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Scandium(III) triflate immobilised in ionic liquids: a novel and recyclable catalytic system for Friedel–Crafts alkylation of aromatic compounds with alkenes

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Scandium(III) triflate catalysed Friedel–Crafts alkylation of aromatic compounds with alkenes proceeded readily in the hydrophobic ionic liquid solvents based on 1,3-dialkylimidazolium salts with easy catalyst/solvent recycling, whereas these reactions did not occur in common organic solvents, water or hydrophilic ionic liquids at all.

The Friedel–Crafts alkylation of aromatic compounds with alkenes is of great synthetic significance in view of laboratory synthesis and particularly industrial production.[1] For example, a number of important industrial processes for ethylbenzene, cumene and linear alkylbenzenes, *etc*. are based on this reaction. In general, this type of reaction is catalysed by $AlCl_3$, H_2SO_4, HF and other acid catalysts. However, a common problem, particularly in industrial processes, is that catalysts cannot be reused after the usual aqueous work-up.

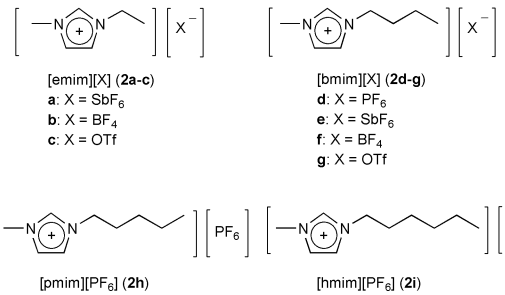
Recently, considerable attention has been focused on the catalytic use of rare earth(III) (RE) salts, especially, RE(III) trifluoromethanesulfonates [$RE(OTf)_3$] as water-tolerant and recyclable Lewis acid catalysts in carbon–carbon bond forming reactions.[2] The RE(III) compound-catalysed Friedel–Crafts alkylations of aromatic compounds using alcohols, mesylates, halides, aldehydes, acetals, *etc*. as alkylating agents have also been reported.[3] However, to the best of our knowledge, there has been no previous report on the use of $RE(OTf)_3$ for the Friedel–Crafts alkylation of aromatics using alkenes as alkylating agents.

We disclose here our preliminary results on the Friedel–Crafts alkylation of aromatics with alkenes using a novel and recyclable catalytic system, $Sc(OTf)_3$ immobilised in air and moisture-stable rt ionic liquids.[4]

To examine the catalytic effect of lanthanide trifluoromethanesulfonates, we first carried out the alkylation of benzene with hex-1-ene in the presence of 20 mol% of $Sc(OTf)_3$ in various organic solvents (none, CH_2Cl_2, acetonitrile, nitromethane and nitrobenzene) or H_2O at 20 °C for 12 h. However, in all cases neither alkylation nor olefin isomerisation took place at all (Table 1, entries 1–6). It is therefore not surprising that there has been no report on the use of $RE(OTf)_3$ for the Friedel–Crafts alkylation of aromatics using alkenes as alkylating agents so far.

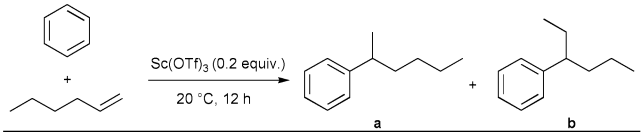
Very interestingly, however, when the same reaction was carried out in air and moisture-stable rt ionic liquids consisting of 1,3-dialkylimidazolium cations and their counter anions **2**,[5] [emim][X] ([emim]$^+$ = 1-ethyl-3-methylimidazolium cation; X = SbF_6 (**2a**), BF_4 (**2b**), OTf (**2c**)), [bmim][X] ([bmim]$^+$ = 1-butyl-3-methylimidazolium cation; X = PF_6 (**2d**), SbF_6 (**2e**), BF_4 (**2f**)and OTf (**2g**)), [pmim][PF_6] ([hmim]$^+$ = 1-pentyl-3-methylimidazolium cation; **2h**) and [hmim][PF_6] ([hmim]$^+$ = 1-hexyl-3-methylimidazolium cation; **2i**), we obtained quite satisfactory results in some cases. In this reaction, the catalytic activity of $Sc(OTf)_3$ was strongly influenced by the nature of the anion [X].

When the hydrophobic ionic liquids such as the [emim][SbF_6] (**2a**), [bmim][PF_6] (**2d**), [bmim][SbF_6] (**2e**),



[pmim][PF_6] (**2h**) or [hmim][PF_6] (**2i**) were used, the desired alkylated products were obtained quantitatively, although $Sc(OTf)_3$ is only slightly soluble and thus exists as a suspended form in these ionic solvents (Table 1, entries 7, 10, 11, 14 and 15).† It is noteworthy here that the rearrangement of alkene takes place prior to the ring substitution, which indicates that the carbonium ion is formed first. Polarity of these ionic solvents leads to the stabilisation of the polar cationic intermediate. In sharp contrast to these results, in the hydrophilic ionic liquids, [emim][BF_4] (**2b**), [emim][OTf] (**2c**), [bmim][BF_4] (**2f**) or [bmim][OTf] (**2g**), the catalyst was highly soluble and thus totally immobilised in these ionic liquids, but the reaction did not occur at all (Table 1, entries 8, 9, 12 and 13). Thus, we next

Table 1 Friedel–Crafts alkylation of benzene with hex-1-ene in the presence of 20 mol% of $Sc(OTf)_3$ in various solvents[a]



Entry	Solvent	Conversion[b] (%) of hex-1-ene	Yield[b] (%) of monoalkylated product (**a**:**b**)
1	None	0	0
2	CH_2Cl_2	0	0
3	CH_3CN	0	0
4	CH_3NO_2	0	0
5	$PhNO_2$	0	0
6	H_2O	0	0
7	[emim][SbF_6] (**2a**)	>99	96 (1.5:1)
8	[emim][BF_4] (**2b**)	0	0
9	[emim][OTf] (**2c**)	0	0
10	[bmim][PF_6] (**2d**)	>99	96 (2:1)
11	[bmim][SbF_6] (**2e**)	~99	93 (1.5:1)
12	[bmim][BF_4] (**2f**)	0	0
13	[bmim][OTf] (**2g**)	0	0
14	[pmim][PF_6] (**2h**)	>99	95 (1.6:1)
15	[hmim][PF_6] (**2i**)	>99	95 (2:1)

[a] Reaction conditions: hex-1-ene (1 mmol), benzene (2 mL), $Sc(OTf)_3$ (0.2 mmol), solvent (1 mL), 20 °C, 12 h. [b] Conversions and yields based on hex-1-ene were determined by the internal standard method in GC.

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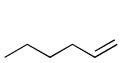
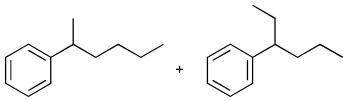
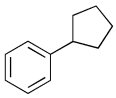
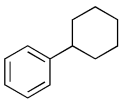
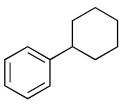
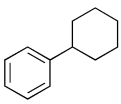
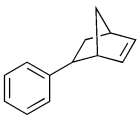
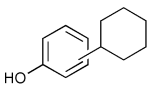
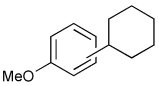
Table 2 $Sc(OTf)_3$ catalysed Friedel–Crafts alkylation of benzene with various alkenes in the ionic liquid **2e**[a]

Entry	Aromatic compound	Alkene	Product	Conversion[b] (%) of alkene	Yield[b] (%) of monoalkylated product
1	Benzene			>99	93[c]
2	Benzene			>99	84
3	Benzene			>99	90
4[d]	Benzene			>99	92
5[e]	Benzene			>99	92
6	Benzene			>99	65
7	Phenol			>99	93[f]
8	Anisole			>99	85[g]

[a] Reaction conditions: alkene (1 mmol), benzene (2 mL), $Sc(OTf)_3$ (0.2 mmol for entries 1–6 and 0.1 mmol for entries 7–8), the ionic liquid **2e** (1 mL), 20 °C, 12 h. [b] Conversions and yields based on alkene were determined using the internal standard method in GC. [c] **a**:**b** = 1.5:1. [d] Reaction was carried out with the ionic liquid **2e** containing $Sc(OTf)_3$ recovered from the reaction in entry 3. [e] Reaction was carried out with the ionic liquid **2e** containing $Sc(OTf)_3$ recovered from the reaction in entry 4. [f] The ratio of *ortho* to *para* product is *ca.* 2.5:1. [g] The ratio of *ortho* to *para* product is *ca.* 1.8:1.

examined Friedel–Crafts alkylation of other substrates only using the ionic liquid **2e**. As shown in Table 2, in all cases the reaction proceeded smoothly to furnish the corresponding alkylation products in quantitative yields. Moreover, the ionic liquid phase containing $Sc(OTf)_3$ was almost quantitatively recovered by simple decantation of the organic layer (the upper phase) after reaction. Second and third reactions of benzene with cyclohexene using the recovered ionic liquid **2e** containing catalyst afforded quantitative yield of cyclohexylbenzene (Table 2, entries 4 and 5).

In a typical reaction, the alkene and aromatic compound are added to the ionic liquid **2e** containing 20 mol% of $Sc(OTf)_3$ directly. Two phases are formed and the mixture is stirred at 20 °C for 12 h. The organic layer is separated to leave the ionic liquid phase containing the catalyst which can be reused.

In summary, Friedel–Crafts alkylation of aromatic compounds with alkenes using the novel reusable catalytic system, $Sc(OTf)_3$-ionic liquid, has been developed. The simple procedures, easy recovery and reuse of this novel catalytic system are expected to contribute to development of benign and waste-free chemical processes for Friedel–Crafts alkylation of aromatics with alkenes.

Notes and references

† $Y(OTf)_3$ (16%), $Ho(OTf)_3$ (16%), $Tm(OTf)_3$ (11%), $Lu(OTf)_3$ (64%) also catalysed the reaction of benzene with cyclohexene in the ionic liquid **2e**. However, the yields of the cyclohexylbenzene were significantly inferior to that with $Sc(OTf)_3$. All other lanthanide(III) triflates were inactive under the same reaction conditions. These results can be ascribed to the stronger Lewis acidity of $Sc(OTf)_3$ than that of lanthanide analogues.

1 For reviews of Friedel–Crafts alkylation reactions, see: G. A. Olah, *Friedel–Crafts and Related Reactions*, Wiley-Interscience, New York, 1964, vol. II, part 1; R. M. Roberts and A. A. Khalaf, *Friedel–Crafts Alkylation Chemistry A Century of Discovery*, Dekker, New York, 1984; G. A. Olah, R. Krishnamurit and G. K. S. Prakash, *Friedel–Crafts Alkylations in Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991.

2 For reviews, see: S. Kobayashi, *Synlett*, 1994, 689; R. W. Marshman, *Aldrichimica Acta*, 1995, **28**, 77; S. Kobayashi, *J. Synth. Org. Chem. Jpn.*, 1995, **53**, 370.

3 N. Mine, Y. Fujiwara and H. Taniguchi, *Chem. Lett.*, 1986, 357; T. Tsuchimoto, T. Hiyama and S. Fukuzawa, *Synlett*, 1996, 557; T. Tsuchimoto, T. Hiyama and S. Fukuzawa, *Chem. Commun.*, 1996, 2345; T. Tsuchimoto, K. Tobita, T. Hiyama and S. Fukuzawa, *J. Org. Chem.*, 1997, **62**, 6997; H. Kotsuki, T. Oshisi and M. Inoue, *Synlett*, 1998, 255.

4 Reviews for ionic liquids: T. Welton, *Chem. Rev.*, 1999, **99**, 2071; K. R. Seddon, *J. Chem. Tech. Biotechnol.*, 1997, **68**, 351; K. R. Seddon, ionic liquid database, QUB School of Chemistry homepage, http://www.ch.qub.ac.uk; Y. Chauvin and H. Olivier, *CHEMTECH*, 1995, 26.

5 Preparation of ionic liquids: For BF_4 and PF_6 salts (**2b**, **2d**, **2f**, **2h** and **2i**): P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza and J. Dupont, *Polyhedron*, 1996, **15**, 1217; The synthesis of the SbF_6 salts (**2a**, **2e**) was similar to that of BF_4 and PF_6 salts with the exception that $NaSbF_6$ was used in place of $NaBF_4$ or $NaPF_6$; For the triflates (**2c**, **2g**): P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168. All ionic liquids used in this paper were pre-dried under reduced pressure (0.5 mmHg) at 50 °C for 24 h.

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