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# Unexpected results from the re-investigation of the Beckmann rearrangement of ketoximes into amides by using TsCl

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ABSTRACT

TsCl (*p*-toluenesulfonyl chloride), a commercially available organosulfonyl chloride, has been widely used as a stoichiometric dehydrogenation reagent in the transformation of ketoximes into corresponding amides via the Beckmann rearrangement. It has been now found to catalyze the Beckmann rearrangement with high catalytic efficiency, converting a wide range of ketoximes into their corresponding amides under mild condition with good to excellent yields (up to 99% of yield with 1–5 mol % of catalyst loading).



## 1. Introduction

The Beckmann rearrangement, as a fundamental tool in organic chemistry,[1] has been successfully utilized for the transformation of cyclohexanone oxime into caprolactam in industry. The rearrangement, however, requires harsh conditions such as a large amount of a strong acid and high reaction temperature. Besides, it also suffers from a considerable large amount of byproduct ammonium sulfate.[2] Hence, extensive efforts have been devoted to the optimization of the catalytic reaction system. Many catalytic systems such as liquid phase system,[3] vapor phase system,[4] supercritical water system,[5] and ionic liquids system[6] have been developed so far. And liquid-phase catalytic Beckmann rearrangement under mild conditions has become a topic of current interest due to its advantages such as easy work-up, and industrial practicability. Various catalysts were developed such as inorganic catalyst $P_2O_5$,[7] $HSO_3Cl$,[8] $PCl_5$,[9] metallic Lewis acid $[RhCl(cod)]_2$,[10] $Yb(OTf)_3$,[11] $RuCl_3$,[12] $HgCl_2$.[13] However, due to drawbacks such as toxicity, high cost, and corrosiveness, these catalysts have not yet been industrially utilized.

Recently, organocatalyst for the Beckmann rearrangement has attracted researchers' attention for its efficiency in catalytic activity and easy to handle during the rearrangement. Cyanuric chloride (CNC),[14] as the first organocatalyst, was reported to be a highly efficient catalyst for the Beckmann rearrangement by Ishihara and his co-workers. In the effort aimed at developing new catalytic system environ-friendly for the Beckmann rearrangement, we have developed BOP-Cl[15] (bis(2-oxo-3-oxazolidinyl)phosphinic chloride) as the first highly efficient organophosphorus catalyst for the Beckmann rearrangement, then the second generation of organophosphorus catalyst triphosphazene (TAPC).[16] On the other hand, a novel mechanism was consequently proposed by Ishihara and co-workers to account for the new generation of organocatalytic Beckmann rearrangement.[14] On the basis of this hypothesis, a similar mechanism was also described for the BOP-Cl[15] and TAPC[16b] catalyzed Beckmann rearrangement. Meanwhile, we also noticed that TsCl has been widely used as a stoichiometric dehydrogenation reagent in the transformation of ketoximes into corresponding amides via the Beckmann rearrangement.[17] As a consequence, we wondered if TsCl, mechanistically similar to BOP-Cl, TAPC and CNC, also can catalyze the Beckmann rearrangement efficiently. In this article, we are going to present our results of the TsCl-catalyzed Beckmann rearrangement of ketoximes to corresponding amides.

## 2. Results and discussion

Initially, *p*-toluenesulfonyl chloride TsCl was chosen for the catalytic Beckmann rearrangement. As shown in Table 1, to our amazement, catalytic amount (10 mol %) of TsCl was found to smoothly convert the acetophenone oxime **1** into acetanilide **2** in excellent yield (99% yield). Furthermore, decrease of the catalytic amount of TsCl to 5 mol % gave acetanilide in 95% yield. It is very clear that TsCl can catalyze the Beckmann rearrangement smoothly and give the rearrangement product in excellent yield. Therefore, it also indicated that a catalytic mechanism shown in Scheme 1, similar to that of BOP-Cl[15] and CNC[14] system, may be accountable for it catalytic behavior. In order to rule out the possibility of potential acid (HCl) catalyzed pathway, a competitive rearrangement experiment of acetophenone oxime **1** was carried out by using 10 mol % of HCl in anhydrous $CH_3CN$ at reflux temperature, and gave no desired amide **2**.

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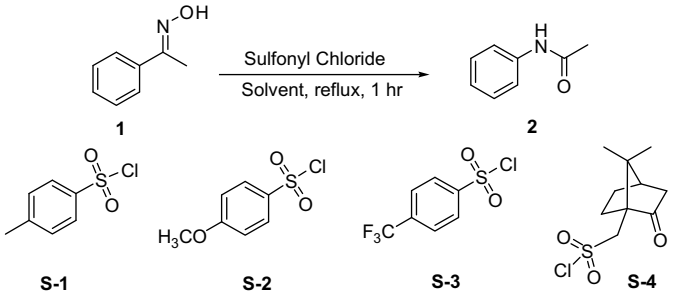
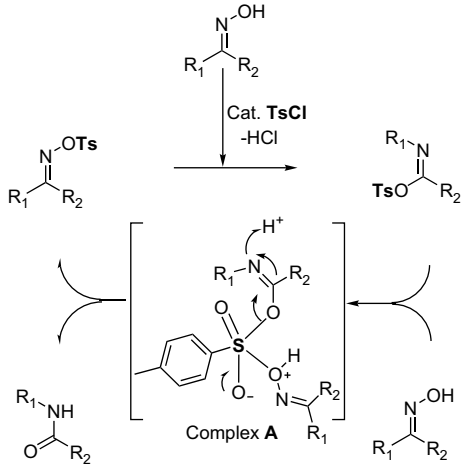
**Table 1**
Sulfonyl chloride catalyzed Beckmann rearrangement of acetophenone oxime




| Entry | Sulfonyl chloride | mol % | Solvent | Yield[a,b] (%) |
|---|---|---|---|---|
| 1 | **S-1** | 10 | $CH_3CN$ | 99 |
| 2 | **S-1** | 5 | $CH_3CN$ | 95 |
| 3 | **S-2** | 5 | $CH_3CN$ | 96 |
| 4 | **S-3** | 5 | $CH_3CN$ | 97 |
| 5 | **S-4** | 5 | $CH_3CN$ | 50 |
| 6 | **S-1** | 5 | Toluene | Trace |
| 7 | **S-1** | 5 | Dioxane | Trace |
| 8 | **S-1** | 5 | THF | Trace |

[a] Ketoximes (2 mmol) were used for the Beckmann rearrangement in anhydrous MeCN (4 mL).
[b] Isolated yields.



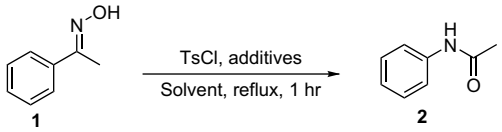

**Scheme 1.** Proposed mechanism for TsCl-catalyzed Beckmann rearrangement.

Further screen of sulfonyl chlorides showed that aryl sulfonyl chloride bearing both electron-donating and electron-withdrawing groups gave the very similar result. However, camphorsulfonyl chloride **S-4** shows moderate catalytic activity and gave its amide in 50% yield. The reason for lower catalytic activity of **S-4** might ascribe to an undetermined electronic effect on the sulfur center causing by different substituents. In terms of availability and chemical stability, combined with above result, TsCl was chosen for further study. Next, we examined the effect of solvents on the Beckmann rearrangement of acetophenone oxime. As shown in Table 1, polar solvent acetonitrile gave its amide in 95% yield (entry 2), while other nonpolar solvents all failed to give their amides in satisfactory yields.

In order to screen the optimal catalytic system, Lewis acids such as $ZnCl_2$, $InCl_3$ were also investigated as co-catalysts to further optimize the rearrangement.

From Table 2, it is clear that with $ZnCl_2$ as co-catalyst, the amount of TsCl could be further decreased to 2 mol % without notable decrease of its catalytic activity. $ZnCl_2$ (5 mol %) gave 99% yield of the amide (entry 2). $ZnCl_2$ exhibits the highest co-catalytic activity among all co-catalysts (entries 4 and 5). Previous report suggests that sole Lewis acid could hardly catalyze the Beckmann rearrangement.[14] In our case, 2 mol % of TsCl solely gave much less catalytic activity for the Beckmann rearrangement of acetophenone oxime. Interestingly, when 0.05 equiv of water and 1 equiv (based on oxime) were added, *N*-acetyl aniline was obtained in 50% (entry 6) and 5% (entry 7), respectively, despite the fact that TsCl shows enough stability in aqueous solution. The same phenomenon was reported in ionic liquid supported sulfonyl chloride catalyzed Beckmann rearrangement.[18] Anhydrous solvent somehow played a key role on the catalytic activity of the Beckmann rearrangement. With all above results together, 5 mol % TsCl and/or 2 mol % TsCl/2 mol % $ZnCl_2$ in anhydrous acetonitrile was chosen as optimal catalytic system for Beckmann rearrangement in our study.

**Table 2**
Effect of acids as co-catalysts on the TsCl-catalyzed Beckmann rearrangement of acetophenone oxime

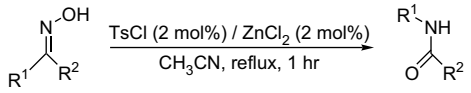



| Entry | TsCl (mol %) | Additive (mol %) | Yield[a,b] (%) |
|---|---|---|---|
| 1 | 5 | None | 95 |
| 2 | 5 | $ZnCl_2$ (5) | 99 |
| 3 | 2 | None | 35 |
| 4 | 2 | $ZnCl_2$ (2) | 96 |
| 5 | 2 | $InCl_3$ (2) | 67 |
| 6 | 2 | $Zn(ClO)_4$ (2) | 94 |
| 7 | 5 | $H_2O$ (5) | 50 |
| 8 | 5 | $H_2O$ (100) | 5 |

[a] Ketoximes (2 mmol) were used for the Beckmann rearrangement in anhydrous MeCN (4 mL).
[b] Isolated yields.

The generality and scope of the Beckmann rearrangement of ketoximes to amides catalyzed by TsCl or TsCl/$ZnCl_2$ catalyst systems were then investigated (Table 3). It is obvious that excellent yields were obtained for most of oximes, aromatic oximes in particular, in acetonitrile under reflux condition for 1 h. TsCl (2 mol %)

**Table 3**
Scope of TsCl/$ZnCl_2$ catalyzed Beckmann rearrangement[a]



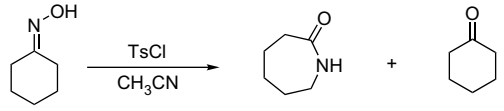

| Entry | $R^1$ | $R^2$ | Yield[b] (%) |
|---|---|---|---|
| 1 (**2a**) | Ph | Me | 96 |
| 2 (**2b**) | Ph | Ph | 99[c] |
| 3 (**2c**) | p-(Me)$C_6H_4$ | Ph | 98[c] |
| 4 (**2d**) | p-(Me)$C_6H_4$ | *p*-(Cl)$C_6H_4$ | 99[c] |
| 5 (**2e**) | p-(Me)$C_6H_4$ | *p*-(MeO)$C_6H_4$ | 98[c] |
| 6 (**2f**) | p-(Cl)$C_6H_4$ | *p*-(MeO)$C_6H_4$ | 98[c] |
| 7 (**2g**) | p-(Me)$C_6H_4$ | Me | 99 |
| 8 (**2h**) | *p*-(MeO)$C_6H_4$ | Me | 98 |
| 9 (**2i**) | *o*-(MeO)$C_6H_4$ | Me | 95 |
| 10 (**2j**) | *m*-(MeO)$C_6H_4$ | Me | 97 |
| 11 (**2k**) | Ph | Et | 98 |
| 12 (**2l**) | *p*-(Cl)$C_6H_4$ | Me | 40 (97[d]) |
| 13 (**2m**) | $(CH_2)_{11}$ | | 99 (99[e]) |
| 14 (**2n**) | $C_8H_{17}$ | Me | 98[f] |
| 15 (**4**) | $(CH_2)_5$ | | <5[c] |

[a] Ketoximes (2 mmol) were used for the Beckmann rearrangement in anhydrous MeCN (4 mL) in the presence of TsCl (2 mol %) and $ZnCl_2$ (2 mol %).
[b] Isolated yields (overall yields of isomeric mixtures for the cases of **2c–f**).
[c] TsCl (2 mol %) was used and the reaction mixture was refluxed for 1 h.
[d] TsCl (10 mol %) was used and the reaction mixture was refluxed for 2 h.
[e] The arrangement of ketoxime (100 mmol) in the MeCN (50 mL) was carried out by using TsCl (1 mol %) and $ZnCl_2$ (1 mol %).
[f] TsCl (5 mol %) and $ZnCl_2$ (5 mol %).

without any co-catalyst could efficiently catalyze Beckmann rearrangement of diaryl ketoxime in almost quantitative yields providing the 5:4 ratio of corresponding isomeric mixtures caused by the 5:4 ratio of *E*/*Z* mixture of corresponding ketoximes (entries 2–6). For acetophenone oxime series, excellent yields were obtained for the monosubstituted ketoxime bearing methyl or methoxy group on aromatic ring (entries 7–10). Unfortunately, 1-(4-chlorophenyl)ethanone oxime gave corresponding amide in only 40% yield under standard reaction condition, which can be improved to 97% when 10 mol % of TsCl was used (entry 12). Furthermore, the Beckmann rearrangement of aliphatic oximes was also investigated. We found that our catalytic system is applicable to aliphatic oximes with a relatively large ring (entry 11). Scale-up test was conducted for the Beckmann rearrangement of cyclododecanone oxime (100 mmol). Perfect yield was obtained with TsCl (1 mol %)/$ZnCl_2$ (1 mol %) (entry 13). The yield of rearrangement product of nonan-2-one oxime reached to 98%, when TsCl (5 mol %)/$ZnCl_2$ (5 mol %) was used as catalyst system (entry 14). However, the rearrangement of cyclohexanone oxime gave only trace amount of ε-caprolactam by using TsCl (5 mol %), and reaction system became sluggish and turned to brown-black after prolonging the reaction time. This result is very similar to that of the CNC,[14] BOP-Cl[15] system.

Interestingly, both conversion and selectivity dramatically increased when the loading of TsCl increased to 20 mol % (entries 2 and 3 in Table 4). Further increased to 30 mol %, better conversion and selectivity were obtained and the decrease of reaction temperature to 60 °C gave very similar conversion and selectivity (entries 5 and 6). When 20 mol % MsCl was employed, almost quantitative conversion and 88% of selectivity were obtained (entry 7).

**Table 4**
The catalytic Beckmann rearrangement of cyclohexanone oxime using TsCl




3 4 5

| Entry | Catalyst (mol %) | Temp | Conv./% | Sel. of **4**[a] (%) |
|---|---|---|---|---|
| 1 | TsCl (5) | Reflux | 12 | 35 |
| 2 | TsCl (10) | Reflux | 24 | 53 |
| 3 | TsCl (20) | Reflux | 66 | 83 |
| 4 | TsCl (20) | 60 °C | 74 | 71 |
| 5 | TsCl (30) | 60 °C | 90 | 94 |
| 6 | TsCl (30) | Reflux | 96 | 93 |
| 7 | MsCl (20) | 60 °C | >99 | 88 |

[a] Ketoximes (2 mmol) were used for the Beckmann rearrangement in anhydrous MeCN (2 mL), and the conversion and selection were determined by GC.

## 3. Conclusion

In summary, we have developed new catalytic system using TsCl as highly efficient organocatalyst for Beckmann rearrangement. In most cases, excellent yields could be obtained by using 5 mol % TsCl or 2 mol % TsCl/2 mol % $ZnCl_2$ in anhydrous acetonitrile. MsCl (20 mol % or 30 mol % of TsCl) was necessary for cyclohexanone oxime case. Further studies will be focusing on exploring more versatile and environ-benign catalytic Beckmann rearrangement system, and clarifying the catalytic mechanism.

## 4. Experimental

### 4.1. General methods

All solvents were distilled under standard procedures prior to use under nitrogen atmosphere (For example: $CH_3CN$ distilled from $CaH_2$; THF, dioxane, toluene distilled from sodium). $^1H$ (400 MHz) and $^{13}C$ (100 MHz) NMR chemical shifts are reported in $CDCl_3$ 7.27 ppm for $^1H$, 77 ppm for $^{13}C$ as standards and coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to designate signal multiplicity: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad.

### 4.2. General procedure A

A solution of ketoxime (2 mmol), 1–5 mol % of TsCl and/or 0–2 mol % Lewis acid in 4 mL of dry MeCN was refluxed under a nitrogen atmosphere. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous sodium hydrogen carbonate. The organic layer was extracted with ethyl acetate, dried over anhydrous sodium sulfate, and concentrated on rotary vacuum evaporator. The resulting crude product was purified by column chromatography on silica gel to give the corresponding amide in high yield.

Since all products are known, only the data of several typical compounds were listed as following.

*4.2.1. Acetanilide (**2a**).* Mp: 114–115 °C (lit.[13] mp 114–116 °C); $^1H$ NMR: $\delta$ 2.17 (s, 3H), 7.10 (t, *J*=7.4 Hz, 1H), 7.30–7.35 (m, 3H), 7.50 (d, *J*=8.0 Hz, 2H); $^{13}C$ NMR: $\delta$ 169.38, 138.18, 128.86, 124.28, 120.35, 24.30.

*4.2.2. N-Phenylbenzamide (**2b**).* Mp: 164–165 °C (lit.[19] mp 164–165 °C); $^1H$ NMR: $\delta$ 8.03 (br s, 1H), 7.87 (d, *J*=7.3 Hz, 2H), 7.66 (d, *J*=7.9 Hz, 2H), 7.54 (t, *J*=7.3 Hz, 1H), 7.46 (t, *J*=7.4 Hz, 2H), 7.37 (t, *J*=7.9 Hz, 2H), 7.16 (t, *J*=7.4 Hz, 1H); $^{13}C$ NMR: $\delta$ 165.88, 137.96, 135.00, 131.81, 129.07, 128.76, 127.06, 124.57, 120.31.

*4.2.3. N-p-Tolylacetamide (**2g**).* Mp: 149–150 °C (lit.[13] mp 149–151 °C); $^1H$ NMR: $\delta$ 8.28 (br s, 1H), 7.40 (d, *J*=8.2 Hz, 2H), 7.09 (d, *J*=8.1 Hz, 2H), 2.30 (s, 3H), 2.12 (s, 3H); $^{13}C$ NMR: $\delta$ 168.95, 135.53, 133.84, 129.36, 120.30, 24.28, 20.84.

*4.2.4. N-Phenylpropionamide (**2k**).* Mp 106–107 °C (lit.[13] mp 103–104 °C); $^1H$ NMR: $\delta$ 8.30 (s, 1H), 7.55 (d, *J*=7.8 Hz, 2H), 7.27 (t, *J*=7.8 Hz, 2H), 7.08 (t, *J*=7.4 Hz, 1H), 2.37 (q, *J*=7.4 Hz, 2H), 1.21 (t, *J*=7.6 Hz, 3H); $^{13}C$ NMR: $\delta$ 172.97, 138.24, 128.84, 124.12, 120.25, 30.55, 9.81.

*4.2.5. Azacyclotridecan-2-one (**2m**).* Mp 150–151 °C (lit.[20] mp 143–145 °C); $^1H$ NMR: $\delta$ 6.07 (br s, 1H), 3.26 (dd, *J*=5.7, 10.5 Hz, 2H), 2.19–2.16 (m, 2H), 1.68–1.62 (m, 2H), 1.55–1.45 (m, 2H), 1.34–1.27 (m, 14H); $^{13}C$ NMR: $\delta$ 173.57, 39.00, 36.82, 28.27, 26.73, 26.32, 26.17, 25.71, 25.20, 24.92, 24.61, 23.90.

For the case of caprolactam (**4**), 5–30 mol % of TsCl or MsCl was used. The conversion and selectivity were analyzed by GC (detailed GC analytical data please see Supplementary data).

## Acknowledgements

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## Supplementary data

The $^1H$ NMR and $^{13}C$ NMR copies of most compounds and the copies of GC data for caprolactam will be attached as Supplementary data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.07.036.

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