Electrogenerated Lewis Acid-Catalyzed Claisen Rearrangement of Allyl Aryl Ethers

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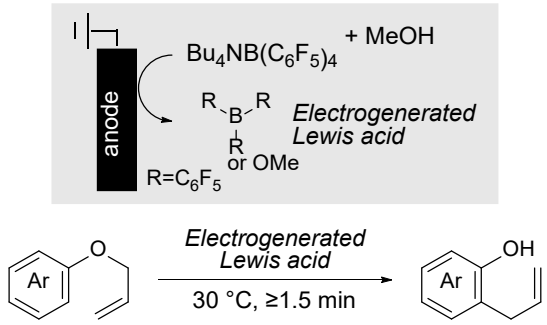
Supporting Information Placeholder



ABSTRACT: Catalysts for Claisen rearrangement have been intensively studied to overcome the need for a high temperature. However, previous studies have encountered challenges, such as the need for heating, a long reaction time and/or the need for equivalent amounts of catalyst. In this study, we introduce an effective electrogenerated boron-based Lewis acid catalyst for the aromatic Claisen rearrangement, which proceeds in a few minutes at ambient temperature. Generation of the electrogenerated Lewis acid catalyst is discussed based on NMR analysis and DFT calculations.

Claisen rearrangement is one of the most widely used reactions in organic synthesis.[1,2] However, the inherent nature of this reaction requires a high temperature, leaving room for improvement. In the past century, catalysts for Claisen rearrangement have been actively studied, and various Lewis acids have been shown to catalyze this reaction.[3,4] The first reported example used a BF_3–acetic acid complex, where the reaction proceeded below 80 °C in 10 minutes.[10] Subsequent research demonstrated that the use of BCl_3 as a catalyst allowed the reaction to occur under milder conditions, specifically at 10 °C within 30 minutes.[11] Despite its utility, BCl_3 poses significant practical challenges due to its rapid decomposition in the presence of moisture and the need for a stoichiometric amount of the catalyst. Given these limitations, numerous Lewis acid catalysts have been developed (Figure 1a).[3-9] However, many of these catalysts still require heating, a long reaction time, and/or stoichiometric loading of the catalyst, and have not yet surpassed BCl_3 in terms of catalytic activity for the Claisen rearrangement. Brønsted acids can also catalyze the reaction, but they often lead to an overreaction, producing dihydrobenzofuran as a major product (Figure 1b).[12-20] Another variation that can provide mild reaction conditions is photo-Claisen rearrangement.[21-23] Despite its simplicity, which only requires irradiation by light, it frequently suffers from low regioselectivity between *ortho* and *para* products, along with generation of deallylated phenol.

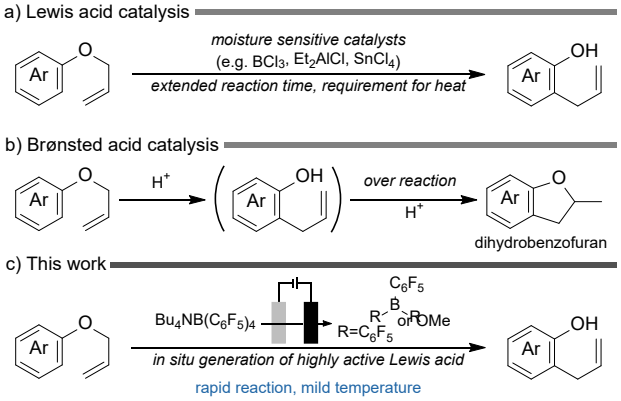


Figure 1. (a) Conventional Lewis acid-catalyzed Claisen rearrangement. (b) Conventional Brønsted acid-catalyzed Claisen rearrangement. (c) Harnessing the electrogenerated Lewis acid to enable rapid Claisen rearrangement at mild temperature.

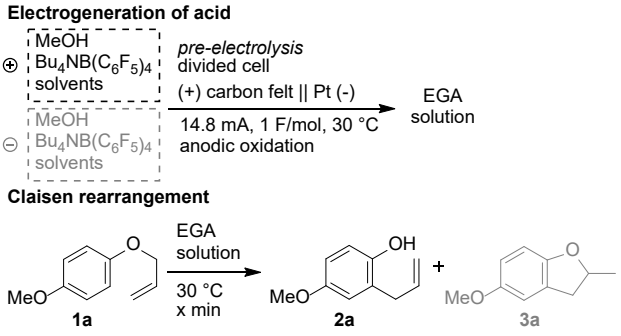
To address these challenges, we explored the use of electrogenerated acids as an alternative approach. Traditionally, electrogenerated acids have been considered a type of Brønsted acid, generated by the oxidation of trace amounts of water or alcohol if used as a solvent in the system.[24-34] The strength of these acids depends on the type of counter anion used as the electrolyte. Recent studies have shown that use of the specific electrolyte $Bu_4NB(C_6F_5)_4$ can significantly enhance reactions that proceed

poorly with other electrolytes, albeit the reason was not clear.[35,36]

Building on these insights, we reconsidered the active species of electrogenerated acid from $Bu_4NB(C_6F_5)_4$, and hypothesized the generation of highly active boron-based Lewis acid (Figure 1c).[37] Herein, we show that this hypothesis could be rationalized by nuclear magnetic resonance (NMR) analysis combined with density functional theory (DFT) calculations, representing the first electrogenerated Lewis acid without the use of specific electrodes or ionic liquids,[38-40] highlighting its potential as a novel catalytic approach. Additionally, using this acid, aromatic Claisen rearrangement could be effectively catalyzed, while mitigating the moisture sensitivity associated with the conventional borane catalysts.

We commenced the experimental investigation by reacting allyl 4-methoxyphenyl ether (**1a**) with electrogenerated acid from $Bu_4NB(C_6F_5)_4$ in different solvents (Table 1). Pre-electrolysis, a procedure for the electrogeneration of acids, was conducted in a divided cell with both the anodic and cathodic chambers charged with MeOH (0.42 mmol), $Bu_4NB(C_6F_5)_4$ (0.64 mmol) and solvent (6.4 mL), with an applied charge of 1 F/mol (based on MeOH). When CH_2Cl_2 was used as a solvent, when the generated acid was reacted with **1a**, 27% of rearrangement product **2a**, along with 6% of dihydrobenzofuran **3a**, were obtained within 20 minutes at 30 °C (entry 1). On the other hand, with CH_3NO_2 as a solvent, no rearrangement product **2a** was obtained, and instead dihydrobenzofuran **3a** was obtained in 51% yield through cyclization of **2a** (entry 2, see the Supporting Information for the time course of the reaction). Since cyclization of **2a** to **3a** mainly occurs in the presence of a Brønsted acid,[12-20] the obtained results suggest the generation of Lewis acid in CH_2Cl_2 and Brønsted acid in CH_3NO_2. With CH_3CN as the solvent, no reaction occurred, as the reactivity of the electrogenerated acid was impaired by the coordinating property of CH_3CN (entry 3). Further reducing the reaction time with CH_2Cl_2 solvent increased the yield of **2a** to 41% (entry 4).

Table 1. Effect of the Solvent on the Electrogenerated Acid-Catalyzed Claisen Rearrangement of Allyl 4-Methoxyphenyl Ether 1a[a]

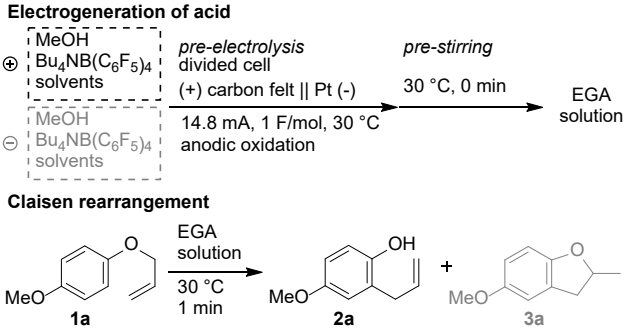


entry	solvents	reaction time (x min)	2a[b]	3a	1a
1	CH_2Cl_2	20 min	27%	6%	trace
2[c, d]	CH_3NO_2	20 min	0%	51%	1%
3	CH_3CN	20 min	0%	0%	99%
4	CH_2Cl_2	1 min	41%	trace	trace

[a] Electrogeneration of the acid was performed with MeOH (0.42 mmol) and $Bu_4NB(C_6F_5)_4$ (0.64 mmol) in 6.4 mL of solvent. Subsequent Claisen rearrangements were performed on a 0.3 mmol scale with 3 mL of the EGA solution. [b] The yields were determined by ^1H NMR analysis using mesitylene as an internal standard. [c] The yields were determined by GC analysis using dodecane as an internal standard. [d] Deallylated 4-methoxyphenol was detected in 33% yield.

Based on these initial findings, the reaction parameters were carefully tuned (Table 2). First, the applied charge was increased to 2 F/mol, followed by an additional 3.3 hours of stirring (pre-stirring). These adjustments increased the yield of **2a** to 55%, which can be attributed to the complete consumption of MeOH to avoid deactivation of the generated Lewis acid and ensure sufficient time for its generation (entry 2, see the Supporting Information for details). Next, removal of MeOH from the cathodic chamber increased the mass balance (entry 3). The divided cell used for the reaction separates the anodic and cathodic chamber with a glass filter (4G), and a trace amount of solution is transferred between the two chambers. Thus, contamination of electrogenerated base, methoxide generated by the cathodic reduction of MeOH, leads to side reactions that decrease the mass balance.[41] Finally, extending the reaction time for Claisen rearrangement to 3 min completely consumed the starting material **1a** to afford **2a** in 72% yield (entry 4).

Table 2. Optimization of the Reaction Parameters[a]



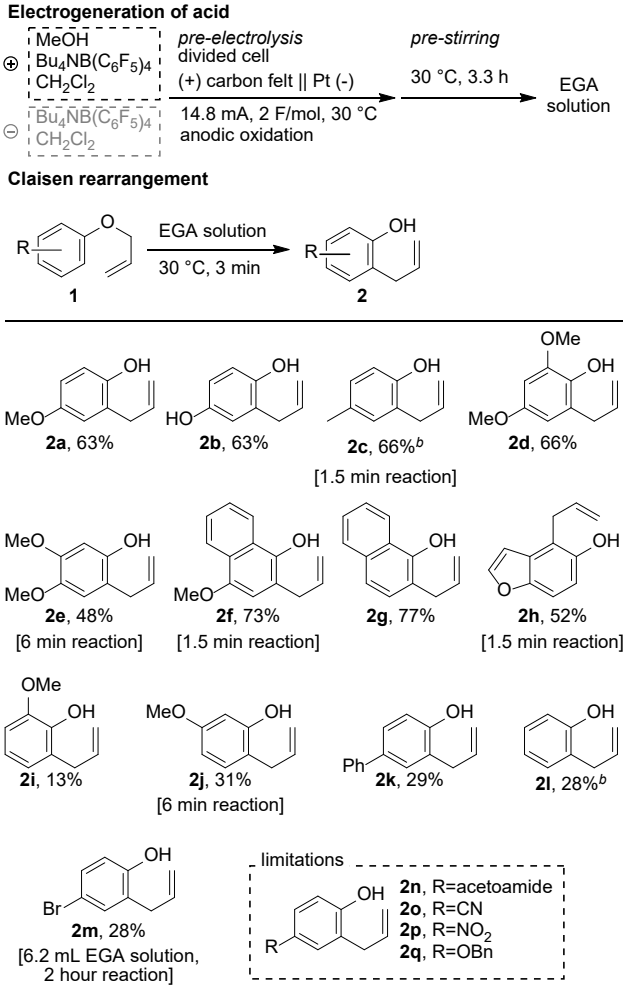
entry	change from initial condition	2a[b]	3a	1a
1	none	41%	trace	trace
2	2 F/mol pre-electrolysis 3.3 h pre-stirring	55%	2%	9%
3	2 F/mol pre-electrolysis 3.3 h pre-stirring no MeOH in the cathodic chamber 1.5 min Claisen rearrangement	55%	trace	37%
4	**2 F/mol pre-electrolysis 3.3 h pre-stirring no MeOH in the cathodic chamber 3 min Claisen rearrangement**	**72% (63%)[c]**	**3%**	**5%**

[a] Electrogeneration of the acid was performed with MeOH (0.42 mmol) and $Bu_4NB(C_6F_5)_4$ (0.64 mmol) in 6.4 mL of CH_2Cl_2. Subsequent Claisen rearrangements were performed on a 0.3 mmol scale with 3 mL of the EGA solution. [b] The yields were determined

by ^{1}H NMR analysis using mesitylene as an internal standard. [c] Isolated yield.

With the optimized conditions in hand, we investigated the substrate scope of this method (Scheme 1). First, the *para* position of the aryl moiety of allyl aryl ether was varied. Electron-donating groups, such as methoxy (**1a**), hydroxy (**1b**) and methyl (**1c**), reacted smoothly to furnish the corresponding products (**2a**-**2c**) with yields ranging from 63% to 66%.The reaction also proceeded well with 2,4-dimethoxy (**1d**) and 3,4-dimethoxy (**1e**) substituents. π-Extended substrates such as 1-(allyloxy)-4-methoxynaphthelene (**1f**), 1-(allyloxy)naphthalene (**1g**) and 5-(allyloxy)benzofuran (**1h**) were also amenable to this reaction (**2f**-**2h**, 52-77%). Allyl 2-methoxyphenyl ether (**1i**), allyl 3-methoxyphenyl ether (**1j**), allyl 4-phenylphnyl ether (**1k**) and allyl phenyl ether (**1l**) were tolerable, albeit they resulted in lower yields. Coordination of the product phenol to the Lewis acid catalyst renders the *para* position of the hydroxy group cationic, which would lead to polymerization with compounds not possessing a substituent at this site. As for an electron-withdrawing substrate, *para*-Br (**2m**) gave the corresponding product in 28% yield after an extended reaction time, with an increased amount of electrogenerated Lewis acid solution. On the other hand, substrates with an acetoamide- (**1n**), cyano- (**1o**), nitro- (**1p**) or benzyloxy- (**1q**) group at the *para* position of the allyloxy group did not give the rearrangement products.

Scheme 1. Scope of Electrogenerated Lewis Acid-Catalyzed Claisen Rearrangement of Allyl Aryl Ether[a]



[a] Electrogeneration of the acid was performed with MeOH (0.42 mmol) and $Bu_4NB(C_6F_5)_4$ (0.64 mmol) in 6.4 mL of CH_2Cl_2. Subsequent Claisen rearrangement was performed on a 0.3 mmol scale with 3 mL of EGA solution. [b] ^{1}H NMR yield. Isolation led to a diminished yield.

Next, we focused our attention on elucidating the electrogenerated Lewis acid. First, direct ^{1}H and ^{11}B NMR analyses of the electrogenerated acid solution from the pre-electrolysis of MeOH and $Bu_4NB(C_6F_5)_4$ in CH_2Cl_2 was conducted (Figure 2). The ^{1}H NMR spectra show the generation of aromatic compounds aside from the signals of tetrabutylammonium. Considering the multiplicity of the signals, they could be attributed to the signal of pentafluorobenzene. Additionally,^{11}B NMR spectra showed three evenly spaced signals at δ 59.5, 40.9 and 22.3 ppm, along with the signal of $Bu_4NB(C_6F_5)_4$ (signal at 0.9 ppm was assigned to the water adduct of $B(C_6F_5)_3$; see the Supporting Information for details). The signal at δ 59.5 ppm was assigned to the boron of $B(C_6F_5)_3$ according to the literature.[42] Considering the reaction system, the signals at δ 40.9 and 22.3 ppm could be attributed to $MeOB(C_6F_5)_2$ and $(MeO)_2B(C_6F_5)$, respectively, which were consistent with the computational prediction of the chemical shift using DFT calculations (see the Supporting Information).[43] From the above, electrogenerated acid from $Bu_4NB(C_6F_5)_4$ in CH_2Cl_2 was rationalized to be a boron-based Lewis acid. We believe that the highly acidic nature of the electrogenerated Brønsted acid from the anodic oxidation of MeOH plays a vital role in this transformation. With these observations, the present Claisen rearrangement was estimated to follow the conventional Lewis acid catalyzed reaction mechanism.[3,4]

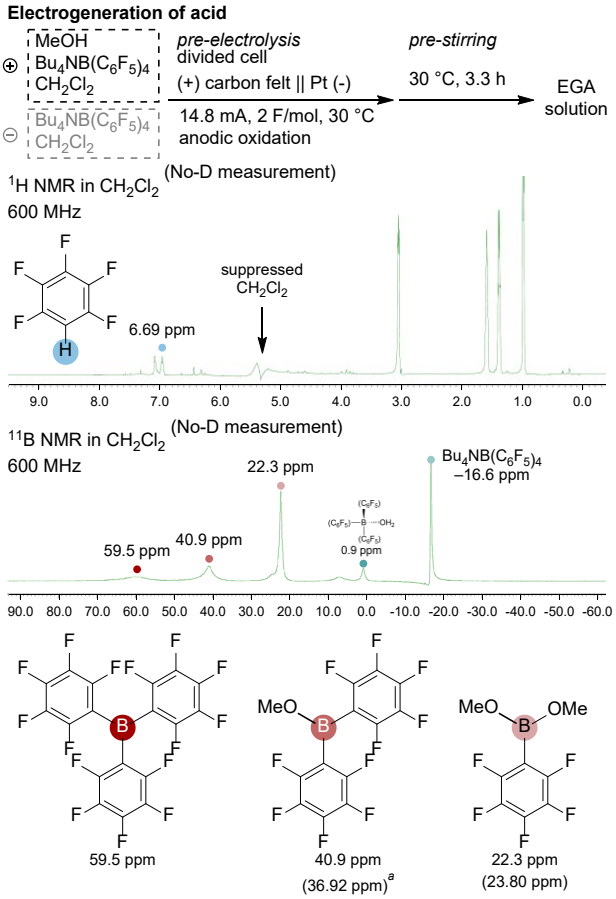


Figure 2. ^{1}H and ^{11}B NMR analyses of EGA solution in CH_2Cl_2. [a] Calculated chemical shifts are shown in parenthesis.

To explain the importance of using CH_2Cl_2 for the electrogenerated Lewis acid, ^1H and ^{11}B NMR analyses were conducted for electrogenerated acid from MeOH and $Bu_4NB(C_6F_5)_4$ in CH_3NO_2 (Figure 3). Although the ^1H NMR spectra showed signals that can be assigned to pentafluorobenzene, ^{11}B NMR showed no signals that can be assigned to $B(C_6F_5)_3$, $MeOB(C_6F_5)_2$ or $(MeO)_2B(C_6F_5)$; instead, a disparate signal emerged at δ 3.5 ppm. The chemical shift of boranes is known to make an upfield shift upon changing its geometry from trigonal planar to tetrahedral. Additionally, the signal of H_2O adduct of $B(C_6F_5)_3$ emerges at δ −0.6 ppm. Thus, this upfield shift giving a signal at δ 3.6 ppm is a prospective change of the geometry to tetrahedral, which seems to be the CH_3NO_2 adduct of $B(C_6F_5)_3$. Altogether, we have reasoned that the boron-based Lewis acid can be generated with solvents other than CH_2Cl_2, but coordination of the solvent reduces its Lewis acidity.

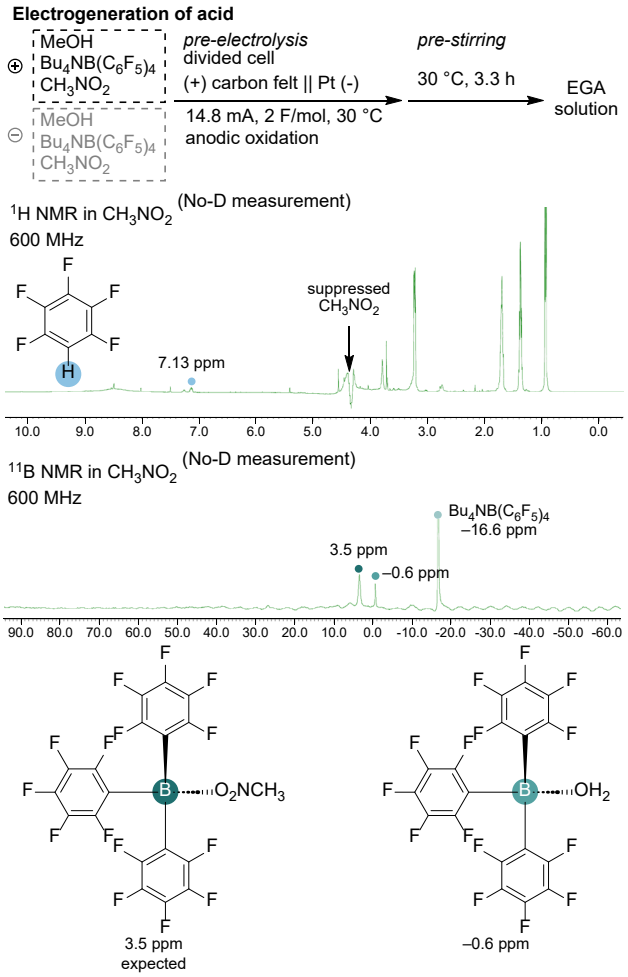


Figure 3. ^1H and ^{11}B NMR analyses of EGA solution in CH_2Cl_2

In summary, we have found that electrogenerated Lewis acid can effectively catalyze Claisen rearrangement of allyl aryl ether, producing the desired product in 1.5 min at 30 °C under the best conditions. Additionally, ^1H and ^{11}B NMR analyses and DFT calculations have unveiled the active species of the electrogenerated acid from $Bu_4NB(C_6F_5)_4$ in CH_2Cl_2: $B(C_6F_5)_3$, $MeOB(C_6F_5)_2$ and $(MeO)_2B(C_6F_5)$. Although stoichiometric use of BCl_3 can achieve the title transformation, our electrochemical method can generate the highly active borane species *in situ* avoiding decomposition by moisture. Additionally, this is the first time that the properties of Lewis acid generated by anodic oxidation have been confirmed. This report demonstrates the utility of a strong Lewis acid without using specific electrodes or ionic liquids, highlighting its potential as a new catalytic approach.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

Additional experimental details, materials, and methods, including NMR spectra for all compounds (PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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