Additions and Corrections

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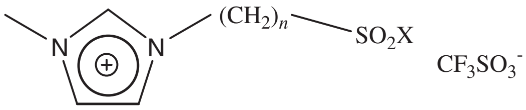
Scheme 1 appeared on page 472 should be changed as follows.



1a, $n = 3$, X = Cl, **1b**, $n = 4$, X = Cl
2a, $n = 3$, X = OH, **2b**, $n = 4$, X = OH

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Novel Acidic Ionic Liquids Catalytic Systems for Friedel–Crafts Alkylation of Aromatic Compounds with Alkenes

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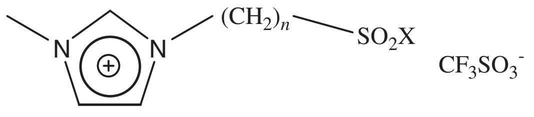
Novel acidic ionic liquids catalytic systems are developed for the Friedel–Crafts alkylation of aromatic compounds with alkenes.

The Friedel–Crafts alkylation of aromatic compounds with alkenes is among the most important processes in chemical industry.[1] Traditionally, this type of reaction is carried out in the presence of $AlCl_3$, HF, or sulfuric acid, which inevitably leads to a series of environment problems as well as operational difficulties in product separation and purification.

Recently, a few of examples of the Friedel–Crafts alkylation of aromatic compounds with alkenes have been reported to be proceeded in room temperature ionic liquids (RTILs), a kind of novel and promising solvents for synthetic chemistry.[2] It is known that these alkylation reactions could be carried out either directly using chloroaluminate ionic liquids, especially in their Lewis acidic form, as catalysts or employing an ionic liquid catalytic system that containing scandium triflate and hydrophobic ionic liquid such as $[BMIm][PF_6]$ (1-butyl-3-methylimidazolium hexafluorophosphate).[1,3]

Unfortunately, from the point of environmental view, both of these catalytic systems have an intrinsic shortage because of their instability. The sensitivity of chloroaluminate ionic liquids toward air and water is already well known. Hydrophobic ionic liquid such as $[BMIm][PF_6]$ is also found to be prone of hydrolysis to emit acidic fume containing HF and other species.[4] In consideration of the possibility of the hydrolysis of hydrophobic ionic liquid, particularly in the presence of acidic metal triflate, it becomes difficult to tell which one, metal triflate or acidic impurity species formed from the hydrolysis of ionic liquid, act as the actual catalysts in the case when catalytic system containing scandium triflate and hydrophobic ionic liquid is utilized for alkylation reactions.

In this paper, we report the research of utilizing a kind of novel acidic ionic liquids catalytic systems for the Friedel–Crafts alkylation of aromatic compounds with alkenes. It includes: (i) a kind of novel Lewis acidic ionic liquids (**1**)[5] is synthesized deriving from Cole's Brønsted acidic ionic liquids (**2**)[6] (Scheme 1), (ii) it is demonstrated that those acidic ionic liquids are effective and reusable catalysts for alkylation of aromatic compounds with styrene, but less active for alkylation of aromatic compounds with other alkenes, (iii) a surprising synergistic effect has been found between those acidic ionic liquids and metal triflate, leading to active catalytic systems for alkylation reactions of aromatic compounds with alkenes that only ionic liquids or metal triflates are ineffective.



1a, $n = 3$, X = Cl, **1b**, $n = 4$, X = Cl
2a, $n = 3$, X = OH, **2b**, $n = 4$, X = OH

Scheme 1. Acidic ionic liquids.

Results of the Friedel–Crafts alkylation of several aromatic compounds with alkenes are summarized in Table 1.[7] To examine the catalytic performance of both the Brønsted and Lewis acidic ionic liquids, we first employed them as catalysts for alkylation of *p*-xylene with styrene, a typical example of the Friedel–Crafts alkylation reactions of aromatic compounds with alkenes that have important practical application in industry.[8] Two different products, i.e. the monostyrenated and the distyrenated, are detected and both are the desired products in industry. It could be seen when *p*-xylene and styrene are treated with the Brønsted acidic ionic liquid **2a** or **2b** (Runs 1and 2), a satisfactory conversion of styrene is achieved after 5 h reaction at 70 °C. The Lewis acidic ionic liquid **1a** is also an effective catalyst for this reaction (Run 3), but with the increasing the length of the side chain, the activity of the Lewis ionic liquid **1b** notably decreased (Run 4), suggesting the difference in the type of acidity, the Brønsted or Lewis acidity, may affect the reaction in some degree.

The reaction is carried out in a biphasic mode, so the products in the upper layer could be easily separated from the ionic liquid by decantation after reaction and the remaining ionic liquid is ready for next run. The Brønsted ionic liquid **2b** has shown good reusability for the alkylation reaction of *p*-xylene with styrene, for example, even after 5 times cycle under the same reaction condition, the conversion of styrene and selectivity to monoalkylated products still kept at 91.6 and 85.3%, respectively (Run 5).

Ionic liquid **2b** could also smoothly catalyze the alkylation reaction of styrene with other aromatic compounds such as benzene and toluene (Runs 6 and 7). Very interesting, however, no reaction is observed when ionic liquid **1a** or **2b** is applied as catalyst for alkylation of benzene with 1-hexene (Runs 8 and 9).[9]

There is also no reaction occurred when only scandium triflate is used as catalyst for alkylation of benzene with 1-hexene (Run 10),[10] which is of in accord with the result observed by Song.[1] A synergistic effect is, however, discovered when the reaction of alkylation of benzene with 1-hexene is carried out in the presence of the mixture of ionic liquid **2b** or **1b** with scandium triflate (Runs 11 and 12). High conversions of 1-hexene are achieved in both cases, but selectivities to monoalkylated products are remarkably varied. Catalytic system containing the Lewis acidic ionic liquid had exhibited higher selectivity for monoalkylated products than that of the Brønsted acidic one.

Then the scandium triflate-Lewis acidic ionic liquid **1b** catalytic system is applied for the alkylation reactions of *p*-xylene or benzene with other different alkenes, including 1-dodecene, cyclopentene and cyclohexene, under unoptimized reaction conditions (Runs 13–16). It could be seen that in all of these cases, the alkylation reactions occurred with medium to high conversions of alkenes and selectivities of monoalkylated products.

Table 1. Friedel–Crafts alkylation reactions of aromatic compounds with alkenes

Run[h]	Arene	Alkene	Catalyst	Conv.[a] (%)	Sel[b] (%)
1	p-xylene	styrene	**2a**[c]	97.4	83.8
2	p-xylene	styrene	**2b**[c]	97.5	80.8
3	p-xylene	styrene	**1a**[c]	97.3	87.8
4	p-xylene	styrene	**1b**[c]	63.8	78.6
5	p-xylene	styrene	**2b**[c,d]	91.6	85.3
6	benzene	styrene	**2b**[c]	99.7	80.7
7	toluene	styrene	**2b**[c]	95.3	82.1
8	benzene	hexene	**2b**[c]	<1	0
9	benzene	hexene	**1b**[c]	<1	0
10	benzene	hexene	**Sc**[e,f]	<1	0
11	benzene	hexene	**Sc+2b**[f]	97.6	69.8
12	benzene	hexene	**Sc+1b**[f]	93.8	88.9
13	p-xylene	hexene	**Sc+1b**[f]	98.8	93.4
14	benzene	dodecene	**Sc+1b**[g]	64.9	67.8
15	benzene	cyclopentene	**Sc+1b**[f]	79.7	61.3
16	benzene	cyclohexene	**Sc+1b**[f]	95.9	84.7

[a] Conversion of alkene: [b] Selectivity of monoalkylated product.

[c] Aromatic compounds: 30 mmol, alkene: 10 mmol, ionic liquid: 10% (mol) of alkene.

[d] Results were obtained after 5 times recycle.

[e] Scandium triflate, 5% (mol) of alkene.

[f] Aromatic compounds: 5.2 mmol, alkenes: 2.6 mmol, scandium triflate, 5% (mol) of alkene, ionic liquids: 5% (mol) of alkene.

[g] Benzene: 5.2 mmol, dodecene: 2.6 mmol, scandium triflate, 10% (mol) of dodecene, ionic liquid: 10% (mol) of dodecene.

[h] Runs 1 to 9 are carried out at 70 °C for 5 h; Runs 10 to 16 are carried out at 80 °C with different reaction time, 10 to 12 are for 4 h, 13 is for 12 h, 14 is for 24 h and 15 to 16 are for 6 h.

There are two major differences distinguish the scandium triflate-acidic ionic liquid catalytic system from Song's scandium triflate-hydrophobic ionic liquid one. One is that scandium triflate is capable of soluble in the acidic ionic liquid under the reaction condition to form a homogenous viscosous solution that is still immiscible with benzene or alkylbenzene. Scandium triflate, on the other hand, is only slightly soluble in the hydrophobic ionic liquids. Another difference is that a visible color change could be seen when scandium triflate is mixed with the acidic ionic liquids, which indicating some kind of reaction happened between scandium triflate and acidic ionic liquids.

The nature of the mechanistic route is not very clear at this stage. On the basis of the above results, however, we are inclined to believe that the observed synergistic effects might proceed via an ionic liquid-metal triflate complex.[11] In this view, the possible reaction route involved the formation of an ionic liquid-scandium triflate complex at first and then followed by the Brønsted or Lewis acidic activation of alkene through the alkene-complex interaction.

In conclusion, novel acidic ionic liquids catalytic systems are developed for the Friedel–Crafts alkylation of aromatic compounds with alkenes. The observed synergistic effect between acidic ionic liquids and scandium triflate might imply an ionic liquid-metal triflate complex act as the real catalyst.

References and Notes

1 C. E. Song, W. H. Shim, E. J. Roh, and J. H. Choi, *Chem. Commun.*, **2000**, 1695, and references cited therein.

2 For recent reviews on ionic liquids, see a) J. Dupont, R. F. de Souza, and P. A. Z. Suarez, *Chem. Rev.*, **102**, 3667 (2002). b) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, **39**, 3772 (2000). c) T. Welton, *Chem. Rev.*, **99**, 2071 (1999). d) C. M. Gordon, *Appl. Catal., A*, **222**, 101 (2001). e) R. A. Sheldon, *Chem. Commun.*, **2001**, 2399.

3 a) K. Qiao and Y. Deng, *J. Mol. Catal. A: Chem.*, **171**, 81 (2001). b) C. DeCastro, E. Sauvage, M. H. Valkenberg, and W. F. Hölderich, *J. Catal.*, **196**, 86 (2000).

4 R. P. Swatloski, J. D. Holbrey, and R. D. Rogers, *Green Chem.*, **5**, 361 (2003).

5 The experimental procedure for preparation of ionic liquids **1** is as follows: thionyl chloride (0.12 mol) was charged into a 50 mL two-neck flask with reflux and magnetic stirrer. Under reflux conditions, the Brønsted acidic ionic liquid **2** (0.1 mol), prepared according to reference 6, was slowly added into the flask, then the reaction was proceeded for another 8 h. Remove the unreacted thionyl chloride by distillation and the residual liquid was product. Then the product was further purified under vacuum at 50 °C for 2 h. DTA analysis shows that the melting point of ionic liquid **1a** and **1b** are 219.8 and 211.8 K, respectively.

6 A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes, and J. H. Davis, Jr., *J. Am. Chem. Soc.*, **124**, 5962 (2002).

7 In a typical experiment, ionic liquid, aromatic compounds and alkene are charged into a 10 mL test tube with magnetic stirrer. Then the reaction is carried out at desired temperature for 5 to 24 h. After reaction, the components in the upper organic layer are analyzed by a gas chromatograph equipped with a FID detector (Shimadzu GC-14A, ULBON HR-52 capillary column 25 m × 0.32 mm).

8 B. S. Kwak and T. J. Kim, *Catal. Lett.*, **59**, 55 (1999), and references cited therein.

9 Lewis acidic ionic liquid **1b** has also no activity for alkylation of benzene with 1-dodecene, cyclopentene and cyclohexene.

10 Other metal triflates, including $Zn(OTf)_2$ (no activity), $La(OTf)_3$ (no activity) and $Yb(OTf)_3$ (about 4% yield) are also examined.

11 O. Mouhtady, H. Gaspard-Iloughmane, N. Roques, and C. L. Roux, *Tetrahedron Lett.*, **44**, 6379 (2003).

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