Synthesis of 5-*tert*-Butyl-1,2,3-trimethylbenzene Catalyzed by [Et₃NH]Cl–AlCl₃¹

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Abstract—Common Lewis acids and Lewis acidic ionic liquid catalysts were applied in the synthesis of 5-*tert*butyl-1,2,3-trimethylbenzene from 1,2,3-trimethylbenzene and 2-chloro-2-methylpropane, where [Et₃NH]Cl– AlCl₃ demonstrated the most promising catalytic potential. The effects of reaction time, temperature, catalyst composition and dosage have been systematically studied in the presence of [Et₃NH]Cl–AlCl₃. The maximum selectivity of 90.32% was achieved upon heating at 10°C for 5 h with a mass fraction of [Et₃NH]Cl–AlCl₃ to 1,2,3-trimethylbenzene of 10%. Activity of the ionic liquid catalyst remained high after several cycles.

Keywords: [Et₃NH]Cl–AlCl₃, alkylation, 1,2,3-trimethylbenzene, ionic liquid **DOI:** 10.1134/S1070363216050303

INTRODUCTION

1,2,3-Trimethylbenzene is an important starting chemical for producing 5-*tert*-butyl-1,2,3-trimethylbenzene, which is mainly used in the synthesis of musk tibetene [1, 2] (Scheme 1).

Ionic liquids demonstrate unique chemical and physical properties and have been widely used as catalysts, solvents, extractants, adsorbents, and performance additives [3–6]. Traditionally AlCl₃ acts as the catalyst in the reaction of 1,2,3-trimethylbenzene with 2-chloro-2-methylpropane [1, 2, 7, 8]. In the current study common Lewis acids and some Lewis acidic ILs were introduced in the alkylation process. [Et₃NH]Cl–AlCl₃ Was determined to be the most efficient catalyst under various conditions.

RESULTS AND DISCUSSION

Alkylation with different catalysts. Influence of molar ratio of reactants upon $AlCl_3$ catalysis is presented in Table 1. At the molar ratio of 2-chloro-2-methylpropane to 1,2,3-trimethylbenzene 1 : 1 or 1.5 : 1, the reactor was filled with pale yellow filaments after

several minutes, retarding the reaction agitation. With the molar ratio 3 : 1 conversion was total and selectivity was 85.02%. The latter was close to the selectivity observed with the molar ratio 2 : 1. Taking in consideration all factors the molar ratio 2 : 1 was considered as the most efficient.

At the following step common Lewis acid and Lewis acidic ionic liquid were introduced in the synthesis of 5-*tert*-butyl-1,2,3-trimethylbenzene (Table 1). AlCl₃ and FeCl₃ demonstrated excellent catalytic performance giving reaction conversion ca 90% and selectivity up to 84.38% and 81.92%, respectively.

Scheme 1. Synthesis of 5-tert-butyl-1,2,3-trimethylbenzene.



¹ The text was submitted by the authors in English.

Run no.	Catalyst	Molar ratio ^b	Dosage, %	Conversion ^c , %	Selectivity ^c , %
1	AlCl ₃	1:1	2	_	_
2	AlCl ₃	1.5 : 1	2	_	_
3	AlCl ₃	2:1	2	99.09	84.38
4	AlCl ₃	3:1	2	100.00	85.02
5	AlCl ₃	2:1	2	99.09	84.38
6	CuCl ₂	2:1	2	0.00	0.00
7	FeCl ₃	2:1	2	99.59	81.92
8	[bmim]–AlCl ₃ ^d	2:1	2	100.00	0.00
9	[bmim]–BF ₄	2:1	2	98.77	0.00
10	[Et ₃ NH]Cl–AlCl ₃ ^e	2:1	2	49.98	63.48
11	[Et ₃ NH]Cl–AlCl ₃	2:1	5	99.81	88.39

Table 1. Effect of molar ratio and different catalysts on alkylation^a

^a Reaction condition: $T = 10^{\circ}$ C, t = 5 h. ^b Molar ratio refers to 2-chloro-2-methylpropane to 1,2,3-trimethylbenzene. ^c 1,2,3-Trimethylbenzene is the key component. ^d Bmim refers to 1-butyl-3-methylimidazolium. ^e Molar ratio of $n(AlCl_3)/n([bmim]) = 2$.

However, it was difficult to separate the products from the catalysts. $CuCl_2$ Demonstrated no catalytic activity. The reaction conversion under the action of [bmim]-AlCl₃ and [bmim]–BF₄ was very high along with poor selectivity. Application of [Et₃NH]Cl–AlCl₃ (2%) as the catalyst in the reaction gave conversion 49.98% and selectivity 63.48%. Increase of the IL quantity to 5% conversion and selectivity improved significantly which could be caused by the increase of quantity of acid sites. Therefore, more specific and detailed research had been performed using [Et₃NH]Cl–AlCl₃.

Effect of composition of IL on alkylation. Acid strength of various ILs greatly affects their catalytic activity. In the study different molar ratio of ionic liquid had been used in catalysis of the alkylation reaction (Table 2). The higher content of aluminum chloride contributed to the improvement of the reaction selectivity. When $n(AlCl_3)/n([Et_3NH]Cl)$ was 1 : 1, the ionic liquid demonstrated no catalytic activity. The higher molar ratio of $AlCl_3$ (1.3 : 1, 1.5 : 1, 1.7 : 1 and 2 : 1) led to the reaction conversion close to 100% [9,10] and higher selectivity which was maximum (90.32%) at $n(AlCl_3)/n([Et_3NH]Cl)$ at 2 : 1.

Effect of IL amount on alkylation. Influence of AlCl₃ content in the ionic liquid is presented in Table 3. Increase in the reaction selectivity could be explained by the fact that the quantity of acid sites was increased with the addition of IL. The reaction rate was high with 10% IL catalysis. Further increase of ILs amount made the reaction uncontrollable, and the temperature

Table 2. Effect of composition of IL on alkylation^a

$n(AlCl_3)/n([Et_3NH]Cl)$	Conversion, %	Selectivity, %
1.0	0	0.00
1.3	100	86.52
1.5	100	86.76
1.7	100	89.14
2.0	100	90.32

^a Reaction conditions: molar ratio 2-chloro-2-methylpropane : 1,2,3trimethylbenzene = 2 : 1, 10% [Et₃NH]Cl–AlCl₃, 5 h, 10°C.

Table 3. Effect of IL	quantity on alkylation ^a

Dosage, %	Conversion, %	Selectivity, %
2	49.98	63.48
5	99.91	88.39
10	100.00	90.32
15	100.00	80.58
20	100.00	76.75

^a Reaction conditions: molar ratio of 2-chloro-2-methylpropane : 1,2,3-trimethylbenzene = 2 : 1, 5 h, 10°C.

<i>T</i> , °C	Conversion, %	Selectivity, %
2	99.94	88.04
5	100.00	88.67
10	100.00	90.32
15	100.00	88.20
20	100.00	86.33

Table 4. Effect of temperature on alkylation^a

^a Reaction conditions: molar ratio of 2-chloro-2-methylpropane : 1,2,3-trimethylbenzene = 2 : 1, 10% [Et₃NH]Cl–AlCl₃, 5 h.

would rise leading to side reactions. It was concluded that 10% of the IL in the alkylation system would have sufficient acid sties for the reaction.

Effect of reaction temperature on alkylation. The reaction conversion was ca 100% in the temperature range from 0 to 20°C. The reaction selectivity demonstrated an upward trend at temperature lower than 10°C and a downward trend at that higher than 10°C, which was comparable with the effect of high quantity of IL. Maximum reaction selectivity was 90.32% at 10°C. High temperature induced side reactions (Table 4).

Effect of reaction time on alkylation. According to the experimental data (Table 5) the reaction conversion was close to 100% after 1 h of the process. The reaction selectivity gradually increased with the extension of time and reached 90.32% after 5 h and then remained stable indicating the reaction equilibrium point. Longer reaction time would result in more side reactions and lower reaction selectivity.

Reusability of the catalyst. Reusability of $[Et_3NH]Cl-AlCl_3$ catalyst was studied in a batch mode (Table 6). Separated with a separation funnel IL catalyst without further treatment was used again in the alkylation of 1,2,3-trimethylbenzene under optimum reaction conditions. Selectivity and conversion of the process remained nearly the same over the first four runs and dropped a little in the fifth run. Probably hydrolysis of AlCl₃ in the ionic liquid could lead to the catalyst deactivation [11, 12].

EXPERIMENTAL

Preparation of ionic liquid. Triethylamine hydrochloride-aluminum chloride were synthesized according to the methods reported earlier [13, 14]. The

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Table 5.	Effect	of react	ion time	on a	ılkyla	tion ^a
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Time, h	Conversion, %	Selectivity, %	
1	99.91	86.75	
2	99.98	89.38	
3	100.00	89.53	
4	100.00	89.69	
5	100.00	90.32	
6	100.00	90.36	

^a Reaction conditions: molar ratio of 2-chloro-2-methylpropane : 1,2,3-trimethylbenzene = 2 : 1, 10% [Et₃NH]Cl–AlCl₃, 10°C.

ILs were prepared by slow addition of the desired amount of AlCl₃ to TEA salt in heptane under the atmosphere of dry N₂. Light brown liquid layer appeared upon storage at room temperature for 0.5 h. The lower liquid lawer was transferred to rotary evaporater to purify the ionic liquid which was stirred for 2 h at 80°C. Color of the ILs varied from brown to black.

1-Butyl-3-methylimidazolium-AlCl₃ and 1-butyl-3methylimidazolium-BF₄ were purchased from Shanghai Cheng Jie Chemical Co. LTD.

Alkylation reaction. Alkylation experiments were carried out in a 50 mL reactor. A low temperature super thermostat bath was used to control the reaction temperature with ethanol as a working fluid. The catalysts and reactants were added in the desired ratio. When metal chlorides acted as the catalytic media, the alkylate needed to be neutralized with a saturated Na₂CO₃, washed with NaCl, and then with water. Upon drying with anhydrous Na₂SO₄ the products were instantly analyzed by a GC-MS Agilent 7890/5975C-Gas Chromatographer (GC)/Mass Selective Detector (MSD); HP-5, MS column, 30 m \times

Table 6. Reuse of ionic liquid in the alkylation reaction^a

Time, h	Conversion, %	Selectivity, %
1	100.00	90.32
2	100.00	90.30
3	100.00	90.01
4	100.00	89.93
5	99.98	89.87

Reaction conditions: molar ratio of 2-chloro-2-methylpropane : 1,2,3-trimethylbenzene = 2 : 1, 10% [Et₃NH]Cl–AlCl₃, 10°C.

250 μm i.d. \times 0.25 μm 120°C–temperature rising 20°C/min–280°.

CONCLUSIONS

Alkylation of 1,2,3-trimethylbenzene with 2chloro-2-methylpropane using different catalysts had been studied. [Et₃NH]Cl–AlCl₃ Was determined to be most promising catalytical substitute for AlCl₃. Temperature of the process, ionic liquid composition, reaction time and amount of IL influenced the reaction conversion and selectivity. The optimum reaction conditions were worked out to be: AlCl₃/[Et₃NH]Cl molar ratio of 2.0, reaction time 5h, temperature 10°C, mass fraction of IL to 1,2,3-trimethylbenzene 10%. Reusability of the ionic liquid [Et₃NH]Cl–AlCl₃ significantly higher than AlCl₃ and its catalytic activity remained high after four cycles.

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