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Ionic liquids - deanol derivatives as the Diels-Alder reaction solvents

Research Article

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Abstract: The Diels-Alder reaction between cyclopentadiene and dienophiles in deanol derivatives containing bis(trifluoromethylsulfonyl)imide anion as media have been studied. The effect of the substituents attached to the cation on the endo:exo selectivity as well as the reaction yield have been evaluated in the absence and presence of Lewis acid catalyst - $Y(OTf)_3$. Catalytic activity of metal triflates and the recycling of chosen catalytic systems have also been investigated

Keywords: *Ionic liquids • Diels-Alder reaction • Lewis acids • Deanol derivatives*

1. Introduction

Diels-Alder reactions belong to the most useful carbon-carbon coupling reactions and are used extensively in the production of fine chemicals, natural products and biologically active molecules. Solvents affect the rate and selectivity of the Diels-Alder reaction [1]. Moreover, Lewis acids catalyze them. The application of ionic liquids (ILs) as environmentally benign reaction solvents for synthesis and catalysis has recently received extensive attention. A number of attempts to accelerate Diels-Alder reactions have been made by using these new reaction media. Seddon and co-workers [2] have initiated the investigations of the Diels-Alder reactions in imidazolium ILs. The majority of research papers have reported the use of ionic liquids based on alkylimidazolium cations. The combination of Lewis acids with imidazolium salts has become the most widely used choice in recent years [3]. The zinc-containing ionic liquids, MX-$ZnCl_2$, where MX was either 1-butyl-3-methylimidazolium chloride (BmimCl), or 1-ethyl-3-methylimidazolium bromide (EmimBr), were described as novel reaction media as well as Lewis acid catalysts for the highly regioselective Diels–Alder reaction of myrcene with acrolein [4]. However, the cations and/or anions from cheap, renewable sources have been pursued for synthesis of ILs lately. These solutions have a reasonable price, are environmentally benign and have a low toxicity of natural feedstocks. For instance, Ishikawa et al. studied the application of the imidazolium salts in lactate, salicylate [5] and camphorsulfonate forms as the medium in the Diels-Alder reaction [6]. Caffeine was also reported as a natural, cheap source of the xanthinium salt, which was used with bismuth(III) triflate for the preparation of a reusable catalytic system [7]. This system proved to be efficient for the Diels-Alder reaction. Recently the combination of imidazolium and pyridinium ionic liquids with erbium triflate has been presented as very effective catalytic systems to promote the Diels-Alder reaction between various dienes and dienophiles [8]. Phosphonium and ammonium ILs are also employed in Diels-Alder reactions but in a smaller range. These cations are cheaper than imidazolium and manufacture of them is lower in both energy and costs. In the group of phosphonium ILs, phosphonium tosylates [9] were investigated as solvents for the Diels-Alder reaction of

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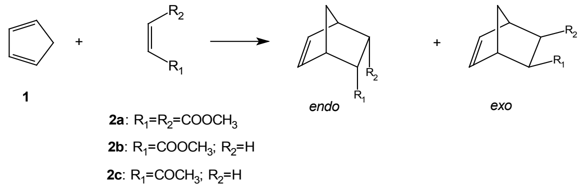
cyclopentadiene or isoprene with various dienophiles, in the absence of metal catalysts. Recently, we have reported catalytic systems consisting of $[P_{6.6.6.14}][NTf_2]$ and metal catalysts as highly effective and possibly reusable in the synthesis of functionalized norbornene via Diels-Alder reactions [10].

This study concerns the application of ammonium ionic liquids formed from deanol (2-dimethylamineethanol). Deanol is a cheap substance, applied in medicine to increase levels of choline and acetylcholine in the blood and brain. One of the deanol derivatives used in the synthesis of ILs is choline chloride. It has a high melting point, thus the unmodified form is not useful as an IL. Abbott and coworkers [11], at first, prepared a range of ionic liquids based on choline chloride. They combined choline chloride, unmodified and modified in the hydroxyethyl group, with $ZnCl_2$ or $SnCl_2$ forming moisture-insensitive Lewis-acidic ionic liquids. Some of them were employed in the Diels-Alder reaction providing high yields, stereoselectivities and easy reuse [12]. However, as authors reported, the alcohol side chain in these ionic liquids reacted with the carbonyl-containing starting materials, especially after recycling. Other ionic liquids, so-called "deep eutectic solvents", were formed from choline chloride and hydrogen-bond donors such as carboxylic acids or amides [13].

Herein we report the use of deanol derivatives containing bis(trifluoromethylsulfonyl)imide anion as the medium of the uncatalyzed and catalyzed Diels-Alder reaction. These deanol derivatives are: alkoxyethyl(2-hydroxyethyl)dimethylammonium, (2-acetoxyethyl)alkoxymethyldimethylammonium, and alkoxymethyl(2-decanoyloxyethyl)dimethylammonium bis(trifluoromethylsulfonyl)imides. Ionic liquids with NTf_2 anion have received a lot of attention because of its low viscosity, hydrophobicity and non-coordinating character. Moreover, the hydrophobicity of NTf_2 anion is comparable to anions such as BF_4 or PF_6, but greater chemical stability is observed for NTf_2. We have tested the reaction of cyclopentadiene (1) with selected dienophiles - dimethyl maleate (2a), methyl acrylate (2b), methyl-vinyl ketone (2c) in these media. The catalytic activity of the catalysts from the group of metal triflates has been compared for chosen dienophiles. The effect of substituents in the cation of used ILs on the reaction yield and stereoselectivity have been also studied.



Scheme 1. The reaction of cyclopentadiene (1) with selected dienophiles - dimethyl maleate (2a), methyl acrylate (2b), methyl-vinyl ketone (2c).

2. Experimental Procedure

2.1. Materials

Deanol of 99.5% purity and decanoyl chloride (98%) were purchased from Aldrich. Acethyl chloride (98%) and tetrabuthylammonium chloride (~95%) were purchased from Fluka. All alcohols (98-99%) to prepare chloromethylalkyl ethers were provided by Fluka, HCl (35-38%) and H_2SO_4 (≥95%) were purchased from POCh, and paraformaldehyde (99%) from Riedel-de Haën. Lithium bis(trifluoromethylsulfonyl)imide (99%) was purchased from Fluka. Hexane (98%) and chloroform (98%) were provided by POCh. Dicyclopentadiene of 95% purity was purchased from Fluka. Dimethyl maleate (96%), methyl acrylate (99%), methylvinyl ketone (99%), and all tested catalysts were provided by Aldrich. The catalysts included: scandium triflate (97%), lithium triflate (99.995%), ytterbium triflate (99.99%), yttrium triflate (98%), magnesium triflate (97%), zinc triflate (98%), copper(II) triflate (98%), and aluminum triflate (99.9%).

2.2. Preparation of ionic liquids based on deanol

All ionic liquids were prepared from deanol. Deanol and its esters, previously prepared by the reaction of deanol with acid chlorides (acetic acid chloride or decanoic acid chloride) under phase transfer catalysis conditions, were reacted with chloromethylalkyl ethers to obtain alkoxymethyl(2-hydroxyethyl)dimethylammonium, (2-acetoxyethyl)-alkoxymethyldimethylammonium, and alkoxymethyl(2-decanoyloxyethyl)dimethylammonium chlorides [14]. Salts formed with bis(trifluoromethylsulfonyl)imide anion were obtained from their respective chlorides by metathesis with lithium bis(trifluoromethylsulfonyl)imide [15]. The purification step of prepared ionic liquids was very important because the chloride anion or water could have an effect on the activity of Lewis acids. Therefore ILs, after dissolving in chloroform, were washed with water until the aqueous residues were chloride anion free. The ionic liquids were then dried under vacuum (4 mbar, 24 h, 90°C). The prepared ILs were characterized *via* ^1H NMR and ^{13}C NMR.

Hexyloxymethyl(2-hydroxyethyl)dimethylammonium bis(trifluoromethylsulfonyl)imide

^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 7.0 Hz, 3H), 1.26 (m, 6H), 1.62 (q, J = 7.0 Hz, 2H), 3.10 (s, 6H), 3.44 (t, J = 4.8 Hz, 2H), 3.76 (t, J = 6.5 Hz, 2H), 4.04 (t, J = 4.7 Hz, 2H), 4.61 (s, 2H); 13C NMR δ ppm = 14.0, 22.7, 25.7, 29.4, 31.9, 48.3, 56.1, 62.5, 73.7, 113.2, 117.4, 121.6, 126.1. Anal. Calcd for $C_{13}H_{26}O_6S_2N_2F_6$: C 32.22, H 5.42, N 5.78; Found: C 32.63, H 5.12, N 5.89.

Decyloxymethyl(2-hydroxyethyl)dimethylammonium bis(trifluoromethylsulfonyl)imide

^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.8 Hz, 3H), 1.26 (m, 14H), 1.63 (q, J = 6.9 Hz, 2H), 3.10 (s, 6H), 3.44 (t, J = 4.8 Hz, 2H), 3.76 (t, J = 6.5 Hz, 2H), 4.04 (t, J = 4.7 Hz, 2H), 4.61 (s, 2H); 13C NMR δ ppm = 14.1, 22.8, 25.7, 29.29, 29.35, 29.42, 29.5, 29.6, 31.9, 48.3, 56.1, 62.5, 73.7, 113.3, 117.4, 121.6, 126.0. Anal. Calcd for $C_{17}H_{34}O_6S_2N_2F_6$: C 37.76, H 6.35, N 5.18; Found: C 37.32, H 6.28, N 5.00.

(2-Acetoxyethyl)imethylpentyloxymethylammonium-bis(trifluoromethylsulfonyl)imide

^{1}H NMR ($CDCl_3$)δ ppm = 4.63 (s, 2H), 4.46 (t, J = 4.7 Hz, 2H), 3.80 (t, J = 6.6 Hz, 2H), 3.64 (t, J = 4.9 Hz, 2H), 3.11 (s, 6H) 2.10 (s, 3H), 1.64 (q, J = 6.9 Hz, 2H), 1.30 (m, 4H), 0.89 (t, J = 6.7 Hz, 3H), ^{13}C NMR ($CDCl_3$) δ ppm = 14.0, 20.0, 22.4, 27.6, 31.6, 48.2, 57.0, 59.8, 73.8, 91.4, 113.4, 117.6, 121.9, 126.1, 169.9. Anal. Calcd for $C_{14}H_{26}O_7S_2N_2F_6$: C 32.80, H 5.12, N 5.47; Found: C 32.43, H 5.01, N 5.27.

(2-Acetoxyethyl)eptyloxymethyldimethylammonium-bis(trifluoromethylsulfonyl)imide

^{1}H NMR ($CDCl_3$) δ ppm = 4.63 (s, 2H), 4.46 (t, J = 4.7 Hz, 2H), 3.80 (t, J = 6.6 Hz, 2H), 3.64 (t, J = 4.8 Hz, 2H), 3.11 (s, 6H) 2.10 (s, 3H), 1.64 (q, J = 7.0 Hz, 2H), 1.30 (m, 8H), 0.89 (t, J = 6.7 Hz, 3H), ^{13}C NMR ($CDCl_3$) δ ppm = 13.9, 20.4, 22.4, 25.5, 28.8, 29.3, 31.5, 48.2, 57.0, 59.8, 73.8, 91.4, 113.4, 117.6, 121.9, 126.1, 169.9. Anal. Calcd for $C_{16}H_{30}O_7S_2N_2F_6$: C 35.54, H 5.60, N 5.18; Found: C 35.82, H 5.38, N 5.29.

Cyclododecyloxymethyl(2-hydroxyethyl)-dimethylammonium bis(trifluoromethylsulfonyl)imide

^{1}H NMR ($CDCl_3$) δ ppm = 1.33 (m, 18H), 1.58 (m, 2H), 1.73 (m, 2H), 2.12 (s, 3H), 3.43 (s, 6H), 4.00 (t, J = 4.9, 2H), 4.00 (q, J = 3.7, 1H), 4.56 (t, J = 4.7, 2H), 5.10 (s, 2H); ^{13}C NMR δ ppm = 19.9, 20.5, 22.6, 22.8, 24.6, 24.8, 28.5, 48.2, 57.1, 59.7, 82.2, 89.9, 113.2, 117.5, 121.7, 126.1, 169.9. Anal. Calcd for $C_{21}H_{38}O_7S_2N_2F_6$: C 41.43, H 6.30, N 4.60; Found: C 41.08, H 6.19, N 4.41.

(2-Decanoyloxyethyl)dimethylnonyloxymethylammonium bis(trifluoromethylsulfonyl)imide

^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.5 Hz, 6H), 1.26 (m, 24H), 1.64 (q, J = 7.3 Hz, 4H), 2.10 (t, J = 7.7 Hz, 2H) 3.11 (s, 6H), 3.64 (t, J = 4.8 Hz, 2H), 3.79 (t, J = 6.7 Hz, 2H), 4.46 (t, J = 4.8 Hz, 2H), 4.63 (s, 2H), 5.49 (s, 1H); ^{13}C NMR δ ppm = 14.0, 22.6, 24.5, 25.6, 29.0, 29.2, 29.37, 29.39, 31.8, 33.8, 48.2, 56.9, 59.9, 73.9, 91.4, 113.2, 117.4, 121.7, 125.9, 172.6. Anal. Calcd for $C_{26}H_{50}O_7S_2N_2F_6$: C 45.85, H 7.42, N 4.11; Found C 46.22, H 7.26, N 4.04.

(2-Decanoyloxyethyl)decyloxymethyldimethylammonium bis(trifluoromethylesulfonyl)imide

^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.5 Hz, 6H), 1.26 (m, 26H), 1.64 (q, J = 7.3 Hz, 4H), 2.10 (t, J = 7.7 Hz, 2H) 3.11 (s, 6H), 3.64 (t, J = 4.8 Hz, 2H), 3.79 (t, J = 6.7 Hz, 2H), 4.46 (t, J = 4.8 Hz, 2H), 4.63 (s, 2H), 5.49 (s, 1H); ^{13}C NMR δ ppm = 14.0, 22.6, 24.5, 25.6, 29.0, 29.2, 29.37, 29.38, 29.39, 31.8, 33.8, 48.2, 56.9, 59.9, 73.9, 91.4, 113.2, 117.4, 121.7, 125.9, 172.6. Anal. Calcd for $C_{27}H_{52}O_7S_2N_2F_6$: C 46.66, H 7.56, N 4.03; Found C 46.32, H 7.77, N 4.23.

2.3. Typical procedure for the Diels-Alder reaction

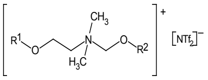
The reaction was conducted as follows: ionic liquid, cyclohexanone (10 µL) as an internal chromatographic standard, dienophile and freshly cracked-cold cyclopentadiene were added into a 4 mL vial containing a small stirring bar. The reaction was conducted at 25°C. The progress of the reaction was monitored by GC analysis over the time needed to obtain quantitative yield or over 24 hours. The yield of products and endo:exo ratios were calculated based on the GC analysis.

If the reaction was performed in the presence of a catalyst, the required portion of the catalyst was weighed first and dissolved in the ionic liquid.

2.4. Recycling experiments

The recycling experiments were performed for the reaction of cyclopentadiene with methylvinyl ketone in (2-decanoyloxyethyl)-nonyloxymethyldimethylammonium bis(trifluoromethylsulfonyl)imide as medium, in the presence of such catalysts as $Y(OTf)_3$, or $Cu(OTf)_2$. The reaction was conducted as described above. The course of the reaction was monitored by GC analysis. When a yield of 90% or higher was achieved (evaluated based on GC analysis), the product was extracted with cyclohexane. The recovered ionic liquid with catalyst dissolved in it, after removal of rest of the solvent under vacuum, was used in subsequent experiments.

Table 1. The yields, stereoselectivities, and reaction rate constants of the Diels-Alder cycloaddition between cyclopentadiene and dienophiles (2a÷c) in ionic liquids prepared based on deanol.



Entry	IL			Dienophile/ Reaction conditions[a]	Yield [%][b]	endo:exo ratio[b]	$k_2 \times 10^6$ [$dm^3\ mol^{-1}\ s^{-1}$]
	Abbreviation	R^1	R^2				
1.	$[(C_6H_{13}Om)DAE][NTf_2]$	H	C_6H_{13}	2a/4 h/45°C	82	3.2:1	32.3
2.	$[(C_{10}H_{21}Om)DAE][NTf_2]$	H	$C_{10}H_{21}$	2a/4 h/45°C	83	3.1:1	30.5
3.	$[(C_5H_{11}Om)AcDAE][NTf_2]$	$CH_3C(O)$	C_5H_{11}	2a/4 h/45°C	80	3.0:1	29.2
4.	$[(C_7H_{15}Om)AcDAE][NTf_2]$	$CH_3C(O)$	C_7H_{15}	2a/4 h/45°C	78	2.8:1	27.3
5.	$[(C_{12}H_{23(c)}Om)AcDAE][NTf_2]$	$CH_3C(O)$	$C_{12}H_{23}$(cycl)	2a/4 h/45°C	82	2.7:1	31.6
6.	$[(C_9H_{19}Om)DecDAE][NTf_2]$	$C_9H_{19}C(O)$	C_9H_{19}	2a/4 h/45°C	86	3.5:1	38.5
7.	$[(C_9H_{19}Om)DecDAE][NTf_2]$	$C_9H_{19}C(O)$	C_9H_{19}	2a/4 h/35°C	72	3.7:1	19.6
8.	$[(C_9H_{19}Om)DecDAE][NTf_2]$	$C_9H_{19}C(O)$	C_9H_{19}	2a/24 h/25°C	90	3.9:1	9.7
9.	$[(C_{10}H_{21}Om)DecDAE][NTf_2]$	$C_9H_{19}C(O)$	$C_{10}H_{21}$	2a/4 h/45°C	82	3.3:1	29.9
10.	$[(C_6H_{13}Om)DAE][NTf_2]$	H	C_6H_{13}	2b/24 h/25°C	95	4.4:1	16.1
11.	$[(C_7H_{15}Om)AcDAE][NTf_2]$	$CH_3C(O)$	C_7H_{15}	2b/24 h/25°C	100	4.0:1	12.7
12.	$[(C_9H_{19}Om)DecDAE][NTf_2]$	$C_9H_{19}C(O)$	C_9H_{19}	2b/24 h/25°C	97	4.3:1	14.2
13.	$[(C_9H_{19}Om)DecDAE][NTf_2]$	$C_9H_{19}C(O)$	C_9H_{19}	2c/2 h/25°C	94	7.2:1	90.1

[a] *1 mL of ionic liquid, 4 mmol of dienophile, 6 mmol of cyclopentadiene*
[b] *monitored and determined by gas chromatography (GC).*

Table 2. Comparison of yield and stereoselectivity of the Diels-Alder reaction between cyclopentadiene and 2a in the presence of $Y(OTf)_3$ in various deanol based ILs[a].

Entry	IL[b]	20 min		40 min	
		Yield [%][c]	endo:exo[c]	Yield [%][c]	endo:exo[c]
1	$[(C_6H_{13}Om)DAE][NTf_2]$	69	9.4:1	82	9.4:1
2	$[(C_{10}H_{21}Om)DAE][NTf_2]$	72	9.7:1	90	9.7:1
3	$[(C_5H_{11}Om)AcDAE][NTf_2]$	80	10.0:1	94	10.0:1
4	$[(C_7H_{15}Om)AcDAE][NTf_2]$	78	9.8:1	91	9.8:1
5	$[(C_{12}H_{23(c)}Om)AcDAE][NTf_2]$	82	9.3:1	96	9.3:1
6	$[(C_9H_{19}Om)DecDAE][NTf_2]$	74	9.4:1	86	9.4:1
7	$[(C_{10}H_{21}Om)DecDAE][NTf_2]$	80	9.3:1	93	9.3:1
8[d]	$[(C_{12}H_{23(c)}Om)AcDAE][NTf_2]$	76	8.9:1	88	8.9:1
9[e]	$[(C_{12}H_{23(c)}Om)AcDAE][NTf_2]$	42	8.5:1	64	8.5:1

[a] *reaction conditions: 1 mL of ionic liquid, 4 mmol of 2a, 6 mmol of cyclopentadiene, 0.04 mmol of $Y(OTf)_3$, reaction temperature: 25°C*
[b] *abbreviations as in Table 1*
[c] *monitored and determined by gas chromatography (GC)*
[d] *2 mL of IL*
[e] *3 mL of IL.*

3. Results and Discussion

The prepared deanol derivatives belong to the quaternary ammonium salts. They are hydrophobic liquids, with thermal stability above 200°C and low viscosity (100 - 300 mPa s).

Diels-Alder reactions of cyclopentadiene with chosen dienophiles proceeded in these ionic liquids at 25°C (Table 1). At this temperature, 24 h of reaction time for dimethyl maleate (2a) and methyl acrylate (2b) as dienophiles, but only 2h for methyl-vinyl ketone (2c) was needed to obtain high yields of products. The increase in temperature to 35°C or 45°C gave a significant increase in the reaction rate with a parallel decrease of endo selectivity (the reaction of cyclopentadiene with dimethyl maleate (2a) - Table 1). The changes to the functional group: hydroxy (R^1=H), acetoxy (R^1=$CH_3C(O)$) or decanoyloxy (R^1=$C_9H_{19}C(O)$) at the end of the ethyl substituent and elongation of the alkoxymethyl substituent (R^2) in ammonium cation, resulted in little effect on the endo:exo selectivity of product. The observed endo:exo selectivities ranged from 2.7:1 to 3.3:1 for the reaction of 2a with cyclopentadiene at 45°C and increased to 3.9:1 at 25°C. For the reaction of 2b, selectivities ranged from 4.0:1 to 4.4:1 and for reaction of 2c endo:exo selectivity

Table 3. Comparison of the catalytic activity of metal triflates in the Diels-Alder reaction between cyclopentadiene and 2a or 2c in deanol based ILs.

Entry	Dienophile	Catalyst (mol%)[c]	Time	Yield (%)[c]	endo:exo[c]
1	2a[a]	$Y(OTf)_3$ (1)	40 min	91	9.8:1
2	2a[a]	$Yb(OTf)_3$ (1)	40 min	95	8.9:1
3	2a[a]	$Mg(OTf)_2$ (1)	2 h	93	8.1:1
4	2a[a]	$Zn(OTf)_2$ (1)	4 h	88	6.1:1
5	2a[a]	LiOTf (2)	6 h	89	8.0:1
6	2c[b]	$Y(OTf)_3$ (1)	6 min	92	8.7:1
7	2c[b]	$Sc(OTf)_3$ (1)	6 min	95	5.3:1
8[d]	2c[b]	$Yb(OTf)_3$ (1)	6 min	78	6.6:1
			35 min	94	6.5:1
9[e]	2c[b]	$Cu(OTf)_2$ (1)	5 min	69	9.7:1
			35 min	91	9.9:1
10	2c[b]	$Zn(OTf)_2$ (1)	6 min	61	8.0:1
			35 min	91	7.7:1
11	2c[b]	Li(OTf) (1)	6 min	44	7.1:1
			35 min	85	7.6:1
			60 min	92	7.6:1
12	2c[b]	$Al(OTf)_3$ (1)	5 min	46	8.1:1
			35 min	82	8.3:1
			60 min	90	8.3:1

[a] *reaction conditions: 1mL of [(C_7H_{15}Om)AcDAE][NTf_2], 4 mmol of 2a, 6 mmol of cyclopentadiene, reaction temperature: 25°C*

[b] *1 mL of [(C_9H_{19}Om)DecDAE][NTf_2] 2 mmol of 2c, 3 mmol of cyclopentadiene, reaction temperature: 25°C*

[c] *mol% of catalyst vs dienophile was given in brackets*

was 7.2:1. Generally, the elongation of the alkoxymethyl chain gives little decrease in selectivities. This trend is analogous to the early reported in alkyldimethyl(2-hydroxyethyl)ammonium bis(trifluoromethylsulfonyl)-imides with the elongation of alkyl substituent. The authors suggested that this phenomenon is due to steric interaction between the transition state and the cation of the IL. Analyzing an influence of functional group at the end of the ethyl substituent on the endo:exo ratio, we observed the highest selectivities for 2a or 2b as dienophiles, when the IL contained a hydroxyl or decanoyloxy moieties. The lowest selectivities appeared in the reaction of both dienophiles with the acetoxy group in the substituent.

The selectivities obtained in deanol derivatives were comparable to those achieved by our group and reported by others in imidazolium ionic liquids, for instance (2a, 25°C, 3.2÷3.7:1) (2b, 25°C, 3.6÷3.8:1) [5] in 1-alkoxymethylimidazolium or 1-alkyimidazolium lactate and salicylate, (2b, rt, 3.8:1), (2c, rt, 6.1:1) [16] in 1-hexyl-3-methylimidazolium tetrafluoroborate and (2a, 25°C, 5.2:1) [5], (2b, rt, 4.3÷6.1:1) [17] in imidazolium bis(trifluoromethylsulfonyl)imides.Therefore, synthesized deanol derivatives could be mentioned as an effective medium comparable to imidazolium ILs.

As part of our research, we decided to study the influence of both ionic liquids and Lewis acids on the Diels-Alder reaction. It is well known that Lewis acids catalyze Diels-Alder reactions and can improve rate and selectivity. The application of ionic liquids could be a way of immobilization and reuse of Lewis acids. Therefore, the other reactions catalyzed by Lewis acids are also tested in these ionic media.

In our work, yttrium triflate was combined with each ionic liquid and used in the reaction of dimethyl maleate, 2a and cyclopentadiene. The endo:exo ratios and yields are summarized in Table 2. Dimethyl maleate was chosen because it was the least active dienophile, so any improvements could be easily observed. On the other hand, yttrium triflate was demonstrated as a very active and universal catalyst for different dienophiles in early papers [10].

As was shown in Table 2, in the presence of $Y(OTf)_3$, almost quantitative yields of product were achieved in 40 minutes in each of the ionic liquids as medium. The presence of the electrophilic (hydroxyl or carbonyl) group in the cation was not the barrier for catalytic activity of metal triflates. Stereoselectivity of this reaction was increased 3-fold in comparison to that without yttrium catalyst and ranged from 9.3:1 to 10.0:1. It can be noted that a little decrease in the endo:exo ratio was found when longer alkoxymethyl chains were used as the substituent (Table 2). Possibly, it was a consequence of a little higher viscosity of the ILs.

The dilution of the reactants by the increase of the volume of ionic liquid versus reactants and catalyst also affected a decrease in the stereoselectivity and the reaction rate (Table 2, entry 5, 8 and 9).

The catalyst $Y(OTf)_3$ was also tested in the reaction of cyclopentadiene with 2b or 2c in deanol derivatives as media. For example, the reaction of 2b was catalyzed by $Y(OTf)_3$ in the IL - $[(C_7H_{15}Om)AcDAE][NTf_2]$ and gave the product in an 8.3:1 endo:exo ratio. However this reaction was stopped after 2 hours with 58% yield because the polymerization of diene was significant and complete conversion of cyclopentadiene was reached after this time.

Methyl-vinyl ketone, 2c was reacted with cyclopentadiene in the presence of $Y(OTf)_3$. For instance, the yield of 92% with 8.7:1 endo:exo stereoselectivity was achieved in $[(C_9H_{19}Om)DecDAE][NTf_2]$ as medium after 6 minutes.

Having established catalytic activity of the yttrium triflate in ionic liquids, we tested other metal triflates with less or similar Lewis acidity. For this study, the reactions of cyclopentadiene with 2a or 2c were chosen due to the different reactivity of these two dienophiles. The yields and selectivities are presented in Table 3.

Table 4. Recycling of the system $[(C_9H_{19}Om)DecDAE][NTf_2]$/catalyst in the reaction of cyclopentadiene with methyl-vinyl ketone (2c).

Catalyst	**Run**			
	1	**2**	**3**	**4**
	Yield (endo:exo ratio)[a]			
$Y(OTf)_3$	92% (8.7:1)[b]	94%(8.9:1)[b]	95%(8.5:1)[b]	93% (8.3:1)[b]
$Cu(OTf)_2$	97% (9.9:1)[c]	97%(9.8:1)[c]	96%(9.4:1)[c]	95% (8.7:1)[c]

[a] *yields and selectivities determined by GC*
[b] *data for reaction time 6 min*
[c] *data for reaction time 60 min*

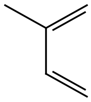
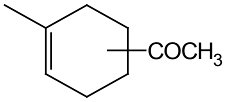
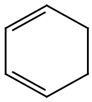
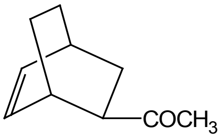
All used catalysts accelerated the Diels-Alder reactions and generally increased endo:exo selectivities. Thus, used ILs - deanol derivatives, proved to be good media to catalyze the reaction.

Reaction of cyclopentadiene with 2a gave the cycloaddition product in yields near or over 90%. The reaction time needed to achieve this yield was longer with Mg, Zn or Li triflates than with Y or Yb catalysts, hence catalytic activity of Mg, Zn, or Li triflates was reduced. Similarly, endo:exo selectivities, for the reaction of 2a, were dependant on the type of metal in catalyst and ranged from 6.1:1 to 9.8:1. For a representative of imidazolium salt, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, comparable activity of metal triflates was obtained.

In the case of the reaction of cyclopentadiene with 2c, copper(II) triflate proved to be the most effective in increasing selectivity (9.9:1) in a short reaction time of 35 min. The other catalysts – Al, Li, Zn, Yb, and Sc triflates were also effective and gave the product with 90% yield or higher after 35 min or 60 min. However, in the case of this dienophile, the increase in the reaction rate was not always parallel with an increase in endo:exo ratio. For example, with Sc or Yb catalysts, the selectivity was less than that achieved in the reaction conducted without catalyst.

Finally, the recyclability of the ionic liquid with catalyst was tested on the representative reaction of cyclopentadiene and 2c. Two catalysts - $Y(OTf)_3$ and $Cu(OTf)_2$ were chosen for these experiments (Table 4). The product was extracted with cyclohexane. As shown in Table 4, the catalytic system consisted of the deanol

Table 5. Yield and selectivity of the Diels-Alder reaction between 2-methyl-1,3-butadiene or 1,3-cyclohexadiene and 2c in deanol based IL[a].

Entry	**Diene**	**Catalyst (mol%)**[b]	**Time/ Temperature**	**Product**	**Yield (%)**	**Isomers ratio**
1		-	6 days/25°C		60	3.6:1[c]
2		$Y(OTf)_3$ (1)	24 h/25°C		89	[d]
3		$Sc(OTf)_3$ (1)	1 h/25°C		90	[d]
4		-	6 days/25°C		32	17.2:1[e]
5		$Y(OTf)_3$ (1)	4 h/25°C		96	35.1:1[e]
6		$Sc(OTf)_3$ (1)	5 min/25°C		97	42.4:1[e]

[a] *reaction conditions: 1mL of $[(C_7H_{15}Om)AcDAE][NTf_2]$, 4 mmol of methyl-vinyl ketone (2c), 6 mmol of diene*
[b] *mol% of catalyst vs. dienophile was given in brackets*
[c] *para:meta*
[d] *only para isomer was detected*
[e] *endo:exo*

based IL and metal triflate, which could be recovered and reused without any noticeable loss of activity. Some decrease in endo:exo selectivity in the presence of copper triflate appeared in the fourth run, which indicated the loss of the catalyst.

The investigations of the Diels-Alder reaction in deanol based ILs have also been extended to the other dienes (Table 5). Isoprene and cyclohexadiene are less reactive than cyclopentadiene. However, the use of the catalytic systems composed of deanol based ILs and Lewis acid catalysts, such as $Y(OTf)_3$ and $Sc(OTf)_3$, gave the product in high yield and high selectivity in a short reaction time at room temperature.

4. Conclusions

We have demonstrated that ammonium ionic liquids based on deanol are effective media for Diels-Alder reactions. The elongation of the alkoxymethyl chain in the ammonium cation resulted in little decrease of endo:exo selectivities. ILs with hydroxy or decanoyloxy moieties in their substituents gave higher selectivities than those with an acetoxy group. The combination of several metal triflates with differently functionalized ammonium cations accelerated the reaction and increased the endo:exo selectivities. The recovery and reuse of deanol based ILs, along with catalyst immobilized in it, could be easily carried out after extraction of product with cyclohexane.

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