Cleavage of Aromatic Methyl Ethers by Chloroaluminate Ionic Liquid Reagents

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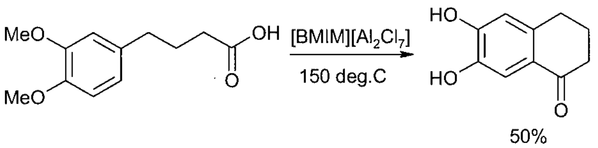
We have discovered serendipitously that chloroaluminate ionic liquids can cleave aromatic methyl ethers under surprisingly mild conditions. Three ionic liquids, viz. [TMAH][Al_2Cl_7], [BMIM][Al_2Cl_7], and [EMIM][Al_2Cl_6I], and aluminum chloride were compared in the selective demethylation of 4,5-dimethoxyindanone at the 4-methoxy-function. The ionic liquids exhibited a remarkably high selectivity (96:4) in comparison with aluminum chloride (70:30). In addition, the reaction time was drastically shortened when the ionic liquids were used. Interestingly, the three ionic liquids displayed the same reactivity in the demethylation of 4,5-dimethoxyindanone. Considering the lower cost and the bulk availability of the precursors of [TMAH][Al_2Cl_7], we conclude that this is the most attractive ionic liquid from an industrial point of view. To make the large-scale application of [TMAH][Al_2Cl_7] feasible, we have developed a safe upscalable method for its preparation. Furthermore, the scope of ether cleavage by the ionic liquid reagent [TMAH][Al_2Cl_7] was investigated and it was found that aromatic methyl-, allyl-, and benzyl-ether cleavage is applicable to a variety of heterocyclic compounds.

Introduction

During the past decade, the scientific interest shown by organic chemists in ionic liquids has escalated tremendously.[1] While the pioneering work was done with chloroaluminate ionic liquids,[2,3,4] the discovery of liquid, water-stable, tetrafluoroborate and hexafluorophosphate salts has boosted the attention of synthetic organic chemists for ionic liquid technology.[5,6] In contrast to chloroaluminate ionic liquids, the water-stable ionic liquids offer opportunities for solvent recycling and are, therefore, considered to be the most revolutionary ionic liquids, especially from an environmental point of view. Although in many cases chloroaluminate ionic liquids cannot be recycled, and certainly not when heteroatomic substrates are involved, they constitute a form of liquid aluminum chloride that, as we report herein, exhibits chemical reactivity completely different to that of its conventional solid counterpart.

Interest in Lewis-acidic ionic liquid technology initiated an investigation of the Friedel−Crafts-type ring closure reactions of phenylbutyric acid analogs (Scheme 1). Heating 3,4-dimethoxyphenylbutanoic acid in chloroaluminate ionic liquid did not give the intended product, 6,7-dimethoxytetralone, but instead the demethylated compound, viz. 6,7-dihydroxytetralone.[7] Further investigation of this reaction revealed that demethylation proceeds readily at room temperature, while ring closure takes place only at elevated temperatures. The use of methoxyaromatics as protected phenols is a useful strategy in the synthesis of multifunctional heterocyclic compounds. Hence, demethylation is often encountered in such syntheses in order to deprotect the phenol and to allow further functionalization at the hydroxyl function concerned. This is normally achieved by treatment with boron tribromide, hydrobromic acid, or aluminum chloride. To investigate whether a novel demethylation methodology had been discovered serendipitously, the ionic liquid-mediated ether cleavage was scrutinized with regard to the amount and the nature of the ionic liquid, as well as other reaction parameters. Furthermore, we describe an economically viable, safe, well-controlled, and, thus, upscalable method for the preparation of a chloroaluminate Lewis-acidic ionic liquid. Finally, the scope of the ionic liquid-mediated ether cleavage is elucidated.



Scheme 1. Ring closure of 3,4-dimethoxyphenyl butanoic acid[7]

Results

Our investigation of the demethylation process started by using 4,5-dimethoxyindanone as the substrate. The choice

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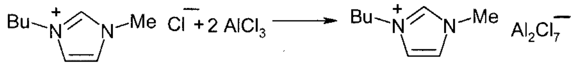
of this compound stemmed from our interest in selective demethylation of this compound at the 4-position, a process that has found application in the synthesis of many pharmaceuticals being currently developed. The demethylation could be achieved by treating the starting compound with aluminum chloride in dichloromethane. Under these conditions, demethylation required 6 days under reflux and resulted in a 7:3 mixture of the desired 4-hydroxy-5-methoxyindanone and its regioisomer. The reason for the observed preference for demethylation at the 4-position lies in the deactivation of the methoxyl group at the 5-position, by the presence of the electron-withdrawing carbonyl function. This effect, however, appears not to be sufficiently strong in the reaction with aluminum chloride as a mixture of two very similar regioisomers is formed. Consequently, the desired regioisomer can be obtained in a pure form from this mixture in moderate yield only. Treatment of 4,5-dimethoxyindanone with the ionic liquid [BMIM][Al_2Cl_7], under the same conditions as above, resulted in complete conversion after 23 hours to a 96:4 ratio of regioisomers. From this mixture, the desired regioisomer could readily be obtained in pure form by crystallization. Three ionic liquids were prepared and used to study the conditions for demethylation with 4,5-dimethoxyindanone as the substrate.

Preparation and Physical Properties of Lewis-Acidic Ionic Liquids

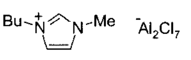
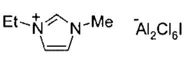
Lewis-acidic chloroaluminate ionic liquids are generally prepared by reaction of an organic halide salt with approximately 2 equivalents of aluminum chloride, as is illustrated in Scheme 2. The first equivalent of aluminum chloride is consumed by reaction with the chloride anion, and the resulting aluminum tetrachloride forms a complex with the remaining "active" aluminum chloride.[8] Hence, in an ionic liquid containing aluminum chloride and an organic halide salt in a 2:1 ratio, several chloroaluminate ions are in equilibrium with each other, of which the [Al_2Cl_7] anion is most prominent.[1,8] This situation has been verified by spectroscopic methods such as Raman[9] and ^{27}Al NMR [9–11] spectroscopies and FAB mass spectroscopy.[12] The ionic liquids employed in this study are shown in Table 1. The preparations[13,14] as well as a variety of applications of Lewis-acidic ionic liquids **2**[15] and **3**[16] have been documented. The fact that the most commonly used ionic liquids consist of imidazolium cations can be explained historically, since these were the first salts that were liquid at room temperature.[17] From an industrial point of view, however, imidazolium-based ionic liquids are too expensive to be used for most applications on large scale. In our study, ionic liquid **1**, based on the trimethylammonium cation, is compared with ionic liquids **2** and **3**. Ionic liquid **1** can be prepared from the readily available and very cheap precursor, trimethylammonium chloride, according to the same experimental procedure as described for **2** and **3**. The experimental procedure described in the literature involves addition of one solid to the other, which is accompanied by tremendous evolution of heat.[15,16] Although on such vigorous reactions can be carried out gram scale, it is not safe to follow this prescription on a larger laboratory scale or in an industrial reactor. We found that the preparation of ionic liquids **1–3** could be controlled very well when the organic halide salt (e.g., trimethylammonium chloride) was added portionwise to a suspension of aluminum chloride in dichloromethane. After stirring for 1 to 2 hours, a clear solution of ionic liquid in dichloromethane had formed. This ionic liquid solution could either be used as such, or the dichloromethane could be evaporated and the ionic liquid stored for later use. In this way, the preparation of ionic liquids **1–3** could be carried out safely on a scale varying between 5 g and 30 kg.



2 [BMIM][Al_2Cl_7]

Scheme 2. The preparation of the Lewis-acidic ionic liquid [BMIM]-[Al_2Cl_7] **2**

Table 1. Structure and physical properties of the ionic liquids prepared and used for this study

No	Structure		*Mw* (g/mol)	ρ (g/mL)	$c(Al_2Cl_7)$ (mol/L)
1	$Me_3\overset{+}{N}H\ \overset{-}{Al_2Cl_7}$	[TMAH][Al_2Cl_7]	362.27	1.23	3.4
2		[BMIM][Al_2Cl_7]	441.39	1.15	2.6
3		[EMIM][Al_2Cl_6I]	504.86	1.41	2.8

For our study it was advantageous to know the molarity of "active" aluminum chloride, present as the [Al_2Cl_7] anion, in the ionic liquids. The molarity of "active" aluminum chloride can be calculated from the density (ρ) and the molecular weight (Mw) of the ionic liquid according to:

$$c(Al_2Cl_7) = \rho/Mw$$

For ionic liquids **1–3** the molecular weights, the measured densities, and the deduced concentrations of "active" aluminum chloride are collected in Table 1.

Study of the Demethylation Conditions Using 4,5-Dimethoxyindanone as the Substrate

To shed light on the role and the amount of ionic liquid required for this reaction, we studied the influence of the number of equivalents of ionic liquid on the conversion of starting compound. This study was done by high-speed synthesis using an Anachem SK233 robot station. By utilizing the derived "active" aluminum chloride concentrations of ionic liquids **1–3** (Table 1), a series of experiments were performed by using a varying amount of ionic liquid. The conversion of the demethylation of 4,5-dimethoxyindanone was followed with time. The data obtained with ionic liquid **1** are plotted in the graph shown in Figure 1. From this graph, we conclude that approximately 3 equivalents of **1** are required to drive the selective demethylation of 4,5-dimethoxyindanone to completion. This proportion appeared to be independent of the ionic liquid deployed, as the same amount of ionic liquids **2** and **3** was required for this reaction. Conceivably, the reactivity of two equivalents of Lewis-acidic ionic liquid is diminished by coordination to oxygen atoms of the carbonyl and second methoxyl functions, respectively.

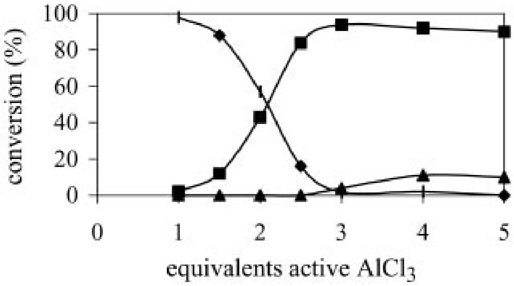


Figure 1. Demethylation of 4,5-dimethoxyindanone by [TMAH][Al_2Cl_7]; [(◆) 4,5-dimethoxyindanone, (■) 4-hydroxy-5-methoxyindanone, (▲) 5-hydroxy-4-methoxyindanone]

In another series of experiments, the activities of the ionic liquids shown in Table 1 and aluminum chloride were compared with each other in the demethylation of 4,5-dimethoxyindanone. This series shed light on the differences with regard to selectivity and reaction rate. With ionic liquids **1−3**, a virtually complete conversion was accomplished within 24 hours. For aluminum chloride, the reaction was stopped after 42 hours. Evidently, the rate of demethylation of 4,5-dimethoxyindanone is much higher when ionic liquids **1−3** are used instead of aluminum chloride. The graph shown in Figure 2 clearly points out that all the ionic liquids are much more selective than aluminum chloride in the demethylation of 4,5-dimethoxyindanone.

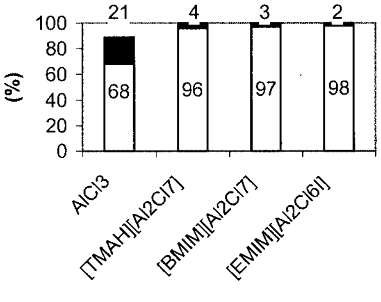
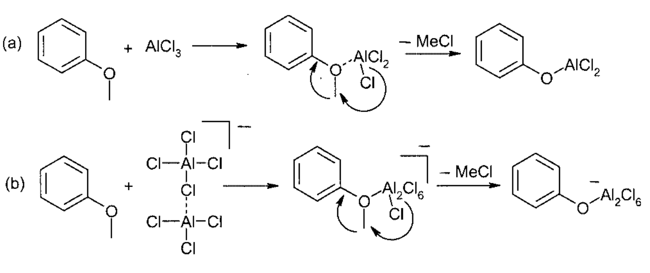


Figure 2. Comparison of the selectivity of ionic liquids **1−3** and $AlCl_3$ in the demethylation of 4,5-dimethoxyindanone. [(□) 4-hydroxy-5-methoxyindanone, (▲) 5-hydroxy-4-methoxyindanone]

With respect to reaction rates and selectivities, ionic liquids **1−3** show nearly identical performances. Considering the much-lower cost of **1** in comparison to **2** and **3**, we conclude that [TMAH][Al_2Cl_7] is the preferred ionic liquid for industrial applications.

The observation that demethylation with ionic liquid is so much faster, than in case when aluminum chloride is used, can be explained mechanistically. The underlying mechanisms of demethylation by ionic liquid and aluminum chloride are identical (Scheme 3). The first step of the demethylation is coordination of aluminum chloride, or the chloroaluminate anion of the ionic liquid, to the oxygen atom of the methoxyl function. This coordination activates the bond between the methyl group and the oxygen atom. This process is followed by attack of a chloride anion to the methyl carbon atom, which is the rate-determining step of the process. This rate-determining step is promoted by a higher concentration of chloride ions. In the ionic liquid, the concentration of chloride ions is much higher than in a solution of aluminum chloride because of the presence of 1 equivalent of $AlCl_4$ for each equivalent of "active" aluminum chloride. In addition, the nucleophilicity of the chloride ions may be enhanced in ionic liquid because of their weaker coordination to anionic chloroaluminate species.



Scheme 3. Demethylation with $AlCl_3$ (a) and ionic liquid (b)

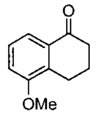
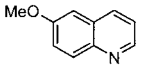
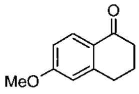
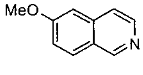
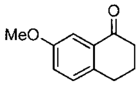
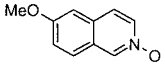
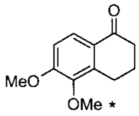
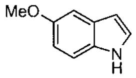
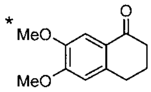
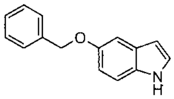
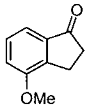
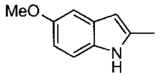
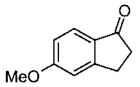
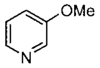
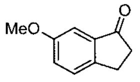
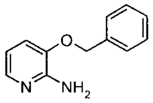
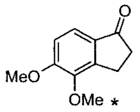
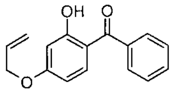
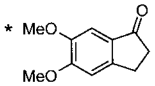
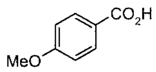
The Scope of the Ionic Liquid-Mediated Ether Cleavage Reaction

Next, the scope of the ether cleavage reaction was explored by subjecting a series of mono- and dimethoxyaromatic compounds, as well as aromatic benzyl and allyl ethers, to [TMAH][Al_2Cl_7]. The performance of [TMAH][Al_2Cl_7] was compared to that of aluminum chloride. The results are collected in Table 2.

Remarkably, although most of the methoxyaromatic compounds were virtually unreactive towards aluminum chloride, demethylation readily took place using the ionic liquid [TMAH][Al_2Cl_7] as demethylating agent. With dimethoxytetralones (entries 4 and 5), the selectivity and yield obtained were similar for reactions conducted with either aluminum chloride or the ionic liquid. The selectivity of the demethylation of dimethoxyindanones (entries 9 and 10) revealed a more confusing picture. For 4,5-dimethoxyindanone, the highest selectivity was obtained with the ionic liquid. In contrast, the selectivity in the reaction of 5,6-dimethoxyindanone was best with aluminum chloride.

As is evident from Table 2, demethylation by the ionic liquid reagent [TMAH][Al_2Cl_7] is compatible with a variety of heterocycles and functional groups. Clearly, the presence of amine, amidine, hydroxyl, keto, and carboxylate functions do not disturb ether cleavage. Interestingly, as shown by entries 15, 18 and 19, allyl and benzyl ethers can also be cleaved employing [TMAH][Al_2Cl_7] as the ether-cleaving agent.

Table 2. Cleavage of aromatic methyl, allyl and benzyl ethers by [TMAH][Al_2Cl_7] (I.L.)[a]

Entry	Substrate	Conversion (%)[b]		Entry	Substrate	Conversion (%)[b]	
		I.L.	$AlCl_3$			I.L.	$AlCl_3$
1		99	0	11		99	36
2		99	63	12		99	0
3		99	9	13		99	0
4		97 (99:1)	97 (99:1)	14		99	0
5		99 (99:1)	97 (99:1)	15		99	0
6		99	0	16		90	0
7		99	56	17		99	99
8		99	0	18		99	0
9		99 (96:4)	89 (70:30)	19		99	72
10		99 (50:50)	91 (90:10)	20		99	0

[a] For entries 1−10 we have proven that [TMAH][Al_2Cl_7] works equally well as [BMIM][Al_2Cl_7]. [b] The conversion was determined after workup by GC and NMR spectroscopy. * Indicates which methoxyl group is cleaved predominantly in the dimethoxyaromatic compounds. The ratio of regioisomers is shown in brackets below the conversion.

Concluding Remarks

Lewis-acidic chloroaluminate ionic liquids constitute a novel class of reagents that are highly effective in the cleavage of aromatic methyl ethers. We have shown that the ionic liquid [TMAH][Al_2Cl_7] exhibits the same reactivity as its more commonly used imidazolium analogs. Since [TMAH]-[Al_2Cl_7] can be prepared in one step from readily available and cheap starting materials, viz. trimethylammonium chloride and aluminum chloride, this ionic liquid does not endanger the economy of the process. Therefore, this ionic liquid seems to be preferred from an industrial point of view. We have presented an upscalable method for the preparation of [TMAH][Al_2Cl_7] and its imidazolium analogs. This method involves addition of trimethylammonium chloride to a suspension of aluminum chloride in dichloromethane, followed by evaporation of the solvent to obtain the ionic liquid in a pure form. The ionic liquid solution can also be used as such for the demethylation reaction.

Surprisingly, selective methyl ether cleavage was observed when 4,5-dimethoxyindanone was treated with [TMAH][Al_2Cl_7] in dichloromethane giving a 96:4 mixture of the pharmaceutically interesting intermediate, 4-hydroxy-5-methoxy-indanone, and its regioisomer. On the contrary, aluminum chloride displayed a very poor regioselectivity in this reaction, resulting in a 7:3 mixture of regioisomers.

Ether cleavage by [TMAH][Al_2Cl_7] was elaborated using several heterocyclic aromatic compounds bearing a variety of functional groups. We have demonstrated that the ionic liquid-mediated ether cleavage is widely applicable. Besides methyl ethers, the ionic liquid reagent also cleaves allyl and benzyl ethers effectively.

In summary, the ionic liquid [TMAH][Al_2Cl_7] can be employed both on laboratory scale and on large scale as an ether-cleaving agent that, with regard to reactivity, is superior to its conventional solid counterpart, aluminum chloride.

Experimental Section

General Remarks: Reactions were monitored on an HP 6890 Series GC and TLC (silica gel). The NMR spectra were recorded on a Bruker DPX-400. Mass spectrometry was performed on a PE Sciex API 165. An Anachem Sk233 Workstation equipped with a Stem RS1000 10 position reactor block was used for the High Speed Experimentation (HSE).

***N*-Butyl-*N*-methylimidazolium Chloride:** A mixture of *N*-methylimidazole (100 g, 1.22 mol) and *n*-butyl chloride (113 g, 1.22 mol) was stirred and heated at 70 °C for 96 h. The reaction mixture was cooled to ambient temperature. The viscous oil was washed three times with ethyl acetate and then the ethyl acetate remaining was removed in vacuo. The resulting oil crystallized as a white solid. Yield: 210 g (98%). NMR (D_2O): $\delta = 8.6$ (s, 1 H), 7.3 (d, 2 H), 4.1 (t, 2 H), 3.8 (s, 3 H), 1.8 (m, 2 H), 1.2 (m, 2 H), 0.8 (t, 3 H) ppm.

***N*-Ethyl-*N*-methylimidazolium Iodide:** *N*-Methylimidazole (32.9 g, 0.4 mol) and ethyl iodide (38.4 mL, 0.48 mol) were dissolved in dichloromethane (100 mL) and heated under reflux for 18 h. The remaining dichloromethane and ethyl iodide were evaporated. The crude product was stirred in diethyl ether and the white crystals that formed were collected by filtration. Yield: 93.3 g (98%). NMR (D_2O): $\delta = 8.6$ (s, 1 H), 7.3 (s, 2 H), 4.1 (q, 2 H), 3.8 (s, 3 H), 1.4 (t, 3 H) ppm.

[TMAH][Al_2Cl_7] (1): Aluminum chloride (173 g, 1.3 mol) was suspended in dichloromethane. The suspension was cooled with an ice bath, and trimethylammonium chloride (62 g, 0.65 mol) was added with stirring. After the addition, the reaction mixture was warmed to ambient temperature and was stirred for 2 h. The clear yellow solution of ionic liquid could be used as such. To obtain the ionic liquid in a pure form, the dichloromethane was evaporated. Yield: 235 g (99%).

The density of the liquid was determined by accurately measuring the weight of 10 mL of sample, and was found to be 1.23 g/mL.

[BMIM][Al_2Cl_7] (2): *N*-Butyl-*N*-methylimidazolium chloride (5 g, 28.6 mmol) was stirred under a stream of nitrogen gas while being cooled with an ice bath. Aluminium chloride was added in small portions to the stirred powder. A highly exothermic reaction took place. After all the aluminium chloride (7.1 g, 53.2 mmol) had been added, the cooling was removed and the reaction mixture was warmed to ambient temperature. This process yielded a yellow liquid (12.1 g, 99%). The density of the liquid was determined by accurately measuring the weight of a 10 mL sample, and was found to be 1.15 g/mL.

[BMIM][Al_2Cl_7] could also be prepared using dichloromethane as a solvent, as described above for [TMAH][Al_2Cl_7].

[EMIM][Al_2Cl_6I] (3): Powdered *N*-ethyl-*N*-methylimidazolium iodide (50 g, 0.21 mol) was stirred and cooled with an ice bath under a flow of nitrogen gas and then powdered aluminium chloride (53.2 g, 0.4 mol) was added in small portions. The cooling bath was removed and after stirring for 1 h, a brown liquid had formed. Yield: 103 g (99%).

The density of the liquid was determined by accurately measuring the weight of 10 mL of sample, and was found to be 1.41 g/mL.

[EMIM][Al_2Cl_6I] could also be prepared by using dichloromethane as a solvent according to the method described for [TMAH][Al_2Cl_7].

Robot Experiments

The solvent for the system was dichloromethane. Reactions were carried out in septum-sealed reactor tubes under a flow of nitrogen. Tubes were dried before use by heating to 150 °C and then cooling under nitrogen. Generally, the starting material (200 mg) was dissolved in dichloromethane such that the total volume including the ionic liquid was 8 mL. To this solution, ionic liquid (**1**, **2**, or **3**) was added dropwise and $AlCl_3$ (3 equiv.) was added manually in portions. The reaction mixture was warmed to 38 °C. Samples were taken after 8, 16, 24, and 48 h. Samples (10 µL) were taken by aspiration of the reaction mixture, and were quenched in 50% saturated NaCl solution/1 N HCl and extracted with ethyl acetate (800 µL). The samples were analyzed off-line by GC.

Laboratory Experiments. General Procedure for Entries 1−20 of Table 2: The substrate was dissolved in dichloromethane (1 g/40 mL). To the stirred solution, ionic liquid (3 equiv. of [TMAH][Al_2Cl_7]) was added dropwise. The reaction mixture was warmed to reflux. The reactions were monitored by GC and TLC. After the reaction was complete, the mixture was poured into dilute hydrochloric acid (1 M). The aqueous layer was extracted three times with ethyl acetate. The ethyl acetate was washed with saturated $NaHCO_3$ and brine, and then the ethyl acetate was dried with $MgSO_4$ and the solvents were evaporated.

In cases where the substrate had basic functional groups, the reaction mixture was poured into water. The aqueous layer was neutralized with a NaOH solution (1 M). The aqueous layer was extracted three times with ethyl acetate, and then the ethyl acetate was washed with brine, dried with $MgSO_4$, and the solvents were evaporated.

4-Hydroxy-5-methoxyindanone. Large-Scale Procedure: A solution of [BMIM][Al_2Cl_7] (250 mL, 2.5 equiv.) in dichloromethane (1 L) was added dropwise to a solution of 4,5-dimethoxyindanone (50 g, 0.26 mol) in dichloromethane (500 mL). The reaction mixture was stirred for 23 h at 40 °C. The reaction mixture was poured into a mixture of water (4 L) and concentrated hydrochloric acid (0.6 L). The aqueous layer was extracted three times with dichloromethane. The organic layer was subsequently dried with $MgSO_4$ and the solvents were evaporated. This process yielded the crude product (45 g, 97%). After recrystallization from a mixture of heptane and ethyl acetate (3:2), the purified product (37 g, 80%) was obtained. The product had a purity of 99.2% according to HPLC. NMR ($CDCl_3$) was in agreement.

This procedure was also followed using [TMAH][Al_2Cl_7] (191 mL, 2.5 equiv.), which gave a similar result.

6,7-Dihydroxytetralone: [TMAH][Al_2Cl_7] (2.5 mL) was added to (3,4-dimethoxyphenyl)butanoic acid (200 mg, 0.893 mmol). No cyclization was observed by TLC after 1 h of reaction time. The temperature was raised to 60 °C, but again no cyclization was observed at this temperature. The solution was then heated to 150 °C overnight. The reaction mixture was cooled and hydrochloric acid (1 M, 15 mL) was added. The reaction mixture was stirred for 30 minutes. The aqueous layer was extracted three times with ethyl acetate. The ethyl acetate phase was washed with saturated aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, and then the solvents were evaporated. This process yielded 6,7-dihydroxytetralone (80 mg, 50%), as was confirmed by NMR spectroscopy ($CDCl_3$ or CD_3OD).

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