



A novel reaction in ionic liquids: selective cyclization of 1-dodecene to cyclododecane under moderate pressure[☆]

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Abstract—A novel reaction of cyclization of 1-dodecene to cyclododecane with high selectivity, especially under moderate pressure, is found in ethanol buffered chloroaluminate ionic liquids with easy separation of product due to the immiscibility with ionic liquids. © 2003 Elsevier Science Ltd. All rights reserved.

Room temperature ionic liquids (RTILs) have recently received recognition as novel and promising solvents for synthetic chemistry.¹ They have essentially no vapor pressure, making them an attractive candidate to replace many of the volatile organic compounds (VOCs) that are currently used as solvents in organic synthesis. They have also been referred to as ‘designer solvents’ for their chemical and physical properties could be adjusted by a careful choice of cation/anion. Examples of their applications in both reactions^{2,3} and separations,^{4,5} showing a number of advantages over conventional organic solvents, have been demonstrated.

The reaction of simple alpha olefin to prepare less readily available products is important in chemical industry. By carefully choosing the reaction conditions and the catalyst, alpha olefin could be converted to linear internal or highly branched internal olefin via different reaction route, including isomerization, dimerization or oligomerization.^{6,7} Example of direct selective cyclization of alpha olefin to cycloalkane, however, is absent from the literatures. For example, no efficient catalyst has been reported for direct cyclization of 1-dodecene to cyclododecane.⁸ Cyclododecane, an important intermediate for manufacturing Nylon, was traditionally prepared by a two-step reaction process, i.e. 1,4-butdiene was firstly trimerized to cyclododec-

triene and then followed by hydrogenation of cyclododecatriene over Ni catalyst to produce cyclododecane.

Ionic liquids containing chloroaluminate (AlCl_4^- , Al_2Cl_7^-) anions could be strong Lewis acids, and therefore, can act as either catalysts or reaction medium for acid catalyzed processes. It has been demonstrated that chloroaluminate ionic liquids are suitable solvents for dimerization and oligomerization of alpha olefins.⁹ Toluene, as cosolvent, is nonetheless necessary for those reactions to achieve optimum activity and selectivity, which indicates that cosolvent, in some ways, would interact with chloroaluminate ionic liquids and play an important role in the reactions. Only non-protic solvents, such as toluene and heptane, have been used as cosolvents with chloroaluminate ionic liquids up to now. The combination of chloroaluminate ionic liquids with protic solvents has been, however, out of consideration all along due to the generation of oxychloroaluminate species ($\text{Al}_3\text{OCl}_8^-$, $\text{Al}_3\text{O}_2\text{Cl}_6^-$) when chloroaluminate ionic liquids were mixed with the protic solvents.¹⁰ Those oxychloroaluminate species are Lewis acidic and therefore, there exists the possibility that the protic solvents buffered chloroaluminate ionic liquids can still function as either acidic catalysts or reaction medium. Here we report the first example of using ethanol buffered chloroaluminate ionic liquids as reaction medium and catalyst for acid catalyzed isomerization of alpha olefin. It was found that 1-dodecene proceeded cyclization reaction to cyclododecane in such a novel reaction medium with high selectivity, especially under moderate pressure. A recyclable and environmentally friendly process for production and separation of cyclododecane was also established by addition of ethanol to the chloroaluminate ionic liquids (Fig. 1).

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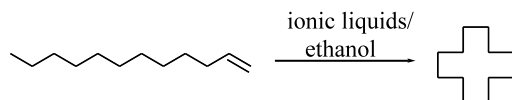


Figure 1. Cyclization of 1-dodecene to cyclododecane in ethanol buffered ionic liquids.

Results of cyclization of 1-dodecene in the ionic liquid consisted of AlCl_3 and 1-butyl-3-methyl imidazolium chloride ([BMIm]Cl) are listed in Table 1.¹¹ GC/MS analysis showed that several products, such as cyclododecane and 9-methyl-2-undecene, etc. were formed, in which the selectivity for cyclododecane reached 55–83%. For the concentration of 1-dodecene was low in the reaction mixture, other by-products, including dimer of 1-dodecene and addition product of 1-dodecene with ethanol were not detected.

Because chloroaluminate ionic liquids were immiscible with 1-dodecene, direct addition of 1-dodecene into the chloroaluminate ionic liquids would result a biphasic liquid mixture only. In this case, the conversion of 1-dodecene and selectivity to cyclododecane was rather low (entry 1). When ethanol, a cosolvent having well solubility with both of chloroaluminate ionic liquids and 1-dodecene, was added into the biphasic liquid mixture, a homogenous liquid mixture formed, which greatly facilitated the cyclization reaction of 1-dodecene. The conversions of 1-dodecene and selectivity to cyclododecane increased remarkably from 4.2 to 12.4% and 73.1 to 82.9%, respectively (entry 2). The physicochemical state of ethanol buffered chloroaluminate ionic liquid was closely associated with the volume ratio of ethanol/ionic liquid. When ethanol was mixed with equal volume of chloroaluminate ionic liquid, for example, it was a very exothermic reaction and the colorless ionic liquid turned into being viscous and opaque after cooling. But a colorless liquid could be regained if more ethanol was added, i.e. the amount of ethanol was excessive than that of chloroaluminate ionic liquid. In our experiments, the volume ratio of ethanol/ionic liquid was about 10, which could ensure us to obtain a monophasic reaction medium for cyclization reaction of 1-dodecene. Therefore, there is no

doubt that oxychloroaluminate, even hydroxychloroaluminate species, would generate as the result of mixing chloroaluminate ionic liquid with ethanol.

The acidity of chloroaluminate ionic liquid, as expected, was also an important factor that affects the reaction. With the molar ratio of AlCl_3 /quaternary ammonium salts decreased from 2:1 to 1:2, i.e. chloroaluminate ionic liquids changed from Lewis acid to Lewis base, the conversion of 1-dodecene and selectivity to cyclo-dodecane also decreased correspondingly (entries 2–5), suggesting that acidic environment was more favorable for cyclo-dodecane formation.

When the cyclization reaction of 1-dodecene was further carried out under moderate inert N_2 pressure ranged from 3.0 to 6.0 MPa, we observed a high selective cyclization of 1-dodecene (entries 6–9). Cyclization of 1-dodecene to cyclododecane is a volume-decreasing reaction (the density of 1-dodecene and cyclododecane was 0.761 and 0.871 g/ml, respectively). One can deduce from the prediction of chemical equilibrium that pressure is favorable for the formation of cyclododecane. The conversion of 1-dodecene and selectivity to cyclododecane was, however, almost unchanged when pressure rose from 3.0 to 6.0 MPa. The reason was still not clear at this stage.

Chloroaluminate ionic liquid as reaction medium and catalyst could be repeatedly used for the cyclization of 1-dodecene. Entry 10 showed that the fifth reaction results of reusing of AlCl_3 -BMImCl (1-*n*-butyl-3-methylimidazolium chloride). It can be seen that, even being reused at the fifth time, the conversion of 1-dodecene and selectivity to cyclododecane still kept at 11.2 and 81.3%, respectively.

Once the reaction was finished, more attention was paid to recovery of product and recycle of ionic liquid and ethanol. As demonstrated by Wheeler et al., incorporation supercritical CO_2 with ionic liquids could form a recyclable process for extraction of non-volatile organic compounds from ionic liquids.¹² We found that addition of ethanol to chloroaluminate ionic liquids could also make a similar recycle of ionic liquids and product

Table 1. Results of cyclization of 1-dodecene in chloroaluminate ionic liquid

Entry	AlCl_3 /[BMIm]Cl (mol/mol)	Pressure (MPa)	Time (h)	Conversion (%)	Selectivity (%)
1 ^a	2:1	N.A.P. ^c	8	4.2	73.1
2	2:1	N.A.P.	8	12.4	82.9
3	1.5:1	N.A.P.	8	8.5	75.2
4	1:1	N.A.P.	8	4.8	67.9
5	0.5:1	N.A.P.	8	3.2	54.8
6	2:1	3	12	23.4	93.4
7	2:1	4	12	24.8	93.1
8	2:1	5	12	27.2	92.4
9	2:1	6	12	25.2	93.8
10 ^b	2:1	N.A.P.	8	11.2	81.3

^a Ethanol was not added.

^b Reused five times.

^c Normal atmospheric pressure.

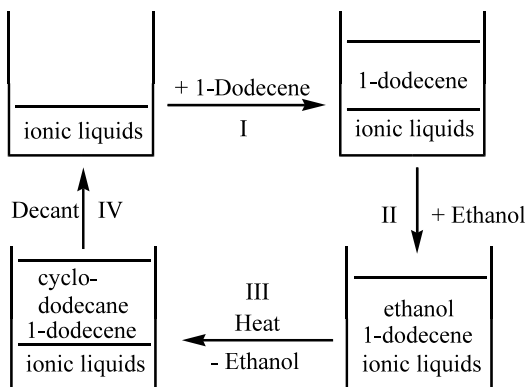


Figure 2. A recyclable ionic liquids/ethanol system for cyclization of 1-dodecene.

recovery in the case of 1-dodecene cyclization reaction, and ethanol was more convenient than supercritical CO_2 to be handled with. Figure 2 illustrates an environmentally benign ionic liquids/ethanol reaction and separation system for cyclization of 1-dodecene. In step I, 1-dodecene was added into the ionic liquid and a two phase system formed due to the immiscibility of ionic liquid with 1-dodecene. Step II involves the addition of ethanol to the above biphasic liquid mixture and a homogenous liquid mixture formed, and then reaction was proceeded. Step III remove the ethanol by heat after the reaction, and a biphasic liquid mixture reformed with the upper layer consisted of product and unreacted substrate. In step IV, The product and unreacted substrate were separated with decantation, and the used ionic liquids are obtained and available for another reaction cycle. For ionic liquids that are non-volatile, the loss of ionic liquids in a reaction recycle could be neglected. Ethanol could also be repeatedly used if distillation was conducted instead of simple heating to remove it.

Cyclization of other alkenes with even number carbon atom, including octene, 1-tetradecene, 1-hexadecene and 1-octadecene, were also tested in ethanol buffered AlCl_3 -MBImCl chloroaluminate ionic liquids. However, desired products from cyclization reactions were not observed, and the major products were various branched isomers of the alkenes. This experimental results suggested that the selectivity to the desired cyclized product was closely related to the alkene itself.

Although the detailed mechanism of cyclization is not clear at this stage, it can be conjectured that the formation of desired cyclization product was dependant upon the conformation of alkene molecule. 1-Dodecene just has the suitable conformation, for example, a head-to-tail one, that could be easily converted to cyclododecane. Other alkenes with either longer or shorter length

of carbon chains than that of 1-dodecene, could not form such a suitable conformation and only branched isomers were obtained.

In conclusion, it is the first time that selective cyclization of alpha olefin to cycloalkane could proceed in a novel protic solvent buffered chloroaluminate ionic liquid under moderate pressure with high selectivity. Also, it was found that ethanol addition into and separation from the chloroaluminate ionic liquids could make both cyclization reaction and product separation much more easier. Such ionic liquid reaction system mediated with second solvent, which could greatly facilitate both reaction and separation, may give some useful revelation for efficient organic syntheses and catalytic reactions.

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- In a typical experiment, chloroaluminate ionic liquids with the amount of AlCl_3 as 0.01 mol and molar ratio of AlCl_3 /quaternary ammonium salts varied from 2 to 1, 10 ml ethanol and 2 ml 1-dodecene (9.3 mmol) were successively added into a 90 ml stainless autoclave with magnetic stirring. The reaction proceeded at 80–140°C for 6–12 h. Remove ethanol by heating at 80–90°C after reaction, then the formation of two layers was observed with the upper layer consisting of products and unreacted substrate. After removal of products and unreacted substrate by decant, the remaining ionic liquids phase was purified at 100°C for 30 min under vacuum for the reusability tests. Composition analysis of the upper layer was carried out using a HP 6890/5973 GC/MS equipped with HP 5MS column, 30 m×0.25 mm×0.25 μm . The concentration of reactant and product was given by the system of GC/MS Chemstation according to the area of each chromatograph peak.
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