

Mg(OTf)₂ + ionic liquid – recyclable catalytic system in diels-alder reaction

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A comparative study of Diels-Alder reaction between cyclopentadiene and dimethyl maleate in catalytic system is reported. The catalytic system was formed from ionic liquid which was made of N-hexylpyridinium bis(trifluoromethylsulfonyl)imide and magnesium trifluoromethanesulfonate. The yields, TONs, TOFs and *endo:exo* ratios were calculated. The optimal catalyst concentration was found in order to obtain the mixture of *endo*, *exo* isomers with the highest yields. Moreover recycling of the catalytic system consisting of Mg(OTf)₂ (2 mol%) and ionic liquid was performed. The distillation was noticed to be a better product removal method than extraction by organic solvent, taking into consideration both the TON and TOF values.

Keywords: Diels-Alder reaction, ionic liquids, Lewis acids, norbornene derivatives.

INTRODUCTION

Diels-Alder reaction is a source of various cyclic and bicyclic compounds that are commonly used in pharmaceuticals, cosmetics, pesticides synthesis¹. Norbornene derivatives were also found to be useful as copolymers for special properties materials^{2,3}.

Nowadays researchers are focused on finding an appropriate solvent for cycloaddition. It should be nontoxic, enhancing reaction rate and selectivity, being recyclable and making the product separation easy. The perfect one comes to everybody's mind is water⁴. Unfortunately using water as solvent is not common because of the limited solubility of organic compounds. Moreover, LiCl, NaCl and LiClO₄ solutions in diethyl ether⁵ or supercritical CO₂⁶ were investigated. Solvents as toluene, acetonitrile and methanol were taken as reaction medias in traditional norbornene derivatives synthesis methods⁷. However they are slowly being replaced by other solvents because of being rather harmful.

Ionic liquids have been successfully applied as alternative solvents in many reactions, also in Diels-Alder cycloaddition. They are classified as green solvents because of specific properties such as negligible vapour pressure, being thermally stable and recyclable. It is known that ionic liquids together with Lewis acids enhance both the yield and selectivity⁸⁻¹⁰. Chloroaluminated ionic liquids were one of the first combinations of Lewis acid and ionic liquid tested in the Diels-Alder reaction between cyclopentadiene and various acrylates¹¹. The other combination was zinc chloride containing system¹². Generally, ionic liquids with Lewis acids show promising performances¹³. Lanthanum¹⁴, erbium triflate¹⁵, scandium triflates^{16,17} and many more were found as active catalysts in many cycloadditions.

If the product exists as a different phase, the main way to remove decantation is used to separate it. If not, products isolation could be provided by distillation or extraction. With those methods catalyst recycling is allowed. Phosphonium¹⁸ and sulfonium¹⁹ ionic liquids together with chlorides and triflates were reported in the literature as excellent reaction recyclable medias.

We investigated the catalytic activity of the system [hpy][NTf₂] and Mg(OTf)₂. Magnesium salt was acting in the system as acidic catalyst resulting in a significant increase of reaction rate, and practical Mg(OTf)₂/IL re-

cover/reuse. Generally, triflates are well known for catalytic activity in many organic reactions, also in the Diels-Alder reactions. Especially the triflates of expensive rare-earth metals, such as yttrium, scandium and lanthanides are used. We proposed triflate of the commonly existing and cheaper metal such as magnesium. Magnesium triflate with ionic liquids has never been investigated as a recyclable catalytic system.

Similar to our studies in cycloaddition between ethyl acrylate and cyclopentadiene, studies have been made with erbium triflate and pyridinium ionic liquids¹⁵. However, in those catalytic systems ionic liquids and metal salts consisted of the same triflate anion. In all the formed systems, the obtained yields and selectivities were higher than in the organic solvent based systems.

EXPERIMENTAL PART

Diels-Alder reaction method

Before the reaction started ionic liquid was dried. Measured by Carl-Fisher method, water content was less than 120 ppm. The reaction was carried out in a small vial of 4 ml capacity equipped with a magnetic stirrer. Into the vial the Mg(OTf)₂ catalyst and ionic liquid N-hexylpyridinium bis(trifluoromethylsulfonyl)imide were put. The vial content was stirred until the magnesium salt was completely dissolved. Next, dimethyl maleate and cyclopentadiene were introduced into the reaction media. The yields and the selectivities were calculated by the GC analysis.

Recycling

The catalyst, together with ionic liquid was placed in a small flask equipped with a magnetic stirrer. Next, dimethyl maleate and cyclopentadiene were added. The reaction was monitored by the GC analysis. The 2,3-di(metoxycarbonyl)-5-norbornene- reaction product was separated from the reaction media by distillation under vacuum pressure or by extraction with an organic solvent.

Results and discussion

Initially, we used the catalytic systems based on Mg(OTf)₂ and N-hexylpyridinium bis(trifluoromethylsulfonyl)imide in the reaction of cyclopentadiene with dimethyl maleate, which leads to a mixture of *endo* and

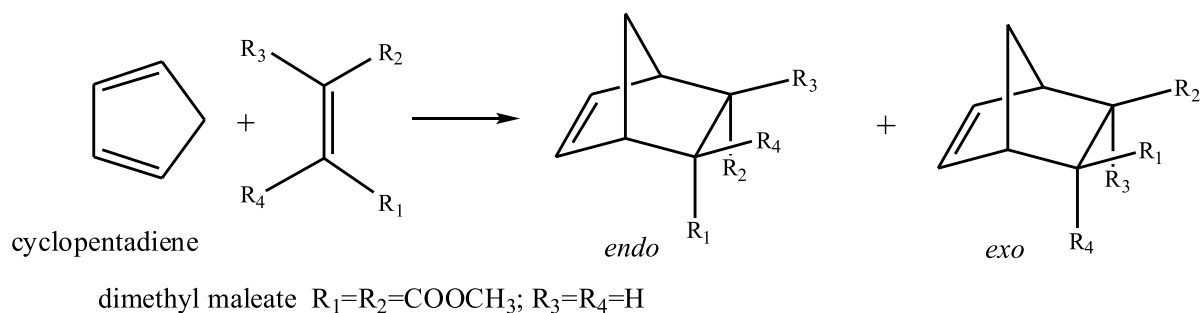


Figure 1. The Diels-Alder reaction between cyclopentadiene and dimethyl maleate

exo products (Fig. 1), as a probe of the efficiency of the $Mg(OTf)_2/IL$ system. The model cycloaddition reactions have been carried out with different catalyst concentrations. The aim was to find the optimal triflate content giving the highest yield in a short cycloaddition time. Fig. 2 suggests that the yield is highly dependent on $Mg(OTf)_2$ concentration. However, the addition of the catalyst does not enhance the selectivity – Fig. 3.

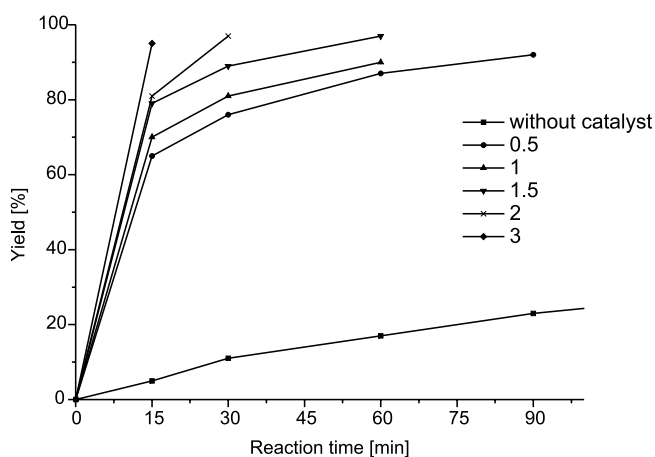


Figure 2. Dependence of the yield on the reaction time for the various catalyst concentrations

In further investigations recycling was performed in 2 catalytic systems. The first one had 1 mol% of $Mg(OTf)_2$ dissolved in ionic liquid. The second one had 2% mol of the catalyst immobilized. The TOFs and TONs values which were calculated after the GC analysis were placed in Table 1.

In the studied systems, containing 1 mol% and 2 mol% of $Mg(OTf)_2$, it was possible to reuse the same reaction media five times. After each cycloaddition the products

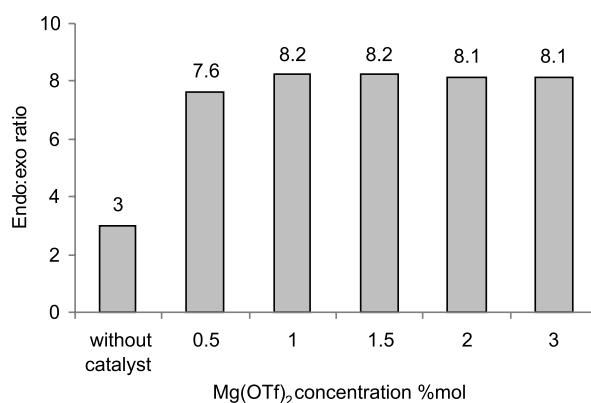


Figure 3. Endo: exo ratio dependence on catalyst concentration

were removed from the system by distillation under vacuum. Comparing the TOF values catalytic system with the immobilized 2 mol% of catalyst was better than the other one, providing twice as high values. The parameters calculated for the system with 1 mol% of catalyst are rather small, less than $50 \text{ mol} \cdot \text{h}^{-1} \cdot \text{mol}^{-1}$. The noticed difference in the TOF values is caused by a different time of reaction. In the system based on ionic liquid and 2 mol% of $Mg(OTf)_2$ high yields were obtained after 30 min. In the second system 2 hours were needed to achieve a good yield. Analyzing the TON values it was observed that together with enhancing the catalyst concentration in the system is, the TON values are decreasing. In our case, twice as much catalyst in the system was causing twice as low TON parameters.

Taking into consideration the short reaction time required to obtain a high yield and corresponding to them high TOF, the catalytic system with 2 mol% of catalyst in ionic liquid is better than the other one and is recommended for use many times in the Diels-Alder reaction leading to the synthesis of 2,3-dimethoxycarbonyl-5-

Table 1. Comparison of the yields, endo:exo ratios, TON and TOF for the catalytic systems consisting of 1 and 2 mol% of $Mg(OTf)_2$ in [hpy][NTf₂]. Dimethyl maleate 8 mmol, cyclopentadiene 12 mmol, (0.08 and 0.16 mmol) $Mg(OTf)_2$, 2 ml of ionic liquids

	1 %mol $Mg(OTf)_2$					2 %mol $Mg(OTf)_2$					
	fresh	I	II	III	IV	fresh	I	II	III	IV	
Yields after 2 h (%)	94	92	91	87	80	Yields after 30 min (%)	98	97	94	91	89
Endo:exo	7.6	7.4	7.5	7.3	7.0	Endo:exo	7.0	7.1	6.8	6.7	6.4
TON (mol ¹ mol ⁻¹)	94	91	91	87	80	TON (mol ¹ mol ⁻¹)	49	48	47	45	44
TOF (mol ¹ mol ⁻¹ h ⁻¹)	47	46	45	43	40	TOF (mol ¹ mol ⁻¹ h ⁻¹)	97	97	94	90	89

I – first recycle; II – second recycle; III – third recycle; IV – forth recycle

endo:exo ratio of isomers *endo* and *exo*-2,3-di(methoxycarbonyl)-5-norbornene.

TON (Turnover Number) – number of substrate moles converted to mole numbers of the used catalyst (mol¹ mol⁻¹). TOF (Turnover Frequency) – number of substrate moles converted to mole numbers of the used catalyst in the time unit (mol¹ mol⁻¹ h⁻¹)

Table 2. Comparison of the yields, endo:exo ratio, TON and TOF for the catalytic systems consisting of 2 mol% of Mg(OTf)₂ in [hpy][NTf₂]. Dimethyl maleate 8 mmol, cyclopentadiene 12 mmol, (0.08 and 0.16 mmol) Mg(OTf)₂, 2 ml of ionic liquids. Product removal by distillation under vacuum pressure and by extraction

	Extraction					Distillation					
	fresh	I	II	III	IV	fresh	I	II	III	IV	
Yield after 30 (%)	96	93	91	86	81	Yield after 30 min (%)	98	97	94	91	89
Endo:exo	7.6	7.4	7.5	7.3	7.0	Endo:exo	7.0	7.1	6.8	6.7	6.4
TON (mol·mol ⁻¹)	48	47	46	43	41	TON (mol·mol ⁻¹)	49	48	47	45	44
TOF (mol·mol ⁻¹ ·h ⁻¹)	96	93	91	86	81	TOF (mol·mol ⁻¹ ·h ⁻¹)	97	97	94	90	89

norbornene. There are two methods of the product removal – products distillation under vacuum and extraction. In order to compare them, the catalytic system containing 2 mol% of the catalyst was investigated in recycling by extraction.

Both the TON and TOF values are smaller in recycling made by extraction than in the distillation method. Moreover, a little loss in ionic liquids amount, probably dissolved in organic solvent, was found and it was another disadvantage.

CONCLUSIONS

In the synthesis of *endo* and *exo* the 2,3-dimethoxycarbonyl-5-norbornene products are obtained with high yields in a short time. The reported method of norbornene derivatives synthesis is properly corresponding to the Green Chemistry principals. It uses a reaction media with negligible vapour pressure – ionic liquid and catalyst, that together are found to be recyclable.

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