

## Friedel–Crafts Sulfonylation in 1-Butyl-3-methylimidazolium Chloroaluminate Ionic Liquids

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1-Butyl-3-methylimidazolium chloroaluminate ionic liquids have been employed as an unconventional reaction media and as Lewis acid catalyst for Friedel–Crafts sulfonylation reaction of benzene and substituted benzenes with 4-methyl benzenesulfonyl chloride. The substrates exhibited enhanced reactivity, furnishing almost quantitative yields of diaryl sulfones, under ambient conditions. Studies concerning the effect of Lewis acidity of the ionic liquid on the initial extent of conversion of this reaction has been carried out.  $^{27}\text{Al}$  NMR spectroscopy has been exploited as a tool to investigate the mechanistic details of the reaction.  $^{27}\text{Al}$  NMR spectral studies show the predominance of  $[\text{Al}_2\text{Cl}_7]^-$  species in  $[\text{bmim}]\text{Cl}-\text{AlCl}_3$ ,  $N = 0.67$ , acidic ionic liquid in the presence of 4-methyl benzenesulfonyl chloride, and after the reaction with the aromatic hydrocarbon,  $[\text{AlCl}_4]^-$  species predominates. This change in speciation of aluminum can be attributed to the interaction of the Lewis acidic species  $[\text{Al}_2\text{Cl}_7]^-$  of the ionic liquid with the formed HCl during the sulfonylation reaction, which is evidenced by the control experiment. Preliminary investigations on Friedel–Crafts acylation further substantiate the argument.

### Introduction

With the rapid advancement in the field of synthetic organic chemistry, more and more environmentally benign and eco-friendly processes are coming up at an overwhelming rate. Fueled by the current scenario of environmental consciousness and green chemistry, it seems that the ionic liquids are here to stay in the present scheme of things. This is because of not only their electrochemical properties<sup>1,2</sup> but also their tremendous potential as solvents. The diversity of the solutes solvated by ionic liquids is vast, ranging from organic to organo-metallic to inorganic substrates. Their properties<sup>3</sup> such as hydrophobicity, hydrophilicity, viscosity, density, Lewis acidity, etc. can be tailored to suit the requirements by fine-tuning of parameters such as an organic cation, inorganic anion, and the length of a side chain hooked to an organic cation. These characteristics offer flexibility to the chemists to design the solvents as per the needs of the process. Other properties such as negligible vapor pressure and recyclability make them useful alternatives to the conventional molecular organic solvents in several reactions, which have been reviewed.<sup>4</sup> Chloroaluminate-based ionic liquids are intriguing and have been the subject of our investigation<sup>5</sup> for quite some time, owing to their Lewis acidity, which can be varied over a range and their intrinsic ability to solvate substances. These properties coupled together offer advantages of homogeneous Lewis acid catalysis that can be aptly exploited in

several synthetically useful reactions. These ionic liquids are prepared from  $\text{AlCl}_3$  and organic halide. We chose to work on the ionic liquids prepared from  $\text{AlCl}_3$  and 1-butyl-3-methylimidazolium chloride  $[\text{bmim}]\text{Cl}$ , as they have an advantage of being liquid at room temperature over a considerable composition range of apparent mole fraction of  $\text{AlCl}_3$ ,  $N = \text{ca. } 0.30\text{--}0.67$ .

### Results and Discussions

With an ever-increasing quest for exploration of newer reactions in chloroaluminate-based ionic liquids, we herein report for the first time Friedel–Crafts sulfonylation reactions in ionic liquids. These reactions have been extensively studied employing various alkyl/aryl sulfonylhalides and sulfonic acids with aromatic hydrocarbons in the presence of different acid catalysts.<sup>6–8</sup> Our interest in sulfonylation stems from the requirement of diaryl sulfones as pendant groups on the monomers for our work on polymerizations. We investigated sulfonylation of benzene and substituted benzenes with 4-methyl benzenesulfonyl chloride ( $\text{TsCl}$ ) in ionic liquids,  $[\text{bmim}]\text{Cl}-\text{AlCl}_3$ ,  $0.67 \geq N > 0.50$  (Scheme 1). The substrates exhibited high reactivity, giving almost quantitative yields of the product, diaryl sulfones under ambient conditions in  $[\text{bmim}]\text{Cl}-\text{AlCl}_3$ ,  $N = 0.67$ .

The Lewis acidity<sup>9</sup> of these ionic liquids can be varied over a wide range as stated earlier by manipulating the relative amounts of organic base and  $\text{AlCl}_3$ . The  $\text{AlCl}_3$  mole fractions less than 0.5 afford basic,  $N = 0.5$  gives

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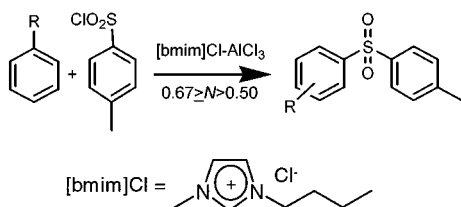
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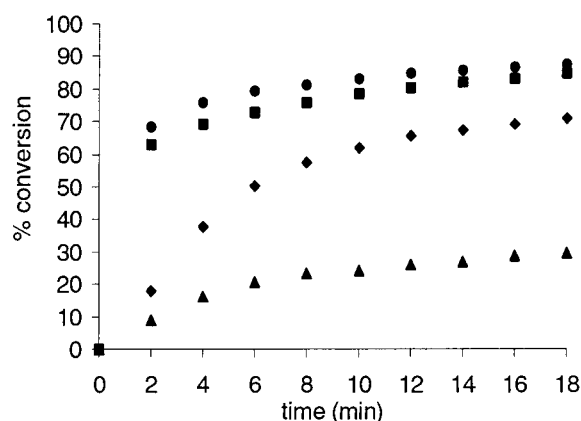
**Scheme 1. Friedel-Crafts Sulfonylation of Benzene and Substituted Benzenes with 4-Methyl Benzenesulfonyl Chloride in Ionic Liquids, [bmim]Cl-AlCl<sub>3</sub> (0.67 ≥ *N* > 0.50)**



**Table 1. Effect of Lewis Acidity on Friedel-Crafts Sulfonylation in Ionic Liquids Using TsCl**

<i>N</i>	% conversion/min	
	for benzene <sup>a</sup>	for methylbenzene <sup>b</sup>
0.50		
0.58	2.8	12.5
0.63	5.1	25.0
0.67	6.9	31.5

<sup>a</sup> Conversions after 10 min. <sup>b</sup> Conversions after 2 min.



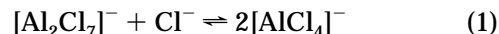
**Figure 1.** Friedel-Crafts sulfonylation of benzene (◆), chlorobenzene (▲), methylbenzene (■), and 1,4-dimethylbenzene (●) with 4-methyl benzenesulfonyl chloride at room temperature in [bmim]Cl-AlCl<sub>3</sub>, *N* = 0.67.

neutral, and those greater than 0.5 afford acidic ionic liquids. The Lewis acidic species in such liquids is [Al<sub>2</sub>Cl<sub>7</sub>]<sup>−</sup>, and its concentration in the liquid is the function of the mole fraction of AlCl<sub>3</sub>. In an attempt to contemplate the effect of Lewis acidity on this reaction, ionic liquids of different compositions were prepared. Benzene and methylbenzene were chosen as model substrates, and the initial extent of conversions of the reactions were monitored in different ionic liquids at room temperature. No reactions were observed in the basic as well as the neutral liquids as expected. However in the liquids of compositions in the range *N* = 0.58–0.67, progressive increase in the initial rates of the reactions was seen due to consequent increase in the concentration of the catalytic species in the liquid. The results are illustrated in Table 1.

Preliminary investigations on sulfonylation in [bmim]Cl-AlCl<sub>3</sub>, *N* = 0.67 encouraged us to carry out the systematic study of the extent of conversion as a function of time for various aromatic hydrocarbons with TsCl. Figure 1 depicts the high initial rates of reactions demonstrating enhanced reactivity of substrates in the ionic liquid at room temperature. The regular trend of the progressive increase in initial rates with increasing

number of hyperconjugative methyl groups on the aromatic nucleus was observed.

The mechanism of sulfonylation based on the kinetics of the reaction by conventional procedure employing AlCl<sub>3</sub> as a Lewis acid in nitrobenzene has been well documented.<sup>10</sup> In an attempt to gain an insight into the mechanism of this reaction in these unconventional ionic liquids, we thought it would be worthwhile to carry out comprehensive <sup>27</sup>Al NMR studies. With a view that <sup>27</sup>Al NMR gives the knowledge of the speciation of aluminum during the course of the reaction, the study was planned to bring to light the intricate details of the mechanism. <sup>27</sup>Al NMR spectroscopy has been applied to the determination of the species<sup>11</sup> prevailing in ionic liquids of varying mole fractions of AlCl<sub>3</sub> and to the studies concerning the chemical exchange rates<sup>12</sup> by spectral simulation. However, surprisingly, no reports regarding the application of this technique pertaining to the mechanistic studies are known to date. The acid/base behavior of these liquids is controlled largely by reaction 1, which is believed to adequately describe the speciation



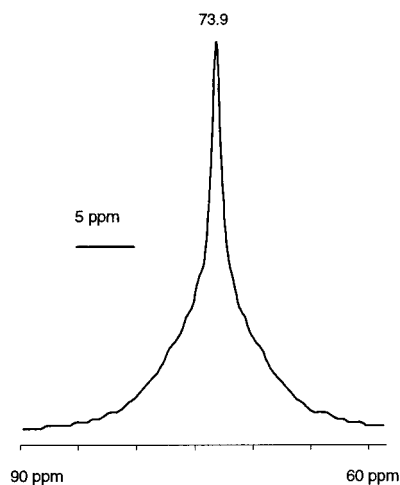
of aluminum in chloroaluminate liquids over a wide range of compositions. The anionic species equilibrium for the dissociation reaction has been investigated by potentiometry.<sup>13,14</sup> The equilibrium constant for this reaction is of the order of 10<sup>17</sup>–10<sup>18</sup> near ambient temperature.<sup>15,16</sup> Hence, in the basic ionic liquids, the predominant anionic species are [AlCl<sub>4</sub>]<sup>−</sup> and Cl<sup>−</sup>, whereas in acidic ionic liquids, [Al<sub>2</sub>Cl<sub>7</sub>]<sup>−</sup> predominates. In highly acidic ionic liquids, larger aluminum chloride adducts may become significant, e.g., [Al<sub>3</sub>Cl<sub>10</sub>]<sup>−</sup> ion.<sup>11,17,18</sup> Our work was mainly confined to the studies in the acidic ionic liquid of *N* = 0.67.

The chemical shifts of [AlCl<sub>4</sub>]<sup>−</sup> and [Al<sub>2</sub>Cl<sub>7</sub>]<sup>−</sup> in the <sup>27</sup>Al NMR spectrum were ascertained by recording the spectra of ionic liquids of compositions *N* ≤ 0.5 and *N* = 0.67, respectively. The values were found to be δ 79.3 and δ 73.9 ppm for [AlCl<sub>4</sub>]<sup>−</sup> and [Al<sub>2</sub>Cl<sub>7</sub>]<sup>−</sup>, respectively. The acidic ionic liquid of *N* = 0.67 showed a broad signal at δ 73.9 ppm. The equimolar mixture of ionic liquid and TsCl (Figure 2) showed no apparent shift in the already existing signal, indicating the formation of coordination complex of TsCl and [Al<sub>2</sub>Cl<sub>7</sub>]<sup>−</sup> species. However the possibility of the initial step (reaction 2) leading to

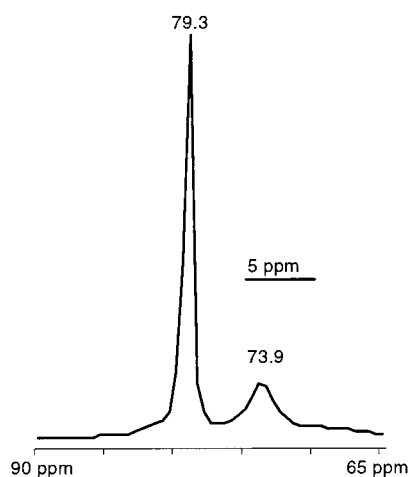


ionization of TsCl (which may be via coordination complex) to yield 4-methyl benzenesulfonylium ion with concomitant transformation of [Al<sub>2</sub>Cl<sub>7</sub>]<sup>−</sup> to [AlCl<sub>4</sub>]<sup>−</sup> species cannot be completely ruled out. This is because the peak for [Al<sub>2</sub>Cl<sub>7</sub>]<sup>−</sup> is broad enough to overlap the [AlCl<sub>4</sub>]<sup>−</sup>

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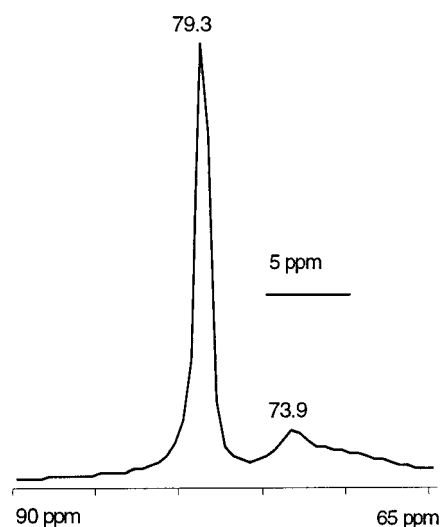


**Figure 2.**  $^{27}\text{Al}$  NMR of equimolar mixture of [bmim]Cl- $\text{AlCl}_3$ ,  $N = 0.67$  and TsCl.



**Figure 3.**  $^{27}\text{Al}$  NMR of [bmim]Cl- $\text{AlCl}_3$ ,  $N = 0.67$ , TsCl, and 1,3,5-trimethylbenzene in the molar proportion 1.0:1.0:1.1, respectively, after 5 min.

peak, particularly at low concentration of  $[\text{AlCl}_4]^-$ . If it is presumed that transformation of  $[\text{Al}_2\text{Cl}_7]^-$  takes place as per reaction 2, then significantly large line width of  $[\text{Al}_2\text{Cl}_7]^-$  indicates the low equilibrium constant of the forward reaction. Detailed investigations are required to establish the participation of either the coordination complex of TsCl with  $[\text{Al}_2\text{Cl}_7]^-$  or completely polarized ion pair  $[\text{Ts}][\text{AlCl}_4]$  in the sulfonylation reaction. The mixture of TsCl, ionic liquid, and 1,3,5-trimethylbenzene in mole proportion of 1.0:1.0:1.1, respectively, showed a peak at  $\delta$  79.3 ppm, after 5 min with the concomitant decrease in the peak at  $\delta$  73.9 ppm, corresponding to  $[\text{Al}_2\text{Cl}_7]^-$  species (Figure 3). 1,3,5-Trimethylbenzene was chosen because it reacts very fast at room temperature to produce sulfonylated aromatic hydrocarbon and HCl. The line width of the peak at  $\delta$  79.3 ppm corresponding to  $[\text{AlCl}_4]^-$  (as indicated from controls) indicates very little  $[\text{Al}_2\text{Cl}_7]^-$  is present. The large difference between the line widths of  $[\text{AlCl}_4]^-$  and  $[\text{Al}_2\text{Cl}_7]^-$  occurs because the  $^{27}\text{Al}$  nucleus in  $[\text{Al}_2\text{Cl}_7]^-$  ion does not exist in an environment of cubic symmetry as in  $[\text{AlCl}_4]^-$  and because the  $[\text{Al}_2\text{Cl}_7]^-$  ion has a large volume than the  $[\text{AlCl}_4]^-$  ion.<sup>12</sup> However, the observation of change in speciation of aluminum, i.e., predominance of  $[\text{AlCl}_4]^-$  from  $[\text{Al}_2\text{Cl}_7]^-$  after the sulfonylation reaction can be rationalized on the basis of work

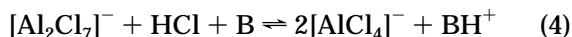


**Figure 4.**  $^{27}\text{Al}$  NMR of equimolar mixture of [bmim]Cl- $\text{AlCl}_3$ ,  $N = 0.67$  and 1,3,5-trimethyl-2-[(4-methylphenyl) sulfonyl]-benzene after treatment with dry HCl gas for 15 min.

done by Smith et al.<sup>19</sup> They concluded that HCl in acidic ionic liquids is a superacid. The strong Lewis acid  $[\text{Al}_2\text{Cl}_7]^-$  present in acidic ionic liquids acts as a chloride sink providing the driving force for the enhanced acidity of HCl (reaction 3). This has been substantiated by the



thermodynamic model of  $\text{AlCl}_3$  and 1-ethyl-3-methylimidazolium chloride ionic liquid, developed by Dymek et al.<sup>20</sup> According to their model, the concentration of chloride ions decreases by a factor of nearly  $5 \times 10^2$  when the  $\text{AlCl}_3$  content of the liquid increases from 55 to 67 mol %, the solubility limit of  $\text{AlCl}_3$  at ambient temperatures. However, the above reaction 3, is driven to the right due to i) the presence of generic base, B which may be the formed product in this case, (reaction 4) and ii) the observed high equilibrium constant for reaction 1 which gives  $[\text{AlCl}_4]^-$ .



To justify the suspicion that the sulfone plays a role of a base, we designed an experiment wherein 1,3,5-trimethyl-2-[(4-methylphenyl) sulfonyl]-benzene was mixed with [bmim]Cl- $\text{AlCl}_3$ ,  $N = 0.67$  in equimolar ratio and a jet of dry HCl gas was bubbled through the mixture for 15 min. The  $^{27}\text{Al}$  NMR of this mixture showed a peak for  $\text{AlCl}_4^-$  at  $\delta$  79.3 ppm (Figure 4), whereas the same mixture before treatment with HCl showed exclusively the peak for  $[\text{Al}_2\text{Cl}_7]^-$  at  $\delta$  73.9 ppm.

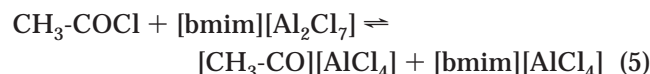
The sulfonylation reactions showed high initial rates as indicated from Figure 1, and later the extent of conversion was very slow, which may be due to participation of some amount of unreacted TsCl as a base (reaction 4) in the presence of high concentration of the liberated HCl. Despite the slower rates in later course, that the

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reaction went almost to completion may be due to differential basicities of TsCl and sulfone. To check whether the equilibrium of the reaction 4 can be driven to the left in the presence of excess of substrate and TsCl, the reaction was carried out where the molar proportion of the ionic liquid was adjusted so that it provided less  $[\text{Al}_2\text{Cl}_7]^-$  than the amount of substrate. A reaction that contained 1,3,5-trimethylbenzene, TsCl, and ionic liquid in a molar proportion of 1.1:1.0:0.5, respectively, afforded incomplete conversion to corresponding sulfone. Interestingly, the percentage conversion in this reaction was found to be slightly greater than the  $[\text{Al}_2\text{Cl}_7]^-$  would permit if consumed but at a slow rate. The reaction carried out by adding 1,3,5-trimethylbenzene (1.2 equiv) to the equimolar mixture of TsCl and  $[\text{bmim}]\text{Cl}-\text{AlCl}_3$ ,  $N = 0.67$  maintained at reduced pressure of 0.01 atm, showed a similar spectrum as Figure 3. This shows that it is practically difficult to drive HCl out of the reaction mixture before it reacts with  $[\text{Al}_2\text{Cl}_7]^-$ , even under reduced pressure. HCl formed in the reaction mixture has a high tendency to react with  $[\text{Al}_2\text{Cl}_7]^-$ , and moreover the medium is considerably viscous to allow the easy removal of HCl. The interactions of the product sulfone with  $[\text{AlCl}_4]^-$  and  $[\text{Al}_2\text{Cl}_7]^-$  ions are inevitable. The oxidizing and the protic impurities known to be present in such ionic liquids may further complicate the processes, rendering them difficult to explain. Substantial experimental evidences of physicochemical nature may prove fruitful in this regard.

Friedel–Crafts alkylation<sup>21</sup> and acylation<sup>22,23</sup> have been investigated in such ionic liquids. The reaction between acetyl chloride and the acidic ionic liquid was followed by  $^1\text{H}$  NMR by Wilkes et al.<sup>22</sup> The results suggested a stoichiometric reaction between  $\text{CH}_3\text{-COCl}$  and  $[\text{Al}_2\text{Cl}_7]^-$  ion. (reaction 5). Indeed, it is possible to isolate the solid,



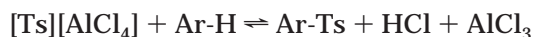
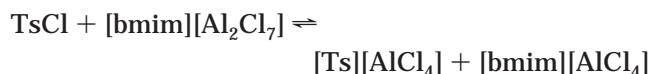
which is suspected to be  $[\text{CH}_3\text{-CO}][\text{AlCl}_4]$ , from the ionic liquid. We however believe that, after the electrophilic substitution with the acyl cation, even if  $[\text{Al}_2\text{Cl}_7]^-$  species is regenerated, it can no longer be completely available for further reaction as a result of its interaction with liberated HCl in the presence of acetylated product. Preliminary investigations employing  $^{27}\text{Al}$  NMR spectroscopy has confirmed this belief. The acylation using acetyl chloride and 1,4-dimethylbenzene in  $[\text{bmim}]\text{Cl}-\text{AlCl}_3$ ,  $N = 0.67$  liquid was followed by  $^{27}\text{Al}$  NMR spectroscopy, which after 10 min of reaction showed no detectable amount of  $[\text{Al}_2\text{Cl}_7]^-$  species. The control experiment of the acylated product in  $[\text{bmim}]\text{Cl}-\text{AlCl}_3$ ,  $N = 0.67$  liquid after treatment with dry HCl as in case of sulfonylation showed the predominance of  $[\text{AlCl}_4]^-$  species. Had this not been the case, the ionic liquids would have revolutionized the field of Friedel–Crafts chemistry and several other synthetically important reactions driven by the Lewis acid catalysts. In the initial phases of the reaction, some amount of HCl formed escapes into the atmosphere even before the  $[\text{Al}_2\text{Cl}_7]^-$  species is

regenerated. Later, after the regeneration of  $[\text{Al}_2\text{Cl}_7]^-$  species, the interaction of  $[\text{Al}_2\text{Cl}_7]^-$  with HCl in the presence of the acylated product and the electrophilic substitution can become competitive. Probably because of these reasons, the reaction is observed to go beyond the extent of what is expected from it if it consumes equimolar amount of  $[\text{Al}_2\text{Cl}_7]^-$  species.  $\text{AlCl}_3$  is known to form a complex with the carbonyl group of the acylated product in the conventional Friedel–Crafts acylations. This complex formation could render the complete recombination of  $\text{AlCl}_3$  with  $[\text{AlCl}_4]^-$  difficult, to give  $[\text{Al}_2\text{Cl}_7]^-$ . However, the  $^{27}\text{Al}$  NMR of the mixture of  $[\text{bmim}]\text{Cl}-\text{AlCl}_3$ ,  $N = 0.67$ , acetyl chloride, and 1,4-dimethylbenzene in molar proportion of 1.0:1.0:1.1, respectively, shows only one peak at  $\delta$  79.3 ppm corresponding to  $[\text{AlCl}_4]^-$  ion, which reflects that no other Al-containing species is present in significant concentration to be detected by NMR. Thus it seems that the equilibrium constant of the reaction 6 is high enough to allow the complex formation. No such complex formation with

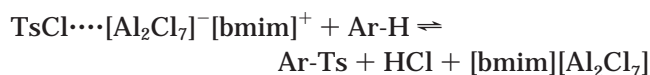
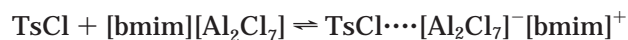


the formed sulfone even in case of the sulfonylation was observed in NMR (Figure 3). The complex of 1,3,5-trimethyl-2-[(4-methylphenyl) sulfonyl]-benzene with  $\text{AlCl}_3$  in a control experiment in NMR showed a peak at 70.9 ppm.

On the basis of the conclusions drawn from the above experiments the plausible mechanisms of sulfonylation in  $[\text{bmim}]\text{Cl}-\text{AlCl}_3$ ,  $N = 0.67$  liquid are as follows:



and




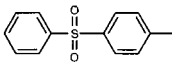

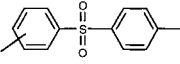

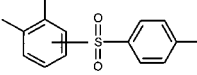

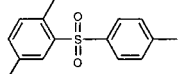

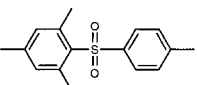

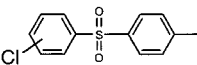
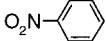
To generalize the procedure, the sulfonylation reactions were carried out on different substrates such as benzene and substituted benzenes. The reactions worked well, and the results are illustrated in Table 2. The optimization of time, temperature, and yields was carried out for the mole ratio 1.1:1.0:1.2 of substrate, TsCl, and ionic liquid, respectively. The reactions were continued until the quantitative conversions at room temperature or a little higher, bearing in mind the ambient quality of the procedure. However, the experimentation revealed that the rates of the reactions in ionic liquid increased with the corresponding increase in the molar proportion of the

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**Table 2.** Friedel–Crafts Sulfonylations of Benzene and Substituted Benzenes in [bmim]Cl–AlCl<sub>3</sub>, *N* = 0.67 with TsCl

Entry	Substrate	Product	Time (h)	Temperature (°C)	Isomer distribution <i>o</i> : <i>p</i>	Yield (%) <sup>a</sup>
1.			5	30	-	89
2.			4	30	34:66	92
3.			3	30	11:89	91
4.			3	30	-	87
5.			3	30	-	90
6.			5	50	5:95	83
7.		-	-	-	-	-

<sup>a</sup> Isolated yields

ionic liquid and temperature, affording quantitative yields of the products in relatively short times.

### Experimental Section

The ionic liquids were prepared as previously described.<sup>24</sup> In a typical experimental procedure, to the weighed quantity of ionic liquid [bmim]Cl–AlCl<sub>3</sub>, *N* = 0.58–0.67, were added TsCl and hydrocarbon in a molar ratio of 1.2:1.0:1.1, respectively, on a 2 mmol scale with respect to TsCl, unless otherwise stated in the text. The reaction mixture was stirred at the desired temperature in an inert atmosphere. All additions were carried out in an inert atmosphere glovebox. The reaction was quenched using 6 M HCl in cold conditions. The resultant solution was extracted using ethyl acetate (3 × 10 mL). The combined organic extracts were evaporated under reduced pressure. The crude extract was assayed on GC, to monitor the conversion and isomer distribution. The products were further purified by silica gel column chromatography and characterized by IR, NMR spectroscopy, and physical con-

stants. The characterization data was found to be consistent with the earlier reports.<sup>8</sup>

**<sup>27</sup>Al NMR Studies.** All spectra were recorded on a 500 MHz spectrometer. The samples were prepared in 5-mm BB probe and the receiver coil of the spectrometer was tuned to optimize the detection of aluminum-27 resonance at 130 MHz. All spectra were referenced to anhydrous AlCl<sub>3</sub> taken as an external standard ( $\delta$  0.0 ppm). The samples used for recording <sup>27</sup>Al NMR spectra were prepared by dissolving 40–50  $\mu$ L of reaction mixtures in 400  $\mu$ L of CD<sub>2</sub>Cl<sub>2</sub>.

**Gas Chromatographic Analysis.** A gas chromatograph equipped with flame ionization detector was employed for the analysis. The detector temperature was maintained at 280 °C. The column was programmed with an initial temperature of 200 °C and was increased thereafter to 270 °C at the rate of 10 °C min<sup>-1</sup>. The column used was liquid-phase ov-17 (length 6 ft).

**Acknowledgment.** We thank National Facility of High Field NMR, TIFR, Mumbai for the spectral recordings.

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