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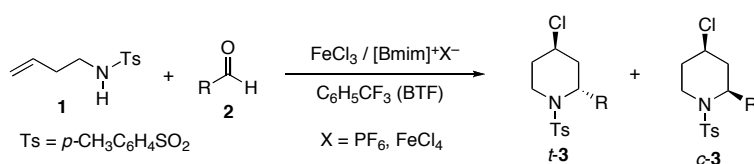
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Application of biphasic reaction procedure using ferric chloride dissolved in an imidazolium salt and benzotrifluoride (FeIm-BTF procedure) to aza-Prins cyclization reaction

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LETTERS

Application of biphasic reaction procedure using ferric chloride dissolved in an imidazolium salt and benzotrifluoride (FeIm-BTF procedure) to aza-Prins cyclization reaction

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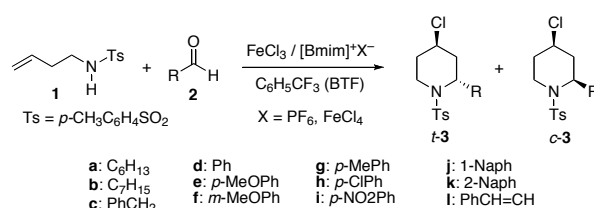
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Abstract—Aza-Prins cyclization reaction of *N*-tosyl-3-butenylamine with aliphatic and aromatic aldehydes was performed using a combination of FeCl₃ and 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆) or 1-butyl-3-methylimidazolium tetrachloroferate (BmimFeCl₄) in benzotrifluoride (BTF). The desired *N*-tosyl-4-chloro-2-substituted piperidines were obtained from aliphatic aldehydes in the comparable yields to those for the previously reported reactions in which FeCl₃ was used in CH₂Cl₂. On the other hand, significant progress for the piperidine synthesis from aromatic aldehydes has been achieved, particularly when BmimFeCl₄ was used with FeCl₃ in BTF. © 2014 Elsevier Science. All rights reserved

We recently developed a novel liquid-liquid biphasic reaction system utilizing a combination of FeCl₃ and 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆) in benzotrifluoride (BTF), named as FeIm-BTF procedure, which could promote certain electron transfer reactions.¹ Both imidazolium salts² and BTF³ are known as environmentally benign solvents. Iron reagents are inexpensive and nontoxic reagents, and FeCl₃ is among the most convenient iron reagents. The FeIm-BTF procedure is therefore compatible with green sustainable chemistry.⁴

It is known that FeCl₃ can be used not only as an oxidizing reagent⁵ but also as a Lewis acid.⁶ FeIm-BTF procedure should, therefore, be principally applicable to Lewis acid-FeCl₃ promoted reactions. We then paid our attention to the FeCl₃ promoted aza-Prins cyclization reaction, recently reported by Martin and Padron.^{7,8} In their efforts, alkenyl or alkynyl *N*-sulfonylamines were reacted with various aldehydes to give chloro substituted piperidines or tetrahydropyridines, some of which have potential bioactivities. However, there are problems because the yields of *N*-heterocyclic products from aromatic aldehydes are relatively low and the use of environmentally less desirable methylene chloride is essential.

In this letter, we report our preliminary observation that a combination of FeCl₃ and BmimPF₆ or 1-butyl-3-methylimidazolium tetrachloroferate (BmimFeCl₄) in BTF was effective to promote the aza-Prins cyclization reaction to give chloro substituted piperidines using both aliphatic and aromatic aldehydes (Scheme 1).⁹ We first examined the reaction of *N*-tosyl-3-butenylamine (**1**) (0.50 mmol) with aliphatic aldehydes such as heptanal (**2a**) and octanal (**2b**) (1.5 equiv) using FeCl₃ (1.5 equiv) and BmimPF₆ (1.5 equiv) in BTF (5.0 ml).¹⁰ Stirring at room temperature for 30 min, the upper BTF layer was taken and subjected to silica-gel chromatography separation to give

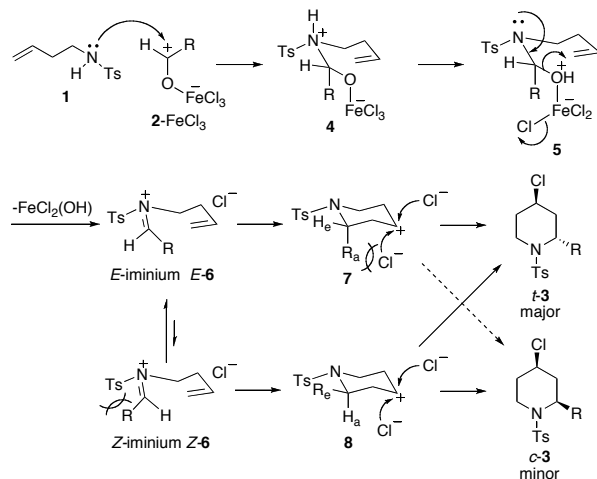


Scheme 1. Substrates and products.

trans-*N*-tosyl-4-chloro-2-hexyl piperidine (**t-3a**) in 63% (98% based on the conversion of **1**) and *trans*-*N*-tosyl-4-chloro-2-heptyl piperidine (**t-3b**) in 81%, respectively. We also conducted the FeCl₃ promoted reaction of **2a** and **2b** in CH₂Cl₂, as reported previously,^{8a} to obtain **t-3a** and **t-3b** in the same yields as 87%. Also, **c-3b** were isolated in 10% in the FeIm-BTF reaction and 6% in CH₂Cl₂, respectively. Notably, when BTF was not used as a solvent, the yield of **t-3b** significantly decreased (47%). On the other hand, when BTF was replaced by the same volume of toluene which is also insoluble in BmimPF₆, the reaction of **2b** did not go to the completion with the recovered **1** (78-39%) giving **3b** (19-40%) as the inseparable mixture with unidentified byproducts. The reaction of phenylacetaldehyde (**2c**), while 14% of **1** was recovered, produced both **t-3c** and **c-3c** in 79% (92 : 8), which is also comparable to the yield (78%, **t-3c** : **c-3c** = 83 : 17) for the reported reaction in CH₂Cl₂.^{7a}

Although the structure of the ferric salt under the FeIm-BTF conditions is not clear at the moment,¹¹ we think that the reaction pathways are similar to those of FeCl₃ promoted reactions (Scheme 2).^{7a} FeCl₃ activated aldehyde (**2**-FeCl₃) is attacked by **1** to give the zwitterionic ammonium intermediate **4**. Proton transfer in **4** either via intramolecular or intermolecular fashion to produce the hydroxonium intermediate **5**. Releasing the ferric salt gives the iminium intermediate **6** whose *E*-form and *Z*-form are in the equilibrium each other. Since *E*-**6** is more stable than

Z-6 due to the steric repulsion between Ts and R groups, the formation of carbocation **7** should be predominant to the isomeric cation **8**, and then **7** is attacked from the less crowded upper side by in situ generated chloride ion. Consequently, exclusive formation of *t*-**3** is plausible.



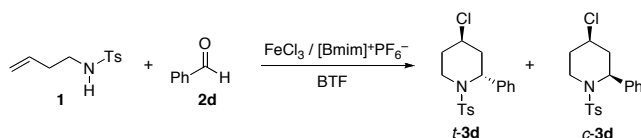
Scheme 2. Plausible reaction pathways.

Above preliminary observations encouraged us to apply FeIm-BTF procedure to the reaction of benzaldehyde (**2d**) with **1**. Representative results are summarized in Table 1.¹⁰ On the basis of Scheme 2, **2d** is expected to be less reactive than **2a-c**. Indeed, the reaction of **2d** with **1** for 2 h under the same condition as that for **2b** resulted in more than 70% recovery of **1** (entry 1). While extending the reaction time to 24 h slightly increased both the conversion of **1** and the yield of **3d** (entry 2), raising the reaction temperature drastically decreased them (entry 3). On the other hand, the quantity of BTF significantly affected the reaction

progress; decreasing the volume of BTF lead to the increasing the conversion of **1** (compare entry 1 with entry 7, entry 2 with entries 4, 6, and 8). Extending the reaction time to 48 h slightly increased the conversion of **1** while the yield of **3d** did not change (entry 5). We also applied the conditions of entry 4 to *p*-anisaldehyde **2e** and *p*-nitrobenzaldehyde **2i** (not shown in Table 1). It was then observed that *t*-**3i** was obtained in 26% at 85% conversion of **1** while no reaction of **2e** proceeded. Most noteworthy was that the use of two times quantity of FeCl₃ significantly increased the yield of **3d** (compare entry 1 with entry 9) while such an effect of FeCl₃ quantity was not obvious under the neat condition (compare entry 8 with 10). It should be noted that the yield of **3d** in the entry 9 is much greater than the previously reported yield of **3d** (46%, *t*-**3d** : *c*-**3d** = 90 : 10) for the reaction in CH₂Cl₂.^{7a}

We next turned our attention to 1-butyl-3-methylimidazolium tetrachloroferrate (BmimFeCl₄). This imidazolium salt is known as a magnetic ionic liquid which therefore has potential applicability to the area of materials science.¹² On the other hand, synthetic application of BmimFeCl₄ has been limited.¹³ We then decided to replace BmimPF₆ by BmimFeCl₄ expecting that BmimFeCl₄ could promote aza-Prins cyclization reaction if FeCl₃ is in situ generated from FeCl₄ counter anion. Results of the reactions of various aldehydes **2** with **1** employing the FeIm-BTF procedure using BmimFeCl₄ are presented in Table 2.¹⁴ Although this idea was not practical (entry 1), desired reaction of **2b** (entry 2) smoothly proceeded on addition of FeCl₃. In the reaction of **2d**, decreasing the quantity of BTF did not significantly influence the yield of **3d** (entries 3-5; compare entry 3 with entry 2 of Table 1) while omission of BTF slightly decreased the yield of **3d**. Then, the condition of entry 3 was applied to aldehydes **2e-l**. In the cases of

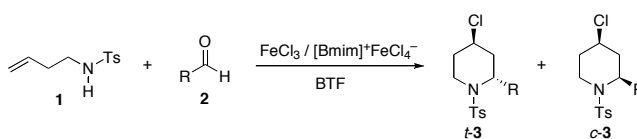
Table 1. Aza-Prins cyclization of **1** with benzaldehyde **2d** promoted by FeCl₃ with BmimPF₆ in BTF^a



Entry	FeCl ₃ (equiv vs 1)	BTF (mL)	Reaction time (h)	Recovery of 1 (%)	Yield of 3 (<i>t</i> - 3 : <i>c</i> - 3) (%) ^b
1	1.5	5.0	2	76	19 (87 : 13)
2	1.5	5.0	24	67	32 (95 : 5)
3 ^c	1.5	5.0	24	90	7 (100 : 0 ^d)
4 ^e	1.5	1.0	24	51	34 (88 : 12)
5	1.5	1.0	48	40	35 (91 : 9)
6	1.5	0.5	24	21	47 (87 : 13)
7 ^f	1.5	0	2	6	36 (90 : 10)
8	1.5	0	24	0	51 (90 : 10)
9	3.0	1.0	24	0	82 (90 : 10)
10	3.0	0	24	0	57 (90 : 10)

^aTosylamine **1** (0.50 mmol), **2d** (1.5 equiv vs **1**), BmimPF₆ (1.5 equiv vs **1**), at room temperature. ^bIsolated yields. ^cHeating at 60 °C. ^dNo *c*-**3d** was isolated.

^eAverage of four experiments. ^fAverage of two experiments.

Table 2. Aza-Prins cyclization of **1** with aldehyde **2** promoted by FeCl₃ with BmimFeCl₄ in BTF^a

Entry	2	R	FeCl ₃ (equiv vs 1)	Recovery of 1 (%)	Yield of 3 (<i>t</i> - 3 : <i>c</i> - 3) (%) ^b
1	2b	C ₇ H ₁₅	0	100	
2	2b	C ₇ H ₁₅	1.5	0	92 (100 : 0)
3 ^c	2d	Ph	1.5	2	93 (89 : 11)
4 ^d	2d	Ph	1.5	0	94 (90 : 10)
5 ^e	2d	Ph	1.5	0	86 (90 : 10)
6	2e	<i>p</i> -MeOPh	1.5	100	
7	2f	<i>m</i> -MeOPh	1.5	20	74 (91 : 9)
8	2g	<i>p</i> -MePh	1.5	26	72 (89 : 11)
9 ^c	2h	<i>p</i> -ClPh	1.5	29	67 (85 : 15)
10	2i	<i>p</i> -NO ₂ Ph	1.5	0	80 (90 : 10) ^f
11	2j	1-Naph	1.5	100	
12	2k	2-Naph	1.5	92	8 (100 : 0)
13	2l	<i>trans</i> -PhCH=CH	1.5	38	48 (100 : 0)

^aTosylamine **1** (0.50 mmol), **2** (1.5-1.6 equiv vs **1**), FeCl₃ (1.5 equiv vs **1**), BmimFeCl₄ (1.5 equiv vs **1**), BTF (5.0 mL), at room temperature, 0.5 h for **2b** and 24 h for **2d-l**. ^bIsolated yields. ^cAverage of two experiments. ^dBTF (1.0 mL). ^eNo BTF was used. ^fRatio was determined by ¹H-NMR.

2f-2i, the corresponding piperidines **3f-i** were obtained in moderate to good yields (entries 7-10). However, the reactions of **2e**, **2j** and **2k** were sluggish (entries 6, 11 and 12). The electron donating methoxy substituent at para position of benzaldehyde must lower the reactivity of **2e-FeCl₃**, and bulky naphthyl substituents of **2j** and **2k** must also deter their reactivities. Also, cinnamaldehyde **2l** was found to be tolerable to the FeIm-BTF procedure to give **3l** in moderate yield (entry 13).

In conclusion, we discovered that the FeIm-BTF procedure was effective to promote aza-Prins cyclization reaction of *N*-tosyl-3-butenylamine with various aldehydes to give chloro substituted piperidines.¹⁵ Particularly noteworthy is that significant progress for the piperidine synthesis from aromatic aldehydes has been achieved. Characteristics of the FeIm-BTF procedure are, 1) a combination of FeCl₃ and BmimPF₆ or BmimFeCl₄ produces a liquid phase ferric reagents, 2) the use of these hybrid reagents together with BTF gives a liquid-liquid biphasic reaction system,¹⁶ 3) BTF layer containing the desired products can be simply taken from the crude reaction mixture when two layers separate well.^{14,17} Although the reaction condition has not been fully optimized yet, the FeIm-BTF procedure is certainly a new entry to promote aza-Prins cyclization reactions, and may have the potential applicability to other ferric salt promoted synthetic reactions.

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 - General reaction procedure. A BTF solution of **1** (112.7 mg, 0.50 mmol) and aldehyde (0.75 mmol) was added to FeCl₃ (121.7-243.3 mg, 0.75-1.50 mmol) and BmimPF₆ (0.16 mL, 213.1 mg, 0.75 mmol) in BTF under N₂. The resulting mixture was stirred under N₂ at room temperature for 30 min - 24 h. Then, a BmimPF₆ layer was rinsed with Et₂O (3 mL × 3) after separation from a BTF layer. The residue obtained after concentration of BTF and Et₂O was purified by silica gel column chromatography (EtOAc / *n*-Hexane solvent systems), and then subjected to TLC (EtOAc / *n*-Hexane solvent systems). Piperidines *t*-**3b**, *c*-**3b**, *t*-**3c**, *c*-**3c**, *t*-**3d**, and *c*-**3d** are known, while the spectroscopic data of minor *cis*-compounds are not reported, and the X-ray crystallographic analysis of *t*-**3c** is reported,^{7a} and thus characterization of the piperidines **3** obtained and determination of their relative stereochemistry were performed by the comparison of their spectral data with those of the reported compounds.
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 - Although BmimFeCl₄ dissolving FeCl₃ and BTF also produces liquid-liquid biphasic system, the etheral extraction was performed because two layers do not separate well as the case of BmimPF₆. General reaction procedure is as follows. A BTF solution of **1** (112.7 mg, 0.50 mmol) and aldehyde (0.75 mmol) was added to FeCl₃ (121.7-243.3 mg, 0.75-1.50 mmol) and BmimFeCl₄ (0.18 mL, 252.7 mg, 0.75 mmol) in BTF under N₂. The resulting mixture was stirred under N₂ at room temperature for 30 min - 24 h. Then, it was extracted with Et₂O (30 mL × 3) after addition of water. The extract was treated with water, satd aqueous Na₂S₂O₃, satd aqueous NaHCO₃, satd aqueous NaCl, and dried over anhydrous MgSO₄. The residue obtained after concentration was purified by silica gel column chromatography (EtOAc / *n*-Hexane solvent systems), and then subjected to TLC (EtOAc / *n*-Hexane solvent systems).
 - Independent reviewers suggested the possibility of the formation of byproducts such as tetrahydropyridines, pyrrolidines, and Tishchenko type products from aldehydes particularly when **3** were obtained in low yields. At present, the formation of such compounds has not been confirmed.
 - Actual roles of BTF and imidazolium salts have not been fully understood yet. Significant progress of the piperidine yields might be ascribed to the liquid phase iron reagents while BTF is particularly beneficial for the separation step.
 - Although the reuse of imidazolium layer is desired, it may not be possible to use again the FeCl₃ in imidazolium salt because stoichiometric amount of chloride ion is consumed to produce **3**. A reviewer suggested the possibility of the use of catalytic amount of FeCl₃ with the excess of other chloride salts such as LiCl and Bu₄NCl. If this devised procedure works, then imidazolium layer might be reusable, which would be certainly the future subject to investigate.

Supplementary Material

Experimental procedures and spectral data and charts of selected products **3**.