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Ionic Liquids as Powerful Solvent Media for Improving Catalytic Performance of Silyl Borate Catalyst to Promote Diels−Alder Reactions

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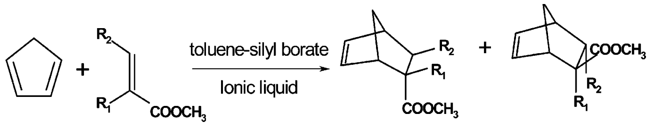
Received May 28, 2007



Use of the acidic chloroaluminate ionic liquid, including the recycled ones, can improve the catalytic activity of the toluene-coordinated silyl borate in enhancing rates, stereoselectivities, and yields of Diels−Alder reactions.

Diels−Alder reactions are accelerated by Lewis acid catalysts. It has been recently demonstrated that a Lewis acid catalyst, such as toluene-coordinated silyl borate, $[Et_3Si(toluene)]B(C_6F_5)_4$, can offer high catalytic activity for promoting Mukaiyama and Diels−Alder reactions.[1] The Diels−Alder reactions of 1,3-cyclohexadiene with methyl acrylate, methyl crotonate, methyl vinyl ketone, and crotonaldehyde and of 2,3-dimethylbutadiene with methyl acrylate proceeded with high yields and endo:exo ratios, but no rate data were reported. As a part of our research program on ionic liquids,[2] we now demonstrate that ionic liquids can further improve the catalytic performance of silyl borate catalyst. The ionic liquids employed in this investigation include 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4], 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6], 1-butyl-3-methylimidazolium hexafluoroantimonate [BMIM][SbF_6], 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4], 1-butyl-3-methylimidazolium iodide [BMIM]I, and 1-octyl-3-methylimidazolium tetrafluoroborate [OMIM][PF_6] (Figure 1). These ionic liquids were chosen because they were easy to synthesize and handle in laboratories. The preference to employ ionic liquids over conventional organic solvents in chemical transformations has been highlighted in several reports.[3]

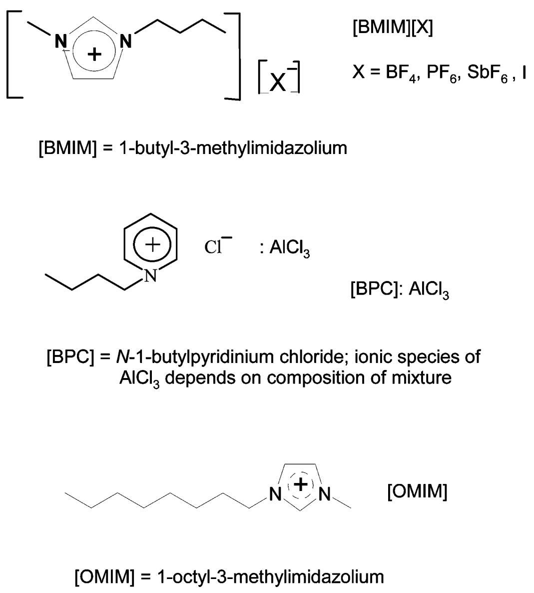
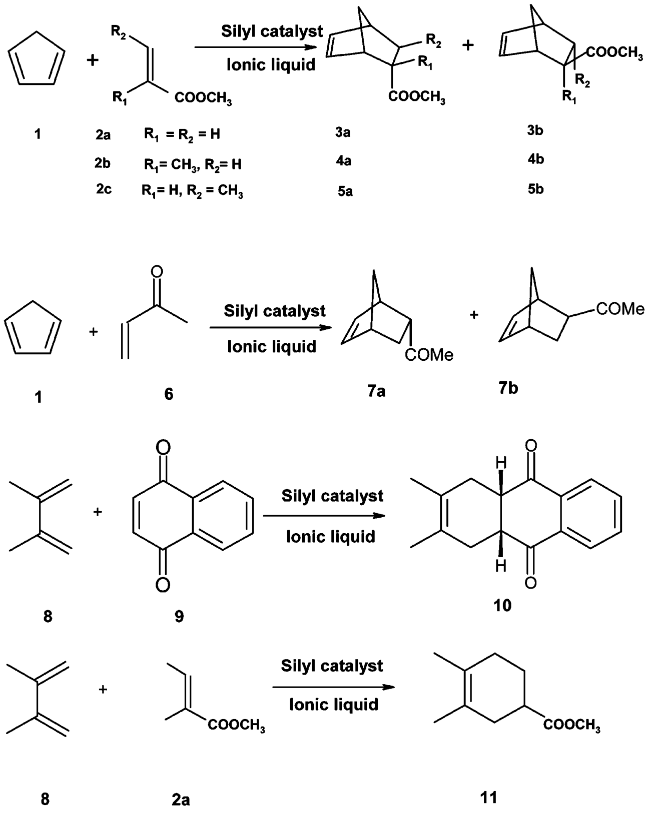


FIGURE 1. Ionic liquids used.

SCHEME 1. Investigated Diels−Alder Reactions



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[3] For example, see: (a) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998. (b) Holbrey, J. D.; Seddon, K. R. *Clean Products and Processes*; Springer: Berlin, 1999; Vol. 1, p 223. (c) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (d) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391. (e)

10.1021/jo071099w CCC: $37.00

TABLE 1. Rates,[a] Yields,[b] Reaction Times,[c] and endo:exo Data[d] for the Reaction of 1 with 2a with and without Silyl Borate Catalyst in Different Media with Catalytic Loading at 27 °C

entry	catalyst/ionic liquid	$10^5 k_2$ ($M^{-1} s^{-1}$)	yield[b] (%), time[c] (h)	endo:exo[d]
1	1 mol % of silyl borate[e]	9.00	85, 2.5	80:20
2	[BMIM][BF_4]	4.52	76, 4.5	74:26
3	0.1 mol % of silyl borate + [BMIM][BF_4]	5.92	84, 4	79:21
4	0.25 mol % of silyl borate + [BMIM][BF_4]	8.00	87, 2.5	82:18
5	0.5 mol % of silyl borate + [BMIM][BF_4]	9.94	90, 2	86:14
6	0.75 mol % of silyl borate + [BMIM][BF_4]	11.51	92, 2	89:11
7	1 mol % of silyl borate + [BMIM][BF_4]	13.22	95, 1.5	93:7
8	1.5 mol % of silyl borate + [BMIM][BF_4]	13.55	95, 1.5	91:9
9	2 mol % of silyl borate + [BMIM][BF_4]	13.98	95, 1.5	92:8
10	[BMIM][PF_6]	3.92	72, 4.5	74:26
11	1 mol % of silyl borate + [BMIM][PF_6]	12.21	90, 2	87:13
12	[BMIM][SbF_6]	3.45	70, 4.5	72:28
13	1 mol % of silyl borate + [BMIM][SbF_6]	11.01	90, 2.5	91:9
14	[EMIM][BF_4]	5.86	73, 4	73:27
15	1 mol % of silyl borate + [EMIM][BF_4]	16.76	85, 2	90:10
16	[OMIM][PF_6]	3.11	70, 5	70:30
15	1 mol % of silyl borate +[OMIM][PF_6]	7.34	70, 5.5	72:28
16	[BMIM]I	2.46	68, 6	68:32
17	1 mol % of silyl borate +[BMIM]I	5.98	72, 4.5	73:27

[a] Standard error of 5%; the reactions were carried out in a 1 mmol scale in 1.5 mL of ionic liquid. [b] Isolated yields. [c] No further increase in yields after the times reported. [d] Determined by GC analysis. [e] Toluene = 1 mL.

The reaction of cyclopentadiene **1** with methyl acrylate **2a** (Scheme 1) was carried out in the presence of the above catalyst in different media (Table 1). This reaction is faster in water as compared to that in conventional organic solvents.[4,5] This reaction gave 85% yield in toluene-coordinated silyl borate catalyst with a rate constant (k_2) ~9 times higher than that observed in 2,2,4-trimethylpentane ($k_2 = 1.03 \times 10^{-5}$ $M^{-1} s^{-1}$, with a yield = 66% in 7 h, endo-stereoisomer = 63%). The use of 1 mol % of the silyl catalyst in [BMIM][BF_4] offered the maximum yield (Table 1, entries 3−9). The reaction was ~3 times faster in 1 mol % of the catalyst with [BMIM][BF_4] as compared to that in ionic liquid alone. This reaction with the silyl catalyst in [BMIM][PF_6], however, resulted in 90% yield with endo:exo = 87:13. The reaction was 3-fold faster in 1 mol % of silyl borate + [BMIM][PF_6] with improvement in yield and with higher endo:exo ratios. The performance of silyl borate catalyst in another ionic liquid, [BMIM][SbF_6], was recorded to be similar to the one achieved in [BMIM][PF_6]. The catalyzed reaction was about 3 times faster in [EMIM][BF_4] than in ionic liquid alone. However, in this case, sufficient improvement was not observed as compared to the reaction catalyzed in the absence of an ionic liquid.

The catalyzed reaction was suppressed in the presence of [OMIM][PF_6] and [BMIM]I. In our recent work, we have demonstrated that Diels−Alder reactions are retarded in ionic liquids with high viscosities due to a diffusion problem.[2a] This seems to be also valid in the present investigation.

Considering the role of chloroaluminate ionic liquids in accelerating the Diels−Alder reaction,[2c] we decided to investigate whether the catalytic performance can be further improved in chloroaluminate ionic liquid. The results are given in Table 2. First, the reaction was carried out in silyl borate with its concentration starting from 0.1 to 1 mol % in the acidic chloroaluminate ionic liquid (*N*-1-butylpyridinium chloride abbreviated as BPC with $AlCl_3$ with mole fraction, *X*, of $AlCl_3$ = 0.6; Supporting Information Figure S1). Both the k_2 and the yields were maximized in 0.3 mol % of silyl borate catalyst in the acidic [BPC][$AlCl_3$]. The reaction was 8 times faster with 20% higher product and endo:exo ratio of 98:2 in 0.3 mol % of catalyst in the acidic [BPC][$AlCl_3$] as compared to that in ionic liquid alone. The catalyzed reaction in 0.3 mol % of silyl borate became slow in the basic chloroaluminate ionic liquid [BPC][$AlCl_3$]. The catalyzed reaction carried in a neutral chloroaluminate gave better results than those obtained in basic chloroaluminate. This clearly shows that the catalytic activity of silyl borate is lowered in basic chloroaluminate ionic liquid. It may be noted that the reaction in 0.3 mol % of silyl borate catalyst in conjunction with the acidic chloroaluminate was 47 times faster than in 2,2,4-trimethylpentane. This shows that the Lewis acid effect imparted by the acidic chloroaluminate ionic liquid is additive to the Lewis acid catalytic effect of the silyl catalyst. A combination of the catalyst in a neutral chloroaluminate ionic liquid offers 86% of cycloadduct with a 78:22 endo:exo product. The use of $AlCl_3$ with and without silyl borate catalyst did not give desirable results as obtained with the use of silyl borate catalyst in ionic liquids.

It is clear from Table 2 that the silyl borate catalyst when used with the acidic chloroaluminate ionic liquid can offer better catalytic performance than that obtained in silyl borate catalyst or ionic liquids alone. Another important experimental observation is that only one-third of the concentration of the catalyst is required in the acidic chloroaluminate ionic liquid as compared to that in other ionic liquids for achieving optimum rates and products.

Considering the utility of the acidic chloroaluminate in improving the performance of the silyl borate catalyst, we decided not to employ other ionic liquids for carrying out these reactions. The exo-selective reaction of **1** with methyl methacrylate, **2b**, in the acidic chloroaluminate ionic liquid gave 60%

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TABLE 2. Kinetic Data for the Reaction of 1 with 2a with the Catalyst Loading of Silyl Borate in the Most Efficient Chloroaluminate Ionic Liquids at 27 °C

entry	catalyst/ionic liquid	$10^5\,k_2$[a] ($M^{-1}\,s^{-1}$)	yield[b] (%), time[c] (h)	endo:exo[d]
1	$AlCl_3$[e]	7.53	77, 7	79:21
2	1 mol % of silyl borate + $AlCl_3$[e]	10.32	87, 5.5	82:18
3	[BPC][$AlCl_3$]	5.81	80, 6.5	72:28
4	0.05 mol % of silyl borate + [BPC][$AlCl_3$][f]	15.40	91, 6	81:19
5	0.1 mol % of silyl borate + [BPC][$AlCl_3$][f]	31.89	93, 4	87:13
6	0.2 mol % of silyl borate + [BPC][$AlCl_3$][f]	44.65	96, 3	94:6
7	0.3 mol % of silyl borate + [BPC][$AlCl_3$][f]	48.5	98, 2	98:2
8	0.5 mol % of silyl borate + [BPC][$AlCl_3$][f]	48	97, 2	97:3
9	0.75 mol % of silyl borate + [BPC][$AlCl_3$][f]	47.6	97, 2	96:4
10	1 mol % of silyl borate + [BPC][$AlCl_3$][f]	47.5	97, 2	97:3
11	1 mol % of silyl borate + [BPC][$AlCl_3$][g]	11.08	86, 3.5	78:22
12	1 mol % of silyl borate + [BPC][$AlCl_3$][h]	8.55	50, 4.5	65:35

[a] Standard error of 5%; the reactions were carried out in a 1 mmol scale in 1.5 mL of ionic liquid. [b] Isolated yields. [c] No further increase in yields after the times reported. [d] Determined by GC analysis. [e] In toluene 1 mL. [f] Acidic, $AlCl_3$ X (mole fraction) = 0.6. [g] Neutral, $AlCl_3$ $X = 0.5$. [h] Basic, $AlCl_3$ $X = 0.45$.

TABLE 3. Diels−Alder Reactions[a] Catalyzed by Silyl Catalyst in Acidic Chloroaluminate at 27 °C

entry	catalyst/ionic liquid	$10^7\,k_2$[b] ($M^{-1}\,s^{-1}$)	yield[c] (%), time[d] (h)	endo:exo[e]
		reaction: **1** + **2b**		
1	silyl borate[f]	6.32	45, 7	40:60
2	[BPC][$AlCl_3$][g]	9.87	47, 5.5	75:25
3	silyl borate + [BPC][$AlCl_3$][g,h]	24.15	60, 4	80:20
		reaction: **1** + **2c**		
4	silyl borate[f]	10.56	45, 5	80:20
5	[BPC][$AlCl_3$][g,h]	18.40	57, 5	86:14
6	silyl borate + [BPC][$AlCl_3$][g]	38.44	70, 2.5	93:7
		reaction: **1** + **6**		
7	silyl borate[f]	79.27	87, 2	85:15
8	[BPC][$AlCl_3$][g,h]	71.52	90, 2	83:17
9	silyl borate + [BPC][$AlCl_3$][g]	179.5	98, 1	98:2
		reaction: **8** + **9**[i]		
10	silyl borate[f]	43.21	95, 30 min	−
11	[BPC][$AlCl_3$][g]	37.34	92, 30 min	
12	silyl borate + [BPC][$AlCl_3$][g]	92.54	99, 10 min	
		reaction: **8** + **2a**[j]		
13	silyl borate[f]	2.05[k]	91, 13[j]	−
14	silyl borate + [BPC][$AlCl_3$][g]	3.53	96, 8	

[a] Diene = dienophile = 8 mmol, silyl borate catalyst = 0.3 mol % used in all experiments given in this table. [b] Standard error of 5%, ionic liquid = 1.5 mL. [c] Yields determined by NMR spectroscopy. [d] No further increase in yields after the times reported. [e] Determined by GC analysis. [f] Toluene = 1 mL. [g] Acidic $X_{AlCl3} = 0.6$. [h] Rrom ref 2b. [i] **8** = 6 mmol, **9** = 2 mmol. [j] From ref 1. [k] Measured by us, not mentioned in ref 1.

product with 80% endo-stereoisomer. It may be noted that the reaction of **1** with **2b**, which offers predominant exo-stereoisomer (60%) in silyl borate (Table 3, entry 1) as in organic solvents,[4] now proceeds with higher endo-stereoselective stereoisomer (80%) in the mixture of silyl borate with the acidic [BPC][$AlCl_3$]. This is clearly an improvement over our recent work, in which we reported the same reaction carried out in chloroaluminate ionic liquids.[2d]

The reaction of **1** with methyl *trans*-crotonate **2c** proceeded in silyl borate + acidic chloroaluminate to give 70% of cycloadduct in 2.5 h with endo:exo ratio of 93:7. This reaction in silyl borate + acidic chloroaluminate proceeded to give 70% of cycloadduct in 2.5 h with endo:exo ratio of 93:7.

The reaction of **1** with methyl vinyl ketone **6** was noted to be 2-fold faster in the silyl borate catalyst + acidic chloroaluminate as compared to that in the silyl borate catalyst. This reaction as catalyzed by scandium triflate in 1-hexyl-3-imidazolium tetrafluoroborate [HMI][BF_4] is reported[6] to give 95% cycloadduct with endo:exo ratio of 93:7. As clear from the data given in Table 3, the reaction in silyl borate + acidic chloroaluminate proceeded faster with comparable yields and the endo/exo ratio as compared to that in the acidic chloroaluminate ionic liquid or the catalyst alone.

The reaction of 2,3-dimethylbutadiene **8** with 1,4-naphthoquinone **9** proceeded in silyl borate + acidic chloroaluminate to give >99% cycloadduct in 10 min when compared to the one catalyzed by silyl borate alone. The use of scandium triflate + [BMIM][BF_4] has been reported to offer 96% cycloadduct with 99% as the endo stereoisomer.[7]

In order to demonstrate the utility of ionic liquids in enhancing the catalytic performance, we repeated the reported reaction of **8** with **2a** under the reported reaction conditions.[1] The reaction proceeded in a mixture of 0.3 mol % of silyl borate with acidic [BPC][$AlCl_3$] to give 96% yield in just 8 h as compared to 91%

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yield in 13 h in silyl borate alone, suggesting that a suitable ionic liquid can further promote the catalyzed reaction with an increase in yield and reduction in reaction time.

We also used the recycled acidic chloroaluminate by extracting the product with Et_2O.[2c,5] The catalyzed reaction of **1** with **2a** in the recycled condition gave 91−95% yield for up to seven recycles (see Supporting Information), thus confirming the active role of the ionic liquid in promoting the reaction.

Above, we have shown that (i) the acidic chloroaluminate ionic liquid can further enhance the catalytic power of an expensive silyl borate catalyst for carrying out Diels−Alder reactions; (ii) less amount of catalyst in the above ionic liquid is required to obtain optimum results; (iii) this is an improvement on the recent work of Hara et al.[1] as evidenced by repeating the reaction carried out by them; and (iv) the used ionic liquid can be recovered and reused in promoting Diels−Alder reactions to offer comparable yields. This study can be expanded to cover more Lewis acid sensitive organic reactions.

Experimental Section

We prepared the catalyst by the procedure of Lambert and Zhang.[8] In a typical run, first the dienophile (8 mmol) was added to the mixture containing the catalyst prepared in toluene (1 mL) and the ionic liquid (1.5 mL). To this was added the diene (8 mmol), and the reaction mixture was magnetically stirred at room temperature. For the reaction of **8** with **9**, 6 mmol of **8** and 2 mmol of **9** were used for obtaining quantitative yields.[9,10] For a standard kinetic run, the dienophile (1 mmol) was added to the ionic liquid (1 mL of ionic liquid) and was allowed to equilibrate at the desired temperature controlled to ±0.01 K. The reaction was initiated by addition of diene (1 mmol in 1 mL). The reaction progress was monitored at appropriate time intervals by extraction of aliquots with ether followed by appropriate dilution and GC analysis. The reported k_2 value is an average of triplicate runs with Fs standard error of 5%. The endo and exo products for the reactions of **1** with **2a** and **2b** were characterized by NMR.[10,11] However, for the reaction of **1** with **2c**, the stereochemical assignments were made by condensing crotonic acid with **1** and the resultant endo and exo bicyclic acids separated by iodolactonization as described by Evans et al. and us.[12,13] The ^1H NMR spectrum of *endo*-ester is also reported by Ikota.[14]

Acknowledgment. Thanks are due to Dr. M. Heilig for his help in preparing the catalyst.

Supporting Information Available: Experimental details, data, ^1H NMR spectra of products, and GC analysis of sample product. This material is available free of charge via the Internet at http://pubs.acs.org.

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