

High Regioselective Diels–Alder Reaction of Myrcene with Acrolein Catalyzed by Zinc-Containing Ionic Liquids

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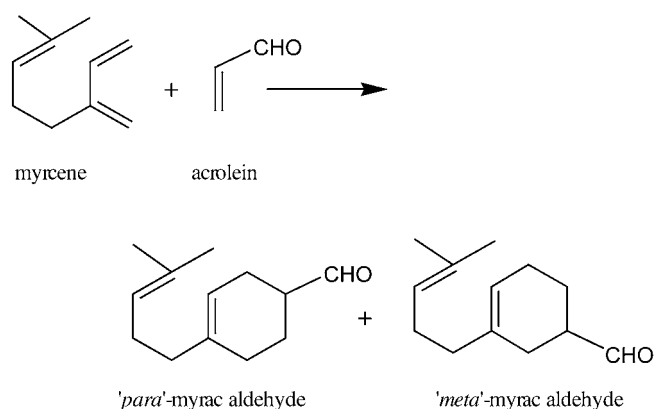
Abstract: The ambient zinc-containing ionic liquids, MX-ZnCl₂, functioning as both Lewis acid catalyst and green solvent, are employed for a high regioselective Diels–Alder reaction of myrcene with acrolein for the first time, where MX is either 1-butyl-3-methylimidazolium chloride (BmimCl), 1-ethyl-3-methylimidazolium bromide (EmimBr), *N*-butylpyridinium bromide (BPyBr), or *N*-ethylpyridinium bromide (EtPyBr). Compared with the analogous reaction performed over a ZnCl₂ catalyst in the conventional solvent dichloromethane, higher regioselectivity of the ‘*para*’ cycloadduct and excellent yield were achieved at shorter reaction time in these ionic liquids with optimized molar compositions of MX and ZnCl₂. These moisture-insensitive ionic liquids can be easily separated from reaction products after simple washing with hexane, allowing their reuse with no obvious loss in activity.

Keywords: acrolein, Diels–Alder reaction, ionic liquids (ILs), myrcene, zinc chloride

Introduction

The Diels–Alder reaction is one of the most useful carbon-carbon bond-forming reactions in organic synthesis and is widely used in the chemical industry for the synthesis of natural products in a regio- and stereo-controlled way. Myrcene (7-methyl-3-methene-1,6-octadiene), prepared by cracking β -pinene from turpentine oil, gives rise to a variety of fragrant compounds and their intermediates when reacted with conjugated alkylene carbonyl compounds.^[1] For example, the Diels–Alder reaction of myrcene with acrolein can yield two regioselective cycloadducts, the ‘*para*’- and ‘*meta*’-myrac aldehyde (4- and 3-(4'-methyl-3'-pentyl)- Δ^3 -cyclohexenecarboxaldehyde) (Scheme 1). It is known that the ‘*para*’-myrac aldehyde has been found to be very useful in perfumes, eau de colognes, cosmetic powders and dryer-added fabric softener articles, as well as in cigarette and smoking tobacco articles.^[2] How to synthesize the ‘*para*’-myrac aldehyde with high regioselectivity is therefore a very in-

teresting question. In our previous reports, rate enhancement and the ‘*para*’ regioselectivity improvement of the reaction has been achieved by the use of homogeneous and heterogeneous ZnCl₂ Lewis acid catalysts.^[3] However, it is known that almost all homogeneous Lewis acids have serious drawbacks, e.g., requirements of large amount of catalyst and laborious work-up procedures, problems of environmentally hazardous waste-streams and difficulty in their reuse. Heterogeneous Lewis acid catalysts can be recycled, but an additional modification of the catalyst is usually required in its preparation procedure; also, the catalytic reaction has to be carried out in large volumes of toxic and volatile organic solvents which may be hazardous to the environment.



Scheme 1. The Diels–Alder reaction of myrcene with acrolein.

Recently, the application of room temperature ionic liquids (ILs) as green solvents and catalysts in different organic transformations has attracted much attention due to their unique physicochemical properties, e.g., non-volatility, non-inflammability, and facility in recycling. It is reported that some ionic liquids, such as 1-butyl-3-methylimidazolium trifluoromethanesulfonate [Bmim][OTf], 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆], 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF₄], and 1-ethyl-3-methyl-

Table 1. The results of Diels–Alder reactions of myrcene with acrolein obtained in ionic liquids at various molar ratios of ZnCl_2 to MX.^[a]

Entry	MX	Molar ratio of ZnCl_2 to MX	Yield [%]	Regioselectivity [<i>p/m</i>]
1	BmimCl	0:1 ^[b]	4.3	75:25
2		0.9:1	21.5	94:6
3		1:1	26.8	94:6
4		1.1:1	47.4	94:6
5		1.5:1	62.3	94:6
6		2:1	97.3	95:5
7		3:1	96.3	95:5
8	EmimBr	0:1 ^[b]	4.1	74:26
9		0.9:1	18.6	93:7
10		1:1	22.8	93:7
11		1.1:1	45.9	94:6
12		1.5:1	66.5	94:6
13		2:1	97.4	94:6
14		3:1	97.5	94:6
15	BPyBr	0:1 ^[b]	4.3	77:23
16		0.9:1	20.4	94:6
17		1:1	25.0	94:6
18		1.1:1	50.0	94:6
19		1.5:1	72.6	94:6
20		2:1	96.9	95:5
21		3:1	97.1	95:5
22	EtPyBr	0:1 ^[b]	3.7	76:24
23		0.9:1	17.9	94:6
24		1:1	22.2	94:6
25		1.1:1	42.7	95:5
26		1.5:1	58.1	95:5
27		2:1	92.2	95:5
28		3:1	94.4	95:5

^[a] The reaction was performed at 15 °C for 2 h.

^[b] Reaction time was 4 h.

midazolium hexafluorophosphate [Emim][PF₆] etc., were favorably reused to accelerate some Diels–Alder reactions.^[4,5] However, in the case of the Diels–Alder reaction catalyzed by Lewis acid, these neutral ILs did not show great advantages due to their weak Lewis acidity. Chloroaluminate ionic liquids have been reported as both solvent and Lewis acid catalyst for several Diels–Alder reactions^[6] but the widespread utilization of chloroaluminate ionic liquids is rather limited due to their moisture sensitivity. Therefore, it is very interesting to find a new type of ionic liquids that possesses both a suitable Lewis acid property and stability to moisture.^[7] In this paper, the Diels–Alder reactions of myrcene with different carbonyl-containing dienophiles in BmimCl– ZnCl_2 , EmimBr– ZnCl_2 , BPyBr– ZnCl_2 and EtPyBr– ZnCl_2 ionic liquids has been examined for the first time. These ionic liquids are favorably moisture-insensitive which allows their repeated use for at least five times, without noticeable decrease in their catalytic activities.

Results and Discussion

Effect of ZnCl_2 Composition in Ionic Liquids on the Reaction

In Table 1 are listed the results of the Diels–Alder reaction between myrcene and acrolein in different ionic liquids at various molar ratios of ZnCl_2 to MCl. Very poor yield and regioselectivity were obtained if the reaction was performed in ZnCl_2 -free BmimCl, EmimBr, BPyBr, or EtPyBr ionic liquids (entries 1, 8, 15 and 22). However, the reaction rate in zinc-containing ionic liquids was very sensitive to the molar ratio of ZnCl_2 to MX in the range from 0.9:1 to 2:1. For example, if the reaction was carried out in the zinc-containing ionic liquid with a molar ratio of ZnCl_2 to BmimCl of 0.9:1, the yield of cycloadducts was only 21.5%, but the regioselectivity of *p/m* (94/6) increased significantly (Entry 2), as compared with that in pure BmimCl. With an increase of the molar fraction of ZnCl_2 from 1:1 to 2:1, the reaction

Table 2. The results of Diels–Alder reactions of myrcene with acrolein in dichloromethane and in ionic liquids.

Entry	Solvent	Catalyst	Time [h]	Yield [%]	Regioselectivity [<i>p/m</i>]
1	CH ₂ Cl ₂ ^[a]	None	6	6.5	72:28
2	CH ₂ Cl ₂ ^[a]	ZnCl ₂	6	69.0	92:8
3	CH ₂ Cl ₂ ^[a]	ZnCl ₂ /NaY	6	83.2	93:7
4	BmimCl–ZnCl ₂ ^[b]	None	2	97.3	95:5
5	EmimBr–ZnCl ₂ ^[b]	None	2	97.4	94:6
6	BPyBr–ZnCl ₂ ^[b]	None	2	96.9	95:5
7	EtPyBr–ZnCl ₂ ^[b]	None	2	92.2	95:5

^[a] Ref.^[3b], the reaction was performed at 30 °C.

^[b] The molar ratio of ZnCl₂ to XCl was 2:1 and the reaction was performed at 15 °C.

rate increased clearly (entries 2–6). Especially at a molar ratio of ZnCl₂ to BmimCl of 2:1, a yield of 97.3% for the cycloadducts with high regioselectivity (*p/m* = 95/5) was obtained at 15 °C after only 2 h (entry 6). Both the yield and regioselectivity (*p/m* ratio) remain almost unchanged with an increase of the molar ratio of ZnCl₂ to BmimCl up to 3:1 (entry 7). Similar reaction rules were obtained for EmimBr–ZnCl₂ (entries 8–14), BPyBr–ZnCl₂ (entries 15–21) and EtPyBr–ZnCl₂ (entries 22–28). The enhancement of the reaction rate and regioselectivity observed here could be attributed to an increase in Lewis acidity as a result of the increase of the amount of ZnCl₂ in each zinc-containing ionic liquid.

Comparison between the Reactions in Dichloromethane and in Ionic Liquids

In Table 2 are summarized the results of the Diels–Alder reactions of myrcene with acrolein carried out in ionic liquids and in the solvent dichloromethane. The thermal reaction rate in dichloromethane was very low with poor regioselectivity (entry 1). In our previous report,^[3] higher yield and regioselectivity of cycloadducts were obtained over the heterogeneous catalyst of ZnCl₂/NaY prepared by treatment with microwave irradiation than that over the typical homogeneous Lewis acid of ZnCl₂ in the conventional solvent of dichloromethane (entries 2 and 3). However, when the reaction was performed in the zinc-containing ionic liquids with different cations, a significant enhancement in the reaction rate was observed. Typically, a higher yield of the cycloadducts with higher regioselectivity was achieved in the zinc-containing ionic liquids after a reaction period of only 2 h at 15 °C (entries 4–7), whereas lower yield and regioselectivity were obtained over homogeneous and heterogeneous ZnCl₂ catalysts in the solvent of dichloromethane even after 6 h reaction at 30 °C (entries 1–3), indicating that the ionic liquid acted here not only as a Lewis acid catalyst but also as a green solvent with polar or ionic characteristics and high internal pressure.^[8] The mid-strength Lewis acid active sites in

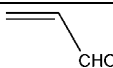
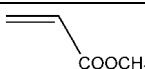
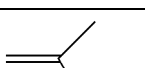
the zinc-containing ionic liquids may play very important roles in the Diels–Alder reaction.

Comparison among Different Carbonyl-Containing Dienophiles

Further, we have carried out the Diels–Alder reactions of myrcene with different carbonyl-containing dienophiles to examine the possibility of the wide use of this kind of ionic liquids. The results of the Diels–Alder reaction in the ionic liquid BmimCl–ZnCl₂ (molar ratio of ZnCl₂ to BmimCl = 2:1) and organic solvents at different reaction temperatures are compared in Table 3. It is observed that the yield and regioselectivity were strongly influenced by the dienophiles and reaction temperature. Compared with the reaction performed in the solvent dichloromethane, the yield of the cycloadducts and the regioselectivity of the ‘*para*’ cycloadduct increased significantly in the ionic liquid BmimCl–ZnCl₂ at 15 °C (entries 1 and 2, 3 and 4, 7 and 8, and 11 and 12). By using the corresponding dienophile as solvent at the reaction temperature of 75 °C, the reaction performed in the ionic liquid also gave a high yield and regioselectivity (entries 5 and 6, 9 and 10, and 13 and 14). The results indicated that the ionic liquid BmimCl–ZnCl₂ acted in the reactions as both Lewis acid catalysis and polar solvent. Moreover, the reaction temperature has a remarkable effect on the ‘*para/meta*’ regioselectivity in BmimCl–ZnCl₂ ionic liquid. The regioselectivity decreased significantly with increasing reaction temperature (entries 4–6, 8–10, and 12–14).

Both the electron density at the carbonyl of dienophile and the steric crowding of the dienophile have great effects on the Diels–Alder reaction rate. It is known that in the Diels–Alder reaction of myrcene catalyzed by Lewis acid the carbonyl of the dienophile is coordinated with the Lewis acid sites of Zn²⁺ to activate the dienophile,^[3a] and therefore the electron density at the carbonyl of the dienophiles should be taken into account. Among the four dienophiles, acrolein has no electron-donating group and the least steric crowding, which gives the highest yield of myrac aldehyde with highest

Table 3. The results of Diels–Alder reactions between myrcene and different dienophiles.^[a]

Entry	Dienophile	Solvent	Temperature [°C]	Time [h]	Yield [%]	Regioselectivity [<i>p/m</i>]
1		CH ₂ Cl ₂ ^[b]	15	6	6.5	72:28
2		BmimCl–ZnCl ₂	15	2	97.3	95:5
acrolein						
3		CH ₂ Cl ₂ ^[b]	15	48	3.8	67:33
4		BmimCl–ZnCl ₂	15	48	85.9	93:7
5		Methyl acrylate ^[c]	75	9	46.3	67:33
6		BmimCl–ZnCl ₂	75	9	95.2	79:21
methyl acrylate						
7		CH ₂ Cl ₂ ^[b]	15	48	1.7	67:33
8		BmimCl–ZnCl ₂	15	48	69.9	92:8
9		methyl methacrylate ^[c]	75	9	10.9	67:33
10		BmimCl–ZnCl ₂	75	9	83.1	77:23
methyl methacrylate						
11		CH ₂ Cl ₂ ^[b]	15	48	2.2	56:44
12		BmimCl–ZnCl ₂	15	48	31.0	90:10
13		mesityl oxide ^[c]	75	9	6.4	70:30
14		BmimCl–ZnCl ₂	75	9	52.3	70:30
mesityl oxide						

^[a] Unless otherwise noted, the reaction conditions were 2 mL of IL, 1.0 mmol of myrcene, and 1.1 mmol of dienophile.

^[b] CH₂Cl₂ (2 mL) was used as the only solvent.

^[c] 10 mmol of methyl acrylate, methyl methacrylate and mesityl oxide were used as dienophile and solvent, respectively.

regioselectivity at a short reaction time (entry 2). However, methyl acrylate and methyl methacrylate with an electron-donating group (–OCH₃) gave poorer yields when used as dienophiles even at a prolonged reaction time (entries 4 and 8). Mesityl oxide gave the lowest yield of cycloadducts and lowest regioselectivity, which is mainly attributed to the difficulty in activating it due to steric crowding (entries 12 and 14). Taking into account the electronic properties and steric hindrance of the dienophiles, the activity sequence for the four dienophiles is as follows: acrolein > methyl acrylate > methyl methacrylate > mesityl oxide, which is in good agreement with the yields of cycloadducts listed in Table 3.

Recycling of the Ionic Liquids in the Diels–Alder Reaction of Myrcene with Acrolein

The Diels–Alder reaction catalyzed by the zinc-containing ionic liquids is a two-phase reaction, namely, the dienophile acrolein dissolves in the ionic liquid, but the less polar diene forms a separate phase. After completion of the reaction the products also form a separate phase on top of the ionic liquid and therefore are easily separated by decanting or removing with a pipette. The isolated products can be distilled under reduced pressure. The remaining ionic liquid is further washed with hexane and is recycled in subsequent runs. All the procedures for recovering the ionic liquids are operated in the

air without special anti-moisture procedures, which shows that the zinc-containing ionic liquids are moisture stable. The above procedure was repeated four times and the results obtained in the ionic liquids are listed in Table 4. It was observed that there was no noticeable decrease in activity even up to 5 subsequent runs. The simple experimental and product isolation procedures as well as the easiness for recovery and reuse of the novel reaction medium may contribute to the development of a green strategy for the high regioselective synthesis of ‘*para*’-myrac aldehyde.

Conclusions

In summary, this paper has described that the zinc-containing ionic liquids are novel reaction media as well as Lewis acid catalysts for the highly regioselective Diels–Alder reaction of myrcene with acrolein. High yields of myrac aldehyde with high regioselectivity were achieved in the zinc-containing ionic liquids at the molar ratio of ZnCl₂ to MX of 2:1 and a short reaction time. The experimental procedure here is quite simple and convenient, the non-volatile and moisture-stable ionic liquids can be conveniently recovered for recycled uses, and thus the generation of wastes and safety-related problems may be avoided. The novel reaction/catalytic media described here may serve as promising replacements of homogeneous and heterogeneous ZnCl₂ in tox-

Table 4. Reuse of ionic liquids in Diels–Alder reactions of myrcene with acrolein.^[a]

Entry	MX-ZnCl ₂	Run time	Yield [%]	Regioselectivity [<i>p/m</i>]
1	BmimCl–ZnCl ₂	1	97.3	95:5
2		2	96.8	95:5
3		3	97.9	94:6
4		4	95.7	94:6
5		5	97.3	94:6
6	EmimBr–ZnCl ₂	1	97.4	94:6
7		2	97.7	94:6
8		3	96.8	94:6
9		4	96.3	94:6
10		5	97.1	94:6
11	BPyBr–ZnCl ₂	1	96.9	95:5
12		2	95.4	95:5
13		3	98.4	94:6
14		4	96.0	94:6
15		5	98.2	94:6
16	EtPyBr–ZnCl ₂	1	92.2	95:5
17		2	93.5	95:5
18		3	94.1	95:5
19		4	90.0	95:5
20		5	91.6	94:6

^[a] The reaction was performed at 15 °C for 2 h and the molar ratio of ZnCl₂ to BmimCl was 2:1.

ic organic solvents and are expected to find wider applications in related organic synthesis.

Experimental Section

Chemicals

Anhydrous ZnCl₂ was prepared by using thionyl chloride (SOCl₂) to dehydrate ZnCl₂·2 H₂O,^[3] the remaining SOCl₂ was then removed by distillation under vacuum, the obtained anhydrous ZnCl₂ was kept in a vacuum desiccator with potassium hydroxide overnight prior to use. Acrolein (from Aldrich), methyl acrylate, methyl methacrylate and mesityl oxide (from Fluka) were fresh distilled before use. Myrcene, pyridine, and 1-methylimidazole supplied by ACROS were used as received. 1-Chlorobutane, bromoethane, *n*-hexane, dichloromethane, and chloroethane were purchased from ABCR (Associação Brasileira de Captadores de Recursos) and freshly distilled before use.

General Procedures for the Synthesis of Ionic Liquids

1-Butyl-3-methylimidazolium chloride (BmimCl), 1-ethyl-3-methylimidazolium bromide (EmimBr), *N*-1-butylpyridinium bromide (BPyBr) and *N*-1-ethylpyridinium bromide (EtPyBr) were synthesized following the procedures described in the literature.^[9]

Synthesis of BmimCl; Typical Procedure

To *N*-methylimidazole (20 mL, 0.25 mmol) as solvent an equal molar amount of *n*-chlorobutane was added into a round-bottomed flask and then the mixture was refluxed at 80 °C for 48 h with stirring. After cooling the reaction mixture to room temperature, the top phase was decanted and the bottom phase was washed with ethyl acetate (5 × 40 mL) to ensure that any unreacted starting material was removed from the bottom phase. The volatile materials were evaporated under high vacuum to obtain BmimCl as a slightly yellow liquid.

Zinc-Containing Ionic Liquids BmimCl–ZnCl₂, EmimBr–ZnCl₂, BPyBr–ZnCl₂ and EtPyBr–ZnCl₂

These were prepared by mixing MX (20 mmol) and appropriate amounts of anhydrous ZnCl₂ followed by heating at 100 °C for 12 h under nitrogen with vigorous stirring. The color of the resulted ionic liquids depended on the kind of MX used.

General Procedures for Diels–Alder Reactions

In a typical reaction, myrcene (1.0 mmol) was added slowly to a solution of zinc-containing ionic liquid (2 mL) and acrolein (1.1 mmol) under vigorous stirring for an appropriate time. After the reaction was completed, the upper clear liquid was pipetted off for gas chromatographic analysis, the remaining ionic liquid phase was washed with hexane (3 × 3 mL), purified under vacuum and directly reused in the subsequent runs. The reaction products was analyzed by gas chromatography on an Agilent Technologies 6890N (FID, HP-5 column, 30 m ×

0.32 mm $\times$ 0.25 μ m), nitrogen as a carrier gas, injector temperature 220 °C, detector temperature 200 °C, oven temperature 150 °C, using *trans*-naphthene as an internal standard. The retention times were: acrolein 2.58 min, myrcene 3.35 min, '*meta*'-myrac aldehyde 12.61 min, and '*para*'-myrac aldehyde 13.89 min, respectively. After distillation and purification of the upper clear liquid under vacuum, the product '*para*'-myrac aldehyde (bp 136–138 °C/500 Pa) was identified by GC-MS, FT-IR (Nicolet Nexus FT-IR Spectrometer), ¹H NMR and ¹³C NMR (INOVA-400-Varian) spectra, the data of which were in good agreement with those of an authentic sample; MS: *m/z* = 192 [*M*⁺ peak], 177 [192-CH₃]⁺, 149 [177-CHO]⁺, 122 [192-CH₂CH=CHO]⁺, 93 [122-CHO]⁺, 69 [(CH₃)₂=CHCH₂]⁺, 41 [CH₂=CH-CH₂]⁺, 29 [-CHO]⁺; IR: ν = 2820, 2720, 1730, 1390, 1370, 1205, 805 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 1.60, 1.68 [2 s, 6 H (CH₃)₂], 1.92–2.10 (m, -CH₂-, -CH₂-CH₂-, -CH₂-), 2.23 (m, =CH-CH₂), 2.46 (m, -CH-), 5.08 [m, =CH-C(CH₃)₂], 5.43 (m, =CH-CH₂), 9.69 (s, -CHO); ¹³C NMR (100 MHz, CDCl₃): δ _C = 17.66 (-CH₃), 22.53 (-CH₃), 24.48 (-CH₂), 25.68 (-CH₂), 26.30 (-CH₂), 26.86 (-CH₂), 37.58 (-CH₂), 46.07 (-CH), 118.34 (=CH), 124.04 (=CH), 131.57 (=C), 138.01 (=C), 204.82 (-CHO).

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