



Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Lewis acid-assisted *N*-fluorobenzenesulfonimide-based electrophilic fluorine catalysis in Beckmann rearrangement

Fukai Xie^{a,b,1}, Chuan Du^{a,b,1}, Yadong Pang^{a,b}, Xu Lian^a, Chentao Xue^a, Yanyu Chen^a, Xuefei Wang^a, Maosheng Cheng^a, Chun Guo^{a,*}, Bin Lin^{a,*}, Yongxiang Liu^{a,b,*}

^a Key Laboratory of Structure-Based Drug Design and Discovery (Shenyang Pharmaceutical University), Ministry of Education, Shenyang 110016, PR China

^b Faculty of Wu Ya, Shenyang Pharmaceutical University, Shenyang 110016, PR China

ARTICLE INFO

Article history:

Received 11 September 2016

Revised 12 November 2016

Accepted 14 November 2016

Available online xxxxx

Keywords:

N-Fluorobenzenesulfonimide

Beckmann rearrangement

Lewis acid assistance

Electrophilic fluorine catalysis

ABSTRACT

A microwave-assisted *N*-fluorobenzenesulfonimide (NFSI)/Lewis acid-catalyzed Beckmann rearrangement was developed. The remarkable promotion to the electrophilicity of NFSI by Lewis acids was illustrated utilizing a series of readily available oxime substrates. The action model between NFSI and Lewis acids was probed by control experiments and theoretical calculations.

© 2016 Elsevier Ltd. All rights reserved.

N-Fluorobenzenesulfonimide (NFSI) is a commercially available, cheap, stable, and easy-to-handle solid compound, which was first synthesized by Differding and Ofner in 1991.¹ As a source of fluorine cation (F⁺), NFSI was originally used as an electrophilic fluorinating reagent.² NFSI also served as an oxidant to generate high-oxidation-state metal complexes in transition-metal catalyzed reactions.³ Recently, NFSI has been employed as a nucleophilic nitrogen or nitrogen radical in many C–N bond formation reactions.⁴ NFSI showed strong electrophilicity owing to the existence of a fluorine cation, which made it a potential non-metallic Lewis acid. However, there were no reports on the Lewis acidity of NFSI in catalyzing organic transformations until our group reported the Meyer-Schuster rearrangement catalyzed by NFSI with the aid of samarium(III) triflate early this year.⁵

Beckmann rearrangement is an acid-catalyzed transformation of oxime to amide in organic synthesis.⁶ Traditionally, Beckmann rearrangement was performed under the catalysis of strongly acidic and dehydrating media such as sulphuric acid,⁷ phosphorus pentachloride⁸ and the mixture of acetic acid, acetic anhydride and hydrogen chloride.⁹ Mild conditions were also developed, which mainly included silica gel^{10a,b} and zeolite-based catalysts,^{10c} metallic Lewis acids^{10d–f} and solid acid catalysts.^{10g,h} Beckmann

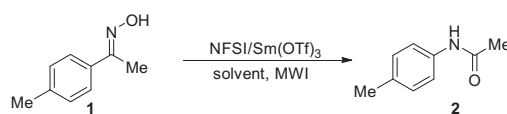
rearrangement in supercritical water¹¹ or ionic liquids media¹² was studied as well. Organocatalysts were also utilized as efficient catalysts in Beckmann rearrangement.¹³ Because of the importance of the products derived from Beckmann rearrangement, continuous efforts on developing facile and robust conditions for this transformation have been made.

Our group recently has introduced a new catalytic system resulted from the combination of NFSI and rare earth metal triflates such as samarium(III) triflate [Sm(OTf)₃] in catalyzing Meyer-Schuster rearrangement, which was featured as mild reaction conditions, short reaction time and simple experimental procedures.⁵ The discovery of the new function of NFSI inspired us to investigate the unique catalytic system in certain Lewis acids catalyzed transformations especially those with harsh conditions and to identify the true catalytic species. In the present study, we aimed at the development of NFSI/Lewis acids system in catalyzing Beckmann rearrangement and the detection of the detailed mechanistic interactions between NFSI and Lewis acids.

An oxime substrate **1** was synthesized firstly to screen the conditions for Beckmann rearrangement under the microwave irradiation. It was found that Sm(OTf)₃ or NFSI alone was not an effective catalyst in catalyzing the transformation (Table 1, entries 1–2). In contrast, a combination of NFSI and Sm(OTf)₃ (1 mol%) could catalyze the reaction to provide the product with excellent isolated yield at 100 °C for 10 min using acetonitrile as the solvent (Table 1, entries 3–4). Decreasing of the catalytic loading of NFSI to 10 mol% or 5 mol% resulted in lower yields (Table 1, entries 5–6).

* Corresponding authors at: Key Laboratory of Structure-Based Drug Design and Discovery (Shenyang Pharmaceutical University), Ministry of Education, Shenyang 110016, PR China (Y. Liu).

¹ These authors contributed equally.

Table 1
Screening of the reaction conditions.

Entry	Solvent	NFSI loading (mol%)	Lewis acid loading (mol%)	Temp (°C)	Time (min)	Yield ^a (%)
1	CH ₃ CN	0	1	100	10	11
2	CH ₃ CN	15	0	100	10	30
3	CH ₃ CN	25	1	100	10	95
4	CH ₃ CN	15	1	100	10	93
5	CH ₃ CN	10	1	100	10	77
6	CH ₃ CN	5	1	100	10	13
7	CH ₃ CN	15	5	100	10	96
8	CH ₃ CN	10	5	100	10	80
9	CH ₃ CN	5	5	100	10	47
10	CH ₃ CN	15	1	100	150	93 ^b
11	THF	15	1	100	30	10
12	DCE	15	1	100	30	80
13	toluene	15	1	100	30	7

Note:

^a Run on a 0.2 mmol scale and isolated yield.^b Run with heating.

Increasing of the Sm(OTf)₃ loading afforded no dramatic improvement in yield (Table 1, entries 7–9). The reaction could be performed with heating by prolonging reaction times (Table 1, entry 10). In screening solventssuch as tetrahydrofuran (THF), dichloroethane (DCE) and toluene, it was observed that DCE could also act as an effective solvent, while THF and toluene were not the optimal choices (Table 1, entries 11–13).

With the optimized conditions in hand, a library of oxime compounds was synthesized with structural and electronic modifications to examine the scope of the NFSI/Sm(OTf)₃ system in catalyzing Beckmann rearrangement. 1-(Aryl)ethanone oximes **1a–1e** were prepared firstly and subjected to the optimal conditions. All the tested substrates gave the *N*-(aryl)acetamide products **2a–2e** in moderate to excellent yields regardless of the aryl rings bearing electron-rich or electron-deficient substitutions (Table 2, entries 1–5). The symmetrical bis(aryl)methanone oxime substrates **1f–1i** were then examined under the standard conditions and corresponding *N*-(aryl)benzamides products **2f–2i** were obtained in excellent yields (Table 2, entries 6–9). The substrates of unsymmetrical bis(aryl)methanone oximes **1j–1k** gave the electron-rich phenyl ring migration *N*-(aryl)benzamide products **2j–2k** as the major products, accompanied with about 30% electron-deficient phenyl ring migration *N*-(aryl)benzamide products (Table 2, entries 10–11).

It is worth mentioning that the reaction could also proceed smoothly under neat conditions without losing any efficiency (Scheme 1). And the reaction temperature could be decreased to 80 °C or 60 °C by prolonging reaction time accompanied by slightly lower yield. The reaction could be performed on a gram scale by heating for relatively longer reaction time.

In order to gain insights into the new catalytic system, we turned towards the evaluation of some available Lewis acid with the combination of NFSI in catalyzing Beckmann rearrangement. Firstly, several rare earth metal triflates were investigated. It was shown that they could catalyze the transformation in about 10% yield in the absence of NFSI, consistent with the result of samarium(III) triflate without addition of NFSI. However, when a mixture of 15 mol% NFSI and 1 mol% rare earth metal triflates was used, the yield was improved significantly (Table 3, entries 1–4). Some non-active Lewis acids with chloride as counterions were also examined.

When the combinations of those Lewis acids with NFSI were employed, acceptable yields were achieved. The blank experiments by using metal chloride afforded only trace amount of products or no products at all (Table 3, entries 5–11). These results demonstrated that in the assistance of Lewis acids, even those with lower catalytic activities the NFSI has much better activity than NFSI alone in catalyzing Beckmann rearrangement.

To identify the real catalytic species, several control experiments were performed. The possibility of the formation of more active Sm[N(SO₂Ph)₂]₃¹⁴ by counterion exchange was excluded by synthesizing the Sm[N(SO₂Ph)₂]₃ using literature reported method.¹⁵ The freshly prepared catalyst showed uncomparable activity with the combination of NFSI and Sm(OTf)₃ (Table 4, entry 1). In contrast, the combination of NFSI and Sm[N(SO₂Ph)₂]₃ provided reasonable yield (Table 4, entry 2). Additionally, to study the influence of electrophilic fluorine on the catalysis, *N*-methylbenzenesulfonimide (NMSI) was prepared. The combination of NMSI and Sm(OTf)₃ showed much weaker catalytic activity than NFSI/Sm(OTf)₃ and the combination of NMSI and CaCl₂ showed no activity at all, which indicated that the fluorine played an essential role in catalyzing the reactions (Table 4, entries 3–4). To shed lights on the catalytic effects of the electrophilic fluorine, two commercially available electrophilic fluorine reagents were examined. As expected, they were able to catalyze the Beckmann rearrangement in 73% and 83% yields respectively (Table 4, entries 5–6). However, the combination of Sm(OTf)₃ and Selectfluor afforded similar yields to Selectfluor itself, which indicated that the electrophilicity of the fluorine of Selectfluor was not further increased by Sm(OTf)₃. It also indicated that the Lewis acids significantly increased the electrophilicity of the fluorine of NFSI to the degree that is comparable to that of the Selectfluor fluorine (Table 4, entry 7).^{2d,16}

From those above findings, a mechanistic proposal on the interaction between NFSI and Lewis acids was presented in Scheme 2. The bidental coordination of Lewis acids with the sulfonyl groups on NFSI in a six-membered ring pattern¹⁷ would decrease the electron density on nitrogen of the counteranion, which would enhance the electrophilicity of fluorine by redistributing the electron density. In order to determine the electronic nature of the fluorine, DFT calculations were performed and the atomic charges

Download English Version:

<https://daneshyari.com/en/article/5260231>

Download Persian Version:

<https://daneshyari.com/article/5260231>

[Daneshyari.com](https://daneshyari.com)