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Triflic Anhydride-Mediated Beckmann Rearrangement Reaction of β-Oximyl Amides: Access to 5-Iminooxazolines

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Abstract. Facile and efficient synthesis of 5-iminooxazolines from α,α-disubstituted β-oximyl amides mediated by triflic anhydride (Tf_2O) in the presence of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) in dichloromethane at room temperature is developed, and a mechanism involving tandem Beckmann rearrangement and intramolecular cyclization reaction is proposed.

Keywords. Beckmann rearrangement; cyclization; β-oximyl amides; oxazolines; triflic anhydride.

1. Introduction

The rearrangement of ketoximes to the corresponding amides, known as the Beckmann reaction, is a classical transformation in organic chemistry and continues to be an active area of current research.[1] In chemical industry, it is successfully employed as a powerful tool for the manufacturing ε-caprolactam.[2] Unfortunately, the conventional Beckmann rearrangement reaction usually requires strong acid catalysts and harsh conditions, such as high reaction temperature and dehydrating media, which meanwhile releases quite a lot of acidic wastes.[1,3] Therefore, mild and efficient organocatalysis of the Beckmann rearrangement reaction has been developed to overcome these drawbacks,[4–6] and some Beckmann rearrangement reactions have been realized in ionic liquids at room temperature[7] and supercritical water.[8] Most reported mild conditions were still associated with the use of rather toxic and/or expensive reagents or solvents.[1,3] The investigation of Beckmann rearrangement reactions with the aim to obtain mild and efficient conditions is still in demand.

During the course our studies on the development of synthetic methodologies for heterocycles from β-oxo amide derivatives, we prepared a series of β-oximyl amides **1** and investigated their reaction behavior under different conditions, and achieved a divergent synthesis of 5-chloro-1*H*-pyrazoles (Path A),[9] 5-arylamino-4-haloethylisoxazoles (Path B and C),[9,10] and spiro-fused pyrazolin-5-ones (Path D)[10] under varied conditions (scheme 1). Contrary to those reported Beckmann rearrangement reactions mediated or catalyzed by the activation of the hydroxyl group by the *p*-toluenesulfonyl or cyanuric chloride,[4,11] the Beckmann rearrangement reaction of β-oximyl amides **1** was not observed under our tested conditions as described in scheme 1. Very recently, we developed a facile synthesis of 2,3-dihydrofuro[3,2-*c*]pyridin-4(5*H*)-ones by the reaction of 1-aminopropenoyl cyclopropane-1-carboxamides in the presence of triflic anhydride (Tf_2O).[12] In connection with these studies and our continuing interest in the further synthetic potential of β-oximyl amides **1**, we investigated their reactivity toward triflic anhydride and other organic anhydrides under different conditions. As a result of this study, we achieved an efficient synthesis of 5-iminooxazolines **2** (scheme 1, Path E) under very mild conditions. In the present work, we wish to report our experimental results and present a proposed mechanism involved.

2. Experimental

2.1 *Reagents and Instrumentation*

All reagents were purchased from commercial sources and used without purification, unless otherwise indicated. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25°C at 300 MHz (or 400 MHz) and 100 MHz, respectively, with TMS as internal standard. IR spectra (KBr) were recorded on FTIR-spectrophotometer in the range

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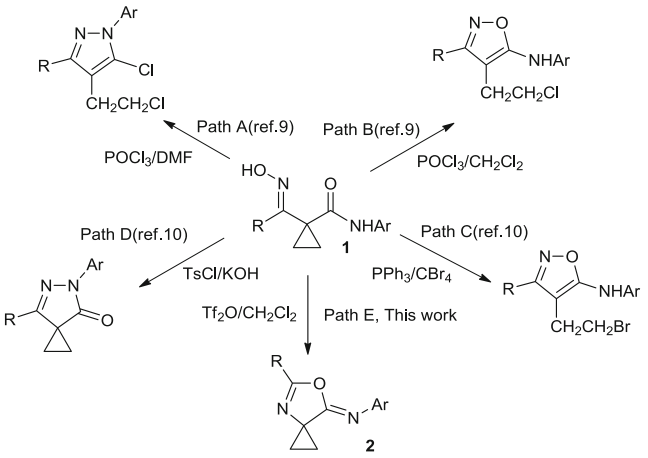


Scheme 1. Reactions of α-Carbamoyl-α-Oximyl Cyclopropanes **1** under different conditions.

of 400-4000 cm^{-1}. Melting points were uncorrected. All reactions were monitored by TLC with GF254 silica gel-coated plates. Chromatography was carried out on silica gel (300−400 mesh).

2.2 *Typical procedure for the synthesis of 2 (2a as an example)*

To a solution of **1a** (1.0 mmol) in DCM (5 mL) at room temperature was added Tf_2O (1.2 mmol) and DBU (1.2 mmol) in one portion. The mixture was stirred at room temperature for 15 min, and then poured into brine (15 mL), which was extracted with DCM (3 × 10 mL). The combined organic phases were washed with water (2 × 10 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 10**:** 1) to give **2a** as a white solid (0.208 g, 89%).

2.3 *Physical Data of Compounds **2** and **3***

2a, 2c, 2d, 2f, 2h, 2i are known compounds, and their analytical data are in good agreement with those in literature [see ref. 14].

2.3a *(Z)-4-Chloro-N-(5-methyl-6-oxa-4-azaspiro[2.4] hept-4-en-7-ylidene)aniline (**2a**)*: White solid, M.p. 179-181°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (t, *J* = 3.6 Hz, 2H), 1.63 (t, *J* = 3.6 Hz, 2H), 2.20 (s, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 18.9, 49.8, 124.3, 128.8, 129.6, 143.9, 162.1, 162.4; IR (KBr) 3132, 3012, 2931, 1718, 1672, 1598, 1544, 1488, 1402, 1240, 1083, 966, 918, 841, 653 cm^{-1}; Anal. Calcd. for $C_{12}H_{11}ClN_2O$: C, 61.41; H, 4.72; N, 11.94. Found: C, 61.16; H, 4.80; N, 11.88. MS calcd. *m*/*z* 234.1, found 235.1 [(M+1)$^+$].

Colorless crystal, *M* = 234.68, Monoclinic, *C2/c*, *a* = 23.827(6) Å, *b* = 7.4104(19) Å, *c* = 14.707(4) Å, α = 90.00°, β = 116.100(5)°, γ = 90.00°, *V* = 2332.0(11) Å^3, *Z* = 8, *T* = 293, F_{000} = 976, R_1 = 0.0553, wR_2 = 0.2452.

2.3b *(Z)-3-Chloro-N-(5-methyl-6-oxa-4-azaspiro[2.4] hept-4-en-7-ylidene)aniline (**2b**)*: Colorless semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.54 (t, *J* = 3.5 Hz, 2H), 1.63 (d, *J* = 3.2, 2H), 2.18 (s, 3H), 6.98 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.12 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8, 18.9, 49.7, 121.1, 123.0, 124.3, 129.6, 134.1, 146.6, 162.0, 162.8. IR (KBr) 3145, 3021, 2938, 1702, 1617, 1488, 1406, 1253, 1038, 1012, 963, 922, 835, 684 cm^{-1}; Anal. Calcd. (%) for $C_{12}H_{11}ClN_2O$: C, 61.41; H, 4.72; N, 11.94; Found (%): C, 61.55; H, 4.75; N, 11.87.

2.3c *(Z)-2-Methyl-N-(5-methyl-6-oxa-4-azaspiro[2.4] hept-4-en-7-ylidene)aniline (**2e**)*: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (t, *J* = 3.2 Hz, 2H), 1.64 (t, *J* = 3.2 Hz, 2H), 2.16 (s, 3H), 2.19 (s, 3H), 6.97-7.04 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 17.7, 18.6, 49.1, 121.1, 124.0, 126.0, 130.0, 130.1, 144.4, 161.1, 162.4; IR (KBr) 3138, 3014, 2946, 1789, 1721, 1633, 1488, 1425, 1402, 1274, 1039, 1014, 965, 926, 838, 691 cm^{-1}; Anal. Calcd. (%) for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found (%): C, 73.05; H, 6.52; N, 13.02.

2.3d *(Z)-N-(5-Phenyl-6-oxa-4-azaspiro[2.4]hept-4-en-7-ylidene)aniline (**2g**)*: White solid, M.p. 117-119°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 2H), 1.82 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 9.0 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 19.8, 50.7, 123.1, 124.5, 126.4, 127.4, 128.7, 128.8, 132.0, 145.3, 161.2, 161.6; IR (KBr) 3136, 3018, 2964, 1797, 1712, 1641, 1488, 1422, 1400, 1269, 1039, 1016, 962, 921, 765, 692 cm^{-1}; Anal. Calcd. (%) for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found (%): C, 77.64; H, 5.43; N, 10.75.

2.3e *(Z)-N-(4,4-Diallyl-2-methyloxazol-5(4H)-ylidene) aniline (**2j**)*: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 3H), 2.43-2.48 (m, 2H), 2.64-2.69

(m, 2H), 5.14-5.22 (m, 4H), 5.57-5.67 (m, 2H), 7.10-7.13 (m, 1H), 7.16 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.0, 40.5, 58.5, 119.7, 122.6, 124.2, 128.6, 130.9, 145.5, 162.9, 165.0; IR (KBr) 3138, 3022, 2914, 1703, 1618, 1594, 1523, 1485, 1411, 1087, 885, 843, 706 cm^{-1}; Anal. Calcd. (%) for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found (%): C, 75.42; H, 7.17; N, 10.93.

2.3f *(Z)-N-(2-Methyl-4,4-di(prop-2-yn-1-yl)oxazol-5(4H)-ylidene)aniline (**2k**)*: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16-2.17 (m, 5H), 2.71-2.72 (m, 4H), 7.15 (t, J = 7.2 Hz, 1H), 7.24 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.3, 25.6, 57.0, 72.3, 77.0, 122.8, 124.6, 128.6, 144.9, 161.6, 163.8; IR (KBr) 3135, 3027, 2921, 1698, 1609, 1562, 1485, 1403, 1092, 876, 837, 768, 705 cm^{-1}; Anal. Calcd. (%) for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found (%): C, 76.60; H, 5.70; N, 11.29.

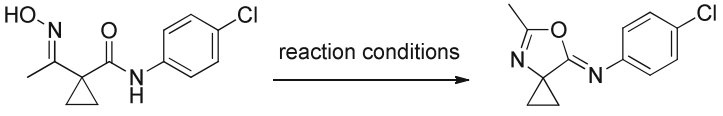
2.3g *(Z)-N-(4,4-Dibenzyl-2-methyloxazol-5(4H)-ylidene)aniline (**2l**)*: White solid, M.p. 102-103°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 3H), 3.14 (d, J = 13.6 Hz, 2H), 3.46 (d, J = 13.6 Hz, 2H), 7.13 (t, J = 7.2 Hz, 3H), 7.21-7.30 (m, 10H), 7.33 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 12.3, 43.2, 62.4, 120.0, 122.9, 124.5, 127.5, 128.6, 128.8, 129.4, 134.9, 136.0, 145.3, 162.8, 164.2; IR (KBr) 3134, 3029, 2916, 1704, 1591, 1487, 1400, 1085, 871, 840, 777, 703 cm^{-1}; Anal. Calcd. (%) for $C_{24}H_{22}N_2O$: C, 81.33; H, 6.26; N, 7.90. Found (%): C, 81.52; H, 6.16; N, 7.95.

2.3h *4-Benzyl-2-methyl-N-phenyloxazol-5-amine (**3m**)*: White solid, M.p. 134-137°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.16 (s, 3H), 3.65 (s, 2H), 5.72 (s, 1H), 6.93-6.99 (m, 3H), 7.16-7.21 (m, 4H), 7.28-7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 9.6, 26.9, 94.1, 115.9, 120.9, 125.7, 127.2, 127.8, 128.2, 137.1, 138.9, 160.0, 160.9; IR (KBr) 3131, 3036, 2927, 1715, 1642, 1583, 1478, 1393, 1094, 868, 832, 759, 696 cm^{-1}; Anal. Calcd. (%) for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found (%): C, 77.03; H, 6.19; N, 10.49.

3. Results and Discussion

The substrates, β-oximyl amides **1**, were prepared by the reaction of β-oxo amides with hydroxylamine ($NH_2OH{\cdot}HCl$) in the presence of NaOAc in methanol at room temperature in high yields.[9] We selected *N*-(4-chlorophenyl)-1-[1-(hydroxyimino)ethyl]cyclopropane carboxamide **1a** as the model compound and examined its behavior in the presence of triflic anhydride. Upon treatment of **1a** with triflic anhydride (1.2 equiv.) in dichloromethane (DCM) at room temperature for 60 min, the reaction proceeded as indicated by TLC,

Table 1. Reaction of **1a** under different conditions.[a]



1a **2a**

Entry	Reagent (equiv)[b]	Base (equiv)[c]	Solvent	Temp (°C)	Time (min)	Yield(%)[d]
1	Tf_2O(1.2)	–	CH_2Cl_2	rt	60	58
2	Tf_2O(1.2)	Et_3N(1.2)	CH_2Cl_2	rt	15	80
3	**Tf_2O(1.2)**	**DBU(1.2)**	**CH_2Cl_2**	**rt**	**15**	**89**
4	Tf_2O(1.2)	Py(1.2)	CH_2Cl_2	rt	15	mixture
5	Tf_2O(1.2)	DBU(1.2)	CH_2Cl_2	40	5	90
6	Tf_2O(1.2)	DBU(1.2)	CH_2Cl_2	0	60	67
7	Tf_2O(1.0)	DBU(1.2)	CH_2Cl_2	rt	10	85
8	Tf_2O(1.2)	DBU(1.0)	CH_2Cl_2	rt	10	81
9	Tf_2O(1.2)	DBU(1.2)	THF	rt	30	58
10	Tf_2O(1.2)	DBU(1.2)	CH_3CN	rt	30	62
11	Ac_2O(1.2)	DBU(1.2)	CH_2Cl_2	rt	18	83
12	TFAA(1.2)	DBU(1.2)	CH_2Cl_2	rt	20	76
13	TfOH(1.2)	DBU(1.2)	CH_2Cl_2	rt	60	n.r.[e]

[a]Reagents and conditions: **1a** (1.0 mmol), solvent (5.0 mL). [b]TFAA: trifluoroacetic anhydride; Ac_2O: acetic anhydride; TfOH: trifluoro-methanesulfonic acid. [c]DBU: 1,8-diazabicyclo(5.4.0)undec-7-ene; Py: pyridine. [d]Isolated yield for **2a**. [e]No reaction.

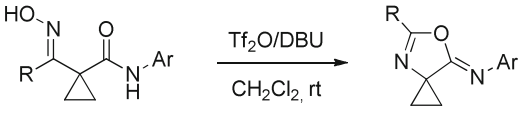
and furnished one product after workup and purification by silica column chromatography. The product was characterized as 4-chloro-*N*-(5-methyl-6-oxa-4-azaspiro[2.4]hept-4-en-7-ylidene) aniline **2a** based on its spectral and analytical data, (table 1, entry 1). Then, we briefly examined the effect of different acidic/basic reagents and their loaded amounts, solvents, and temperature on the success of the cyclization reaction to **2a**. It was found that the yield of **2a** could reach 80% when the reaction was performed with triethylamine (NEt_3) (table 1, entry 2). Subjecting **1a**, Tf_2O (1.2 equiv.) and DBU (1.2 equiv.) to DCM, the reaction could afford **2a** in 89% yield (table 1, entry 3). However, a complex mixture was formed when the reaction of **1a** and Tf_2O was conducted in pyridine (table 1, entry 4). Recently, Wray and co-workers discovered that the base played a key role on the reaction of a ketoximes with an adjacent amino group to selectively produce *N*-arylindazoles or benzimidazoles, and the stronger bases favoured the formation of benzimidazole products via the Beckmann rearrangement reaction.[13] Our results are consistent with their discovery. It was observed that the increase of reaction temperature to 40°C had no significant influence on the yield of **2a**, but did reduce the reaction time (table 1, entry 5), whereas the reaction required prolonged reaction time along with lower yield when performed at 0°C (table 1, entry 6). The decrease of loading of either Tf_2O or DBU would result in slightly lower yield of **2a** (table 1, entries 7 and 8). The reaction of **1a** with Tf_2O could take place in THF or CH_3CN, but the yields of **2a** were not good in comparison to that in DCM (table 1, entries 9 and 10). The experiments revealed that Tf_2O was most effective among those tested anhydrides (table 1, entries 11 and 12). No reaction was even observed when **1a** was subjected to TfOH (table 1, entry13).

Under the conditions as for **2a** in entry 3 (table 1), a series of reactions of α-carbamoyl-α-oximyl cyclopropanes **1** and Tf_2O and DBU were carried out, and some of the results are listed in table 2. It was observed that the reactions of α-carbamoyl-α-oximyl cyclopropanes **1b-f** bearing varied electron-withdrawing and electron-donating aryl amide groups proceeded efficiently to afford the corresponding 5-iminooxazolines **2b-f** in good to high yields (table 2, entries 2-6). The versatility of the 5-iminooxazoline synthesis was further evaluated by reacting **1g** bearing phenyl group R with Tf_2O and DBU in DCM (table 2, entry 7). The structure of **2a** was further elucidated by X-ray single crystal analysis as shown in figure 1. It should be mentioned that most recently Li and co-workers conducted the reaction of α-carbamoyl-α-oximyl cyclopropanes in the presence of DAST (diethylaminosulfur trifluride), and obtained the same compound **2a**.[14]

The efficiency of the synthesis of 5-iminooxazolines **2** was next examined by subjecting α,α-disubstituted β-oximyl amides **1h-l** to the cyclization reaction under identical conditions. It was found that the reactions could furnish the corresponding 5-iminooxazolines **2h-l** in good to high yields (table 3, entries 1-5). To the best of our knowledge, this is the first example for the triflic anhydride-mediated Beckmann Rearrangement reaction of ketoximes. In comparison to the conventio nal Beckmann rearrangement reaction of ketoximes, our protocol is associated with very mild conditions, such as room temperature, short reaction time of less than an hour, simple execution and no strong acid was required.

To expand the general applicability of the synthesis of 5-iminooxazolines **2**, we also carried out the reaction of α-monosubstituted β-oximyl amides **1m** in the same fashion. The reaction could proceed smoothly and furnished a product, which was characterized as 4-benzyl-2-methyl-*N*-phenyloxazol-5-amine **3m** based on its spectral and analytical data (scheme 2). Obviously, product **3m** is the isomer of the corresponding

Table 2. Synthesis of 5-Iminooxazolines **2** from α-Carbamoyl-α-Oximyl Cyclopropanes **1**[a].



1 **2**

Entry	**1**	Ar	R	**2**	Yield(%)[b]
1	**1a**	4-ClC_6H_4	Me	**2a**	89
2	**1b**	3-ClC_6H_4	Me	**2b**	85
3	**1c**	4-MeC_6H_4	Me	**2c**	83
4	**1d**	2,4-$Me_2C_6H_3$	Me	**2d**	74
5	**1e**	2-MeC_6H_4	Me	**2e**	75
6	**1f**	Ph	Me	**2f**	83
7	**1g**	Ph	Ph	**2g**	66

[a]Reagents and conditions: **1** (1.0 mmol), Tf_2O (1.2 mmol), DBU (1.2 mmol), DCM (5.0 mL), r.t., 15-30 min. [b]Isolated yield.

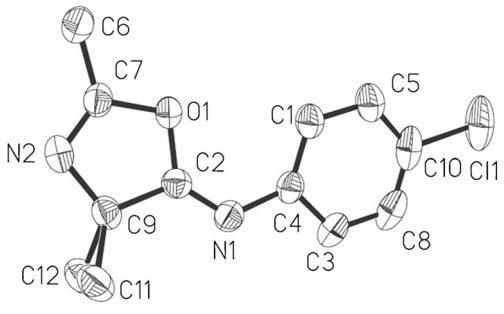
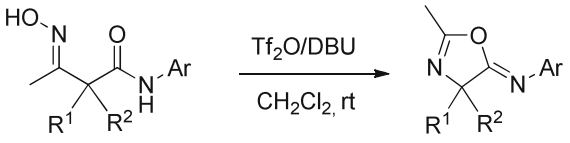


Figure 1. ORTEP drawing of **2a**.

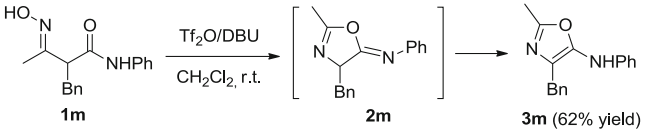
Table 3. Synthesis of 5-iminooxazolines **2** from α,α-Disubstituted β-Oximyl Amides **1**.[a]



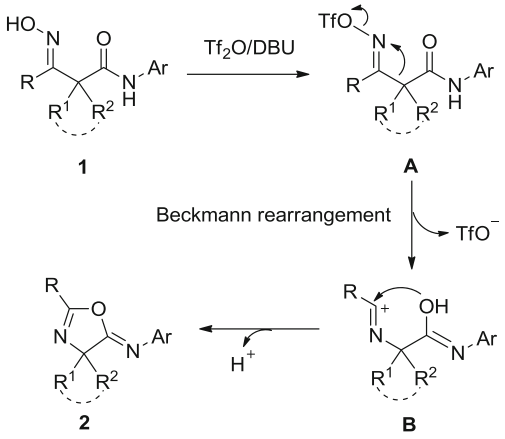
1 **2**

Entry	**1**	Ar	R^1	R^2	**2**	Yield(%)[b]
1	**1h**	Ph	Me	Me	**2h**	68
2	**1i**	Ph	Et	Et	**2i**	91
3	**1j**	Ph	Allyl	Allyl	**2j**	94
4	**1k**	Ph	Propargyl	Propargyl	**2k**	88
5	**1l**	Ph	Bn	Bn	**2l**	77

[a]Reagents and conditions: **1** (1.0 mmol), Tf_2O (1.2 mmol), DBU (1.2 mmol), DCM (5.0 mL), r.t., 15-30 min. [b]Isolated yield.



Scheme 2. The reaction of **1m** with Tf_2O in DCM.



Scheme 3. Plausible mechanism for the reaction of **1** with Tf_2O in DCM.

5-iminooxazoline **2m**. Therefore, we provided herewith an alternative synthetic route to 5-iminooxazolines **2** and 5-aminooxazoles **3**. Actually, oxazoline unit is the core moiety present in numerous natural products and synthetic organic compounds along with a variety of biological activities, such as melatonin receptor agonist, antimycobacterial, anticancer, and elastase inhibitor agents.[15–17]

On the basis of the above experimental results together with some literature reports,[18,19] a mechanism for the synthesis of 5-Iminooxazolines **2** is proposed as depicted in scheme 3. In the presence of DBU, tosylation of β-oximyl amide **1** occurs to give an intermediate **A**,[18] which undergoes the Beckmann rearrangement reaction to afford intermediate **B**,[19] followed by intramolecular cyclization to form substituted 5-iminooxazoline of type **2**.

4. Conclusions

In summary, a facile and efficient one-pot synthesis of 5-iminooxazolines **2** is developed *via* triflic anhydride-mediated Beckmann rearrangement reaction of readily available β-oximyl amides **1**. The protocol was successfully expanded to the synthesis of 5-aminooxazoles **3**. The ready availability of substrates, mild reaction conditions, simple execution, and synthetic potential of the products make this novel protocol very attractive.

Supplementary Information (SI)

Copies of NMR spectra for products **2** and **3** are available at www.ias.ac.in/chemsci. CCDC deposition number: 1063953. The crystallographic data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223 336 033; or deposit@ccdc.cam.ac.uk).

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