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An efficient and highly selective ortho-*tert*-butylation of *p*-cresol with *tert*-butyl methyl ether catalyzed by sulfonated ionic liquids

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Abstract: A novel series of sulfonic acid-functionalized ionic liquids (SFILs) was found to act as efficient catalysts for ortho-*tert*-butylation of *p*-cresol with *tert*-butyl methyl ether (MTBE) as the *tert*-butylating agent without an added solvent. The mono *o*-*tert*-butylated product was obtained in up to 85.8 % isolated yield and 95.2 % selectivity under such green conditions. No *O*-*tert*-butylated byproducts were formed.

Keywords: *tert*-butylation; 2-*tert*-butyl-*p*-cresol; *p*-cresol; sulfonated ionic liquid.

INTRODUCTION

C-Alkylated phenols have received great attention as industrially important intermediates for the preparation of several antioxidants and agrochemicals. For the synthesis of these materials by alkylation reactions, various alkylating agents, such as olefins, alcohols and ethers, have been used in the presence of a catalyst.[1] In particular, 2-*tert*-butyl-*p*-cresol (TBC) and 2,6-di-*tert*-butyl-*p*-cresol (DTBC), which are commercially known as butylated hydroxyl toluene (BHT), are produced by ortho-*tert*-butylation of *p*-cresol under different reaction conditions. TBC and DTBC have found wide applications as dyes, antioxidants, rubbers, UV-absorbers, agrochemicals, non-ionic detergents, emulsifiers and pharmaceuticals. They have also been used for the preparation of surfactants, phenolic resins, and inhibitors of polymerizable activated olefin monomers.[2,3] Considering these aforementioned applications, the preparation of ortho-*tert*-butylated *p*-cresols *via* efficient approaches has been an active area of research.

There are several literature methods for the ortho-*tert*-butylation of *p*-cresol in the presence of homogeneous or heterogeneous catalytic systems, including Brønsted acids,[4] Lewis acids,[5] cation-exchange resins,[6] mesoporous materials,[7] zeolites,[8] molecular sieves, and also supercritical or near-supercritical water.[9]

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Ortho-*tert*-butylation of *p*-cresol was achieved employing various *tert*-butylating agents, particularly *tert*-butyl methyl ether (MTBE) was used in the presence of UDCaT-1 catalyst (a hexagonal mesoporous silica with sulfate modified zirconia).[10] Under the above conditions, the products were obtained in 45 % conversion and 97 % selectivity for TBC. In some cases, the ortho-*tert*-butylation of *p*-cresol was accomplished using *tert*-butanol (TBA) as the C-*tert*-butylating agent. For the promotion of this process, solid-supported catalysts consisting of 12-tungstophosphoric acid (TPA) on zirconia (TPA/ZrO_2),[11] on titania (TPA/TiO_2)[12] or on mesoporous silica (TPA/MCM-41),[13] and WO_x/ZrO_2,[14] have been applied. Despite the benefits of these methods, some suffer from disadvantages, such as unsatisfactory conversion, prolonged reaction time, expensive catalyst, low selectivity, use of toxic solvents, tedious work-up, requirement of special equipment, or harsh reaction conditions. Thus, the development of an efficient, easy, highly selective, and environmentally benign method using novel catalysts for the preparation of C-*tert*-butylated phenols is desirable.

During the last two decades, ionic liquids (ILs) have received great attention as catalysts and solvents in organic chemistry due to their environmentally friendly nature, non-volatility, high polarity, and good chemical and thermal stabilities. High yields of the products and high selectivity in short reaction times, and clean reaction procedures are often observed in ILs as reaction media.[15–18] Furthermore, their hydrophobicity/hydrophilicity can be optimized by appropriate modification of the cation or anion part.[19] ILs containing a Lewis or a Brønsted acid group have been used in various chemical transformations.[20] Recently, significant advances in the field have been witnessed, whereby a functional group is covalently bonded to the IL.[21] The incorporation of sulfonic acid groups to ILs significantly increases their acidic property as well as their water solubility. Such SO_3H-functionalized ILs (SFILs) have been used as substitutes for conventional homogenous and heterogeneous acid catalysts.[22] Moreover their polar nature makes them useful for solvent-free conditions.[23–25] Recently, ortho--*tert*-butylation of *p*-cresol was reported in which TBA was used as the *tert*--butylating agent in the presence of SFILs, such as 1-(4-sulfobutyl)pyridinium hydrogensulfate,[26] (4-sulfobutyl)triethylammonium hydrogensulfate,[27] and polysulfonated ILs,[28] whereby TBC was afforded in good to excellent conversion and selectivity.

In continuation of interest in the application of green methodologies in organic synthesis,[29–32] herein an efficient and green procedure for the ortho-*tert*-butylation of *p*-cresol using MTBE in the presence of the SFILs, presented in Fig. 1, as the catalyst–solvent medium, is described (Scheme 1).

EXPERIMENTAL

Commercially available solvents and chemicals were used without further purification. The SFILs **1**–**3** were prepared according to procedures outlined in the literature[25,33] and were

characterized by NMR spectroscopy on a Bruker DPX 3300-300 MHz. Quantitative product analysis was conducted by gas chromatography on a Hewlett Packard HP-5890 instrument equipped with HP-1 column (30 m long, 0.5 mm diameter), and flame ionization detector (FID), using N_2 as the carrier gas at a flow rate of 2 mL min^{-1}.

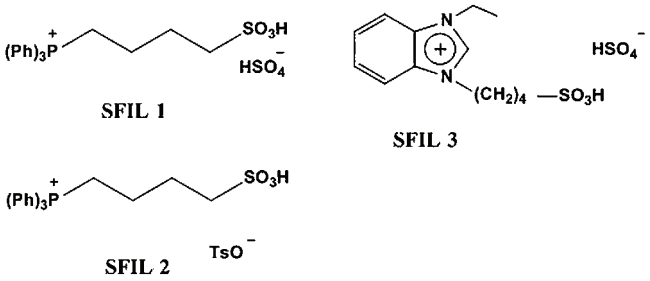
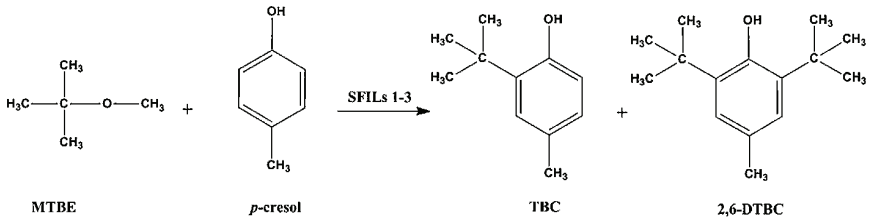


Fig. 1. Structures of the SFILs used in this study; SFIL **1** – triphenyl(4-sulfobutyl)-phosphonium hydrogensulfate ($[Ph_3P(CH_2)_4SO_3H][HSO_4]$), SFIL **2** – triphenyl(4-sulfobutyl)phosphonium tosylate ($[Ph_3P(CH_2)_4SO_3H][TsO]$) and SFIL **3** – 1-ethyl-3-(4--sulfobutyl)-1*H*-benzimidazolium hydrogensulfate ([bSebim]HSO_4).



Scheme 1. Ortho-*tert*-butylation of *p*-cresol with MTBE using SFILs **1**–**3**.

Synthesis and characterization of the SFILs

*Synthesis of triphenyl(4-sulfobutyl)phosphonium hydrogensulfate (SFIL **1**) and triphenyl-(4-sulfobutyl)phosphonium tosylate (SFIL **2**).* The triphenyl(4-sulfobutyl)phosphonium hydrogensulfate and triphenyl(4-sulfobutyl)phosphonium tosylate ionic liquids were prepared according to procedures outlined in the literature.[25] Triphenylphosphine was mixed with 1,4-butane sulftone in toluene at 110–120 °C for 12–24 h. After solidification of mass, the product (zwitterion) was washed three times with diethyl ether and then dried *in vacuo*. A stoichiometric amount of *p*-toluenesulfonic acid or sulfuric acid was added to the precursor zwitterion. The mixture was heated at 80 °C for 24 h, during which time the solids liquefied, resulting in the formation of triphenyl(4-sulfobutyl)phosphonium tosylate or triphenyl(4--sulfobutyl)phosphonium hydrogensulfate. The ILs phase were then washed repeatedly with toluene and diethyl ether to remove the non-ionic residues, and dried *in vacuo*.

*$[Ph_3P(CH_2)_4SO_3H][HSO_4]$ (SFIL **1**).* ^{1}H-NMR (300 MHz, D_2O, δ / ppm): 7.63–7.23 (15H, *m*, Ar-H), 3.05 (2H, *m*, $(CH_2)_3C\mathbf{H}_2SO_3H$), 2.63–2.56 (2H, *t*, J = 7.53 Hz, $C\mathbf{H}_2(CH_2)_3SO_3H$), 1.64 (2H, *m*, $(CH_2)_2C\mathbf{H}_2CH_2SO_3H$), 1.56 (2H, *m*, $CH_2C\mathbf{H}_2(CH_2)_2SO_3H$).

*$[Ph_3P(CH_2)_4SO_3H][TsO]$ (SFIL **2**).* ^{1}H-NMR (300 MHz, D_2O, δ / ppm); 7.4 (2H, *m*, *p*-TsO), 7.27–7.23 (15H, *m*, Ar-H), 6.82–6.79 (2H, *d*, J = 9.00 Hz, *p*-TsO), 2.83–2.79 (2H, *m*, $(CH_2)_3C\mathbf{H}_2SO_3H$), 2.53–2.48 (2H, *t*, J = 7.56 Hz, $C\mathbf{H}_2(CH_2)_3SO_3H$), 1.87 (3H, *s*, *p*-TsO), 1.57–1.54 (2H, *m*, $(CH_2)_2C\mathbf{H}_2CH_2SO_3H$), 1.32 (2H, *m*, $CH_2C\mathbf{H}_2(CH_2)_2SO_3H$).

*Synthesis of 1-ethyl-3-(4-sulfobutyl)-1*H*-benzimidazolium hydrogensulfate (SFIL **3**)*. The 1-ethyl-3-(4-sulfobutyl)benzimidazolium hydrogen sulfate ionic liquid was prepared according to a procedure outlined in the literature.[33] Under vigorous stirring, the required amounts of benzimidazole and tetrabutylammonium bromide were dissolved in a 30 % aqueous solution of sodium hydroxide, the stoichiometric amount of bromoethane was added dropwise and then the mixture was heated at 45 °C for 12 h until two phases formed. The organic phase (upper phase) was washed with deionized water and ethyl acetate and dried *in vacuo* at 50 °C for 3 h, giving 1-ethylbenzimidazole (Ebim) as a colorless liquid. The required amount of 1,4-butane sulftone was dissolved in toluene under vigorous stirring. The stoichiometric amount of Ebim was added to the solution dropwise and cooling to maintain the temperature at 0–5 °C. After completion of the addition, the mixture was slowly heated up to room temperature and stirred for 2 h, whereby a precipitate formed. The precipitate was recovered by filtration, washed three times with diethyl ether and dried at 100 °C for 5 h, giving 1-ethyl-3-(4-sulfobutyl)-1H-benzimidazolium inner salt (Ebim-BS) as a white powder. An amount of Ebim-BS was dissolved in water and a stoichiometric amount of sulfuric acid was added dropwise at room temperature. After completion of the addition, the mixture was slowly heated to 90 °C and stirred for 2 h and then the water was removed *in vacuo* at 70 °C for 3 h, giving [bSebim]HSO_4 as a colorless solid.

*[bSebim]HSO_4 (SFIL **3**)*. ^{1}H-NMR (300 MHz, D_2O, δ / ppm): 9.07 (1H, *s*, NCHN), 7.61 (2H, *m*, Ar-H), 7.37 (2H, *m*, Ar-H), 4.30 (2H, *m*, $N(CH_2)_3C\mathbf{H}_2SO_3H$), 4.23 (2H, *m*, $NC\mathbf{H}_2CH_3$), 2.74 (2H, *t*, *J* = 6.52 Hz, $NC\mathbf{H}_2(CH_2)_3SO_3H$), 1.90 (2H, *m*, $N(CH_2)_2C\mathbf{H}_2CH_2SO_3H$), 1.59 (2H, *m*, $NCH_2C\mathbf{H}_2(CH_2)_2SO_3H$), 1.38 (3H, *t*, *J* = 7.58 Hz, $NCH_2C\mathbf{H}_3$).

Ortho-tert-*butylation of* p-*cresol with MTBE in the presence of SFILs **1**–**3***

The SFIL (1 mmol) was added to a mixture of *p*-cresol (1 mmol, 108 mg) and MTBE (1 mmol, 119 μL) in a 25 mL round-bottom flask and the reaction mixture was heated for the required time and at the chosen temperature as indicated (12 h at 90 °C or 7 h at 100 °C). The progress of the reaction was monitored by TLC on silica gel using ethyl acetate/hexane 2:1 as the eluent. After the given time, the mixture was cooled to room temperature and extracted with ethyl acetate (3×5 mL). The recovered SFIL was dried *in vacuo*, and ^{1}H-NMR analysis attested its high purity, showing no traces of reactants or products. The recovered SFIL could be directly reused without further drying.

The ethyl acetate phase containing the products was analyzed by gas chromatography isothermally at 110 °C. Before injecting the sample into the chromatographic column, dichlorobenzene (as an internal standard, 3.40 mmol, 50 mg) was added to all samples. The carrier gas pressure at the beginning of the chromatographic column was about 13 psi*. Total elution time was 31.35 min and the elution times of dichlorobenzene, *p*-cresol, 2-*tert*-butyl-*p*--cresol and 2,6-di-*tert*-butyl-*p*-cresol in the ethyl acetate phase were 4.7, 5.16, 9.3 and 12.19 min, respectively.

RESULTS AND DISCUSSION

*Assessment of SFILs **1**–**3** as catalysts*

The evaluation of the efficiency of SFILs **1**–**3** in the ortho-*tert*-butylation of *p*-cresol for 12 h at 90 °C revealed 1-ethyl-3-(4-sulfobutyl)benzimidazolium

* 1 psi = 6.895 kPa

hydrogensulfate ([bSebim][HSO_4], SFIL **3**) to be the most effective catalyst. As given in Table I, it led to 75.4 % conversion with 93.3 % selectivity for TBC. For optimization purposes, various reaction conditions in the presence of SFIL **3** were examined.

TABLE I. Ortho-*tert*-butylation of *p*-cresol with MTBE using SFILs **1**–**3**; reaction conditions: 12 h at 90 °C

Entry	Catalyst	Mole ratio *p*-cresol:MTBE:SFIL	Conversion %	Selectivity, %	
				TBC	DTBC
1	[$Ph_3P(CH_2)_4SO_3H$][HSO_4]	1:1:1	56.3	76.3	23.7
2	[$Ph_3P(CH_2)_4SO_3H$][TsO]	1:1:1	35.5	100	0
3	[bSebim][HSO_4]	1:1:1	75.4	93.3	6.7

Effect of the reaction time

The effect of reaction time on the ortho-*tert*-butylation of *p*-cresol with MTBE in the presence of SFIL **3** was studied at 100 °C. Figure 2 shows that increasing the reaction time had a positive impact on enhancing the conversion of *p*-cresol and the selectivity for TBC. The highest conversion and selectivity for TBC were obtained at 7 h and prolonging the reaction time did not lead to any improvement. The maximum conversion of *p*-cresol at 7 h was 85.8 % and the selectivity for TBC 95.2 %.

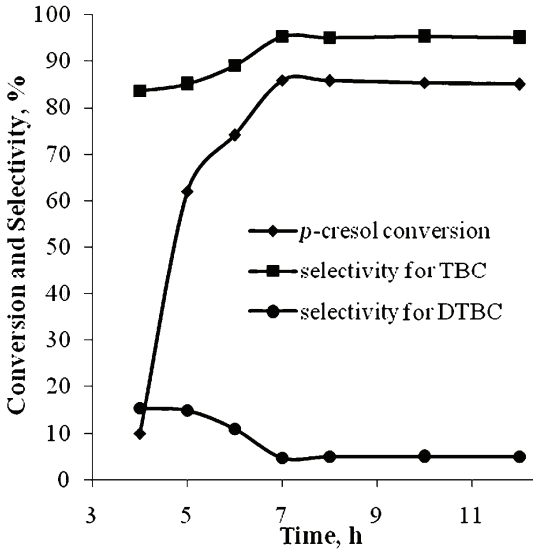
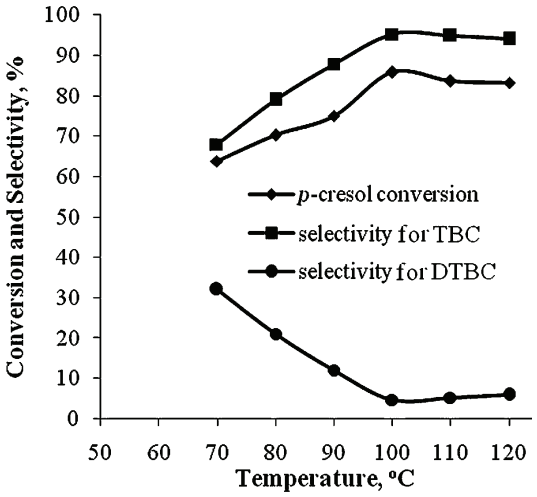


Fig. 2. *p*-Cresol conversion and products selectivity *vs.* reaction time. Reaction conditions: mole ratio of *p*-cresol:MTBE:[bSebim][HSO_4] = 1:1:1; heating at 100 °C.

Effect of the reaction temperature

The ortho-*tert*-butylation of *p*-cresol with MTBE for 7 h was studied at temperatures from 70 to 120 °C. As shown in Fig. 3, conducting the reaction at inc-

reasing temperatures up to 100 °C increased the conversion of *p*-cresol and further increases to above 100 °C did not improve this result. Thus, the optimum reaction temperature was 100 °C leading up to 85.8 % conversion and 95.2 % selectivity for TBC.



Fig, 3. *p*-Cresol conversion and products selectivity *vs.* reaction temperature. Reaction conditions: mole ratio of *p*-cresol:MTBE:[bSebim][HSO_4] = = 1:1:1; heating for 7 h.

Effect of the MTBE:p-*cresol mole ratio*

The influence of MTBE:*p*-cresol mole ratio was studied at 100 °C (reaction for 7 h) while maintaining the [bSebim][HSO_4]:*p*-cresol mole ratio at 1:1 (Fig. 4). Various mole ratios of MTBE:*p*-cresol varying from 0.5–2 were tested. These experiments demonstrated that increasing the mole ratio of MTBE:*p*-cresol

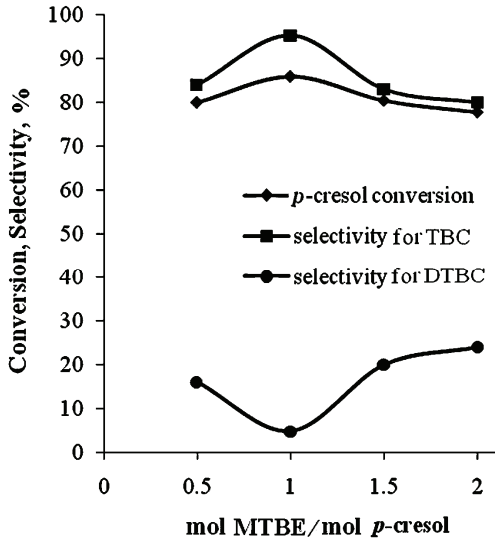


Fig. 4. *p*-Cresol conversion and products selectivity *vs.* amount of MTBE. Reaction conditions: mole ratio of [bSebim][HSO_4]: :*p*-cresol = 1:1; heating for 7 h at 100 °C.

increased the conversion of *p*-cresol, reaching a maximum of 85.8 % from a 1:1 ratio. However, the selectivity for TBC first improved to some extent (a 13 % increase) going from 0.5 to 1 and then decreased. This could be attributed to its transformation into DTBC with more MTBE available. As shown in Fig. 4, the maximum of 85.8 % conversion of *p*-cresol with a 95.2 % TBC selectivity were observed when the MTBE:*p*-cresol ratio was 1:1. Noteworthy, the DTBC selectivity increased when the mole ratio MTBE:*p*-cresol was greater than 1.

*Effect of [bSebim][HSO$_4$]:*p*-cresol mole ratio*

The effect of the mole ratio of [bSebim][HSO$_4$]:*p*-cresol on the reaction was studied under the optimized conditions, *i.e.*, reaction for 7 h at 100 °C with a MTBE:*p*-cresol mole ratio of 1:1. As shown in Fig. 5, with increasing mole ratio of [bSebim][HSO$_4$]:*p*-cresol from 0.5 to 1, both the conversion of *p*-cresol and the selectivity for TBC increased. This is understandable as the progress of catalyzed reactions is proportional to the catalyst loading. However, the best result of 85.8 % conversion and 95.2 % selectivity for TBC was obtained using a [bSebim][HSO$_4$]:*p*-cresol ratio of 1:1, as increasing this ratio did not improve the selectivity.

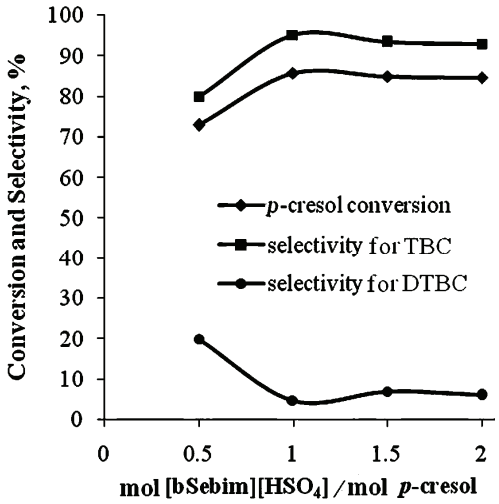


Fig. 5. *p*-Cresol conversion and products selectivity *vs.* amount of [bSebim][HSO$_4$] (SFIL **3**). Reaction conditions: mole ratio of MTBE:*p*-cresol = 1:1; heating for 7 h at 100 °C.

*Recycling of SFIL **3***

In order to examine the recoverability and reusability of [bSebim][HSO$_4$] (SFIL **3**), after completion of the reaction, ethyl acetate (3×5 mL) was added resulting in two layers. The upper phase contained the products and the lower phase the SFIL. After further extractions (2×5 mL ethyl acetate) and phase separation, the SFIL was dried under vacuum for 5 h at 70 °C. Recycle test results for

[bSebim][HSO_4] are shown in Table II, indicating no major decrease (< 5 %) in the conversion of *p*-cresol and selectivity for the products in up to three runs.

TABLE II. Recycling of 1-ethyl-3-(4-sulfobutyl)benzimidazolium hydrogensulfate ([bSebim][HSO_4], SFIL **3**); reaction conditions: mole ratios of [bSebim][HSO_4]:*p*-cresol:MTBE = 1:1:1; heating for 7 h at 100 °C

Entry	SFIL **3** Experimental run	Conversion, %	Selectivity, %	
			TBC	DTBC
1	Fresh	85.8	95.2	4.8
2	Recycle 1	81.7	97.8	2.2
3	Recycle 2	80.3	91.8	8.2

*Comparison of efficiencies of SFILs **1**–**3** with those of other SFIL catalysts*

The efficiencies of the prepared SFILs **1**–**3** were compared with those of other literature SFILs for the ortho-*tert*-butylation of *p*-cresol (Table III). As tabulated, all the SFILs led to TBC with high conversion and good selectivity, but the in the literature known di(SO_3H)-functionalized IL based on imidazolium (SFIL **9**) and [bSebim][HSO_4] (SFIL **3**) afforded the best results. The advantage of SFIL **3** is its ease of preparation compared to the former.

TABLE III. Comparison of various SFIL catalysts for the ortho-*tert*-butylation of *p*-cresol with TBA or MTBE

Reactants	Catalyst	Mole ratio *p*-cresol:TBA or MTBE:SFIL	*t* / °C	Conversion %	Selectivity, %		Ref.
					TBC	DTBC	
p-cresol/MTBE	SFIL **1**	1:1:0.5	90	78.4	90.7	9.3	This study
p-cresol/MTBE	SFIL **2**	1:1.25:1	90	44.8	88.6	11.4	This study
p-cresol/MTBE	SFIL **3**	1:1:1	100	85.8	95.2	4.8	This study
p-cresol/TBA	SFIL **4**[a]	1:1:1	70	80.7	90.0	9.5	27
p-cresol/TBA	SFIL **4**[a]	3:1:1	70	85.0	66.8	32.3	27
p-cresol/TBA	SFIL **5**[b]	1:1:1	70	82.6	80.5	16.7	26
p-cresol/TBA	SFIL **6**[c]	1:1:1	70	70.8	70.6	3.5	26
p-cresol/TBA	SFIL **6**[c]	2:1:1	70	84.0	72.0	27.0	27
p-cresol/TBA	SFIL **7**[d]	1:1:1	70	80.0	91.0	8.9	27
p-cresol/TBA	SFIL **8**[e]	1:1:1	70	66.9	69.2	3.9	26
p-cresol/TBA	SFIL **9**[f]	1:1:0.5	70	85.3	95.2	1.4	28

[a]SFIL **4**: (4-sulfobutyl)triethylammonium hydrogensulfate; [b]SFIL **5**: 1-(3-sulfopropyl)pyridinium tosylate; [c]SFIL **6**: 1-(4-sulfobutyl)pyridinium hydrogensulfate; [d]SFIL **7**: 1-methyl-3-(4-sulfobutyl)imidazolium hydrogensulfate; [e]SFIL **8**: 1-(4-sulfobutyl)pyridinium tosylate; [f]SFIL **9**: a di(SO_3H)-functionalized IL based on 1,1′-(1,4-butanediyl)bis[3-(4-sulfobutyl)-1*H*-imidazolium] bis(hydrogensulfate)

Ortho-tert-*butylation of* p-*cresol with MTBE in the presence of SFIL **3** on the 50 mmol scale*

To a 1000 mL round-bottom flask containing a mixture of *p*-cresol (50 mmol, 5.4 g) and MTBE (50 mmol, 5.95 ml) was added SFIL **3** (50 mmol, 16.20 g) and

the mixture was heated at 100 °C. After 7 h, the reaction mixture was cooled to room temperature and ethyl acetate (3×50 mL) was added leading to the separation of SFIL **3**. The crude product was purified by column chromatography on silica gel using hexane/ethyl acetate 2:1 as eluent that afforded TBC (yellow solid, 6.435 g, 78 % isolated yield) and DTBC (white solid, 0.525 g, 5 % isolated yield). Gas chromatography analysis of the crude product indicated 84.7 % conversion of *p*-cresol and 93.7 % selectivity to TBC.

CONCLUSIONS

A series of SO_3H-functionalized ILs was prepared and their dual catalyst–solvent performances for ortho-*tert*-butylation of *p*-cresol with MTBE examined. The best results were obtained in the presence of [bSebim][HSO_4] (SFIL **3**), and an optimization study was conducted. This Brønsted acidic IL has some advantages, such as up to 85.8 % conversion and 95.2 % selectivity for the mono ortho-*tert*-butylated product TBC, and it could be easily reused avoiding thus the use of solvents and toxic catalysts. The present approach represents an efficient method for the ortho-*tert*-butylation of *p*-cresol to TBC without formation of ortho-*tert*-butylated products and without the use of added solvents.

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ИЗВОД

ЕФИКАСНО И СЕЛЕКТИВНО ОРТО-*ТЕРЦ*-БУТИЛОВАЊЕ *p*-КРЕЗОЛА *ТЕРЦ*-БУТИЛ МЕТИЛ-ЕТРОМ КАТАЛИЗОВАНО СУЛФОНОВАНИМ ЈОНСКИМ ТЕЧНОСТИМА

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Утврђено је да серија нових јонских течности типа сулфонских киселина ефикасно катализује орто-*терц*-бутиловање *p*-крезола *терц*-бутил метил-етром (MTBE) као реагенсом за *терц*-бутиловање, без присутног растварача. Моно орто-*терц*-бутиловани производ настаје у приносу до 80,4 % изолованог производа и уз 95,2 % селективности. Не настаје *O*-*терц*-бутиловани производ.

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REFERENCES

1. A. V. Krishnan, K. Ojha, N. C. Pradhan, *Org. Proc. Res. Dev.* **6** (2002) 132
2. J. Pospisil, *Polym. Degrad. Stab.* **20** (1988) 181
3. J. Murphy, in: Additives *for Plastics Handbook*, 2nd ed., Ch. 2., Elsevier, Amsterdam, 2001
4. L. Tian, F. H. Cao, D. Y. Fang, S. Z. Guo, *Chin. J. Chem. Eng.* **15** (2007) 680
5. T. Zhang, F. Q. Zhang, D. Mei, G. F. Wang, J. G. Wang, *Catal. Commun.* **6** (2005) 385
6. M. A. Harmer, Q. Sen, *Appl. Catal., A* **221** (2001) 45
7. M. Selvaraj, S. Kawi, *Micropor. Mesopor. Mater.* **98** (2007) 143

8. K. Zhang, H. Zhang, G. Xiang, D. Xu, S. Liu, H. Li, *Appl. Catal., A* **207** (2001) 183
9. T. Sato, G. Sekiguchi, T. Adschiri, K. Arai, *Chem. Commun.* **17** (2001) 1566
10. G. D. Yadav, A. A. Pujari, A. V. Joshi, *Green Chem.* **1** (1999) 269
11. B. M. Devassy, G. V. Shanbhag, F. Lefebvre, S. B. Halligudi, *J. Mol. Catal., A* **210** (2004) 125
12. S. M. Kumbar, G. V. Shanbhag, F. Lefebvre, S. B. Halligudi, *J. Mol. Catal., A* **256** (2006) 324
13. G. Kamalakar, K. Komura, Y. Sugi, *Catal. Lett.* **108** (2006) 31
14. S. Sarisha, B. M. Devassy, S. B. Halligudi, *J. Mol. Catal., A* **235** (2005) 44
15. S. Chowdhury, R. S. Mohan, J. L. Scott, *Tetrahedron* **63** (2007) 2363
16. P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **39** (2000) 3772
17. J. Safaei-Ghomi, M. A. Ghasemzadeh, *J. Serb. Chem. Soc.* **77** (2012) 733
18. a) T. Welton, *Chem. Rev.* **99** (1999) 2071; b) V. I. Parvulescu, C. Hardacre, *Chem. Rev.* **107** (2007) 2615
19. J. L. Anderson, R. Ding, A. Ellern, D. W. Armstrong, *J. Am. Chem. Soc.* **127** (2005) 593
20. W. J. Swindall, *Clean Technol. Envir.* **6** (2004) 149
21. P. Wasserscheid, M. Sesing, W. Korth, *Green Chem.* **4** (2002) 134
22. D. C. Forbes, K. J. Weaver, *J. Mol. Catal., A* **214** (2004) 129
23. Y. Gu, F. Shi, Y. Deng, *J. Mol. Catal., A* **212** (2004) 71
24. J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu, Z. Sun, *Catal. Commun.* **5** (2004) 473
25. A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes, J. H. Davis, *J. Am. Chem. Soc.* **124** (2002) 5962
26. X. Liu, J. Zhou, X. Guo, M. Lin, X. Ma, C. Song, C. Wang, *Ind. Eng. Chem. Res.* **47** (2008) 5298
27. K. Kondamudi, P. Elavarasan, P. J. Dyson, S. J. Upadhyayula, *J. Mol. Catal., A* **321** (2010) 34
28. S. Bao, N. Quan, J. Zhang, J. Yang, *Chin. J. Chem. Eng*, **19** (2011) 64
29. R. Fareghi-Alamdari, Z. Hosseinabadi, M. Farhadi-Khouzani, *J. Chem. Sci.* **124** (2012) 827
30. N. Zekri, R. Fareghi-Alamdari, A. Khalafi-Nezhad, *Bull. Chem. Soc. Ethiop*. **24** (2010) 299
31. N. Zekri, R. Fareghi-Alamdari, *Can. J. Chem.* **88** (2010) 563
32. A. Khalafi-Nazhad, R. Fareghi-Alamdari, N. Zekri, *Tetrahedron* **56** (2000) 7503
33. Y. Wang, D. Jiang, L. J. Dai, *Catal. Commun.* **9** (2008) 2475.