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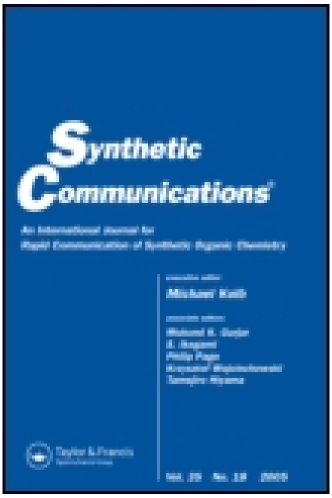

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Microwave-Assisted Beckmann Rearrangement of Aryl Ketoximes Catalyzed by In(OTf)$_3$ in Ionic Liquid

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MICROWAVE-ASSISTED BECKMANN REARRANGEMENT OF ARYL KETOXIMES CATALYZED BY In(OTf)$_3$ IN IONIC LIQUID

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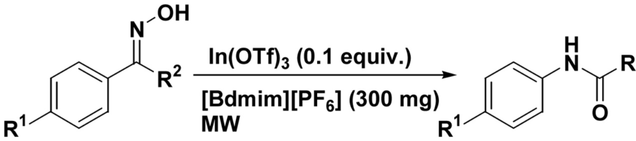
GRAPHICAL ABSTRACT



Abstract *Beckmann rearrangement of aryl ketoximes catalyzed by In(OTf)$_3$ gave amides in ionic liquid under microwave irradiation. Aryl ketoximes were converted to corresponding amides in good yield within very short times (10–270 s). The catalyst and the ionic liquid were easily recovered and reused.*

Keywords Beckmann rearrangement; In(OTf)$_3$; ionic liquid; microwave

The rearrangement of ketoxime to the corresponding amide, known as the Beckmann rearrangement, is a common method used in organic chemistry and is a topic of current interest. It accomplishes both the cleavage of the carbon–carbon bond and the formation of a carbon–nitrogen bond, and this reaction generally requires high reaction temperatures and a large amount of a strong Brønsted acid and dehydrating media, causing large numbers of by-products and serious corrosion problems. In recent years, Beckmann rearrangements using catalysts such as $InCl_3$,[1] H_2SO_3H,[2] $Nd(OTf)_3$,[3] $RuCl_3$,[4] chlorosulfonic acid,[5] BOPCl-$ZnCl_2$,[6] silica sulfate,[7] PTSA-$ZnCl_2$,[8] and 1,3,5-triazo-2,4,6-triphosphorine-2,2,4,4,6,6-chloride[9] in organic solvents have been carried out. Nevertheless, a relatively large amount of organic solvent is generally needed. Consequently, there still exists a need for novel and facile methods for efficient conversion of ketoximes into the corresponding amides via Beckmann rearrangement. Room-temperature ionic liquids (RTILs)

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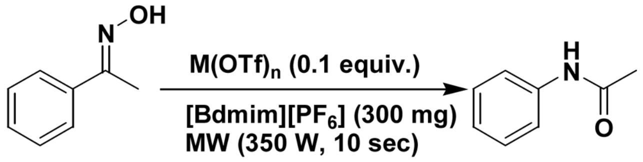
Table 1. Effect of metal triflate in the Beckmann rearrangement of **1**

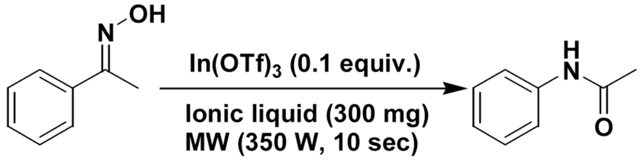


1 (1 mmol) **2**

		Run 1		Run 2		Run 3		Run 4	
Entry	$M(OTf)_n$	Yield (%)	Recov. of **1** (%)	Yield (%)	Recov. of **1** (%)	Yield (%)	Recov. of **1** (%)	Yield (%)	Recov. of **1** (%)
1	$Sc(OTf)_3$	89	1	82	11	78	17	52	41
2	$In(OTf)_3$	89	4	86	7	87	4	86	6
3	$Hf(OTf)_4$	79	1	80	1	83	13	79	11
4	$Sm(OTf)_3$	89	0	81	4	64	29	48	37
5	$Yb(OTf)_3$	88	3	89	15	77	10	4	94

are attracting increasing interest as green solvents in many organic transformations.[10] Efforts to use RTILs as reaction media for the Beckmann rearrangement have been reported.[11–15] Moreover, using Brønsted acidic RTILs as catalyst has been tried for the Beckmann rearrangement.[16–19] However, reusable catalytic

Table 2. Effect of ionic liquid in the Beckmann rearrangement of **1**



1 (1 mmol) **2**

		Run 1		Run 2	
Entry	Ionic liquid[a]	Yield (%)	Recov. of **1** (%)	Yield (%)	Recov. of **1** (%)
1	$[Bmim][PF_6]$	84	5	60	34
2	$[Bmim][BF_4]$	67	19	—[b]	—[b]
3	$[Bmim][OcSO_4]$	0	97	—[b]	—[b]
4	$[Bmim][NTf_2]$	0	95	—[b]	—[b]
4	$[Emim][PF_6]$	92	1	52	47
5	$[Bdimim][PF_6]$	89	4	86	7

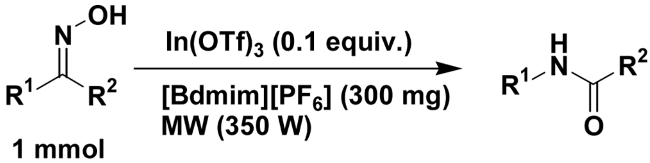
[a] Abbreviations: $[Bmim][PF_6]$, 1-butyl-3-methylimidazolium hexafluorophosphate; $[Bmim][BF_4]$, 1-butyl-3-methylimidazolium tetrafluoroborate; $[Bmim][OcSO_4]$, 1-butyl-3-methylmidazolium octylsulfate; $[Bmim][NTf_2]$, 1-butyl-3-methylmidazolium bis(trifluoromethylsulfonyl)imide; $[Emim][PF_6]$, 1-ethyl-3-methylimidazolium hexafluorophosphate; and $[Bdimim][PF_6]$, 1-butyl-1,3-dimethylimidazolium hexafluorophosphate.

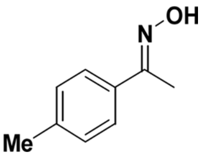
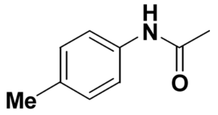
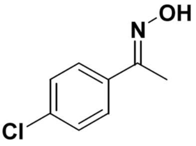
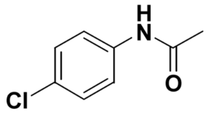
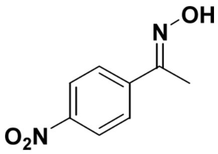
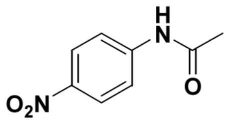
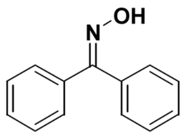
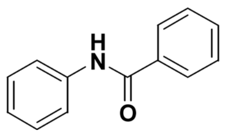
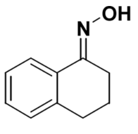
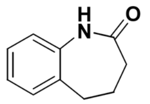
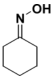
[b] Not examined.

systems are few.[19] Herein, we report our results for the microwave-assisted Beckmann rearrangement of aryl ketoximes catalyzed by In(OTf)$_3$ in ionic liquid. The ionic liquid and the catalyst were easily recovered and reused.

The activity and recyclability of various metal triflate were initially evaluated with Beckmann rearrangement of acetophenone oxime (**1**) as shown in Table 1. The reaction was performed in the presence of 0.1 equiv. of various metal triflate and 300 mg of 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([Bdmim][PF$_6$]) under microwave irradiation for 10 s. Importantly, isolation of the product and

Table 3. Beckmann rearrangement of various ketoximes by In(OTf)$_3$ and [Bdmim][PF$_6$] under microwave irradiation



Entry	Substrate	Time	Product	Yield (%)
1		30		84
2		30 × 2		73
3		20 × 4		70
4		20		92
5		90 × 3		54
6		60	Complex mixture	

substrate was easily accomplished by extraction with diisopropyl ether, and the [Bdmim][PF]$_6$ layer containing metal triflate was reused with a new loading substrate. In every case, the reaction proceeded smoothly to give acetanilide (**2**) on the first run. However, the activity of the recovered catalysts, such as Sc(OTf)$_3$, Sm(OTf)$_3$, and Yb(OTf)$_3$, decreased as repeated runs increased (entries 1, 4, and 5). In contrast, the recovered ionic liquid phase containing the catalyst, such as In(OTf)$_3$ and Hf(OTf)$_4$, was reused for four runs without any loss of activity (entries 2 and 3). As shown in entry 2, a better result was obtained using In(OTf)$_3$.

The recycling performance of various RTILs was investigated in the Beckmann rearrangement of **1** in the presence of a catalytic amount of In(OTf)$_3$ under microwave irradiation for 10 s, as shown in Table 2. The reaction proceeded smoothly to give **2** in the case of 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF$_6$]), 1-ethyl-3-methylimidazolium hexafluorophosphate ([Emim][PF$_6$]), and [Bdmim][PF$_6$] on the first run (entries 1, 5, and 6). However, the activity of the recovered ionic liquid and catalyst were low in the case of [Bmim][PF$_6$] and [Emim][PF$_6$]. In the case of [Bmim][PF$_6$] and [Emim][PF$_6$], the poor yield was presumably caused by the formation of a hydrogen bond between C$_2$-H in imidazolium cation and oxygen in the oxime as reported in the literature.[19] When 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$]) was used as solvent, the reaction of **1** gave **2** in only 67% yield (entry 2). On the other hand, no reaction took place in the presence of 1-butyl-3-methylmidazolium octylsulfate ([Bmim][OcSO$_4$]) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][NTf$_2$]) (entries 3 and 4). The combined use of [Bdmim][PF$_6$] and In(OTf)$_3$ was the most suitable for the Beckmann rearrangement under microwave irradiation.

Next, we tried the Beckmann rearrangement of some ketoximes in the presence of 0.1 equiv. of In(OTf)$_3$ and 300 mg of [Bdmim][PF$_6$] under microwave irradiation (Table 3). Aryl ketoximes were converted into the corresponding amides in good yields within very short times (entries 1–4). The cyclic ketoxime, such as α-tetralone oxime, gave the amide in 54% yield (entry 5). However, cyclohexanone oxime gave complex mixtures (entry 6).

In conclusion, the Beckmann rearrangement of aryl ketoximes was successfully carried out using In(OTf)$_3$ as the catalyst in ionic liquid [Bdmim][PF$_6$] under microwave irradiation. In this reaction, the catalyst and ionic liquid are reasily recovered and reused.

EXPERIMENTAL

General

All starting materials were purchased form Wako Pure Chemical Industries, Ltd. (Japan) and used without further purification. All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples. Melting points were determined on a Yanaco MP-500P micromelting-point apparatus (Japan). Infrared (IR) spectra were measured on a Hitachi IR 270–30 spectrometer (Japan). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using tetramethylsilane as an internal reference on a Bruker AC-250P instrument. High-resolution mass spectrometry (HRMS) was performed on a Hitachi M-2000 AM mass spectrometer (Japan) in electron impact (EI) mode at 70 eV.

Typical Procedure

A mixture of acetophenone oxime **1** (135 mg, 1.0 mmol), $In(OTf)_3$(56 mg, 0.1 mmol), and $[Bdmim][PF_6]$ (300 mg) in a glass tube was irradiated in a domestic microwave oven (Elabitax Eor-17, Yoshii Electric Co., Ltd., Japan, 2450 MHz, 350 W) for 10 s. After 5 mL of diisopropyl ether were added to reaction mixture, the resulting biphasic solution was treated with ultrasonic cleaner bath (200 W) for 1 min. The upper diisopropyl ether containing the expected products was separated by decantation. This extraction process was repeated three times. The diisopropyl ether was evaporated under reduced pressure to afford the crude product. The product was purified by flash-column chromatography on silica gel to give acetanilide **2** (120 mg) in 89% yield along with **1** (1 mg) in 4% yield. The other hand, the bottom phase of the $[Bdmim][PF_6]$ containing $In(OTf)_3$ was reused on the next run.

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