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An ionic liquid-mediated expeditious route to the syntheses of diaryl sulfoxides

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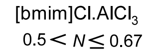
Abstract—A fast and efficient protocol is proposed for the synthesis of diaryl sulfoxides in the ionic liquid 1-butyl-3-methylimidazolium chloroaluminate, [bmim]Cl·$AlCl_3$, $N = 0.67$, by employing arenes and thionyl chloride. The ionic liquid plays a dual role of Lewis acid catalyst and solvent, under ambient conditions, offering good yields of the product. The influence of the Lewis acidity of the ionic liquid on the extent of conversion is studied. © 2003 Elsevier Science Ltd. All rights reserved.

Sulfoxides and sulfones have fascinated organic chemists for a long time owing to their varied reactivity as a functional group for transformation into a variety of organo sulfur compounds. These transformations are useful for the synthesis of drugs and sulfur-substituted natural products.[1,2] Optically active[3] sulfoxides continue to deserve much attention as important chiral auxiliaries in asymmetric synthesis[4] and in C–C bond forming reactions.[5] Syntheses of diaryl sulfoxides also provide a convenient route to triarylsulfonium salts which are used as photoactive cationic initiators[6] and for the photogeneration of protonic acids in the lithographic resist field.[7]

Methodologies for the direct synthesis of sulfoxides are rarely observed in the literature. Usually the synthesis of sulfoxides is accomplished by the oxidation of sulfides,[8] indirect reduction of sulfones[9] and by the reaction of organometallic reagents with sulfinic acid esters, mixed anhydrides or sulfines. A direct method for the synthesis of diaryl sulfoxides is Friedel–Crafts sulfinylation of arenes using a catalyst such as $AlCl_3$[10] or trifluoromethane sulfonic acid.[11] Sulfoxide synthesis is also achieved by dehydration of arenes and SO_2 mediated by magic acid (FSO_3H/SbF_5).[12] The most recent reports on sulfoxide synthesis include their formation from thionyl chloride and arenes employing trifluoromethane sulfonic acid[13] or scandium triflate[14] as the catalyst. The direct preparation of sulfoxides often suffers from the formation of mixtures of products containing sulfonium salts and chlorinated by-products along with the desired sulfoxides.[15]

The discovery of ionic liquids has widened the horizons for newer synthetic strategies in the area of organic chemistry. These innovative fluids are organic salts, whose cation, anion and the alkyl chain attached to organic cation can be varied virtually at will, to change their chemical and physical properties as per the needs of the chemical process. A key feature of these liquids is their intrinsic ability to solvate a wide array of organic and inorganic substrates. They are blessed with qualities such as incredibly large liquidus ranges, negligible vapour pressure and recyclability.[16] In short, these ionic liquids have enlightened the way to complete environmentally benign procedures.[17] Due to their intriguing properties, these liquids have fascinated us. We have studied the applicability of ionic liquids in various synthetically useful transformations.[18] Chloroaluminate ionic liquids remain important.[19,20] In continuation of our research to explore new reactions in ionic liquids, we thought it would be worthwhile to investigate the direct synthesis of diaryl sulfoxides in these liquids. We report herein, for the first time, syntheses of diaryl sulfoxides by the reaction of thionyl chloride with arenes in the Lewis acidic 1-butyl-3-methylimidazolium chloroaluminate, [bmim]Cl·$AlCl_3$, $0.5<N\leq 0.67$, ionic liquids (Scheme 1).



$$\text{Ar-H} \xrightarrow[\text{[bmim]Cl.AlCl}_3,\ 0.5 < N \leq 0.67]{\text{SOCl}_2} \text{Ar-SO-Ar}$$

Scheme 1. Synthesis of diaryl sulfoxides from arenes and thionyl chloride in the [bmim]Cl·$AlCl_3$, $0.5<N\leq 0.67$, ionic liquid.

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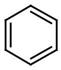
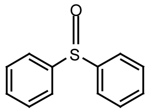
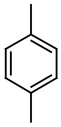
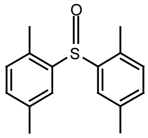
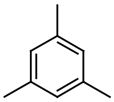
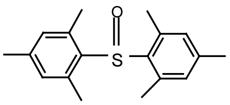
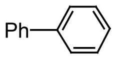
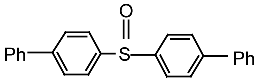
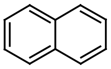
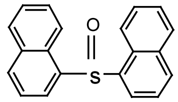
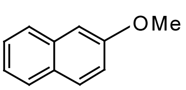
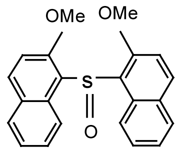
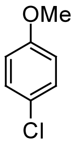
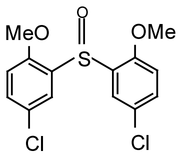
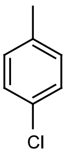
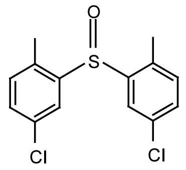
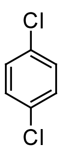
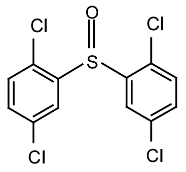
Table 1. Syntheses of diaryl sulfoxides in the ionic liquid, [bmim]Cl·$AlCl_3$, $N=0.67$

Entry	Substrate	Product	%Yield[a]
1.			85
2.			95
3.			96
4.			95
5.			94
6.			92
7.			90
8.			93
9.			91

a = isolated yields

Initially, we investigated the synthesis of sulfoxides in basic, neutral and acidic chloroaluminate ionic liquids by changing the apparent mole fraction of $AlCl_3$ in the liquid, N, over the range 0–0.5, 0.5 and 0.5–0.67, respectively. No reaction was observed in liquids corresponding to $N=0$–0.5, even after 3 h at 100°C. Only

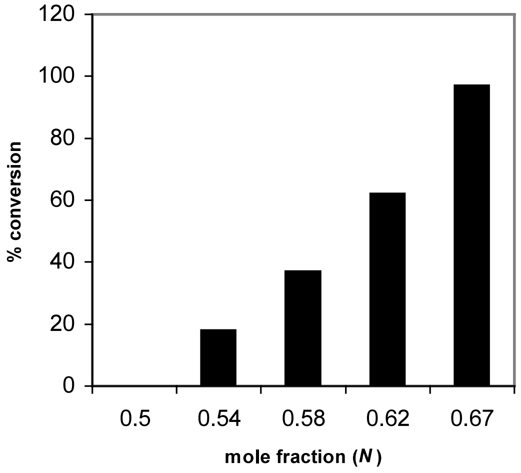


Figure 1. Effect of the mole fraction of $AlCl_3$ (N), in [bmim]Cl·$AlCl_3$, $0.5<N\leq 0.67$, on the % conversion of toluene to ditoluyl sulfoxide.

Table 2. The effect of the position of substituent(s) in mono- and di-substituted benzenes on the isomer distribution of the products in [bmim]Cl·$AlCl_3$, $N=0.67$ mediated reactions of thionyl chloride with arenes

Substrate	Isomer distribution[a] (%)		
	p,p′	*o,p*	*o,o′*
Toluene	79	13	2
o-Xylene	87	2.5	0.5
m-Xylene	85	4	2
o-Cl-anisole	86	2.0	0.5

[a] The % of *p,p′*-, *o,p*- and *o,o′*-diaryl sulfoxides was determined by GC–MS.[22]

acidic ionic liquids gave us positive results.[21] We had earlier explored the effects of the variable Lewis acidity of chloroaluminate ionic liquids in the Fries rearrangement[18a] and Friedel–Crafts sulfonylation.[18b] This unique feature of ionic liquids encouraged us to monitor the influence of the Lewis acidity on the extent of the conversion. A series of experiments was carried out with toluene as a model substrate. The composition of the ionic liquid in terms of the mole fraction of $AlCl_3$ in the liquid N, was varied from 0.50–0.67. A progressive increase in conversion with an increase in the catalytic species $Al_2Cl_7^-$ was observed (Fig. 1). The results indicated that the ionic liquid corresponding to $N=0.67$ offered maximum conversion within 5 min and hence was employed for all further studies.

To generalize the procedure, the reactions were carried out on different arenes. Nearly quantitative yields were obtained in almost all cases when the arene, thionyl chloride and ionic liquid ($N=0.67$) were used in a molar ratio 2:1:1, respectively. The ionic liquid provided drastic reduction in the reaction time under ambient conditions.[21] With arenes such as benzene, *p*-disubstituted benzenes, naphthalene and biphenyl, exclusively, a single product was obtained as illustrated in Table 1. To check the effect of substituents on the isomer distribution of products, we carried out reactions with toluene, *o*-xylene, *m*-xylene and *o*-Cl-anisole under the same reaction conditions.[21] The results are depicted in Table 2. As evident from the results, in all cases the major product obtained was the *p,p′*-disubstituted sulfoxide, with small amounts of *o,p*- and *o,o′*-products.

In conclusion, the ionic liquid [bmim]Cl·$AlCl_3$, $N=0.67$, furnished a homogeneous Lewis acidic medium which catalyses the syntheses of sulfoxides employing arenes and thionyl chloride. The experimental procedure is simple and time saving. Further investigations on the synthesis of asymmetric diaryl sulfoxides using aryl sulfinyl chloride and arenes in these liquids are underway. As a part of our studies of mechanistic details of the Friedel–Crafts reactions in these ionic liquids,[18b] we also intend to exploit ^{33}S and ^{27}Al NMR spectroscopy for rationalizing the mechanism of these reactions.

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21. **Experimental procedure**: In a typical experimental procedure, to the weighed quantity of the arene [10 mmol] and thionyl chloride [5 mmol], the ionic liquid [bmim]Cl·$AlCl_3$, $N = 0.50–0.67$, [5 mmol], was added and the reaction mixture was stirred for 5 min at room temperature. All additions were carried out in an inert atmosphere glove box. The reactions were quenched using 6 M HCl under cold conditions. The resultant solution was extracted using ethyl acetate (3×10 ml). The combined organic extracts were dried using anhydrous sodium sulphate, evaporated under reduced pressure and assayed on GC. The crude products were chromatographed using silica gel column chromatography to yield pure compounds that were characterised by IR, NMR, MS and physical constants.
22. GC–MS analysis was performed using a Shimadzu, QP-5050 instrument equipped with a hp-5 column. The detector temperature was set at 300°C. The column was programmed initially at 60°C for 5 min and then with a gradient of 10°C/min to 250°C.