish to introduce a novel protic acidic ionic-liquid catalyst for organic synthesis. To reach this goal, we have synthesized *N*,*N*-diethyl-*N*-sulfoethanaminium

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*Corresponding author. E-mail: abdolkarimzare@pnu.ac.ir methanesulfonate ([Et_3N-SO_3H][$MeSO_3$]), and characterized it by means of FT-IR, ^1H NMR, ^{13}C NMR and mass spectra. Then, we have successfully applied the ionic liquid as an efficient catalyst for the solvent-free reaction of 2-naphthol with arylaldehydes to provide 14-aryl-14*H*-dibenzo[*a,j*]xanthenes.

EXPERIMENTAL

All chemicals were purchased from Fluka or Merck Chemical Companies. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by thin layer chromatography (TLC). The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The ^1H NMR (250, 300 or 400 MHz) and ^{13}C NMR (62.5, 75 or 100 MHz) were run on a Bruker Avance DPX, FT-NMR spectrometers, δ in ppm. Mass spectra were obtained with Shimadzu GC–MS-QP 1100 EX model.

Procedure for the synthesis of [Et_3N-SO_3H][$MeSO_3$]

A solution of triethylamine (0.50 g, 5 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise to a stirring solution of chlorosulfonic acid (0.58 g, 5 mmol) in dry CH_2Cl_2 (20 mL) over a period of 10 min at 10 °C. Afterward, the reaction mixture was stirred at room temperature for 4 h. The solvent was evaporated, and the liquid residue was triturated with *t*-butylmethyl ether (3×10 mL) and dried under vacuum at 90 °C to give [Et_3N-SO_3H]Cl as a viscous pale yellow oil in 93% yield [7]. Then, methanesulfonic acid (0.481 g, 5 mmol) was added dropwise to [Et_3N-SO_3H]Cl (1.089 g, 5 mmol) over a period of 5 min at room temperature under pressure of nitrogen gas (to remove HCl produced during the reaction). The resulting mixture was stirred for 10 h at room temperature and 2 h at 60 °C under a continuous flow of nitrogen gas to give [Et_3N-SO_3H][$MeSO_3$] as a viscous pale yellow oil in 99% yield. IR (KBr) ν: 881, 1045, 1173, 1469, 2841, 2300-3500 cm^{-1}. ^1H NMR (250 MHz, DMSO-d_6) δ_H: 1.31 (9H, t, J = 7.5 Hz), 2.63 (3H, s), 3.22 (6H, q, J = 7.5 Hz), 9.19 (1H, br.). ^{13}C NMR (125 MHz, DMSO-d_6) δ_C: 9.0, 40.1, 46.3. Mass *m/z*: 277 (M^+).

General procedure for the preparation of 14-aryl-14H-dibenzo[a,j]xanthenes

A mixture of aldehyde (1 mmol), 2-naphthol (2 mmol, 0.288 g) and [Et_3N-SO_3H][$MeSO_3$] (0.25 mmol, 0.069 g) was stirred by a small glass rod at 110 °C. After the reaction was completed (as monitored by TLC), the reaction mixture was cooled to room temperature, and the resulting precipitate was recrystallized from ethanol (95%) to give the pure product.

Selected spectroscopic data of 14-aryl-14H-dibenzo[a,j]xanthenes

*14-Phenyl-14H-dibenzo[a,j]xanthene (**1**).* ^1H NMR (400 MHz, DMSO-d_6) δ_H: 6.74 (1H, s), 6.97 (1H, t, J = 7.6 Hz), 7.14 (2H, t, J = 7.6 Hz), 7.45 (2H, t, J = 7.2 Hz), 7.57 (2H, d, J = 8.8 Hz), 7.62-7.66 (4H, m), 7.91-7.93 (4H, m), 8.70 (2H, d, J = 8.8 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 37.0, 117.9, 118.2, 123.9, 124.9, 126.7, 127.4, 128.4, 128.8, 129.1, 129.5, 131.1, 131.4, 146.0, 148.5.

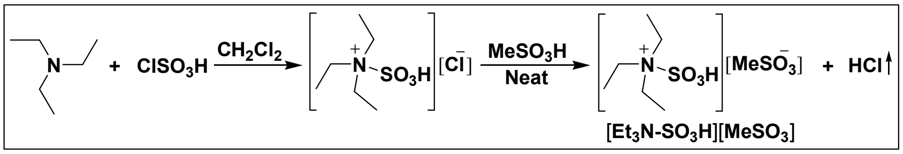
*14-(2-Nitrophenyl)-14H-dibenzo[a,j]xanthene (**4**).* ^1H NMR (300 MHz, DMSO-d_6) δ_H: 6.94 (1H, s), 7.41-7.46 (3H, m), 7.56-7.65 (4H, m), 7.79 (1H, d, J = 2.1 Hz), 7.89-7.94 (4H, m), 8.13 (1H, d, J = 7.8 Hz), 8.45 (1H, s), 8.70 (2H, d, J = 6.0 Hz). ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 36.4, 116.9, 118.1, 122.0, 122.5, 123.6, 125.2, 127.7, 129.1, 130.0, 130.4, 131.1, 134.7, 138.2, 147.9, 148.3, 148.6.

*14-(3-Chlorophenyl)-14H-dibenzo[a,j]xanthene (**6**).* ^{1}H NMR (300 MHz, DMSO-d$_6$) δ_H: 6.74 (1H, s), 7.01 (1H, d, J = 8.1 Hz), 7.13 (1H, t, J = 7.8 Hz), 7.42 (2H, t, J = 7.2 Hz), 7.52-7.66 (6H, m), 7.91 (4H, d, J = 8.7 Hz), 8.67 (2H, d, J = 8.7 Hz). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 36.5, 117.2, 118.1, 123.7, 125.1, 126.8, 127.0, 127.5, 127.9, 129.1, 129.7, 130.7, 131.1, 131.2, 133.5, 148.2, 148.5.

*14-(4-Methylphenyl)-14H-dibenzo[a,j]xanthene (**9**).* ^{1}H NMR (300 MHz, DMSO-d$_6$) δ_H: 2.01 (3H, s), 6.63 (1H, s), 6.90 (2H, d, J = 7.2 Hz), 7.40-7.61 (8H, m), 7.88 (4H, t, J = 2.7 Hz), 8.61 (2H, d, *J* = 8.7 Hz). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 20.8, 37.4, 117.9, 118.1, 123.8, 124.9, 127.3, 128.2, 129.0, 129.3, 129.3, 131.1, 131.3, 135.8, 143.0, 148.3.

RESULTS AND DISCUSSION

To develop our researches on the production and catalytic application of a new class of acidic ILs in which a SO_3H group bonded to a positive tertiary nitrogen [5-8], we have prepared a novel member of this ILs, namely *N*,*N*-diethyl-*N*-sulfoethanaminium methanesulfonate ([Et_3N-SO_3H][$MeSO_3$]), according to Scheme 1.



Scheme 1. The synthesis of [Et_3N-SO_3H][$MeSO_3$].

Characterization of the ionic liquid was achieved by studying its FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectral data; the corresponding data have been reported in the experimental section. The FT-IR data verified presence of the expected functional groups and bonds in [Et_3N-SO_3H][$MeSO_3$] (Table 1).

Table 1. The IR data of [Et_3N-SO_3H][$MeSO_3$].

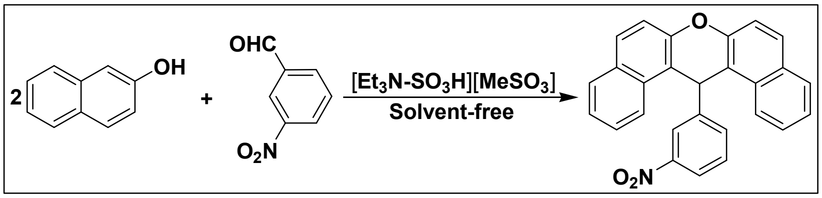
Peak (cm^{-1})	Related functional group or bond
881	Symmetric N-S stretching vibration
1045	Bending of S-OH
1173	Stretching of S=O in methanesulfonate
1469	Bending of C-H
2841	Stretching of C-H
2300-3500	OH group of the SO_3H

In the ^{1}H NMR spectrum of [Et_3N-SO_3H][$MeSO_3$], the peak corresponded to nine hydrogens of the three methyl groups was observed at 1.31 ppm as triplet. The peak appeared at 2.63 ppm as singlet is related to the methyl group of metanesulfonate. The peak related to six hydrogens of the three methylene groups appeared at 3.22 ppm as a quartet. The peak pertaining to the acidic hydrogen was seen at 9.19 ppm.

In the ^{13}C NMR spectrum, three peaks observed at 9.0, 40.1 and 46.3 ppm are related to the carbons of CH_3 of ethyl, CH_3 of methanesulfonate and CH_2, correspondingly.

The mass spectrum of the [Et_3N-SO_3H][$MeSO_3$] showed the peak related to molecular mass [M^+] at *m/z* 277. In addition, the negative mode of mass spectrum showed the peaks corresponded to [M^+], [$M^+ + 1$] and [$M^+ + 2$] of the anion (methanesulfonate) at *m/z* 95, 96 and 97, respectively.

After that the ionic liquid was characterized, its catalytic activity was studied for the production of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes. With the aim of optimizing the reaction conditions, the condensation of 2-naphthol with *m*-nitrobenzaldehyde (Scheme 2) was checked in the presence of various amounts (15-27 mol%) of [Et_3N-SO_3H][$MeSO_3$] at a range of 100-115 °C under solvent-free conditions and also in some solvents; the results are summarized in Table 2. As this Table indicates, the best results were obtained when the reaction was carried out using 25 mol% of the catalyst at 110 °C in the absence of solvent (Table 2, entry 3). The reaction was also examined in the presence of the reactants for the preparation of the catalyst (Table 2, entries 10-12); however, the reaction results were better when [Et_3N-SO_3H][$MeSO_3$] was applied as catalyst. Thus, our program for the synthesis of [Et_3N-SO_3H][$MeSO_3$] was logical.



Scheme 2. The model reaction.

Table 2. Effect of the catalyst amount and temperature on the reaction of 2-naphthol with *m*-nitrobenzaldehyde.

Entry	Catalyst	Solvent	Mol% of catalyst	Temp. (ºC)	Time (min)	Yield[a] (%)
1	[Et_3N-SO_3H][$MeSO_3$]	Solvent-free	15	110	75	77
2	[Et_3N-SO_3H][$MeSO_3$]	Solvent-free	20	110	70	83
3	[Et_3N-SO_3H][$MeSO_3$]	Solvent-free	25	110	55	98
4	[Et_3N-SO_3H][$MeSO_3$]	Solvent-free	27	110	55	98
5	[Et_3N-SO_3H][$MeSO_3$]	Solvent-free	25	100	70	86
6	[Et_3N-SO_3H][$MeSO_3$]	Solvent-free	25	115	55	98
7	[Et_3N-SO_3H][$MeSO_3$]	EtOH	25	Reflux	120	35
8	[Et_3N-SO_3H][$MeSO_3$]	EtOAc	25	Reflux	120	16
9	[Et_3N-SO_3H][$MeSO_3$]	DMF	25	110	60	73
10	[Et_3N-SO_3H][Cl]	Solvent-free	25	110	60	91
11	$MeSO_3H$	Solvent-free	25	110	75	87
12	$ClSO_3H$	Solvent-free	25	110	70	90

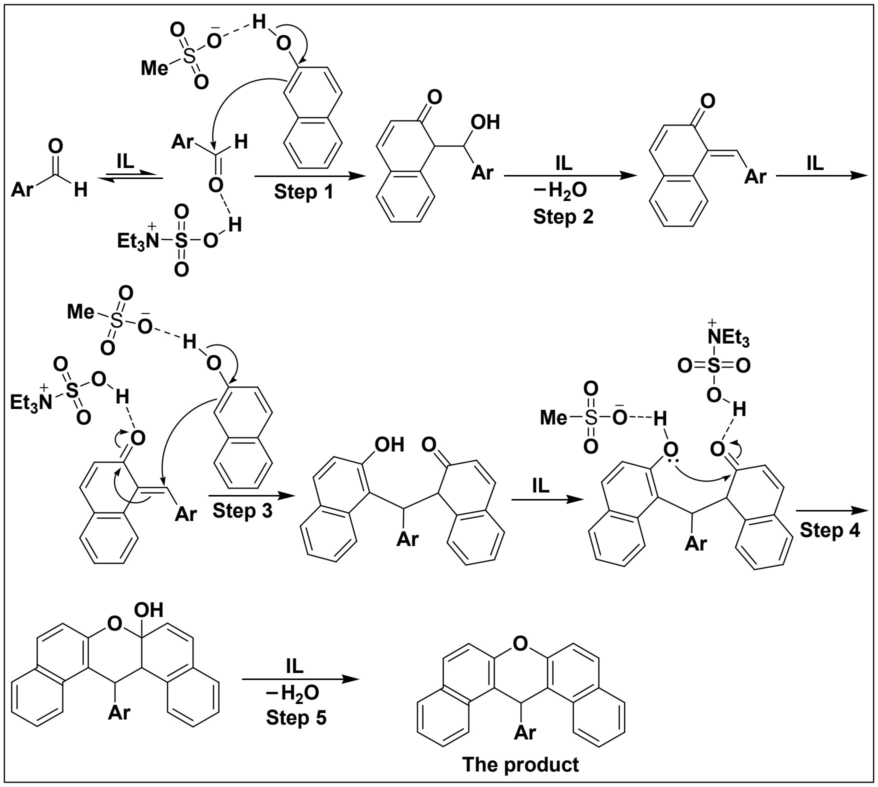
[a] Isolated yield.

After optimizing the reaction conditions, effectiveness and scope of the catalyst were evaluated by examining the reaction of various arylaldehydes with 2-naphthol; the results are demonstrated in Table 3. As it can be seen in this Table, all aldehydes (benzaldehyde and arylaldehydes bearing electron-withdrawing, halogen or electron-donating substituents) afforded the relevant products in high to excellent yields and in short reaction times; these excellent results showed high efficacy and generality of [Et_3N-SO_3H][$MeSO_3$] to catalyze the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes.

Table 3. The production of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes using [Et_3N-SO_3H][$MeSO_3$].

Product No.	Ar	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
1	C_6H_5	35	96	180-182 (181-184) [22]
2	*p*-$O_2NC_6H_4$	45	97	312-314 (313-315) [26]
3	*m*-$O_2NC_6H_4$	55	98	209-211 (208-210) [19]
4	*o*-$O_2NC_6H_4$	55	95	215-217 (212-214) [21]
5	*p*-ClC_6H_4	60	98	291-293 (288-289) [23]
6	*m*-ClC_6H_4	55	95	210-212 (207-209) [21]
7	*o*-ClC_6H_4	35	93	214-216 (215-216) [26]
8	*p*-BrC_6H_4	55	97	296-298 (296-297) [26]
9	*p*-MeC_6H_4	30	95	226-228 (226) [19]
10	*p*-$MeOC_6H_4$	45	95	199-201 (200-202) [21]
11	2,4-$Cl_2C_6H_3$	40	94	251-253 (252-253) [28]
12	3,4-$(MeO)_2C_6H_3$	45	97	196-198 (198-199) [28]

[a] Isolated yield.



Scheme 3. The proposed mechanism for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes.

In fact, our novel ionic liquid (IL) is a dual-functional catalyst, because it has both acidic and basic sites (SO_3H group is acidic, and methanesulfonate is basic); this subject has been reported for another member of this class of ILs [6]. So, $[Et_3N\text{-}SO_3H][MeSO_3]$ can particularly apply as a highly effectual and general catalyst for reactions which need to both acidic and basic catalysts simultaneously; e.g. the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes; this issue is shown in the mechanism (Scheme 3). The SO_3H group activates the carbonyl groups (electrophiles) to accept nucleophilic attacks (steps 1, 3 and 4); the acidic group also accelerates removing H_2O from the intermediates *via* hydrogen bonding with OH groups (steps 2 and 5). In the other hand, the methanesulfonate anion can speed up steps 1, 3 and 4 by activating the nucleophiles; this basic site also accelerates removal of H_2O from the intermediates by assistance to abstracting a proton (steps 2 and 5). The mechanism is supported by the literature [6, 21, 26].

CONCLUSION

In summary, we have reported synthesis, characterization and catalytic performance of a novel protic acidic ionic liquid in organic synthesis. $[Et_3N\text{-}SO_3H][MeSO_3]$ successfully catalyzed the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes; the benefits of this method include effectiveness, generality, high yields, short reaction times, easy purification of the products, simple synthesis of the catalyst from easy-available reactants, and application of solvent-free conditions in the reaction.

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