

N-hexylpyridinium bis(trifluoromethylsulfonyl)imide and Lewis acids – catalytic systems for Diels-Alder reaction

Research Article

Bożena Bittner*, Ewa Janus, Eugeniusz Milchert

Institute of Organic Chemical Technology, West Pomeranian University of Technology, Szczecin, 70-310 Szczecin, Poland

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Abstract: A comparative study of the Diels–Alder reactions between cyclopentadiene (1) and dienophiles (2 a – c) in N-hexylpyridinium bis(trifluoromethylsulfonyl)imide in a temperature range of 20 – 45°C is reported. The reaction rate constants and activation energies were calculated. Moreover, the catalytic systems based on N-hexylpyridinium bis(trifluoromethylsulfonyl)imide and Lewis acids were tested as a reaction media to perform the Diels-Alder reaction. Yb, Y, Mg, Zn triflates and chlorides (0.005 to 0.1 mmol) were used as catalysts. The recycling of catalytic system consisted of YCl₃ and ionic liquid was performed.

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

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1. Introduction

The Diels-Alder reaction is an example of pericyclic reaction, resulting in the formation of cyclic product formed from a diene and a dienophile. This reaction is of primary importance in organic chemistry [1] and comprises a convenient way to form a cyclic or bicyclic product, sometimes with a heteroatom inside of the ring.

A search for an appropriate solvent for the cycloaddition has been a focus of intense research. Such a solvent should meet the following requirements: it should be nontoxic, enhance both the reaction yield and stereoselectivity, facilitate the separation of reaction products, and should be fully recyclable and cheap.

The norbornene derivatives have many important applications. They are used as monomers to produce high performance polymeric materials. The polymerization process can be performed by ROMP (Ring Opening Metathesis Polymerization) [2-5], a radical polymerization [6-8] or an additive polymerization [9-11]. The norbornene derivatives have been widely used as electron transport species [12], in batteries [13] and in drug deliveries [14,15], specifically as ion [16] and gene transporters [17]. These derivatives are also used as a template for nanoparticle synthesis [18]. They are also used as an additive to poly(methyl methacrylate) to improve its

optical properties, and to enhance the thermal stability of polymers [19] or to polymers used for packaging applications. The first Diels-Alder cycloaddition between maleate anhydride and furan [20] was performed in water as a solvent. According to the suggestion of Breslow and Rideout the hydrophobic effect, caused by water, is responsible for the high reaction rate [21-23]. Moreover, the hydrogen bond, formed *in situ*, activates the dienophile and causes a significant enhancement of stereoselectivity [24,25]. However, water is not a perfect medium to perform this reaction, mostly because of the very low solubility of the organic reagents.

Due to an increasing interest in new solvents called ionic liquids, the Diels-Alder reaction was also carried out in such solvents. The first solvent used for this purpose was ethylammonium nitrate in the cycloaddition of cyclopentadiene and methyl-vinyl ketone [26]. Due to the following properties of ionic liquids: very low vapour pressure, non-flammability, non-explosiveness, thermal stability, and their ability to dissolve substrates and metal catalysts, these liquids are widely used in the reaction media [27,28]. Ionic liquids such as imidazolium [29-31], phosphonium [32,33], sulfonium [34] were used in cycloaddition reactions.

Ionic liquids are also used with metal chlorides as catalysts [35-38]. A combination of metal chloride and

* E-mail: bozena.bittner@gmail.com

pyridinium-based ionic liquid was investigated in the cycloaddition between cyclopentadiene and dimethyl maleate [39]. The acidic character of this system resulted in higher yields and higher stereoselectivities in comparison with other solvents such as water, ethanol and microemulsions. The application of chlorides as catalysts requires non-aqueous conditions. Water, even in low amounts, causes the deactivation of the catalyst. A new generation of catalysts resistant to water was also developed [40]. Trifluoromethanesulfonates of metals were used in the ionic liquids or other solvents in order to increase the reaction rate and stereoselectivity [41-45].

Ionic liquids such as 1-ethylpyridinium tetrafluoroborate and 1-ethylpyridinium trifluoroacetate were investigated in the cycloadditions of isoprene with dienophiles such as acrylonitrile, acrylic acid and methacrylic acid [46]. The ionic liquid 1-ethylpyridinium trifluoroacetate was found to be an excellent reaction solvent enhancing both selectivity and reaction rate. The Diels-Alder reactions were studied in catalytic systems based on 1, 5, 10, and 20 mol% of erbium trifluoromethanesulfonate $\text{Er}(\text{OTf})_3$ immobilized in the 1-methylpyridinium trifluoromethanesulfonate [47]. The addition of the catalyst significantly enhanced reaction rates in the cycloadditions of cyclopentadiene and dienophiles such as acrolein and ethyl acrylate. Moreover, it is known from the literature that catalytic systems consisting of 1-N-butylpyridinium or 1-ethyl-3-methyl-imidazolium chlorides used in conjunction with AlCl_3 in the Diels-Alder reaction between cyclopentadiene and acrylates enhance both reaction rates and stereoselectivity [48]. Also the acidic chloroaluminate ionic liquids were found to improve the catalytic activity of the toluene-coordinated silyl borate, enhancing reaction rates, stereoselectivity and yields of the Diels-Alder reactions [49].

Our investigations were carried out with bis(trifluoromethylsulfonyl)imide as an ionic liquid having low viscosity and high thermal stability. Therefore, it was possible to investigate the catalyst's activity because the influence of an anion in the ionic liquid will not be so essential due to its weak coordinating properties. The same ionic liquid, N-hexylpyridinium bis(trifluoromethylsulfonyl) imide, has already been used as a reaction medium in the intermolecular Diels-Alder reaction [50].

A survey of the literature concerning the influence of viscosity reveals that the longer the alkyl chain on the nitrogen of a cation is, the measured ionic liquid's viscosity correspondingly increased [51]. The viscosity of the ionic liquid should be relatively low in order to ensure increased contact of the reagents in the reaction

medium. However, the addition of more methyl groups to the pyridinium ring increases viscosity, as was observed by comparison of N-hexylpyridinium [hpy][NTf₂] ($\eta=80\text{mPa}\cdot\text{s}$) with N-hexyl-3-methylpyridinium [hmpy][NTf₂] ($\eta=85\text{mPa}\cdot\text{s}$) and N-hexyl-3,5-dimethylpyridinium [hmmpy][NTf₂] ($\eta=104\text{mPa}\cdot\text{s}$).

The pyridinium ionic liquids are also used in the photo-induced electron transfer (PET) [52], the accelerated amine-catalyzed Morita-Baylis-Hillman reaction [53], for the tetrahydropyranylation of alcohols [54], as the ionic liquid catalysts and media for the Fischer esterification [55], in the extractive desulfurization of fuel [56] and the Friedel-Crafts alkylation [57].

2. Experimental Procedure

2.1. Materials

The ionic liquid, N-hexylpyridinium bis(trifluoromethylsulfonyl)imide 98% pure, with water concentration less than 120 ppm was supplied by Merck and was additionally dried at a temperature of 45°C under a pressure of 3 mbar for 24 hours before use. Dimethyl maleate 96%, methyl-vinyl ketone 99% and ethyl acrylate 99% were purchased from Aldrich. Cyclopentadiene was obtained as a result of thermal cracking of dicyclopentadiene $\geq 95\%$ pure, purchased from Fluka. Trifluoromethanesulfonates of ytterbium (99.99%), yttrium (98%), magnesium (97%), zinc (98%) and chlorides of yttrium (99.99%), ytterbium (99.9%), magnesium (98%), and zinc (99.7%) were used as catalysts and purchased from Aldrich. Cyclohexanone 99%, used in the GC analysis, was obtained from Merck.

2.2. Measurements

Gas chromatographic (GC) measurement were performed on a Carlo Erba GC 8000 TOP gas chromatograph equipped with FID detector, RXI™-17 column: 30 m \times 0.53 mm \times 1.5 μm film layer column (Restek). The quantitative analyses were performed according to the internal standard method.

The water content has a significant influence on the reaction course because it affects the physical properties of ionic liquids such as viscosity [58]. The catalysts undergo deactivation in the presence of water; therefore it is essential to ensure an anhydrous medium. The water content of the ionic liquids used in this study were measured using the Karl-Fischer titration. If the results were lower than 120 ppm, then it was assumed not to have any effect on the viscosity.

2.3. Procedure for the Diels-Alder reaction

The reactions were carried out in 4 mL vials. A mixture of N-hexylpyridinium bis(trifluoromethylsulfonium)imide (1 mmol) and dienophile: dimethyl maleate, methyl-vinyl ketone or ethyl acrylate (1 mmol), was stirred at different temperatures (20, 25, 30, 35 and 45°C). The reaction time was measured after the addition of cyclopentadiene. The reaction progress was monitored by GC analysis until the reaction went to completion. The reaction was carried out over the time needed to obtain a yield exceeding 90% or 24 hours, whichever came first. When the reaction was performed in the catalytic system based on the metal salts and hexylpyridinium bis(trifluoromethylsulfonium)imide, a catalyst was added to the ionic liquid before adding the dienophile.

2.4. Recycling

YCl_3 (0.08 mmol) was added into a 5 mL round bottom flask. The chloride was dissolved in 1 mL of the ionic liquid. Dimethyl maleate (4 mmol) was added and reaction mixture was stirred with a magnetic stirrer. Cyclopentadiene (6 mmol) was introduced into the flask placed in the thermostatic bath at a constant temperature in the range of 20–45°C. The reaction products, *endo* and *exo* isomers 2,3-bis(methoxycarbonyl)-5-norbornene, were distilled under 1 mbar pressure at a temperature of 85°C. After the distillation was complete, the reagents were introduced into the reaction mixture in order to start the successive synthesis.

3. Results and Discussion

In our work we have developed new and efficient catalytic systems based on the pyridinium ionic liquid and the Lewis acid catalysts for the synthesis of a mixture of the *endo* and *exo* isomers 2,3-bis(methoxycarbonyl)-5-norbornene, 2-acetyl-5-norbornene and 2-ethoxycarbonyl-5-norbornene. The examined catalytic system consisted of N-hexylpyridinium

bis(trifluoromethylsulfonium)imide, as ionic liquid and Y, Yb, Mg, Zn chlorides or trifluorometanosulfonates, as the Lewis acid catalysts for the reaction of cyclopentadiene (1) and dienophiles (2 a – c): dimethyl maleate, methyl-vinyl ketone, ethyl acrylate (Fig. 1).

The values of activation energies and the reaction rate constants, obtained without catalyst, are presented in Table 1. The reaction rate constants referring to methyl-vinyl ketone are the highest. Dienophile reactivity facilitated by electron-withdrawing groups on the substituent influences the reaction rate constants in the cycloaddition between cyclopentadiene and methyl-vinyl ketone. A carbonyl group adjacent to the double bond made this reagent the most active. An ester functional group of the second dienophile (2b) did not promote the cycloaddition to such a degree. Dienophile with two ester groups (2c) was even less active; therefore the second order reaction rate constants were the smallest. Due to the rather small reaction rate constant and high activation energy in the Diels-Alder reaction between cyclopentadiene and dimethyl maleate, a new catalytic system must be developed in order to enhance the reaction rate.

Yields and stereoselectivities of cycloadditions carried out in the ionic liquids were compared with those performed in different catalytic systems in order to demonstrate the advantage of using Lewis acids with ionic liquids. The catalytic activity of each system was presented using TON TOF values (Table 2).

Methyl-vinyl ketone is the most reactive dienophile. Due to the presence of an electron-withdrawing group, the double bond becomes weaker, which facilitates the Diels-Alder reaction. For this reason, even the reaction carried only in the ionic liquid proceeded relatively fast, which is supported by the TON TOF values in Table 2. The reaction was almost complete after 90 min with stereoselectivity *endo:exo* 85:15 without catalyst. To enhance the *endo:exo* ratio, the application of the catalytic system as a reaction medium was useful. The selectivity with Y and Yb chlorides was increased to 92:8 after

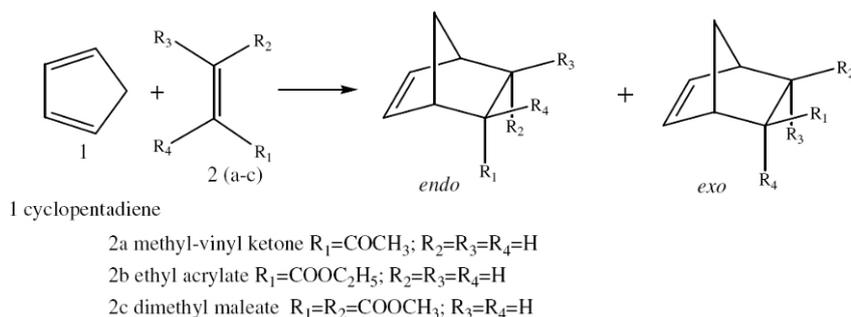


Figure 1. The Diels-Alder reaction between cyclopentadiene and various dienophiles: dimethyl maleate, methyl-vinyl ketone or ethyl acrylate in catalytic system, based on N-hexylpyridinium bis(trifluoromethylsulfonium) imide and Y, Yb, Mg, Zn chlorides or trifluorometanosulfonates, as Lewis acid catalysts

Table 1. The second order reaction rate constants in the Diels-Alder reaction between cyclopentadiene and various dienophiles: dimethyl maleate, methyl-vinyl ketone or ethyl acrylate

Diene	Dienophile	Activation energy (kJ mol ⁻¹)	Temperature (°C)	k × 10 ⁵ (dm ³ mol ⁻¹ s ⁻¹)
1	2 a	22.3	20	14.33
			25	15.67
			30	19.33
	2 b	40.6	25	1.80
			35	2.58
			45	5.18
	2 c	57.0	25	0.68
			35	1.70
			45	2.99

Table 2. TON and *endo:exo* ratios in the Diels-Alder reaction between cyclopentadiene (1) and dienophiles (2a-c) carried in catalytic systems metal salt + [hpy][NTf₂]

Dienophiles Catalyst	2 a		2 b		2 c	
	TON [mol mol ⁻¹]	<i>Endo:exo</i> ratio	TON [mol mol ⁻¹]	<i>Endo:exo</i> ratio	TON [mol mol ⁻¹]	<i>Endo:exo</i> ratio
Y(OTf) ₃	97	90:10	26	93:7	97	89:11
Yb(OTf) ₃	97	90:10	19	90:10	98	89:11
Mg(OTf) ₂	45	88:12	18	82:18	70	88:12
Zn(OTf) ₂	91	92:8	16	84:16	81	90:10
YCl ₃	96	92:8	40	91:9	96	93:07
YbCl ₃	97	92:8	29	90:10	92	90:10
MgCl ₂	45	84:14	4	84:16	12	75:25
ZnCl ₂	96	96:4	37	85:15	14	89:11

30 min. In order to achieve the highest stereoselectivity, a number of catalysts were examined. It was found that ZnCl₂ was the most active catalyst. With this catalyst, after the reaction proceeded for 30 min, the product was obtained with 94:6 *endo:exo* ratio, which exceeds the initial value of 85:15 measured for the cycloaddition carried only in hexylpyridinium bis(trifluoromethylsulfonyl) imide [hpy][NTf₂].

Moreover, it was demonstrated that the presence of triflates in the Diels-Alder reaction between cyclopentadiene and ethyl acrylate does not guarantee high TON TOF values (Table 2). The product that was obtained after 24 h gave a lower yield than in the reaction carried only in [hpy][NTf₂]. The only reason for using triflates as catalysts is to increase *endo:exo* ratio, as was noticed with the ketone. For example, the selectivity ranged from 75:25 to 90:10 with Yb(OTf)₃ and when the ionic liquid was a reaction medium. It was found that *endo:exo* ratios obtained in the catalytic systems with chlorides were four times higher than those in the ionic liquid. A comparison of TOF values for triflates and chlorides clearly indicated that chlorides were more effective catalysts for the cycloaddition. Among the chlorides, YCl₃ and YbCl₃ stood out when taking into account the TON TOF values and stereoselectivities.

In further investigations of the cycloaddition between ethyl acrylate and cyclopentadiene, the chlorides of yttrium, ytterbium, magnesium, and zinc were used as

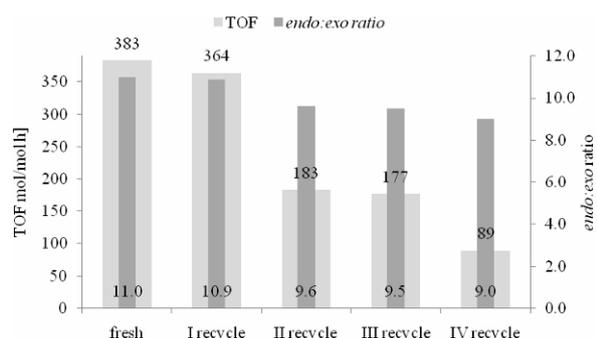
catalysts. The influence of the catalyst concentration on yields and stereoselectivity was observed. The use of larger amounts of catalyst in the system enhanced the yield significantly, which caused an increase in TOF values. Examples are presented in Table 3. In the catalytic system YCl₃ + [hpy][NTf₂], the obtained TOF was 80 [mol mol⁻¹ h⁻¹] for 1 mol% of the catalyst, while for 5 mol% of the catalyst the TOF value increased to 180 [mol mol⁻¹ h⁻¹]. The same tendency was noticed for all chlorides. However, analysing the *endo:exo* selectivities demonstrate that there are no significant differences for YCl₃ and YbCl₃. It was found that for ZnCl₂, it ranges from 85:15 (1 mol%) to 93:7 (5 mol%). Taking into account the obtained results, it was found that the search for appropriate catalysts for the Diels-Alder reaction between ethyl acrylate and cyclopentadiene was very difficult.

For some catalysts from the triflate group, such as scandium, bismuth, indium, copper and aluminium, oligomerization occurs which appears to be competitive with the Diels-Alder reaction. This negative influence of oligomerization has already been noted in previous studies [34]. The catalytic systems consisting of yttrium, ytterbium and zinc triflates also caused a side reaction of oligomerization in the Diels-Alder reaction between dimethyl maleate and cyclopentadiene.

The Diels-Alder reaction between cyclopentadiene and dimethyl maleate conducted in [hpy][NTf₂] in

Table 3. TON, TOF and endo:exo ratios dependence on catalyst concentration in the reaction between ethyl acrylate and cyclopentadiene

Catalyst mol%	YCl ₃			YbCl ₃			MgCl ₂		ZnCl ₂	
	1	3	5	1	3	5	1	5	1	5
TOF	80	150	180	58	72	177	4	29	37	71
TON	87	31	18	75	28	19	69	16	69	18
Endo:exo ratio	91:9	91:9	90:10	89:11	90:10	91:9	84:16	89:11	85:15	93:7

TOF [mol mol⁻¹ h⁻¹] calculated 30 min after reaction startedTON [mol mol⁻¹] calculated 3 h after reaction started**Figure 2.** The effect of number of recycle runs on TOF values and endo:exo ratios

the presence of yttrium or ytterbium triflates and chlorides results in the highest values of TON (Table 2). For this reason, the high yields were obtained for all catalytic systems. The use of ionic liquids without catalyst required 24 h to obtain the product with a yield of 90%. The reaction time was shortened to less than 1 h in the presence of the catalyst. However, the oligomerization was sometimes observed together with the cycloaddition in this catalytic system. Moreover, the obtained selectivities were not as high as in the chloride systems.

On the other hand, yttrium and ytterbium chlorides affected the Diels-Alder reaction positively, by enhancing yields and selectivities similar to what was previously observed for ethyl acrylate. For YCl₃ the obtained endo:exo selectivity was 94:6. The highest endo:exo ratio for this catalytic system was obtained with 2 mol% of YCl₃.

In addition, the recycling studies were performed for the most active catalytic system in the Diels-Alder reaction between cyclopentadiene and dimethyl maleate. The removal of product can be carried out by extraction or distillation under low pressure. In our studies, the product was separated by distillation. However, the main drawback of this method is a gradual darkening of distillation residue due to thermal decomposition of ionic liquid and the polymerization of reaction product. Other researchers observed this effect as well [59]. The decomposition temperature depends primarily on the nature of the coordinating anion. In the case of the ionic liquids containing halides, the decomposition

temperature is lower than that of bistriflimides ([hpy][NTf₂] T_{decomp} = 665 K, [hpy][Cl] T_{decomp} = 511 K). It is known from the literature [60] that the nature of the cation has little influence on the decomposition temperature. The length of the alkyl chain in the cation of these ionic liquids influences to a small degree the decomposition temperature e.g. N-butyl-3-methylpyridinium = [bmpy] = 670 K, N-hexyl-3-methylpyridinium = [hmpy] = 672 K and N-octyl-3-methylpyridinium = [ompy] = 667 K. It is more advantageous to use [hpy][NTf₂], despite the fact that the decomposition temperature for [bmpy][NTf₂] is the highest, but first measurable losses of mass were observed at 590 K. For [hmpy] cation, these losses were observed at 605 K. The difference between the decomposition temperature of hexylpyridinium cation (T_{decomp} = 665 K) in [NTf₂], and the cation, containing one more substituent in the hexylmethylpyridium ring, is very small.

The TOF values and the ratio of endo:exo isomers in the successive syntheses with recirculation of the catalytic system ionic liquid [hpy][NTf₂] and YbCl₃ in the reaction between dimethyl maleate and cyclopentadiene are shown in Fig. 2. Probably, a decrease in the TOF values was caused by catalyst deactivation after oligomerization of products remaining in the reaction media. The time required to achieve a 90% yield increased in every cycle. The IR and UV-Vis analysis of the ionic liquid under distillation conditions did not reveal any significant changes in the spectra.

4. Conclusion

The cycloaddition of cyclopentadiene with dimethyl maleate, methyl-vinyl ketone or ethyl acrylate proceeds smoothly in the presence of the catalytic systems N-hexylpyridinium bis(trifluoromethylsulfonyl)imide and metal chlorides or triflates. In particular, chlorides were identified to strongly affect both the yield and stereoselectivities of the cycloaddition. The possibility to carry out the reaction in the catalytic systems, with the metal salt immobilized in the ionic liquids, enables the reuse of the reaction media several times without a significant loss of activity.

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