[bmim]OH-Promoted one-pot three-component synthesis of β-nitro sulfides in water

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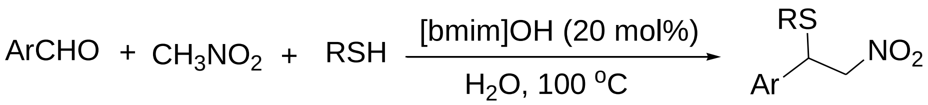
A task-specific ionic liquid, [bmim]OH, has been found to be a highly efficient catalyst for one-pot three-component coupling of aryl aldehydes, nitromethane, and thiols for the synthesis of β-nitro sulfides in water. The main advantages of the present protocol include the use of inexpensive simple substrates and an ionic liquid as a basic catalyst.



Keywords: β-Nitro sulfides; ionic liquids; thiols; aldehydes; nitromethane

1. Introduction

Organic reactions in aqueous media have attracted considerable attention in recent years, since they offer a powerful tool for minimizing waste production and harmful organic solvent disposal.[1-3] Some properties of water make this solvent very attractive (i.e. non-toxicity, non- inflammability, high heat capacity, possibility of controlling pH, isolating insoluble solid products by filtration and recycling inorganic catalysts and water itself), allowing organic processes in aqueous media to be safer, very efficient, and highly selective.[1]

The utilization of multi-component reaction (MCRs) to synthesize novel chemicals, drug-like scaffolds, and natural product compounds has pervaded in organic transformation.[4-5] This is due to the fact that these products can be proposed directly in a single step and diversity can be achieved simply by varying the reaction substrates.[6] Ionic liquids (ILs) have attracted increasing interest in organic synthesis owing to their great potential not only as alternative green reaction media but also as new catalysts and reagents, and because they are also easy to recycle.[7-14]

Nitro olefins have been recognized as versatile building blocks and synthetic intermediates due to their easy conversion into a variety of diverse functionalities.[15-21] These compounds are markedly electron-deficient and powerful dienophiles in the Diels-Alder reaction.[18] Alternatively, these electrophilic alkenes readily undergo Michael addition with many different nucleophiles because of the strong electron-withdrawing nature of the nitro group. Heteroatom-centered nucleophiles such as sulfur, oxygen, nitrogen, and phosphorous anions are good nucleophiles for the Michael addition to nitroalkenes, which provides a useful method for the introduction of two heteroatoms on vicinal positions, in which the nitro group can be readily converted into other functional groups such as keto (the Nef reaction), cyano, and amino groups.[18, 22-27]

The reaction of thiols with nitroalkenes in the presence of a base is the most common method for the preparation of β-nitro sulfides.[28-36] The treatment of β-nitro acetals with thiols in the presence of triethylamine has also been reported for the preparation of β-nitro sulfides.[37] Recently, ionic liquids such as *n*-Bu_4NBr,[38] and Me_4NF[39] have been introduced as efficient catalyst for the Michael addition of thiols to α,β-unsaturated carbonyl compounds, as well as limited numbers of nitroolefins. Several other procedures for the preparation of β-nitro sulfides from thiols and β-nitrostyrenes have been introduced, using ammonium chloride as a catalyst,[40] and catalyst-free reaction under neat condition[41] or in water[42] as medium.

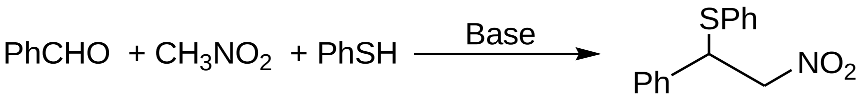
2. Results and Discussion

In recent years, basic ionic liquids (BILs) have been used as environmentally friendly solvents and catalysts with high activity and selectivity and easily recoverable materials which can replace traditional bases such as KOH, H_2CO_3, NaOAc, and Et_3N. 1-Butyl-3-methylimidazolinium hydroxide, [bmim]OH, is one such BILs which acts as reaction medium as well as basic catalyst and has got varied applications in the field of synthetic methodology development.[43-47]

All procedures reported above have performed the synthesis of β-nitro sulfides, utilizing the already available nitroolefins. To the best of our knowledge, there is no report of constructing β-nitro sulfides by a one-pot, three-component reaction of an aryl aldehyde, nitromethane, and thiols. Considering the above points along with our ongoing efforts to develop new one-pot synthetic processes,[48-55] we report herein the first ionic liquid [bmim]OH-promoted synthesis of β-nitro sulfides using a three-component coupling reaction of aromatic aldehydes, nitromethane, and thiols in water at 100 ºC.

To find the optimal conditions, a mixture of benzaldehyde (1.0 mmol), nitromethane (1.0 mmol), and thiophenol (1.0 mmol) was examined under various conditions (Table 1); the effect of

Table1. Optimization of the base-catalyzed one-pot reaction of benzaldehyde, nitromethane and thiophenol[a]



Entry	Solvent	Base (mol %)	Temp. (°C)	Yield (%)[b]
1	CH_3CN	DIPEA (20)	85	35
2	CH_3CN	Et_3N (20)	85	30
3	CH_3CN	DABCO (20)	85	32
4	CH_3CN	DBU (20)	85	21
5	CH_3CN	K_3PO_4 (20)	85	45
6	CH_3CN	KO^tBu (20)	85	26
7	CH_3CN	Cs_2CO_3 (20)	85	20
8	CH_3CN	KF/Al_2O_3(40 wt%)	85	34
9	CH_3CN	$[bmim]BF_4$ (20)	85	40
10	CH_3CN	[bmim]OH (20)	85	75
11	CH_3CN	[bmim]OH (20)	75	60
12	–	[bmim]OH (20)	100	54
13	H_2O	[bmim]OH (20)	100	86
14	H_2O	[bmim]OH (15)	100	70
15	H_2O	[bmim]OH (40)	100	87
16	DMSO	[bmim]OH (20)	100	63
17	$PhCH_3$	[bmim]OH (20)	100	10
18	DMF	[bmim]OH (20)	100	45

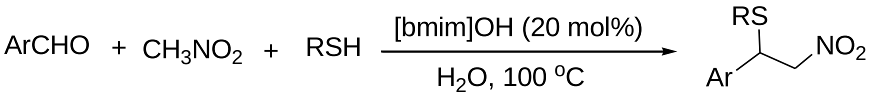
[a] Reaction conditions: benzaldehyde (1.0 mmol), nitromethane (1.0 mmol), thiophenol (1.0 mmol), base, solvent (2 ml), 6 h.

[b] Yield of isolated and purified product.

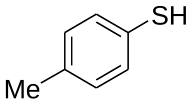
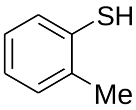
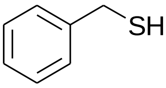
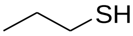
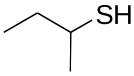
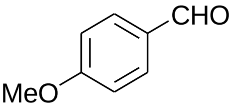
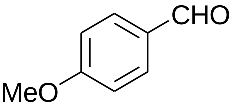
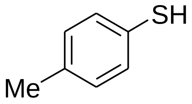
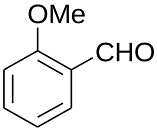
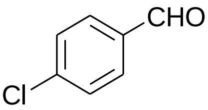
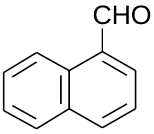
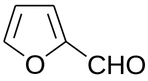
different solvents, temperatures, basic catalysts as well as ionic liquids were examined. The best result (86%) was obtained by carrying out the reaction in the presence of [bmim]OH ionic liquid. The use of other ionic liquids and basic catalysts resulted in a considerable drop in yields (Table 1, Entries 1-9). Also, optimization of the solvent was investigated and it was found that among acetonitrile, dimethyl sulfoxide, *N*,*N*-dimethylformamide, toluene, water, and even solvent-free conditions, the best result in terms of yield was obtained with water (Table 1, Entries 12-18). The effect of the reaction temperature was also checked, and the best performance was observed at 100 ºC. The optimum catalyst loading for the ionic liquid [bmim]OH was found to be 20 mol% (Table 1, Entry 13); however, a catalyst loading lower than 20 mol% gave decreased yield (Table 1, Entry 14), while an increase in the catalyst concentration to 40 mol% did not appreciably increase the yield (Table 1, Entry 15). Therefore, it was decided to use [bmim]OH as the catalyst, H_2O as the solvent, and 20 mol% of the catalyst at 100 ºC as the optimum conditions in further studies.

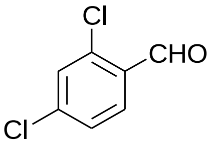
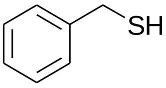
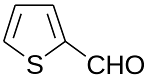
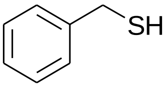
To survey the generality of the catalytic protocol, we studied this thia-Michael reaction using various aryl and heteroaryl aldehydes as well as different thiols including aromatic thiols and alkyl thiols under the optimized reaction conditions. The results are listed in Table 2, and β-nitro sulfides could be obtained in good to excellent yields (75-96%). Generally, the reaction rate of aromatic thiols was found to be faster than that of alkyl thiols (Table 2, Entrie 1-6). The reaction was almost equally facile with both electron-donating and moderate electron-withdrawing substituents on

Table 2. One-pot three-component [bmim]OH-promoted synthesis of β-nitro sulfides [a]



1 **2** **3**

Entry	Aldehyde	Thiol	Product	Time (h)	Yield (%)[b]
1	PhCHO	PhSH	**3a**	6	86
2	PhCHO		**3b**	6	95
3	PhCHO		**3c**	6	91
4	PhCHO		**3d**	6	90
5	PhCHO		**3e**	12	84
6	PhCHO		**3f**	12	85
7		PhSH	**3g**	6	94
8			**3h**	5	96
9		PhSH	**3i**	6	83
10		PhSH	**3j**	6	87
11		PhSH	**3k**	8	84
12		PhSH	**3l**	12	75

13			**3m**	12	78
14			**3n**	6	85

[a] Reaction conditions: aldehyde (1.0 mmol), nitromethane (1.0 mmol), and thiol (1.0 mmol), catalyst (20 mol%), H_2O (2 ml), 100 ºC.

[b] Yield of isolated and purified product.

the aldehydes (Table 2, Entries 7, 10 and 13). However, the reaction of sterically hindered 2-methoxybenzaldehyde with thiophenol gave lower yield than 4-methoxybenzaldehyde (Table 2, Entries 7 and 9). Heteroaryl aldehydes such as furfural and thiophene-2-carbaldehyde also reacted with thiols to give the products in good to high yields (Table 2, Entries 12 and 14).

3. Conclusion

In summary, a simple and very efficient one-pot three-component procedure for the synthesis of β-nitro sulfides starting from aldehydes, niromethane, and thiols in water using a task-specific ionic liquid, [bmIm]OH, has been developed. This method offers marked improvements with regard to operational simplicity, greenness of procedure, avoiding hazardous organic solvents and toxic catalysts, general applicability, reaction conditions, high isolated yields, and thus it provides a better and practical alternative to the existing procedures.[28-42]

4. Experimental section

4.1. *Chemicals*

All chemicals were purchased from Merck and Fluka chemical companies. Melting points were determined on a Büchi melting point B-540 apparatus.

4.2. *Apparatus*

Fourier transform infrared (FT-IR) spectra were recorded on an ABB Bomem Model FTLA 2000 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded at 300 (^{1}H) and 75.4 (^{13}C) MHz, on a commercial Bruker DMX-300 instrument using $CDCl_3$ as solvent. Chemical shifts were determined by reference to residual $CHCl_3$ in $CDCl_3$.

4.2.1 *General procedure*

A mixture of an aromatic aldehyde (1.0 mmol), nitromethane (1.0 mmol), thiol (1.0 mmol), and [bmim]OH (20 mol%) in water (2 ml) was stirred at 100 °C for an appropriate time of 5-12 h (Table 2). The course of the reaction was monitored by thin layer chromatography (TLC) until the starting materials disappeared completely. Then, water (8 ml) was added to the reaction mixture, and extracted with diethyl ether (2 × 10 ml). The combined organic layer was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure, and the crude product thus obtained was purified by preparative TLC (silica gel, eluent EtOAc/*n*-hexane = 1:10) to obtain pure products. The remaining ionic liquid was rinsed with ether (5 ml), dried under vacuum at 90 °C for 2 h to eliminate any water trapped and reused for subsequent runs [45].

4.2.1.1 *(2-Nitro-1-phenylethyl)(phenyl)sulfane* **(3a):** White crystals; mp 72-73 ºC; IR (neat)/υ(cm^{-1}): 1553, 1376; ^{1}H NMR ($CDCl_3$, 300 MHz)/δ ppm: 4.73 (dd, *J* = 11.8, 5.3 Hz, 1H), 4.79-4.94 (m, 2H), 7.26-7.43 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz)/δ ppm: 49.9, 78.5, 127.7, 128.6, 128.8, 129.0, 129.4, 131.9, 133.8, 136.3.

4.2.1.2 *(2-Nitro-1-phenylethyl)(p-tolyl)sulfane* **(3b):** White crystals; mp 76-77 ºC; IR (neat)/υ(cm^{-1}): 1557, 1374; ^{1}H NMR ($CDCl_3$, 300 MHz)/δ ppm: 2.35 (s, 3H), 4.70 (dd, *J* = 16.8, 10.5 Hz, 1H), 4.80-4.88 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.25-7.38(m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz)/δ ppm: 21.2, 50.1, 78.5, 127.6, 128.1, 128.6, 128.9, 130.1, 134.3, 136.4, 139.2.

4.2.1.3 *(2-Nitro-1-phenylethyl)(o-tolyl)sulfane* **(3c):** White crystals; mp 62-63 ºC; IR (neat)/υ(cm^{-1}): 1556, 1379; ^{1}H NMR ($CDCl_3$, 300 MHz)/δ ppm: 2.37 (s, 3H), 4.71 (dd, *J* = 9.2, 2.6 Hz, 1H), 4.77-4.91 (m, 2H), 7.20-7.41 (m, 8H), 7.44 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz)/δ ppm: 14.7, 51.3, 79.8, 126.6, 127.9, 129.1, 129.20, 129.25, 132.5, 133.1, 135.0, 138.9, 140.9.

4.2.1.4 *Benzyl(2-nitro-1-phenylethyl)sulfane* **(3d):** Yellow oil; IR (neat)/υ(cm^{-1}): 1559, 1373; ^{1}H NMR ($CDCl_3$, 300 MHz)/δ ppm: 3.63 (d, *J* = 13.5 Hz, 1H), 3.72 (d, *J* = 13.5 Hz, 1H), 4.47(dd, *J* = 8.8, 6.8 Hz, 1H), 4.67 (dd, *J* = 12.8, 6.8 Hz, 1H), 4.73 (dd, *J* = 12.8, 8.8 Hz, 1H), 7.29-7.39 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz)/δ ppm: 36.0, 45.9, 79.1, 127.6, 127.9, 128.5, 128.8, 129.01, 129.09, 137.0, 137.1.

4.2.1.5 *(2-Nitro-1-phenylethyl)(propyl)sulfane* **(3e):** Pale yellow oil; IR (neat)/υ(cm^{-1}): 1556, 1376; ^{1}H NMR ($CDCl_3$, 300 MHz)/δ ppm: 0.94 (t, *J* = 7.2 Hz, 3H), 1.57(sext, *J* = 7.2 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 4.55 (t, *J* = 7.8 Hz, 1H), 4.75 (d, *J* = 7.5 Hz, 2H), 7.26-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz)/δ ppm: 13.4, 22.6, 33.7, 46.5, 79.4, 127.7, 128.5, 129.1, 137.5.

4.2.1.6 *(1-(4-Methoxyphenyl)-2-nitroethyl)(p-tolyl)sulfane* **(3h):** White crystals; mp= 72-73 ºC; IR (neat)/υ(cm^{-1}): 1554, 1377; ^{1}H NMR ($CDCl_3$, 300 MHz)/δ ppm: 2.35 (s, 3H), 3.79 (s, 3H), 4.67 (dd, *J* =

16.9, 10.3 Hz, 1H), 4.76-4.85 (m, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.2 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz)/δ ppm: 21.2, 49.6, 55.3, 78.7, 114.3, 128.2, 128.4, 128.8, 130.1, 134.2, 139.1, 159.6.

4.2.1.7 *Benzyl(1-(2,4-dichlorophenyl)-2-nitroethyl)sulfane* **(3m):** Yellow oil; IR (neat)/υ(cm^{-1}): 1581, 1379; ^{1}H NMR ($CDCl_3$, 300 MHz)/δ ppm: 3.48(s, 2H), 3.58 (t, *J* = 7.4 Hz, 1H), 4.56 (dd, *J* = 13.1, 7.1 Hz, 1H), 4.72 (dd, *J* = 13.1, 8.0 Hz, 1H), 7.13-7.49 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz)/δ ppm: 29.7, 46.9, 79.3, 127.1, 128.8, 128.9, 129.1, 129.9, 133.3, 134.3, 136.5, 137.5, 138.4.

4.2.1.8 *2-(1-(Benzylthio)-2-nitroethyl)thiophene* **(3n):** Yellow oil; IR (neat)/υ(cm^{-1}): 1595, 1374; ^{1}H NMR ($CDCl_3$, 300 MHz)/δ ppm: 3.70 (d, *J* = 13.4 Hz, 1H), 3.78 (d, *J* = 13.4 Hz, 1H), 4.61-4.77 (m, 3H), 6.96 (d, *J* = 3.2 Hz, 2H), 7.27-7.38 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz)/δ ppm: 36.1, 41.3, 79.6, 126.2, 126.7, 127.0, 127.6, 128.8, 129.0, 136.7, 140.9 .

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