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Brønsted Acidic Ionic Liquid-Catalyzed Synthesis of 14-Aryl-14*H*-dibenzo[*a*,*j*]xanthenes with Controlled Microwave Heating under Solvent-Free Conditions

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Abstract—1-Methyl-3-sulfo-1*H*-imidazol-3-ium chloride ([Msim]Cl) catalyzed the condensation of β-naphthol with aromatic aldehydes under microwave irradiation. This method is efficient to synthesize dibenzoxanthene derivatives in excellent yields, and the catalyst can be reused up to three times without significant loss of activity.

Keywords: benzoxanthene, β-naphthol, Brønsted acidic ionic liquids, microwave irradiation

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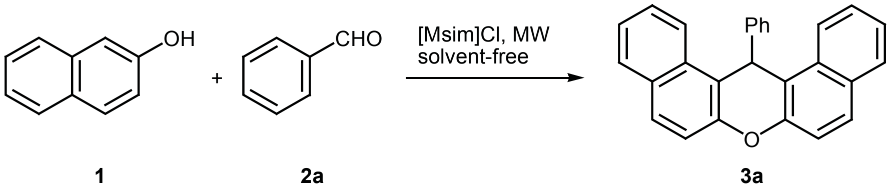
Ionic liquids have recently attracted considerable attention from chemists due to their unique properties such as nonvolatility, non-inflammability, wide range of liquefaction, high thermal stability, and recyclability [1–3]. Recently, increasing interest in ionic liquids has focused on designing Brønsted acidic ionic liquids to replace traditional Brønsted acids such as H_2SO_4, HCl, HNO_3, and H_3PO_4 in organic syntheses. Brønsted acidic ionic liquids constitute one of the most useful classes of ionic liquids capable of acting as solvent and catalyst in organic reactions [4, 5]. Benzoxanthenes are important organic compounds possessing a wide range of biological, therapeutic, and other applications (e.g., as dyes) [6–12]. The existing methods for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes involve the condensation of β-naphthol with aldehydes in the presence of a Brønsted or Lewis acid as catalyst, such as AcOH [13], molecular iodine [14], $KAl(SO_4)_2{\cdot}12H_2O$ [15], metal triflates [16–18], $Fe(HSO_4)_3$ [19], silica-supported Brønsted acids [20–22], $InCl_3$ [23], ruthenium complex [24], ionic liquids [25, 26], PEG-SO_3H [27], mesoporous zirconia [28], sulfonated carbon nanotubes [29], graphene oxide [30], H_3PO_4/Al_2O_3 [31], $NbCl_2$ [32], and many others. Although these synthetic approaches were useful developments, some of them suffer from disadvantages such as low yield, long reaction time, expensive catalyst, or harsh reaction conditions. Consequently, the development of more convenient, economical, and eco-friendly methodology for the synthesis of dibenzoxanthenes is highly desirable. In continuation of our interest in the development of new synthetic methods, we report herein an efficient and facile procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes by reacting β-naphthol with various aromatic aldehydes in the presence of a Brønsted acidic ionic liquid, 1-methyl-3-sulfo-1*H*-imidazol-3-ium chloride [Msim]Cl, under solvent-free microwave irradiation. This is the first application of microwave irradiation in the synthesis of dibenzoxanthenes catalyzed by [Msim]Cl ionic liquid.

1-Methyl-3-sulfo-1*H*-imidazol-3-ium chloride [Msim]Cl was prepared by reacting 1-methyl-1*H*-imidazole with chlorosulfonic acid without a solvent under microwave irradiation at 60°C (20 min). The yield of [Msim]Cl was 94% (Scheme 1). This method provided a higher yield within a shorter reaction time than those reported for the existing methods [33].

Herein we describe a green and straightforward method for the preparation of dibenzoxanthene derivatives from β-naphthol (**1**, 2 mmol) and a number of substituted benzaldehydes (1 mmol) under solvent-free

Scheme 1.

Scheme 2.



conditions. The reaction conditions were optimized using the reaction of **1** with benzaldehyde (**2a**) as a model (Scheme 2); the results are presented in Table 1. First, the influence of catalyst loading was studied. It was found that 15 mol % of [Msim]Cl was sufficient for the formation of dibenzoxanthene **3a** in a high yield. The optimal temperature was found to be 120°C; in this case, the complete conversion was achieved in 30 min. All attempts to carry out the reaction in other conditions led to diminished yields. Furthermore, [Msim]Cl catalyzed the formation of 14-phenyl-14*H*-dibenzo[*a*,*j*]xanthene (**3a**) with a higher yield and in a shorter time than did other catalysts used for the preparation of dibenzoxanthenes, such as $KAl(SO_4)_2 \cdot 12H_2O$ [15], $Yb(OTf)_3$/[BPy]BF_4 [17], and [Hmim]HSO_4 [34].

Under the optimal conditions, the scope of the proposed synthetic protocol was investigated by reacting β-naphthol with a wide range of aromatic aldehydes **2a**–**2n** to afford the corresponding 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes **3a**–**3n** (Scheme 3) in excellent yields 80–96% under microwave irradiation (30 min). The results are summarized in Table 2. Aldehydes with electron-withdrawing groups or halogens (Table 2, entry nos. 2–10) provided better yields than those bearing electron-donating groups (Table 2, entry nos. 11–14) under the same conditions. The reactivity of mono-substituted benzaldehydes can be ranked as follows: chlorobenzaldehyde > nitrobenzaldehyde > fluorobenzaldehyde ≈ bromobenzaldehyde > *tert*-butylbenzaldehyde > methylbenzaldehyde > methoxybenzaldehyde. In addition, the yield from *ortho*-substituted aromatic aldehydes was generally lower than from the corresponding *meta* or *para* isomer, presumably due to the steric effect. The synthesis of 14-phenyl-14*H*-dibenzo[*a*,*j*]xanthene (**3a**) was also carried out in the presence of 15 mol % of [Msim]Cl under conventional heating at 120°C. The product was obtained in 90% yield after 150 min. Thus, microwave activation improves the yield and shortens the reaction time.

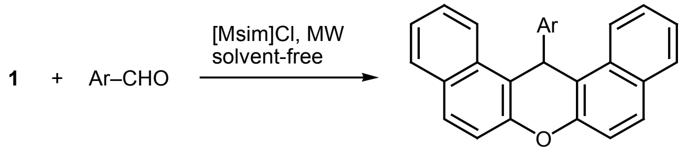
The same model reaction was employed to estimate the reusability of [Msim]Cl. After each reaction cycle, the catalyst was recovered by a simple workup procedure and then re-subjected to the next cycle without further purification (the ^{1}H and ^{13}C NMR spectral data

Table 1. Optimization of the reaction conditions

Entry no.	Temperature, °C	Time, min	Molar ratio **1**:PhCHO:[Msim]Cl	Yield,[a] %
1	100	20	2:1:0.15	63
2	100	30	2:1:0.15	68
3	100	60	2:1:0.15	76
4	110	20	2:1:0.15	75
5	110	30	2:1:0.15	80
6	110	60	2:1:0.15	85
7	120	20	2:1:0.15	82
8	120	30	2:1:0.10	80
9	120	30	2:1:0.15	93
10	120	30	2:1:0.20	91
11	120	30	2:1:0.30	90
12	120	30	2:1:0.40	85
13	120	60	2:1:0.15	93
14	130	20	2:1:0.15	90
15	130	30	2:1:0.15	91
16	130	60	2:1:0.15	90

[a] Isolated yield.

Scheme 3.



2a–2n **3a–3n**

For Ar, see Table 2.

of the recovered catalyst were consistent with those of pure [Msim]Cl). The catalyst was stable after three consecutive cycles without noticeable loss of catalytic activity. In particular, the yield of **3a** was 93, 91, 90, and 87% in the first, second, third, and fourth runs, respectively. Hence, this result may be useful for future industrial applications.

Table 3 compares the proposed procedure with some previously reported methods. It is seen that [Msim]Cl is an efficient catalyst in the one-pot synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes.

In summary, we have proposed a novel and efficient method for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]-xanthenes by condensation of β-naphthol with aromatic aldehydes using 1-methyl-3-sulfo-1*H*-imidazol-3-ium chloride [Msim]Cl under monomode microwave irradiation. The air- and moisture-stable ionic liquid is able to promote the synthesis of dibenzoxanthene derivatives under solvent-free condition, and the use of microwave irradiation enables both significant acceleration of the reactions and improvement of the yield. Moreover, the possibility of recycling without loss of

Table 2. [Msim]Cl-catalyzed synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes[a]

Entry no.	Compound no.	Ar	Yield,[b] %	mp, °C	Reported mp, °C
1	**3a**	Ph	93	183–185	183–185 [34]
2	**3b**	4-FC_6H_4	94	238–240	236–238 [34]
3	**3c**	3-FC_6H_4	92	257–259	258–260 [35]
4	**3d**	2-FC_6H_4	85	232–233	233–234 [32]
5	**3e**	4-ClC_6H_4	96	288–290	289–291 [34]
6	**3f**	3-ClC_6H_4	93	208–210	207–209 [34]
7	**3g**	2-ClC_6H_4	92	212–214	211–213 [34]
8	**3h**	4-BrC_6H_4	94	296–298	298–300 [34]
9	**3i**	4-$O_2NC_6H_4$	95	313–315	312–314 [34]
10	**3j**	2-$O_2NC_6H_4$	86	290–292	290–293 [34]
11	**3k**	4-MeC_6H_4	90	226–228	225–227 [34]
12	**3l**	4-(*t*-Bu)C_6H_4	92	300–302	303–304 [27]
13	**3m**	4-$MeOC_6H_4$	88	202–204	204–207 [34]
14	**3n**	4-HO-3-$MeOC_6H_3$	80	206–208	206–207 [36]

[a] Reaction conditions: β-naphthol (2 mmol), benzaldehyde (1 mmol) and [Msim]Cl (0.15 mmol) at 120 °C for 30 min.

[b] Isolated yield.

Table 3. Catalytic activity of [Msim]Cl and some other catalysts in the synthesis of 14-phenyl-14*H*-dibenzo[*a*,*j*]xanthene (**3a**)

Catalyst	Catalyst loading, mol %	Time, min	Temperature, °C	Yield, %
I_2	25	20	90–95	90 [14]
$KAl(SO_4)_2 \cdot 12H_2O$	50	180	100	90 [15]
$Yb(OTf)_3$/[BPy]BF_4	10	420	110	89 [17]
[Hmim][HSO_4]	12	90	125	85 [34]
PEG–SO_3H	1	10	125	95 [27]
$NbCl_5$	25	288	–	90 [32]
[Msim]Cl	15	30	120	93[a]

[a] Present work.

activity makes the proposed catalyst convenient for large-scale syntheses. Thus, the attractive features of this protocol are simple and green procedure, short reaction time, high yield, and reusability of the catalyst.

EXPERIMENTAL

All chemicals were purchased from Merck and Sigma-Aldrich and were used without further purification. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-500 spectrometer using $CDCl_3$ as solvent and solvent peaks or TMS as internal standards. The high-resolution mass spectra (electrospray ionization) were recorded on a Bruker micrOTOF-QII MS instrument. Microwave irradiation was performed on a CEM Discover BenchMate apparatus, which offers microwave synthesis with safe pressure regulation using a 10-mL pressurized glass tube with Teflon-coated septum and vertically focused IR temperature sensor controlling the reaction temperature. Flash column chromatography (length 60 cm, internal diameter 1.5 cm) was performed on silica gel.

1-Methyl-3-sulfo-1*H*-imidazol-3-ium chloride [Msim]Cl. A microwave tube was charged with 1-methyl-1*H*-imidazole (0.082 g, 1 mmol) and chlorosulfonic acid (0.116 g, 1 mmol). The mixture was heated at 60°C for 20 min in a monomode microwave oven. After cooling, the mixture was then washed with diethyl ether and dried in a Christ Alpha 1-2 LD Plus freeze-dryer to afford [Msim]Cl as a colorless viscous oil in 94% yield.

General procedure for the preparation of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes 3a–3n. A microwave tube containing a mixture of β-naphthol (2 mmol), aromatic aldehyde **2a**–**2n** (1 mmol), and [Msim]Cl (0.15 mmol) was heated under microwave irradiation at 120°C for 30 min. After cooling to room temperature, the mixture was washed with water to remove the catalyst. The crude product was purified by recrystallization from an appropriate solvent. The products were identified by comparing their melting points and spectral characteristics (^{1}H and ^{13}C NMR and mass spectra) with those of samples reported previously (Table 2).

Recycling of [Msim]Cl. The water layer containing the ionic liquid catalyst was collected and washed with ethyl acetate (3×10 mL) to remove organic impurities. Water was then evaporated at 80°C under reduced pressure, and the catalyst was dried at 60°C for 4 h and reused.

CONFLICT OF INTEREST

No conflict of interest is declared by the authors.

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