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# Diels–Alder Reaction of Cyclopentadiene and Alkyl Acrylates in the Presence of Pyrrolidinium Ionic Liquids with Various Anions

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**Abstract** The conversion and stereoselectivity of transformation to *endo* and *exo* norbornene derivatives was determined in the Diels–Alder reaction of cyclopentadiene with alkyl acrylates. The reactions were carried out in the pyrrolidinium ionic liquids in the presence of metal chlorides and trifluoromethanesulfonates as the catalysts. Shorter reaction times and higher conversions of dienophile were observed in a comparison with analogous cycloadditions carried out in the presence of conventional organic solvents. A higher stereoselectivity to the *endo* isomer was found in the majority of cases. The ionic liquids composed of 1-butyl-1-methylpyrrolidinium cation (Pyr<sub>1,4</sub>) and various anions were used. The influence of ionic liquid anion and several metal chlorides and metal triflates used as the catalysts on the conversion was determined.

**Keywords** Diels–Alder reaction · Ionic liquids · Lewis acids

## 1 Introduction

The Diels–Alder reaction is a particularly useful method for the synthesis of compounds with cyclic structure [1]. The majority of syntheses proceed with the formation of a mixture of isomers and the yield and reaction stereoselectivity depends to a large degree on the nature of solvent and catalyst. An enhancement in the reaction stereoselectivity can be achieved through the introduction into the reaction

medium of water [2], surfactants [3], lithium perchlorate(VII) [4], alkyl ammonium nitrate [5], tetrahydrofuran–hydrogen bromide (HBr–THF) complex [6], and Lewis acid. In recent years, the ionic liquids [7–13] have been used as the Diels–Alder reaction medium instead of conventional organic solvents. A good solubility of the catalysts has been of crucial importance in their applications. The catalysts of these cycloaddition reactions are frequently trifluoromethanesulfonates and chlorides of the rare-earth elements such as: M(OTf)<sub>3</sub>, MCl<sub>3</sub> (M = Sc, La, Ce, Y, OTf = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) [10–19]. The ionic liquids used in this type of reaction include the salts containing imidazolium [20], pyridinium [21], phosphonium [22] cation and bis(trifluoromethylsulfonyl)imide as the anion. The reaction of cyclopentadiene with acrolein is an exemplary of such application of the ionic liquids. In the medium of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide-bmim[NTf<sub>2</sub>] and InCl<sub>3</sub> as the catalyst, the stereoselectivity of *endo* isomer amounted to 16, whereas it was 8.8 in the EtOH/InCl<sub>3</sub> medium [12].

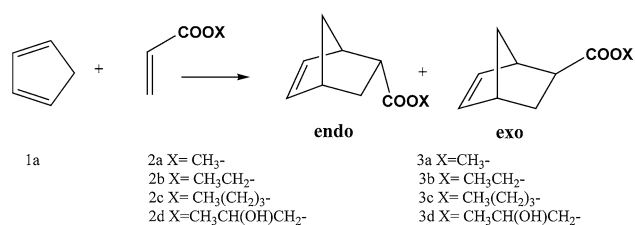
In this work the pyrrolidinium ionic liquids were used in the Diels–Alder reaction of cyclopentadiene with esters of acrylic acids. The catalysts selected for this study were trifluoromethanesulfonates and chlorides of alkali metals, alkaline earth metals, transition metals and rare-earth elements as well as chlorides of aluminum, tin and indium. The course of reaction was presented on Scheme 1.

## 2 Experimental

### 2.1 Raw Materials

The ionic liquids included: 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide Pyr<sub>1,4</sub>[NTf<sub>2</sub>] (98% pure

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**Scheme 1** The reaction of cyclopentadiene with dienophiles

Solvent Innovation), 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonates Pyr<sub>1,4</sub>[OTf] (98% pure Solvent Innovation), 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphates Pyr<sub>1,4</sub>[FAP] (>99% Merck). The liquids were dried in a vacuum drier, at temperature of 95 °C, under pressure of 5 mbar over 24 h. The water content in the ionic liquids was determined by coulometric Karl–Fischer titration using Metrohm 831 KF Coulometers. Cyclopentadiene was obtained as a results of thermal cracking of dicyclopentadiene (>95% pure) purchased from Fluka. As dienophiles were used the following acrylates: methyl (MeAkr) (99% Aldrich), ethyl (EtAkr) (99% Aldrich), butyl (BuAkr) (99% Aldrich) and 2-hydroxypropyl (HpAkr) (98% Aldrich). Gas chromatographic (GC) measurements were performed using cyclohexanone (CH) (>99% Merck) as an internal standard. As the catalysts were the following used chlorides: scandium ScCl<sub>3</sub> (99.9% Aldrich), ytterbium YbCl<sub>3</sub> (99.9% Aldrich), yttrium YCl<sub>3</sub> (99.99% Aldrich), lanthanum LaCl<sub>3</sub> (99.9% Aldrich), magnesium MgCl<sub>2</sub> (99.9% Aldrich), trifluoromethanesulfonates: bismuth Bi(OTf)<sub>3</sub> (99.9% Aldrich), cerium Ce(OTf)<sub>3</sub> (99% Acros Organics), zinc Zn(OTf)<sub>2</sub> (98% Aldrich), tin Sn(OTf)<sub>2</sub> (98% Acros Organics), aluminum Al(OTf)<sub>3</sub> (99.9% Aldrich), indium In(OTf)<sub>3</sub> (99.9% Aldrich), ytterbium hydrate Yb(OTf)<sub>3</sub>·H<sub>2</sub>O (25–28% Yb Aldrich), ytterbium Yb(OTf)<sub>3</sub> (99.99% Aldrich), yttrium Y(OTf)<sub>3</sub> (98% Aldrich), lanthanum hydrate La(OTf)<sub>3</sub>·H<sub>2</sub>O (99.9% Aldrich), lanthanum La(OTf)<sub>3</sub> (99% Acros Organics), magnesium Mg(OTf)<sub>2</sub> (97% Aldrich), cuprum Cu(OTf)<sub>2</sub> (98% Aldrich), neodymium Nd(OTf)<sub>3</sub> (99% Acros Organics), scandium Sc(OTf)<sub>3</sub> (>97% Chemica), sodium NaOTf (98% Aldrich), calcium Ca(OTf)<sub>2</sub> (99.9% Aldrich).

## 2.2 Procedure for the Reaction

The reactions were carried out in 4 mL screwed vials equipped with a magnetic stirrer. The vial was charged with the ionic liquid in the amount of 250 μL, cyclohexanone—20 μL (0.0198 g) and with dienophile in the amount corresponding to 1 mmol. A sample was collected from such prepared mixture and was subjected to GC analysis. The peak area ratio (dienophile/internal standard) was calculated from obtained chromatograms. After the

addition of 0.0996 g (1.5 mmol) of cyclopentadiene, the vial was located in the thermostat bath at temperature of 25 °C and was stirred. The content of dienophile in the reaction mixture was determined by GC method every 30 min over 4 h, or until the conversion of dienophile was over 90% (the reaction time was calculated from a moment of cyclopentadiene addition). The peak area ratio of dienophile to the internal standard was again determined and the dienophile conversion was calculated. The conversion determined in such a way is the same as the yield of norbornene derivative. The dienophile undergoes the reaction only with the formation of *endo* and *exo* derivative of norbornene. The *endo/exo* ratio was calculated based on the GC analysis, whereas in the case of 2-hydroxypropyl acrylate based on the analysis of H<sup>1</sup> NMR and C<sup>13</sup> NMR spectra. In the case of reaction carried out in the presence of catalyst, the catalyst was first weighed in the amount corresponding to 1 or 3 mol% in relation to the dienophile and a constant amount of ionic liquids—250 μL was added. The catalyst concentration in the ionic liquid amounted to 0.04 or 0.12 mol/dm<sup>3</sup>. The catalyst was stirred in the ionic liquid until the complete dissolution.

## 3 Results and Discussion

The results of reaction of cyclopentadiene with selected alkyl acrylates (Scheme 1) in ionic liquids as the reaction medium without the catalyst were presented in Table 1. The reaction of cyclopentadiene with methyl acrylate and ethyl acrylate proceeded very fast in the medium of 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonates Pyr<sub>1,4</sub>[OTf], whereas at much lower rate in 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate Pyr<sub>1,4</sub>[FAP]. The Diels–Alder reaction of cyclopentadiene with methyl acrylate gave the largest fraction of *endo* isomer (84%) in the liquid with [OTf]<sup>−</sup> anion, whereas lower (81%) in the case of remaining liquids. In the reaction of cyclopentadiene with ethyl acrylate the highest stereoselectivity of the *endo* isomer was achieved in the ionic liquids with [OTf]<sup>−</sup> anion (84%), whereas a lower stereoselectivity was obtained with [NTf<sub>2</sub>]<sup>−</sup> (82%) and [FAP]<sup>−</sup> (81%). The stereoselectivity did not change during the course of process. The reaction of cyclopentadiene with butyl acrylate proceeded very fast and with the highest conversion of dienophile in the presence of liquid with [OTf]<sup>−</sup> anion, whereas at the lowest rate in the liquid with [NTf<sub>2</sub>]<sup>−</sup> anion. The highest selectivity of *endo* isomer in this reaction amounted to 84% when the ionic liquid was with [NTf<sub>2</sub>]<sup>−</sup> anion, in the remaining liquids was 82%. Among all considered dienophiles the highest conversion equal to 70% was achieved after 2 h for the reaction of cyclopentadiene with 2-hydroxypropyl acrylate, and that carried out in the presence of liquid with [NTf<sub>2</sub>]<sup>−</sup> anion.

**Table 1** Conversion and stereoselectivity of the reaction of cyclopentadiene with selected alkyl esters of acrylic acid in ionic liquids as the reaction medium without the catalyst

Ionic liquid	CP + MeAcr			CP + EtAcr			CP + BuAcr			CP + 2HpAcr		
	Conversion [mol %]		Stereoselectivity <i>endo:exo</i> (%)	Conversion [mol %]		Stereoselectivity <i>endo:exo</i> (%)	Conversion [mol %]		Stereoselectivity <i>endo:exo</i> (%)	Conversion [mol %]		Stereoselectivity <i>endo:exo</i> (%)
	2 h	4 h		2 h	4 h		2 h	4 h		2 h	4 h	
Pyrr <sub>1,4</sub> [NTf <sub>2</sub> ]	45	63	81:19	36	57	82:18	26	48	84:16	70	82	100:0
Pyrr <sub>1,4</sub> [FAP]	39	66	81:19	35	52	81:19	35	52	82:18	56	88	100:0
Pyrr <sub>1,4</sub> [OTf]	48	67	84:16	59	73	84:16	73	83	82:18	55	82	100:0
Products	2-methoxycarbonyl-5-norbornene			2-ethoxycarbonyl-5-norbornene			2-butoxycarbonyl-5-norbornene			2-(2-hydroxypropyl)oxy-carbonyl-5-norbornene		

[NTf<sub>2</sub>] = (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, [FAP] = (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>, [OTf] = CF<sub>3</sub>SO<sub>3</sub>

In this cycloaddition but also carried out in the presence of [FAP]<sup>−</sup> anion was obtained the highest conversion (88%) after 4 h. In the ionic liquid with [OTf]<sup>−</sup> anion a high conversion (80%) was also obtained after 4 h. The *endo* stereoisomer is formed exclusively in all ionic liquids tested during the synthesis of norbornene derivative. Its presence was confirmed on the basis of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum and by the literature data [23]. A comparison of acrylates used in these syntheses, reveals that their reactivity is similar in the liquids with [NTf<sub>2</sub>]<sup>−</sup> and [FAP]<sup>−</sup> anions. In a series of methyl, ethyl, butyl acrylate, the reactivity in the presence of [NTf<sub>2</sub>]<sup>−</sup> and [FAP]<sup>−</sup> anions decreases along with an extension of the chain length of the ester groups and is always lower than that in the presence of [OTf]<sup>−</sup> anion. In the reaction of cyclopentadiene with butyl acrylate in the presence of [NTf<sub>2</sub>]<sup>−</sup> after 4 h, the product was obtained with 48% yield. In the ionic liquid with [OTf]<sup>−</sup> anion, the conversion of butyl acrylate was the highest in the considered series of acrylates and the ionic liquids. The conversion amounted to 73% after 2 h, whereas 83% after 4 h. The reaction of 2-hydroxypropyl acrylate proceeded in a different manner. Its conversion was similar after 4 h, and has the highest value among the used acrylates irrespective of the ionic liquid.

The studies of catalysts activity in the form of metal chlorides and trifluoromethanesulfonates were performed for the reaction of cyclopentadiene with methyl acrylate in the presence of ionic liquid Pyrr<sub>1,4</sub>[NTf<sub>2</sub>] (Table 2). It was found that not all the compounds caused an increase in the rate and the stereoselectivity of transformation in the direction of *endo* isomer in a comparison with the reaction carried out without the catalyst. The conversion of methyl acrylate in the liquid Pyrr<sub>1,4</sub>[NTf<sub>2</sub>] without the catalyst amounted to 63% after 4 h. In a group of triflates used in the amount of 1% mol in relation to methyl acrylates, the largest increase of conversion was obtained for trifluoromethanesulfonates of lanthanum La(OTf)<sub>3</sub>, magnesium Mg(OTf)<sub>3</sub>, calcium Ca(OTf)<sub>3</sub>, and neodymium Nd(OTf)<sub>3</sub>. The largest increase in

the stereoselectivity of the *endo* isomer up to a value of 93% in a comparison with the reaction without the catalyst (81%) was obtained in Pyrr<sub>1,4</sub>[NTf<sub>2</sub>] liquid in the presence of the catalysts: Sc(OTf)<sub>3</sub> and Y(OTf)<sub>3</sub>. However, a competitive reaction of cyclopentadiene oligomerization proceeded in the presence of these catalysts in Pyrr<sub>1,4</sub>[NTf<sub>2</sub>] liquid and after about 30 min the changes of yield of the main reaction product practically were not observed. In the case of the catalysts: Cu(OTf)<sub>2</sub>, Al(OTf)<sub>3</sub>, Bi(OTf)<sub>3</sub>, Ce(OTf)<sub>3</sub>, In(OTf)<sub>3</sub>, and Sn(OTf)<sub>2</sub>, the oligomerization of cyclopentadiene was prevailing and 2-methoxycarbonyl-5-norbornene was formed with a low yield (below 1%). It was found that the addition of cyclopentadiene caused turbidity of the reaction mixture and subsequently produced a darkening effect and solidification. The reaction was accompanied by the release of heat. The reaction, when conducted in the Pyrr<sub>1,4</sub>[NTf<sub>2</sub>] liquid with scandium and yttrium trifluoromethanesulfonates used in the amount of 3 mol% gave higher stereoselectivities of *endo* isomer (93–94%). However, these catalysts caused the formation of 2-methoxycarbonyl-5-norbornene with lower yields due to accelerated the oligomerization of cyclopentadiene. The other catalysts e.g. Nd(OTf)<sub>3</sub>, La(OTf)<sub>3</sub>, used at higher concentrations (3 mol%), slightly increased the conversion and stereoselectivity of the *endo* isomer in relation to the values obtained at concentration of 1%. An increase in the concentration of Mg(OTf)<sub>3</sub> from 1 to 3 mol% did not cause any changes of the conversion and reaction stereoselectivity.

The chloride catalyst used in the amount of 1 mol% in relation to methyl acrylate in the ionic liquid with [NTf<sub>2</sub>]<sup>−</sup> anion exhibited the highest activity in the case of ytterbium. The largest increase in the stereoselectivity of *endo* isomer in the ionic liquid Pyrr<sub>1,4</sub>[NTf<sub>2</sub>] in relation to the reaction without the catalyst was obtained in the presence of ytterbium and scandium chlorides. An increase of the catalyst amount to 3 mol%, in the case of liquid Pyrr<sub>1,4</sub>[NTf<sub>2</sub>] demonstrated a high activity of yttrium, ytterbium and scandium chlorides. The conversion of 96%

**Table 2** Conversion and stereoselectivity of reaction of cyclopentadiene with methyl acrylate in the ionic liquid Pyr<sub>1,4</sub>[NTf<sub>2</sub>]

Entry	Catalyst	Conversion [mol %]		Stereoselectivity <i>endo:exo</i> %
		2 h	4 h	
1	Y(OTf) <sub>3</sub>	44 <sup>a</sup>		91:9
2	Y(OTf) <sub>3</sub> <sup>c</sup>	74 <sup>a</sup>		93:7
3	Yb(OTf) <sub>3</sub>	46	61	86:14
4	Yb(OTf) <sub>3</sub> <sup>c</sup>	73	90	91:9
5	Sc(OTf) <sub>3</sub>	31 <sup>a</sup>		93:7
6	Sc(OTf) <sub>3</sub> <sup>c</sup>	54 <sup>a</sup>		94:6
7	La(OTf) <sub>3</sub>	50	80	86:14
8	La(OTf) <sub>3</sub> <sup>c</sup>	63	84	87:13
9	La(OTf) <sub>3</sub> ·H <sub>2</sub> O	42	62	84:16
10	Yb(OTf) <sub>3</sub> ·H <sub>2</sub> O	34	48	84:16
11	Nd(OTf) <sub>3</sub>	56	71	86:16
12	Nd(OTf) <sub>3</sub> <sup>c</sup>	84	92	89:11
13	Zn(OTf) <sub>2</sub>	34	54	85:15
14	Ca(OTf) <sub>2</sub>	54	71	82:18
15	Mg(OTf) <sub>2</sub>	52	71	83:17
16	Mg(OTf) <sub>2</sub> <sup>c</sup>	52	72	82:18
17	YCl <sub>3</sub>	48	62	82:18
18	YCl <sub>3</sub> <sup>c</sup>	99		91:9
19	YbCl <sub>3</sub>	73	82	88:12
20	YbCl <sub>3</sub> <sup>c</sup>	96 <sup>a</sup>		91:9
21	ScCl <sub>3</sub>	49	63	88:12
22	ScCl <sub>3</sub> <sup>c</sup>	96 <sup>b</sup>		91:9
23	MgCl <sub>2</sub>	43	64	81:19
24	LaCl <sub>3</sub>	48	53	75:25

<sup>a</sup> Conversion after 1 h,<sup>b</sup> Conversion after 15 min<sup>c</sup> Catalyst 3 mol% vs methyl acrylate

was achieved just after 15 min in the presence of scandium chloride. The same conversion was obtained after 1 h for ytterbium chloride, whereas for yttrium chloride the conversion was 99% after 2 h. The stereoselectivity to the *endo* isomer amounted to 91% in the presence of each of these chlorides.

The reaction of cyclopentadiene with butyl acrylate and in the presence of several most active catalysts was carried out in three pyrrolidinium ionic liquids: Pyr<sub>1,4</sub>[NTf<sub>2</sub>], Pyr<sub>1,4</sub>[OTf], liquid Pyr<sub>1,4</sub>[FAP] (Table 3). All the reactions proceeded with higher yields in the liquid with [NTf<sub>2</sub>]<sup>-</sup> anion. In the presence of the trifluoromethanesulfonate catalysts: scandium, yttrium, ytterbium and the ionic liquid Pyr<sub>1,4</sub>[FAP] proceeded the oligomerization of cyclopentadiene. Similarly as in the case of the reaction of cyclopentadiene with methyl acrylate, the highest activity

in the Diels–Alder reaction exhibited the catalysts: ScCl<sub>3</sub> and YbCl<sub>3</sub>. High conversions of butyl acrylate occurred in the presence of YCl<sub>3</sub> (86%) and YbCl<sub>3</sub> (85%) in the medium of Pyr<sub>1,4</sub>[NTf<sub>2</sub>]. The highest stereoselectivity expressed by a percentage fraction of the *endo* isomer in the product was obtained in the reactions catalyzed by scandium and yttrium trifluoromethanesulfonates (94%), in the presence of ionic liquid Pyr<sub>1,4</sub>[NTf<sub>2</sub>]. A high stereoselectivity of the *endo* isomer (93%) was also achieved in the reaction catalyzed by YCl<sub>3</sub> in the liquid Pyr<sub>1,4</sub>[FAP].

The reaction of cyclopentadiene with ethyl (2b), butyl (2c) and 2-hydroxypropyl acrylates (2d) in the liquid Pyr<sub>1,4</sub>[NTf<sub>2</sub>] (Table 4) in the presence of the most active catalysts: ScCl<sub>3</sub>, YbCl<sub>3</sub> and YCl<sub>3</sub> also exhibits a significant increase of the conversion of acrylates and the stereoselectivity towards the *endo* isomer. In the case of scandium (III) chloride the product was obtained with the quantitative yield after 60 min whereas with yttrium (III) chloride after 120 min. In the presence of triflates Y, Yb and Sc after a period of 2–3 h, a significant conversion of dienophile was not observed. The stereoselectivity of transformation to the *endo* isomer in the presence of each of the catalysts was significantly larger than that without the catalyst. The highest stereoselectivity in the reaction of cyclopentadiene with ethyl acrylate (2b) was obtained in the presence of the catalysts Sc(OTf)<sub>3</sub> and Y(OTf)<sub>3</sub> (93%). In the reaction of cyclopentadiene with butyl acrylate (2c) the highest conversion was observed in the case of ScCl<sub>3</sub> (99% after 15 min) and the highest stereoselectivities of *endo* 2-butoxycarbonyl-5-norbornene (92–94%) occurred in the presence of triflates Y, Yb, and Sc. The reaction of cyclopentadiene with 2-hydroxypropyl acrylate has confirmed the regularity previously found. The conversion of dienophile amounted to 92% in the presence of ScCl<sub>3</sub> already after 15 min. Similar conversions after longer reaction times were obtained with the remaining catalysts: YbCl<sub>3</sub>-93% after 1 h, YCl<sub>3</sub>-94% after 2 h. In the presence of triflates: scandium yttrium and ytterbium, the dienophile conversion at a level of about 90% occurred after 4 h. In the reaction of 2-hydroxypropyl acrylate was formed exclusively *endo* 2-(2-hydroxypropyl)oxycarbonyl-5-norbornene. During the reaction of selected alkyl acrylates with cyclopentadiene in the medium of ionic liquid Pyr<sub>1,4</sub>[NTf<sub>2</sub>] the most active catalysts are: ScCl<sub>3</sub>, YbCl<sub>3</sub> and YCl<sub>3</sub>. The formation of norbornene derivatives proceeds very fast in their presence with a high stereoselectivity of the *endo* isomer (over 89%). However, in the presence of triflates Sc, Yb and Y the conversions of acrylates were found to be lower and the reactions proceed at a slower rate. A side reaction of cyclopentadiene oligomerization proceeds in this case.

**Table 3** Conversion and stereoselectivity reaction of cyclopentadiene with butyl acrylate in pyrrolidinium ionic liquids with various anions

Entry	Catalyst <sup>a</sup>	Pyrr <sub>1,4</sub> [NTf <sub>2</sub> ]		Pyrr <sub>1,4</sub> [OTf]		Pyrr <sub>1,4</sub> [FAP]	
		Conversion [mol %] 0.25 h	Stereoselectivity <i>endo:exo</i> (%)	Conversion [mol %] 0.25 h	Stereoselectivity <i>endo:exo</i> (%)	Conversion [mol %] 0.25 h	Stereoselectivity <i>endo:exo</i> (%)
1	ScCl <sub>3</sub>	99	89:11	82	91:9	46	82:12
2	Sc(OTf) <sub>3</sub>	73	89:11	61	90:10	–	–
3	YCl <sub>3</sub>	88	94:6	63	88:12	63	93:7
4	Y(OTf) <sub>3</sub>	51	91:9	47	90:10	–	–
5	YbCl <sub>3</sub>	96	94:6	61	88:12	61	91:9
6	Yb(OTf) <sub>3</sub>	60	90:10	46	89:11	–	–

<sup>a</sup> Catalyst 3 mol% vs dienophile

**Table 4** Conversion and stereoselectivity reaction of cyclopentadiene with alkyl acrylates in ionic liquid Pyrr<sub>1,4</sub>[NTf<sub>2</sub>]

Entry	Catalyst	Cyclopentadiene + 2b			Cyclopentadiene + 2c			Cyclopentadiene + 2d	
		Conversion [mol %]		Stereoselectivity <i>endo:exo</i> %	Conversion [mol %]		Stereoselectivity <i>endo:exo</i> %	Conversion [mol %]	
		2 h	4 h		2 h	4 h		2 h	4 h
1	ScCl <sub>3</sub>	96 <sup>b</sup>		92:8	99 <sup>a</sup>		89:11	92 <sup>a</sup>	
2	Sc(OTf) <sub>3</sub>	70		93:7	87	89	94:6	85	91
3	YCl <sub>3</sub>	95		91:9	95 <sup>b</sup>		90:10	94	
4	Y(OTf) <sub>3</sub>	86	91	93:7	87	93	94:6	80	86
5	YbCl <sub>3</sub>	93 <sup>c</sup>		92:8	96 <sup>a</sup>		90:10	93 <sup>c</sup>	
6	Yb(OTf) <sub>3</sub>	80	83	91:9	80	82	92:8	83	90

<sup>a</sup> Conversion after 15 min

<sup>b</sup> Conversion after 30 min

<sup>c</sup> Conversion after 1 h

Cyclopentadiene concentration 6 mol/dm<sup>3</sup>, alkyl acrylate concentration 4 mol/dm<sup>3</sup>, catalyst 3 mol% versus alkyl acrylate

## 4 Conclusions

The ionic liquids composed of 1-butyl-1-methylpyrrolidinium cation and anions: bis(trifluoromethylsulfonyl)imide [NTf<sub>2</sub>]<sup>−</sup>, trifluoromethanesulfonate [OTf]<sup>−</sup>, tris(pentafluoroethyl)trifluorophosphate [FAP]<sup>−</sup> are convenient media for the Diels–Alder reaction between cyclopentadiene and alkyl esters of acrylic acid. The reaction already proceeds at room temperature without the catalyst and in the presence of ionic liquids (Table 1), and the dienophile conversion and stereoselectivity depends on the kind of dienophile and anion in the ionic liquid. The above mentioned pyrrolidinium ionic liquids in several case form the effective catalytic systems with chlorides and trifluoromethanesulfonates of metals. These catalysts enhance the conversion of acrylates, the yield of norbornene derivatives and the stereoselectivity of the *endo* isomer. However, some of them show significant increase in the oligomerization rate of cyclopentadiene. The most active catalysts of the reaction of cyclopentadiene with alkyl acrylates are ScCl<sub>3</sub>, YbCl<sub>3</sub> and YCl<sub>3</sub>. The norbornene

derivatives are obtained with the yield over 90% at temperature 25 °C in the presence 3 mol% of catalyst in relation to the dienophile (the catalyst concentration in the ionic liquid amounts 0.012 mol/dm<sup>3</sup>). The reaction times required to achieve such yields amount from 30 to 120 min. The stereoselectivity of the *endo* isomer amounts over 89% in this case and varies widely depending on the kind of metal atom in the chloride or triflate and the type of dienophile.

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