

Erbium triflate in ionic liquids: A recyclable system of improving selectivity in Diels–Alder reactions

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ABSTRACT

The efficiency of $\text{Er}(\text{OTf})_3$ in promoting the Diels–Alder reactions between different dienes and dienophiles in ionic liquids has been investigated. Compared with the analogous cycloadditions performed in conventional solvents shorter reaction times are required to obtain good/excellent yields. In most cases an enhancement of regio- and *endo:exo* selectivity was observed. The role of the ionic liquid, as a function of the cationic part, i.e. the imidazolium based or the pyridinium based, is discussed well. The ILs containing the catalyst can be readily separated from the reaction products and recovered in very high purity for direct reuse, up to six cycles.

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1. Introduction

The Diels–Alder reaction is one of the most important method for the formation of cyclic structures [1] and it is widely used in the chemical industry for the synthesis of natural products in a regio- and stereo-controlled way. Many Diels–Alder reactions usually afforded a mixture of isomers, being the selectivity strongly influenced both by the presence of Lewis acids and by the solvent nature. Therefore, the reaction has been investigated using water [2], surfactants [3], lithium amides [4], alkylammonium nitrate [5], borane–tetrahydrofuran (BH_3 –THF) complexes [6], etc. Considering the practical importance and the broad applications of the Diels–Alder reaction in organic synthesis, an increased attention has been recently focused on the development of “green” methods for the purpose of improving rate and selectivity of this cycloaddition.

Rare earth metal triflates $\text{M}(\text{OTf})_3$ ($\text{M} = \text{Sc}, \text{La}, \text{Ce}, \text{Y}$; $\text{OTf}^- = \text{CF}_3\text{SO}_3^-$) have been efficiently used also to promote Diels–Alder reactions with a significant increase of product yield and *endo:exo* stereoselectivity [7–16].

In particular four of these studies [13–16] have been performed in ionic liquids [17,18], with all the distinct advantages pertaining to these solvents as no measurable vapor pressure, easy catalyst and solvent recover/recycle [19] and high solubility of the Lewis acid in these media. Ionic liquids (ILs) have received in last years a

good deal of attention since classical organic reactions, including cycloadditions reactions, can be performed in these media with great advantages (yield and selectivity) as compared to conventional conditions [20–28]. Support to this point may be found for example in the work of Dyson [15] on the Sc- or In-catalyzed cycloaddition of cyclopentadiene and acrolein in $\text{bmim}[\text{Tf}_2\text{N}]$ that afforded the expected [4 + 2] derivative in an *endo:exo* ratio of 16.0 (94:6). The same reaction conducted in EtOH-InCl_3 or in $\text{H}_2\text{O-InCl}_3$ furnished products with an *endo:exo* ratio of 8.8 (90:10) and 8.5 (89:11), respectively.

The first study of a Diels–Alder reaction in a ionic liquid was performed by Jaeger using ethylammonium nitrate [29]. Most recently a number of applications of this reaction in imidazolium based [30], pyridinium based [31] or phosphonium based [32] ionic liquids have been described. Beside the already mentioned rare earth metal triflates [33], chloroaluminate ionic liquids [34] and ZnCl_2 -containing ILs [28] have also shown very promising performances.

In recent years our group published several studies on the use of lanthanide derivatives, in particular cerium and erbium triflates, as efficient Lewis acid catalysts in Friedel–Crafts acylation, in the rearrangement of epoxides to carbonyl compounds, in protection and deprotection methods [35–41]. In this paper we report a study on a number of simple Diels–Alder reactions, catalyzed by erbium triflate, in different achiral and chiral ionic liquids, resulting in a significant increase of the regio- and *endo:exo* selectivity, up to 99:1, and practical $\text{Er}(\text{OTf})_3/\text{IL}$ recover/reuse. Major advantages in the utilization of this catalyst are the low toxicity and the cost, when compared with other active lanthanide triflates [42]. The

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various cycloadditions, carried out both in imidazolium based and pyridinium based ionic liquids, allowed a direct evaluation of the two classes of ILs taking into consideration that the influence of the imidazolium ionic liquids on the reaction is explained by the solvophobic effect. Moreover, catalytic effect is attributed to the proton at C2 or to the nitrogen of the imidazole ring [25]. Overall, increased product yields, better selectivities and shorter reaction times were observed with respect to conventional conditions, i.e. $\text{Er}(\text{OTf})_3/\text{CH}_2\text{Cl}_2$.

2. Experimental

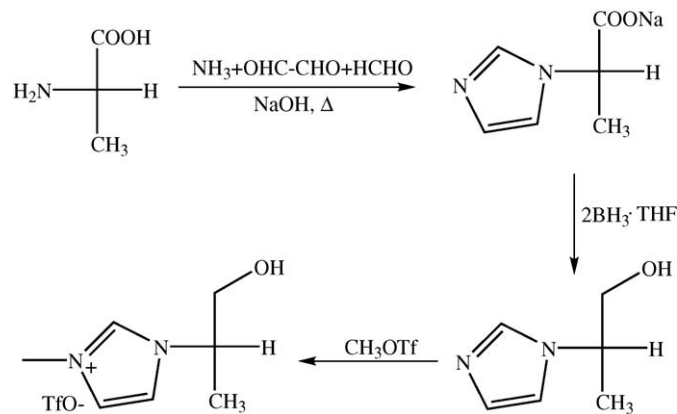
2.1. Synthesis of ionic liquids

L-1-methyl-3-(1'-hydroxy-2'-propanyl)imidazolium trifluoromethane sulfonate [mhyimp][OTf] was obtained according to the procedure described by W. Bao [43] with the following modifications. Formaldehyde water solution (36%, 16.7 g) and glyoxal water solution (32%, 36.2 g) were mixed in a 250 mL three-necked flask equipped with a stirrer and reflux condenser. The solution was heated at 50 °C by stirring and a mixture of alanine (17.8 g, 0.2 mol), ammonia solution (28%, 12.1 g) and sodium hydroxide solution (10%, 80 g) were added in small portions during 0.5 h period. The reaction was stirred for additional 4 h, at 50 °C. Water was removed under reduced pressure and the residue was dried in a vacuum desiccator over P_2O_5 , Scheme 1.

The carboxylic acid sodium salt (31.5 g) was reduced to L-2-(1-imidazolyl) propanol by two molar equivalents of borane–THF (350 mL, 0.43 mol) in THF (195 mL) under N_2 at room temperature, followed by acid hydrolysis with HCl (37%) and subsequent basic hydrolysis with KOH. The solution of BH_3 in THF was added slowly by stirring and the slurry was stirred for additional 3 h before removing THF under reduced pressure. The L-1-methyl-3-(1'-hydroxy-2'-propanyl)imidazolium trifluoromethane sulfonate [mhyimp][OTf] was obtained through direct alkylation by methyl triflate, see next section for details.

1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][OTf]) and 1-methyl pyridinium trifluoromethanesulfonate ([MPy][OTf]) were synthesized according to the following modified solvent-free procedure. In a three-necked flask, at 0 °C and dry conditions, 0.3 mol of methyl trifluoromethanesulfonate were slowly added to 0.29 mol of 1-alkylimidazole or pyridine. The liquid was stirred for 24 h, poured into 150 mL of CH_2Cl_2 , treated with decolorizing carbon, filtered and dried under vacuum to give a colorless-to-pale yellow liquid product, yield 95% and 96%, respectively. The characterization of [bmim][OTf], [MPy][OTf] and [mhyimp][OTf] was obtained by comparison of the corresponding ^1H NMR and ^{13}C NMR spectra with literature reports [27,43,44].

Cyclopentadiene was freshly cracked from dicyclopentadiene (Merck) prior to its use. All reagents were used as obtained from M/S Aldrich Chem. Co., ^1H NMR and ^{13}C NMR spectra were recorded in



Scheme 1. Synthesis of L-1-methyl-3-(1'-hydroxy-2'-propanyl)imidazolium trifluoromethane sulfonate.

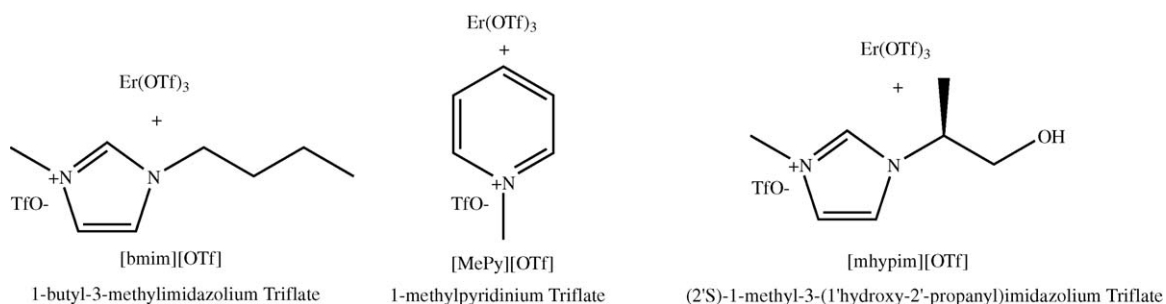
CDCl_3 using tetramethylsilane as internal standard. Mass spectra are obtained by a Shimadzu GC/MS.

2.2. General procedure for Diels–Alder reaction

In a typical reaction, the diene (1.0 mmol) was slowly added to a solution of Erbium triflate and dienophile (1.1 mmol) dissolved in the ionic liquid (2 mL). The reaction mixture was stirred at room temperature and monitored by TLC using precoated silica gel aluminum plates. After 2 h the crude was extracted with diethyl ether (3×5 mL) and the solvent was removed under vacuum. The product was purified by column chromatography over silica gel. The reaction products were analyzed using a Shimadzu GC/MS equipped with an HP-5 column, 30 m, coated with a 0.25 mm film, nitrogen as a carrier gas, injector temperature 250 °C, oven temperature program: 100 °C hold at 2 min, ramp 16 °C/min to 250 °C and hold for 5 min. The remaining ionic liquid phase, containing $\text{Er}(\text{OTf})_3$, was washed with hexane (3×3 mL), purified under vacuum and directly reused in the subsequent runs at least five times, see Section 3.

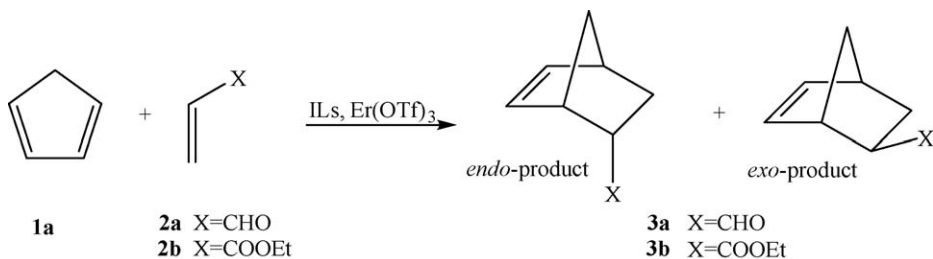
3. Results and discussion

Initially we have used the reaction of cyclopentadiene **1a** with two dienophiles, i.e. acrolein **2a** and ethyl acrylate **2b** which leads to a mixture of *endo* and *exo* products, as a probe of the efficiency of the $\text{Er}(\text{OTf})_3/\text{ILs}$ system. The model cycloaddition reactions have been carried out in three different ionic liquids: 1-butyl-3-methylimidazolium triflate, a pyridinium base derivative 1-methylpyridinium triflate and a chiral imidazolium compound (2'S)-1-methyl-3-(1'-hydroxy-2'-propanyl)imidazolium triflate, prepared through a modified, shortest and simple procedure, see Section 2 (Scheme 2).



Scheme 2.

Table 1
Diels–Alder reactions of cyclopentadiene with **2a** and **2b**, catalyzed by $\text{Er}(\text{OTf})_3$, in ionic liquids.



Entry	Diene	ILs	Time (h)	Product	Conversion ^a (%) (yield ^b (%))	Endo:exo ratio
1	2a	[bmim][OTf]	2	3a	98 (94)	79:21
2	2a	[mPy][OTf]	2	3a	99 (95)	86:14
3	2a	[mhyvim][OTf]	2	3a	99 (95)	80:20
4	2b	[bmim][OTf]	4	3b	86 (81)	90:10
5	2b	[mPy][OTf]	4	3b	86 (80)	65:35
6	2b	[mhyvim][OTf]	4	3b	87 (81)	65:35

^a Determined by GC.

^b Isolated yield.

Alkylimidazolium based on ionic liquids are the most commonly used derivatives for a number of reasons [17,18] and most studies on Diels–Alder cycloaddition reactions have been performed in these media. Pyridinium derived ionic liquids have shown to increase the efficiency of this reaction also in the absence of catalysis [31]. [Mhyvim][OTf] has been used for the first time in this reaction with the double aim of studying the role of the hydroxyl group on the alkyl chain and to investigate a possible asymmetric induction. To avoid exchange reactions, the triflate anion was maintained both in the catalyst and as anion of the ionic liquids. In all cases the ILs recycle/reuse was very efficient.

Reactions were performed at 25 °C for either 2 h for acrolein or 4 h for the less activated ethyl acrylate and the pertinent results are listed in Table 1. All the reactants were added at 0 °C to suppress polymerization of the substrates, that can occur at room temperature. The reaction of cyclopentadiene with acrolein afforded the corresponding cycloaddition products **3a** in high yield and an optimal *endo:exo* ratio of 86:14 obtained in methyl pyridinium triflate (entry 2), selectivity not too far from what has observed in the presence of $\text{Sc}(\text{OTf})_3$ catalysis [15,16].

Also the results obtained for the cycloaddition of **1a** with ethyl acrylate are comparable with literature reports with a large prevalence of the *endo* isomer, formed in a ratio of 90:10 (entry 4), thus proving that Er(III) derivatives may compete with the more expensive Sc(III) based catalysts [42].

The Er(III) catalyzed cycloaddition between cyclopentadiene and acrolein was used to examine both the catalyst loading and the reusability of the ionic liquids as shown in Table 2 negligible product formation is observed in the absence of $\text{Er}(\text{OTf})_3$ even after long reaction times (15 h). A significant increase of product yield was detected by increasing the catalyst up to 10 mol%, value that was used as optimized loading for this study. To note that the different amounts of the catalyst affected the product yield, not the *endo:exo* ratio of the reaction.

The fundamental role of the catalyst is evident also from the data shown in Fig. 1, that compare the rate of the reaction between cyclopentadiene and acrolein performed in bmim[OTf] and in a “classical” solvent as CH_2Cl_2 .

The important effect on the rate of the IL/ $\text{Er}(\text{OTf})_3$ vs. CH_2Cl_2 / $\text{Er}(\text{OTf})_3$ system, observed from the beginning of the reaction (1 h) may be tentatively ascribed to the weakly coordinating and weakly

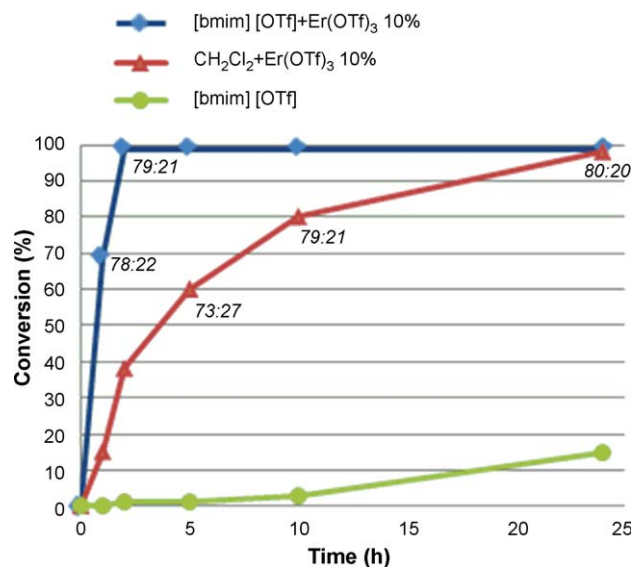


Fig. 1. Diels–Alder reactions of cyclopentadiene and acrolein in different solvents and $\text{Er}(\text{OTf})_3$ loading. Numbers on single point refer to *endo:exo* selectivity.

Table 2
Diels–Alder reactions of cyclopentadiene with **2a** catalyzed by $\text{Er}(\text{OTf})_3$ in ionic liquids as a function of catalyst loading.

Entry	Catalyst loading	Time (h)	Conversion ^a (%)
1	–	15	7
2	$\text{Er}(\text{OTf})_3$ 1 mol%	2	18
3	$\text{Er}(\text{OTf})_3$ 5 mol%	2	52
4	$\text{Er}(\text{OTf})_3$ 10 mol%	2	98
5	$\text{Er}(\text{OTf})_3$ 20 mol%	2	98

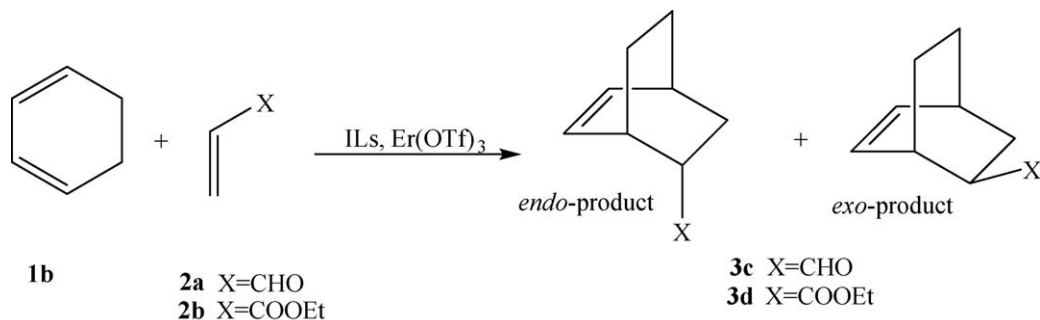
^a Determined by GC.

Table 3
Recovery and reuse of [ILs + $\text{Er}(\text{OTf})_3$] in the reaction between cyclopentadiene and acrolein.

Recycling	Recovered [ILs + $\text{Er}(\text{OTf})_3$] (wt%)	Conversion ^a (%)
1	97	98
2	96	97
3	96	98
4	94	95
5	95	97
6	95	97

^a Determined by GC.

Table 4
Diels–Alder reactions of cyclohexadiene with **2a–b** catalyzed by $\text{Er}(\text{OTf})_3$ in ionic liquids.



Entry	Diene	ILs	Time (h)	Products	Conversion ^a (%) (yield ^b (%))	Endo:exo ratio
1	2a	[bmim][OTf]	2	3c	99 (95)	97:3
2	2a	[mPy][OTf]	4	3c	99 (96)	98:2
3	2a	[mhyvim][OTf]	2	3c	95 (91)	97:3
4	2b	[bmim][OTf]	15	3d	–	–
5	2b	[mPy][OTf]	15	3d	–	–
6	2b	[mhyvim][OTf]	15	3d	–	–

^a Determined by GC.

^b Isolated yield.

solvating attitudes of the ionic liquid with respect to the catalyst [33].

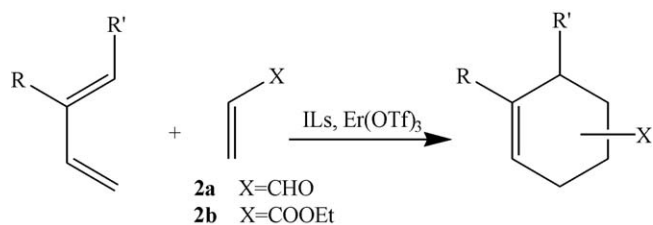
The data pertaining to the recovery and re-use of the couple ionic liquid/ $\text{Er}(\text{OTf})_3$ are collected in Table 3 [18]. After the first cycloaddition reaction the ionic liquid containing the catalyst is separated from the organic layer, washed with hexane (3×5 mL) and dried at 65°C under vacuum. Successive runs were performed by reacting fresh cyclopentadiene and acrolein, at the usual conditions, in the recycled ionic liquid/ $\text{Er}(\text{OTf})_3$. As shown in Table

3, the ionic liquid/ $\text{Er}(\text{OTf})_3$ could be recovered quantitatively and reused without any loss of activity or selectivity.

With these results in our hands, we next extended the Diels–Alder reaction to cyclohexadiene, Table 4, and to a set of acyclic dienes, i.e. butadiene, 2-methylbutadiene, butadiene acetate.

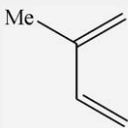
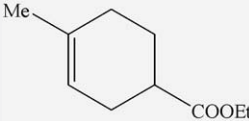
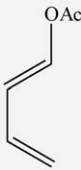
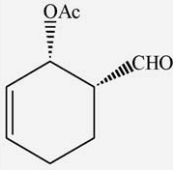
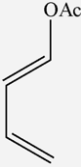
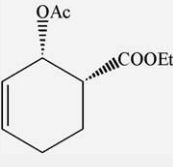
Excellent results were obtained from the reaction of 1,3-cyclohexadiene with acrolein, that afforded almost quantitative yields of **3c** and a remarkable *endo* selectivity up to 98:2. To our surprise, change in the dienophile from acrolein to ethyl acrylate

Table 5
Diels–Alder reactions of acyclic dienes with **2a–b** catalyzed by $\text{Er}(\text{OTf})_3$ in ionic liquids.



Entry	Diene	Dienophile	ILs	Product	Yield ^a (%)	Regioselect.
1		2a	[bmim][OTf]		3e	99 ^b
2			[mPy][OTf]			90 ^b
3			[mhyvim][OTf]			97 ^b
4		2b	[bmim][OTf]		3f	87 ^d
5			[mPy][OTf]			77 ^d
6			[mhyvim][OTf]			97 ^c
7		2a	[bmim][OTf]		3g	85 ^b
8			[mPy][OTf]			85 ^b
9			[mhyvim][OTf]			85 ^c

Table 5 (Continued)

Entry	Diene	Dienophile	ILs	Product	Yield ^a (%)	Regioselect.
10 11 12		2b	[bmim][OTf] [mPy][OTf] [mhyvim][OTf]		3h 72 ^d 71 ^d 85 ^c	99:1 >99:1 >99:1
13 14 15		2a	[bmim][OTf] [mPy][OTf] [mhyvim][OTf]		3i^e 92 ^c 97 ^c 92 ^c	99:1 99:1 >99:1
16 17 18		2b	[bmim][OTf] [mPy][OTf] [mhyvim][OTf]		3j^e 5 ^f 6 ^f 3 ^f	– – –

^aIsolated yield.^bReaction time 2 h.^cReaction time 3 h.^dReaction time 4 h.^e*Endo:exo* ratio 99:1.^fReaction time 20 h.

turns out to give no Diels–Alder cycloaddition reactions with **1b** (entries 4–6). A similar behavior was reported by Aoyama et al. [45] and most recently by Harman on dienes coordinated to π -bases [46].

The known ability of Lewis acids to increase the reaction rate of the cycloadditions is confirmed by the data of Table 5. Butadiene and 2-methyl butadiene undergo cycloaddition with **2a–b**, at room temperature, in reasonable reaction times (2–4 h) and good yields. Worthy of note, the reaction of 2-methyl butadiene with acrolein or ethyl acrylate is highly regioselective, affording almost exclusively **3g** or **3h** in a ratio *para* [3] adduct: *meta* [2] adduct $\geq 99:1$ [1,32,47,48].

Furthermore, the reaction of acrolein with butadiene acetate regioselectively and stereoselectively afforded only *ortho*[1]-*endo*-adduct **3i**, with an *endo:exo* ratio of 99:1 [49]. On the other hand, the cycloaddition of butadiene acetate with ethyl acrylate is quite inefficient, with the formation of small amounts of **3j** in long reaction times. The Diels–Alder reaction of butadiene acetate both with acrolein and ethyl acrylate have been investigated by Dauben et al. in diethyl ether at high pressure, with formation of **3i** and **3j** in 81% and 19% yield, respectively [50]. The significant diversity in product yields may be ascribed to the energy difference between the HOMO of the diene and the LUMO of the dienophiles that differ of about 6.2 kcal/mol in a comparison of the two cases [51]. The even more marked gap of the yields in Table 5 (entries 13–15 vs. 16–18) may be only partially attributed to this energy difference, since in our case a major role should be played by the presence of the Lewis acid catalyst. It is well known that the choice of the Lewis acid depends upon the dienophile to be used. As an example, acrylate esters require Lewis acids very acidic, if compared to acrolein or alkyl vinyl ketones. Therefore $\text{Er}(\text{OTf})_3$ and more in general rare earth metal triflates $\text{M}(\text{OTf})_3$ ($\text{M} = \text{Sc}, \text{La}, \text{Ce}, \text{Y}$; $\text{OTf}^- = \text{CF}_3\text{SO}_3^-$) may not be sufficiently acidic to promote an efficient cycloaddition with acrylate esters.

Many Diels–Alder reactions demonstrated the strong solvent dependence and the ionic liquids shown to have beneficial effects

on this reaction in most cases. As an example, Welton et al. reported a substantial increase of *endo*-selectivity in ionic liquids with a strong hydrogen-bond donor cation and a rate enhancement when compared to non-polar solvents [25]. According to these findings our results were expected to show a remarkable increase of the selectivity using [mhyvim]OTf, due to the presence of the hydroxyl function, but this was not the case. On the other hand, and according to what reported by Kumar and Sarma [14], if the Diels–Alder reaction is carried out in the presence of a Lewis acid catalyst the role of the ionic liquid is in some way flattened. Fig. 1 reports the comparison of the cycloaddition reactions between cyclopentadiene and acrolein in different conditions $\text{IL}/\text{Er}(\text{OTf})_3$; $\text{IL}; \text{CH}_2\text{Cl}_2/\text{Er}(\text{OTf})_3$ and the *endo:exo* selectivities of the ongoing reactions are highlighted. The *endo:exo* selectivity is dominated by the presence of the catalyst independently from the solvent, that comes into play on the reaction rate. In all the cases investigated in this study, in fact, the cycloaddition reactions in $\text{IL}/\text{Er}(\text{OTf})_3$ are faster than in conventional conditions. As an example, in the Diels–Alder reaction of cyclohexadiene with acrolein a quantitative conversion to product is obtained at 2 h for $\text{bmim}(\text{OTf})-\text{Er}(\text{OTf})_3$ and at 3.5 h for $\text{CH}_2\text{Cl}_2-\text{Er}(\text{OTf})_3$. Finally and contrary to our expectations an almost insignificant enantiomeric excess ($ee < 5\%$) was achieved for these reactions when carried out in chiral ILs as mhyvim(OTf).

4. Conclusions

In this study we have demonstrated that $\text{Er}(\text{OTf})_3$ may compete with other more expensive rare earth metal triflates $\text{M}(\text{OTf})_3$ ($\text{M} = \text{Sc}, \text{La}, \text{Ce}, \text{Y}$; $\text{OTf}^- = \text{CF}_3\text{SO}_3^-$) in promoting Diels–Alder reactions between different dienes and dienophiles in ionic liquids. In most cases an enhancement of regio- and *endo:exo* selectivity was observed. From a comparison with conventional solvents the role of the Er-catalyst and of the ionic liquids is clarified. The catalyst is fundamental in determining the *endo:exo* selectivity, the combination $\text{IL}/\text{Er}(\text{OTf})_3$ has an important effect on the rate. The ILs

containing the catalyst can be readily separated from the reaction products and recovered in excellent purity for direct reuse, up to six cycles.

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