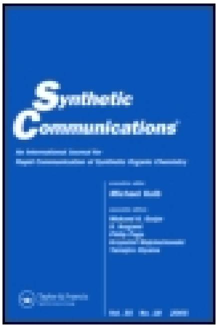

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Green, Catalyst-Free Protocol for the Efficient Synthesis of N-Sulfonyl Aldimines and Ketimines in Ionic Liquid [Bmim]Br

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Green, Catalyst-Free Protocol for the Efficient Synthesis of N-Sulfonyl Aldimines and Ketimines in Ionic Liquid [Bmim]Br

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Abstract: Sulfonamides are efficiently condensed with aldehydes as well as ketones in the absence of catalyst in 1-butyl-3-methylimidazolium bromide ([bmim]Br) under microwave irradiation to afford N-sulfonyl aldimines and ketimines in good to excellent yields in short reaction times.

Keywords: Catalyst-free, ionic liquid, microwave, N-sulfonyl aldimine, N-sulfonyl ketimine, sulfonamide

In recent years, catalyst-free reactions have attracted increasing interest because of the ease of experimental procedure as well as workup, low cost, possibility of using acid- or base-sensitive substrates, and environmentally benign process.[1] This useful technique has been used in several organic transformations, such as synthesis of benzoic esters and benzyl esters,[1a] regioselective conversion of epoxides to vicinal halohydrins,[1b]

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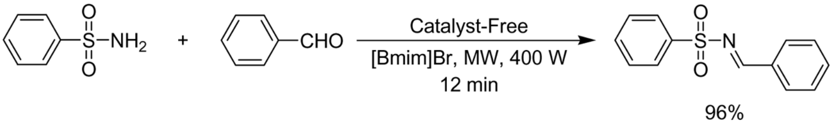
synthesis of dithiocarbamates,[1c] synthesis of 2-aminothiazoles,[1d] transesterification of triglycerides,[1e] N-benzyloxycarbonylation of amines,[1f] synthesis of polyorganosiloxanes,[1g] gem-bisallylation of carboxylic acid derivatives,[1h] and Michael-type addition of amines to electron-deficient alkenes.[1i] As a continuation of our interest in developing the efficient synthetic methodologies in organic synthesis,[2] we have initiated a program to study useful organic transformations in the absence of catalyst. Herein, we found that the synthesis of N-sulfonyl imines from sulfonamides and carbonyl compounds can be efficiently achieved without catalyst in [bmim]Br under microwave irradiation.

Currently, ionic liquids are the subject of considerable interest as benign reaction media in organic synthesis because of their unique properties, such as nonvolatility, nonflammability, recyclability, high thermal stability, and ability to dissolve a wide range of materials. During the past decade, a variety of ionic liquids have been demonstrated as efficient and practical alternatives to volatile organic solvents for many important organic reactions, including carbon–carbon, carbon–oxygen, carbon–sulfur, carbon–nitrogen, and carbon–phosphorus bond formation.[3] Together with the substitution of common molecular solvents, nonconventional activation methods, mainly microwave irradiation, have appeared as powerful techniques to decrease reaction times and to enhance reaction rates.[4]

The preparation of N-sulfonyl imines has attracted much attention in recent years for the versatile usage of the $C=N$ bond in organic synthesis.[5–13] For example, they are excellent substrates in nucleophilic additions,[6] reductions,[7] cycloadditions,[8] aza-Henry reactions,[9] aza Diels–Alder reactions,[10] aziridine,[11] and oxaziridine synthesis,[12] as well as ene reactions.[13] Several synthetic methods for the preparation of N-sulfonyl imines have been reported in the literature.[14–16] Most of them involve the condensation of sulfonamides with aldehydes or ketones in the presence of a strong Lewis or protic acid.[15] In many cases, strongly acidic conditions are not compatible with other functionalities present in a given substrate. Some methods need two-step procedures, are expensive methods, or generate toxic by-products. Several methods also require the preparation of starting materials such as oxime, sulfinylimine, and/or aziridine. Moreover, most of the reported methods are not efficient for the synthesis of aliphatic N-sulfonyl aldimines or N-sulfonyl ketimines. Unsatisfactory yields and long reaction times are also disadvantages of some methods. Moreover, recently we have introduced some new methods for the synthesis of N-sulfonyl imines via the condensation of sulfonamides with carbonyl compounds.[16] However, these methods are associated with one or more of the following disadvantages: (i) nonrecyclability of the catalyst, (ii) moderate yield, (iii) no agreement with



Scheme 1. Condensation of benzenesulfonamide with benzaldehyde.

the green chemistry protocols by the use of volatile organic solvents, and (iv) inefficiency of the procedure when ketones instead of aldehydes are applied in the reaction. Furthermore, there is no catalyst-free protocol for the synthesis of N-sulfonyl imines in the literature. Because of the limitations of the reported methods, development of an efficient, general, rapid, and catalyst-free protocol for the synthesis of N-sulfonyl imines under neutral conditions in one step would be desirable. To reach this goal, in this work we report a new method for the synthesis of N-sulfonyl aldimines and ketimines via the catalyst-free condensation of sulfonamide with aldehydes as well as ketones in [bmim]Br as a relatively neutral ionic liquid under microwave irradiation (Scheme 1). To the best of our knowledge, this is the first catalyst-free protocol for the synthesis of N-sulfonyl imines. It is also important to note that this presented work has none of the previously mentioned drawbacks.

At first, we examined the condensation of benzenesulfonamide (1 mmol) with benzaldehyde (1 mmol) without catalyst under solvent-free and microwave conditions at 400 W of microwave power but these conditions afforded the corresponding N-sulfonyl imine in trace yield after 20 min (Scheme 1, Table 1). Increasing the reaction time or the microwave power did not improve the yield. The yield increased to 96% when the reaction was performed in [bmim]Br (0.25 g) at 400 W (max. 110°C) (Table 1). The reaction was also checked in [bmim]Cl and [bmim]I (Table 1). As Table 1 indicates, [bmim]Br gave the best results. In another study, the reaction of benzenesulfonamide with

Table 1. Catalyst-free condensation of benzenesulfonamide with benzaldehyde under solvent-free conditions as well as in ionic liquids promoted by microwave irradiation (400 W, max. 110°C)

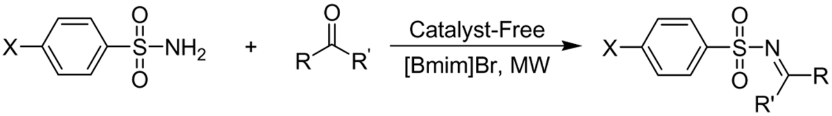
Entry	Solvent	Time (min)	Yield[a] (%)
1	Solvent-free	20	Trace
2	[bmim]Br	12	96
3	[bmim]Cl	12	78
4	[bmim]I	12	67

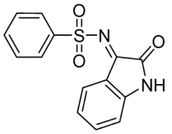
[a] Isolated yield.

benzaldehyde in [bmim]Br was tested at different microwave powers (100–600 W) at range of 100–140°C. The reasonable results were obtained at 400 W and 110°C.

After optimization of the reaction conditions, sulfonamides were reacted with structurally diverse aromatic and aliphatic aldehydes as well as ketones to recognize the efficiency and the scope of the catalyst-free procedure. The results are displayed in Table 2. As can be seen from Table 2, all reactions proceeded efficiently, and the desired products were produced in good to excellent yields and in short reaction times. It must

Table 2. Catalyst-free synthesis of N-sulfonyl imines in [bmim]Br under microwave irradiation (400 W, max. 110°C)



Entry	X	R	R'	Time (min)	Yield[a] (%)	Mp°C (lit[Ref].)
1	H	C_6H_5	H	12	96	76–78 (76–78[16a])
2	H	p-$CH_3C_6H_4$	H	16	92	114–116 (116–118[15a])
3	H	m-$CH_3C_6H_4$	H	16	91	87–89 (85–88[15b])
4	H	p-$N(CH_3)_2C_6H_4$	H	19	85	206–207 (206–207[16b])
5	H	p-$NO_2C_6H_4$	H	18	73	163–164 (164–165[16a])
6	H	p-BrC_6H_4	H	17	87	205–207 (205–207[16a])
7	H	p-ClC_6H_4	H	17	85	131–133 (127–130[15a])
8	H	m-ClC_6H_4	H	17	88	97–99 (92–94[15b])
9				20	81	(144–145)
10	CH_3	C_6H_5	H	12	97	109–110 (108[16d])
11	CH_3	p-(isopropyl)C_6H_4	H	15	95	109–111 (110–112[16a])
12	CH_3	p-$OCH_3C_6H_4$	H	18	96	127–129 (128–129[14a])
13	CH_3	p-$NO_2C_6H_4$	H	18	69	163–164 (164–166[16a])
14	CH_3	p-CNC_6H_4	H	18	74	172–173 (172–173[16d])
15	CH_3	p-ClC_6H_4	H	16	83	168–169 (172–173[14a])
16	CH_3	2-Furyl	H	15	91	99–100 (101[14a])
17	CH_3	$CH_3(CH_2)_5CH_2$	H	18	76	136–137 (138[17])
18[b]	CH_3	C_6H_5	CH_3	25	54	84–86 (88–89[14b])

[a] Isolated yield.

[b] This reaction was carried out at 130°C.

be mentioned that the presence of electron-releasing substituents CH_3 and OCH_3 on the aromatic ring of aldehydes had no significant effect on the reaction yields (Table 2, entries 2, 3, 11, and 12); however, $N(CH_3)_2$ and halogens slightly decreased the yields (Table 2, entries 4, 6–8, and 15). Electron-withdrawing substituents also decreased the yields (Table 2, entries 5, 13, and 14). Interestingly, the catalyst-free method was successfully applied for the reaction of sulfonamides with aliphatic aldehydes as well as ketones (Table 2, entries 9, 17, and 18). However, most of the reported methods are not efficient when aliphatic aldehydes or ketones are used in the reaction.

One of the most interesting properties of ionic liquids is their ease of recycling. For the reaction of benzenesulfonamide with benzaldehyde, no significant loss of the product yield was observed when [bmim]Br was reused even after three times.

In summary, we have reported the first catalyst-free method for the condensation of sulfonamides with aldehydes as well as ketones. The promising points for the presented methodology are efficiency, generality, good yield, short reaction time, low cost, cleaner reaction profile, ease of product isolation, simplicity, potential for recycling of the solvent, and finally agreement with the green chemistry protocols, which makes it a useful and attractive process for the synthesis of N-sulfonyl aldimines and ketimines.

EXPERIMENTAL

All chemicals were purchased from Merck or Fluka Chemical Companies. The ionic liquid was prepared according to the reported methods.[18] All reactions were carried out using a laboratory microwave oven (MicroSYNTH, Milestone Company, Italy). The ^1H NMR (250 MHz) and ^{13}C NMR (62.5 MHz) spectra were run on a Bruker Avance DPX-250, FT-NMR spectrometer, δ in parts per million (ppm). Mass spectra (MS) were recorded on a Shimadzu GC MS-QP 1000 EX apparatus. Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

General Procedure for the Catalyst-Free Synthesis of N-Sulfonyl Imines

[bmim]Br (0.25 g) was added to a mixture of sulfonamide (1 mmol) and carbonyl compound (1 mmol) in a microwave vessel and mixed carefully with a small rod. The resulting mixture was irradiated in a microwave

oven at 400 W for the appropriate time (Table 2). The microwave was programmed to give a maximum internal temperature of 110°C. Afterward, the reaction mixture was cooled to room temperature and was extracted with Et_2O (3×15 mL). The organic extracts were then combined and washed with saturated solution of $NaHSO_3$ (2×20 mL). The organic layer was separated and dried with $CaCl_2$. The solvent was evaporated, and the crude product was dissolved in warm ethyl acetate (2 mL), treated with *n*-hexane (6 mL), and allowed to stand at room temperature for 5–6 h. During this time, the target molecules were produced and then collected by filtration, washed with *n*-hexane, and dried. After isolation of the product, the remaining Et_2O in [bmim]Br was evaporated, and it was used for the next run under identical reaction conditions.

Some Selected Spectral Data of the Products

(E)-N-Benzylidenebenzenesulfonamide (Table 2, Entry 1)

White solid; ^{1}H NMR ($CDCl_3$): δ 7.61 (m, 6H), 8.02 (m, 4H), 9.05 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 127.1, 128.3, 129.5, 130.3, 131.7, 132.8, 134.0, 136.1.0, 171.2; MS (m/z): 245 (M^+). Anal. calcd. for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.52; N, 5.71. Found: C, 63.47; H, 4.37; N, 5.90.

(E)-N-(2-Oxoindolin-3-ylidene)benzenesulfonamide (Table 2, Entry 9)

Orange solid; ^{1}H NMR (DMSO-d_6): δ 6.89 (m, 1H), 7.05 (m, 1H), 7.34 (m, 2H), 7.48 (m, 1H), 7.56 (m, 2H), 7.84 (m, 2H), 11.00 (s, 1H);^{13}C NMR (DMSO-d_6): δ 112.2, 117.8, 122.7, 124.6, 125.5, 128.8, 131.7, 138.3, 144.1, 150.7, 159.3, 184.3; MS (m/z): 286 (M^+). Anal. calcd. for $C_{14}H_{10}N_2O_3S$: C, 58.73; H, 3.52; N, 9.78. Found: C, 58.52; H, 3.68; N, 9.61%.

(E)-N-(4-Isoperopyl-benzylidene)-4-methylbenzenesulfonamide (Table 2, Entry 11)

White solid; ^{1}H NMR ($CDCl_3$): δ 1.20 (d, $J = 7$ Hz, 6H), 2.33 (s, 3H), 2.93 (m, 1H), 7.18–7.80 (m, 8H), 8.91 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 22.4, 22.5, 32.9, 126.1, 126.7, 128.6, 129.3, 130.3, 130.9, 132.9, 156.7, 171.4; MS (m/z): 301 (M^+). Anal. calcd. for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.91; H, 6.57; N, 4.41%.

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