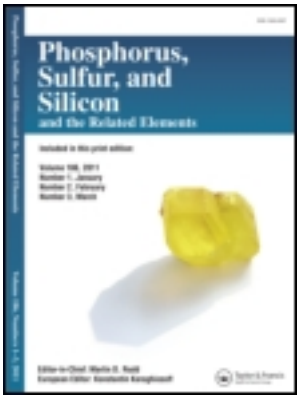

Phosphorus, Sulfur, and Silicon and the Related Elements

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A Simple and Highly Efficient One-Pot Procedure for the Synthesis of Amides via Beckmann Rearrangements Using 1-Tosylimidazole (TsIm)

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A SIMPLE AND HIGHLY EFFICIENT ONE-POT PROCEDURE FOR THE SYNTHESIS OF AMIDES VIA BECKMANN REARRANGEMENTS USING 1-TOSYLIMIDAZOLE (TsIm)

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A facile and highly efficient method for one-pot Beckmann rearrangement of ketoximes into N-substituted amides using N-(p-toluenesulfonyl)imidazole (TsIm) is described. In this method, ketoximes are refluxed with TsIm and Cs_2CO_3 in the presence of SiO_2 as a recyclable catalyst in DMF affording the corresponding amides in high yields. This methodology is highly efficient and regioselective for various structurally diverse ketoximes including symmetrical and unsymmetrical as well as cyclic oximes. The results of quantum mechanical studies used to rationalize the experimental outcomes are discussed.

Keywords Amide; Beckmann rearrangement; ketoxime; SiO_2; *N*-(*p*-toluenesulfonyl)imidazole (TsIm)

INTRODUCTION

Amides and lactams are potential precursors for the synthesis of various natural products as well as synthetic intermediates for medicinal drugs and materials.[1] There are numerous general methods for accessing amides.[2] Among these, perhaps the best known transformation of ketoximes into *N*-substituted amides is the Beckmann rearrangement (BR).[2,3] BR has been extensively used and is a fundamental reaction in organic synthesis, which has led to numerous applications due to the ease with which nitrogen can be inserted into carbon chains starting from readily available ketones. It also represents a powerful method particularly for manufacturing ε-caprolactam as a precursor of nylon-6 in the chemical industry. The conventional BR, however, generally requires relatively high reaction temperature, large amounts of strong Lewis or Brønsted acids, dehydrating media, and harsh reaction conditions, and causes a large number of byproducts and wastes that can not be used with sensitive substrates. On this basis, mild conditions were explored and

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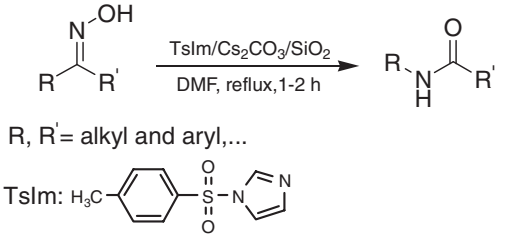
several variants were developed that essentially focused on the formation of activated oxime derivatives that rearrange to the corresponding amides. For instance, cyanuric chloride in DMF[4a] or MeCN,[4b] chloral,[5] solid metaboric acid,[6] $[RhCl(cod)_2]/(p\text{-tol})_3P$,[7] sulfamic acid,[8] ethyl chloroformate/boron trifluoride etherate,[9] *O*-alkyl-*N,N*-dimethyl formamidium salt,[10] and chlorosulfonic acid[11] have been used for BR. Recently, BR in supercritical water[12] and ionic liquid[13] have also been reported. The BR of oxime sulfonates[14] is usually preferred due to their high reactivity, ease of handling, and facile preparation from oxime using TsCl or MsCl.[14c,d,15] Although this method possesses synthetic value, all reported procedures involve the isolation of the starting oxime sulfonates, some of which lack stability, followed with a tedious workup and cumbersome separation processes. Furthermore, working with harmful and toxic sulfonyl halides remains a problem. Therefore, the in situ generation of *O*-ketoxime-sulfonates with a cheap, nontoxic, and stable sulfonating reagent would seem to be a suitable and attractive strategy, and indeed there are a few reports that have explained the one-pot BR of ketoximes via the oxime sulfonate intermediates.[16]

The aforementioned methods have several drawbacks such as non-generality for various types of ketoximes, the use of harmful and/or expensive reagents, undesirable side reactions, formation of large amounts of byproducts and wastes, long reaction times, and low yields. So, there is still a need to extend and improve a practical, efficient, and selective method for the Beckmann rearrangement. Recently, we reported *N*-(*p*-toluenesulfonyl) imidazole (TsIm) as a highly efficient, cheap, and stable reagent for various organic transformations including one-pot conversion of alcohols to alkyl azides,[17a] alcohols to nitriles,[17b] esterification of alcohols,[17c] and *N*-alkylation of nucleobases.[17d] In continuation of our interest in application of TsIm in organic synthesis, in this article we report that symmetrical and unsymmetrical ketoximes can be efficiently converted into their corresponding amides using TsIm/SiO_2 in the presence of Cs_2CO_3 in refluxing DMF (Scheme 1).

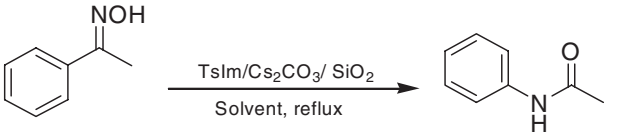


Scheme 1

RESULTS AND DISCUSSION

The first step of this synthetic approach involved the optimization of reaction conditions. Initially, the effect of various solvents on the model reaction of acetophenone oxime in the presence of freshly prepared TsIm[17a] (1.2 equiv) and SiO_2 (1 g) as a catalyst was studied. The results are depicted in Table I. As the data in Table I demonstrate, DMF (entry 2) was the most efficient solvent; thus it was the solvent of choice for all reactions. Using DMSO, MeCN, and HMPA (Table I, entries 1, 5, and 6) also afforded high yields of the corresponding amide; however, the reaction time for completion was longer.

Table I Effect of various solvents on the conversion of acetophenone oxime into *N*-phenyl acetamide

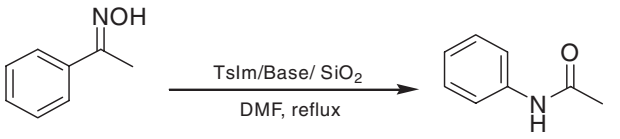


Entry	Solvent	Time (h)	Yield[a] (%)
1	DMSO	3	90
2	DMF	1	96
3	DMF[b]	12	NR[c]
4	THF	48	NR[c]
5	MeCN	4	84
6	HMPA	4	86
7	Toluene	48	Trace
8	Acetone/H_2O[d]	10	30
9	H_2O	48	Trace

[a]Isolated yield.
[b]Anhydrous DMF.
[c]No reaction.
[d](1:1) ratio.

The choice of the base for activation of the ketoximes to react with TsIm and subsequent conversion into amides had a great significance. In this case, we evaluated the potency of several organic and inorganic bases on the model reaction (Table II). In absence of the base, the reaction was not achieved at all or achieved in trace amounts even after prolonged reaction time. As the results in Table II indicate, among the examined bases in this experiment, Cs_2CO_3 (Table II, entry 6) proved to be the most efficient base for the

Table II Effect of various bases on the conversion of acetophenone oxime into *N*-phenyl acetamide



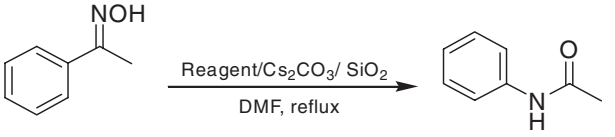
Entry	Base	Time (h)	Yield[a] (%)
1	None	24	trace
2	DBU	7	30
3	DABCO	12	25
4	DMAP	18	10
5	MgO	10	20
6	Cs_2CO_3	1	96
7	K_2CO_3	4	63
8	TEA	10	20
9	Al_2O_3[b]	4	75

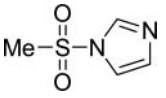
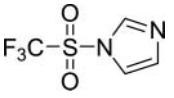
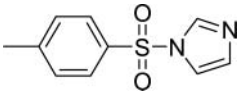
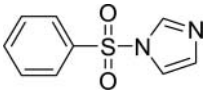
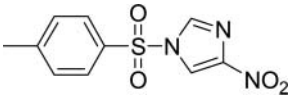
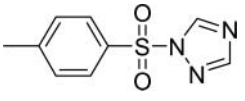
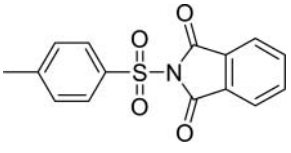
[a]Isolated yield.
[b]Basic alumina.

conversion of acetophenone oxime into *N*-phenyl acetamide. Other bases such as K_2CO_3 and Al_2O_3 (Table II, entries 7 and 9) afforded lower yields of amide.

The optimized amount of TsIm was found to be 1.2–2.0 equiv. per equivalent of ketoxime. We also investigated other TsIm analogues (Table III). As the data in Table III indicate, using TsIm (Table III, entry 3) increased the reaction rate and yield in comparison

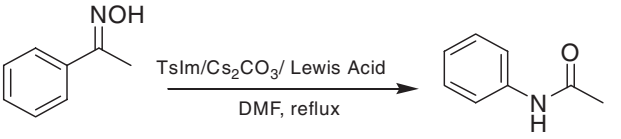
Table III Comparison of TsIm reactivity with analogues on the conversion of acetophenone oxime into *N*-phenyl acetamide



Entry	Reagent	Time (h)	Yield[a] (%)
1		7	65
2		6	58
3		1	96
4		7	60
5		12	54
6		12	49
7		48	NR[b]

[a]Isolated yield.
[b]No reaction.

Table IV Effect of various Lewis acids on the conversion of acetophenone oxime into *N*-phenyl acetamide



Entry	Lewis acid	Time (h)	Yield[a] (%)
1	None	8	42
2	LiCl	5	82
3	SiO_2	1	96
4	$Al(OAc)_3$	2	91
5	$MnCl_2.4H_2O$	18	15
6	$CdCl_2.H_2O$	2	88
7	$NiCl_2.6H_2O$	8	30
8	$FeCl_2.4H_2O$	3	90
9	$SnCl_2.2H_2O$	10	38
10	$ZnCl_2$	5	45
11	CuCl	10	20

[a]Isolated yield.

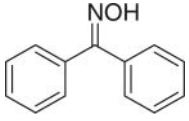
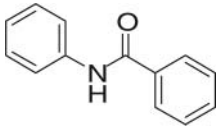
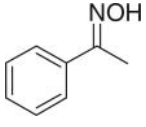
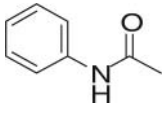
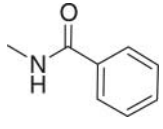
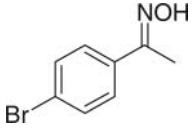
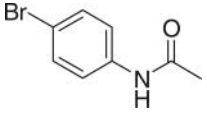
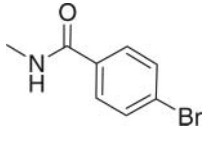
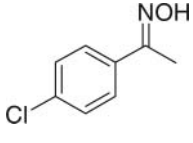
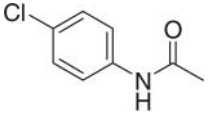
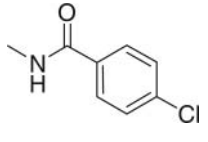
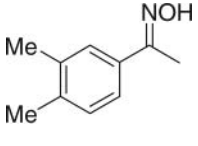
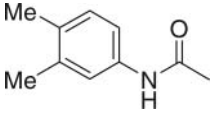
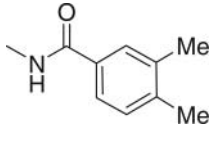
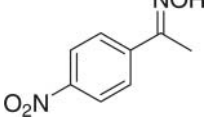
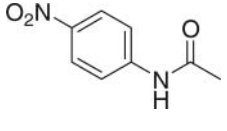
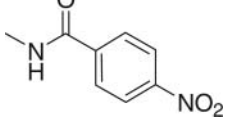
with other sulfonyl analogues. Replacing the tolyl in TsIm with methyl, trifluoromethyl, and phenyl did not afford satisfactory results (Table III, entries 1, 2, and 4). Furthermore, other azole analogues of TsIm were not as effective as imidazole (Table III, entries 5 and 6). *N*-Tosyl phthalimide (Table III, entry 7) was inactive for the conversion of acetophenone oxime into *N*-phenyl acetamide even after refluxing for 48 h.

We also evaluated the role of several Lewis acids as catalysts on the reaction model (Table IV). In the absence of catalyst, the reaction occurred but only in moderate yield. However, using SiO_2 (Table IV, entry 3) shortened the reaction time and remarkably increased the yield. The use of $Al(OAc)_3$, $CdCl_2.H_2O$, and $FeCl_2.4H_2O$ (Table IV, entries 4, 6, and 8) also afforded good results. However, SiO_2 was preferred for use not only because of higher yield and reasonable reaction rate but also because of it is cheap, easy to handle, and readily available. Moreover, SiO_2 is a heterogeneous and reusable catalyst that can be removed from the reaction mixture easily by simple filtration.[19]

The generality and versatility of this method was demonstrated by its application to various structurally different ketoximes (Table V). As the results in Table V indicate, both symmetrical and unsymmetrical ketoximes were successfully converted into the amides in good yields. Most of the oximes used in this research are commercially available or can be easily prepared by the procedure explained in the literature.[20] By this method, both (*E*)- and (*Z*)-isomers of ketoximes can be converted into amides and in most cases a mixture of (*Z*)- and (*E*)-isomers was used.

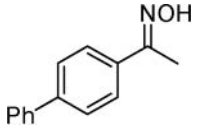
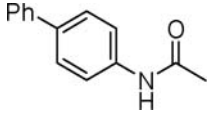
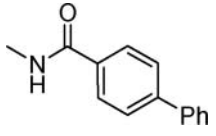
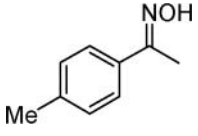
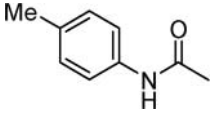
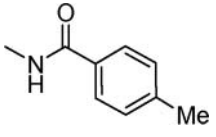
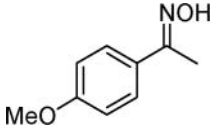
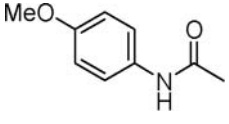
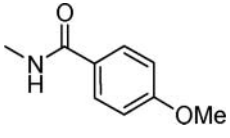
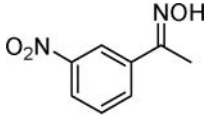
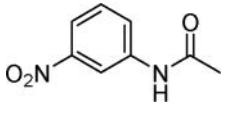
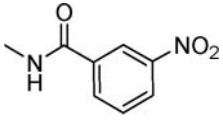
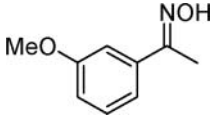
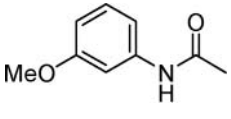
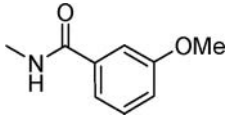
The BR mechanism of ketoximes and its *O*-sulfonate derivatives is well discussed in many articles.[14g,21] Both *Z*- and *E*-*O*-oxime sulfonates are prone to BR, which in most cases an alkyl or aryl residue *anti* to the leaving group is prior to migrate.[14g,21] Since we simultaneously have *Z*- and *E*-*O*-oxime sulfonates in our reaction mixture, the synthesis of two isomer amides is expected. Furthermore, BR attempts of pure *E*- or *Z*-oxime isomers or *O*-oximes sulfonates did not furnish the synthesis of an amide isomer exclusively.[22]

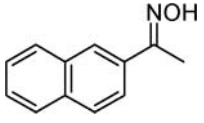
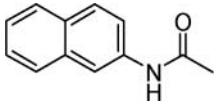
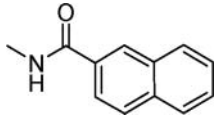
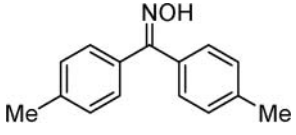
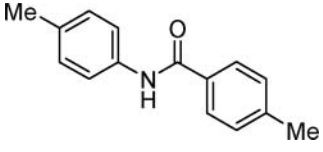
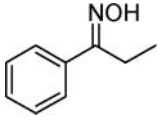
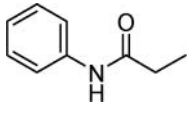
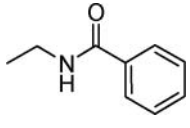
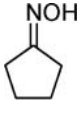
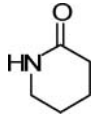
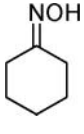
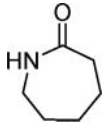
Table V Beckmann rearrangement of ketoximes using TsIm/SiO2/Cs2CO3 in refluxing DMF

Entry[Ref]	Ketoxime	Amide (a)[a]	Amide (b)[a]	Time (h)	Yield (a)[b] (%)	Yield (b)[b] (%)
1[5,7–9,11a,18a,18c]			—	1	95	—
2[4,5,8,9,11a,18a,18c]				1	95	5
3[5,18a]				2	90	4
4[5,18a]				2	89	7
5[18d]				2	91	4
6[11a]				2	86	8

(Continued on next page)

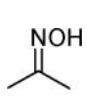
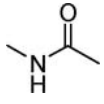
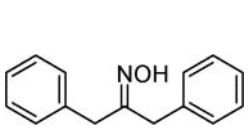
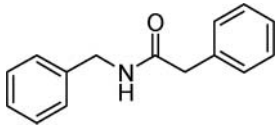
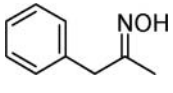
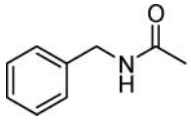
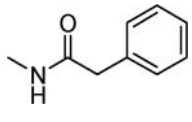
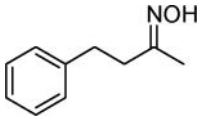
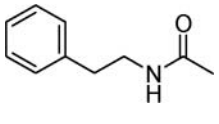
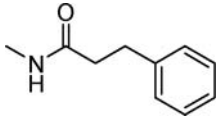
Table VI Beckmann rearrangement of ketoximes using TsIm/SiO2/Cs2CO3 in refluxing DMF *(Continued)*

Entry[Ref]	Ketoxime	Amide (a)[a]	Amide (b)[a]	Time (h)	Yield (a)[b] (%)	Yield (b)[b] (%)
7[18a]				2	91	5
8[5,9,11a,18a]				1.5	94	6
9[4b,5,11a,18a]				1	95	4
10[4a,11a]				2	88	5
11[4b]				1.5	93	7

12[4,5,8]				2	90	5
13[7]			—	1.5	92	—
14[5,7,18c]				2	98	2
15[8,11a]			—	2	88	—
16[4a,8,11a,18c]			—	2	74	—

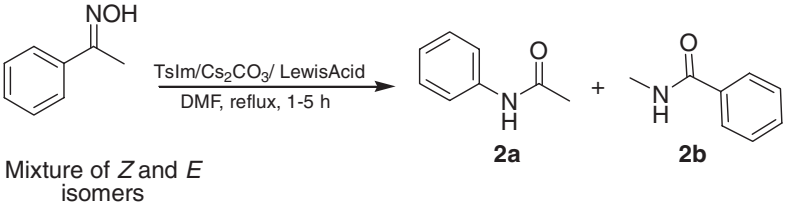
(Continued on next page)

Table V Beckmann rearrangement of ketoximes using TsIm/SiO2/Cs2CO3 in refluxing DMF *(Continued)*

Entry[Ref]	Ketoxime	Amide (a)[a]	Amide (b)[a]	Time (h)	Yield (a)[b] (%)	Yield (b)[b] (%)
17[8,11a]			—	2	85	—
18[9]			—	2	90	—
19[18b,c]				2	91	7
20[9,18c]				2	89	4

[a]All products were characterized by ^{1}H and ^{13}C-NMR, IR, CHN and MS analysis.
[b]Isolated yield.

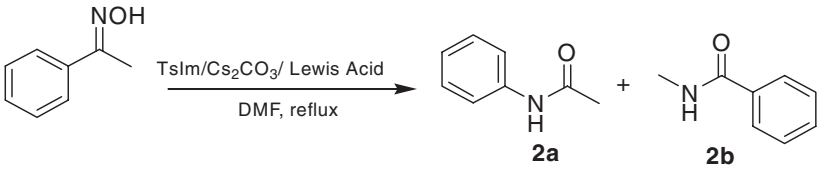
It is well demonstrated and fully established that both *Z*- and *E*-oxime isomers can be interconverted by nitroso-oxime tautomerization ([1,3]-H shift).[23] In addition, isomeric interconversion can happen for *Z* and *E*-*O*-oxime sulfonates in strong acidic media.[16a] These isomeric interconversions annihilate the effort for selective synthesis of one isomer amide and often lead to cumbersome and tedious separation of isomers from a complicated reaction mixture. However, comparing the ratio of synthesized amides from acetophenoxime using our method that employs SiO_2 with other effective Lewis acids (Scheme 2) shown in Table IV, we experienced that ratios of two amide isomers can be altered by changing the Lewis acid. The results are depicted in Table VI.



Scheme 2

As the data in Table VI indicate, among the effective Lewis acids used in our experiments (see Table IV), SiO_2 is proven to exhibit the better selectivity for catalyzing BR of *E*-acetophenoxime that affords *N*-phenyl acetamide (**2a**) mainly with a trace amount of **2b** isomer. Although the better migratory aptitude is for anti phenyl moiety in *E*-isomer in comparison with anti methyl in *Z*-isomer, however, because of nitroso-oxime tautomeric interconvertion of the *E*- and *Z*-isomer, the generation of amide **2b** is inevitable, and this was indicated by TLC and HPLC analysis. One may assume the weaker Lewis acid property of SiO_2 compared to other Lewis acids in Table VI is the reason for the higher selectivity. Nevertheless, using *ab initio* (Hartree-Fock; 6–31G, run on Gaussian 98 version 9.2 software) and semi-empirical [Austin Model 1 (AM1) and Parameterized Model 3 (PM3) run on MOPAC in CS Chem 3D Ultra 8; 2004 Cambridge Soft and Hyperchem,

Table VI Effect of various Lewis acids on the ratio of *N*-phenyl acetamide (**2a**)/*N*-methyl benzamide (**2b**)



Entry	Lewis acid	Time (h)	**2a/2b**[a]
1	LiCl	5	7.0/3.0
2	SiO_2	1	9.5/0.5
3	$Al(OAc)_3$	2	6.5/3.5
4	$CdCl_2.H_2O$	2	7.5/2.5
5	$FeCl_2.4H_2O$	3	8.0/2.0

[a]The ratios were attained by HPLC analysis.

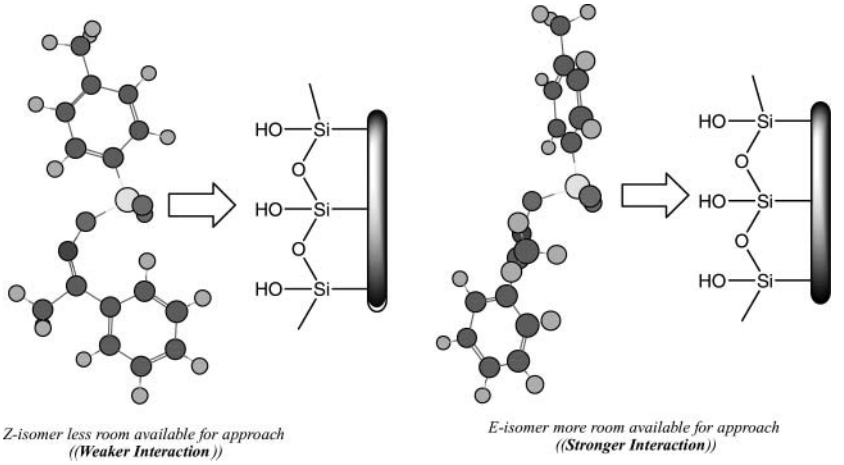
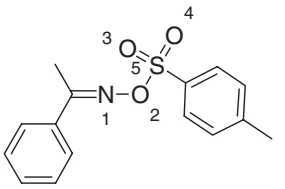


Figure 1 Binding of *Z*- and *E*-*O*-acetophenoxime sulfonate at surface of silica gel.

Hypercube Inc., version 7] quantum mechanical calculations[24] to rationalize this result has manifested more accurate standpoints. The studies indicate that higher reactivity of *E*-*O*-acetophenoxime sulfonate does not merely depend on phenyl moiety anti to leaving group, but also depends on differences in the geometrical and spatial orientation between *Z*- and *E*-*O*-acetophenoxime sulfonate. In Figure 1, the approaches of the optimized geometry of *Z*- and *E*-*O*- acetophenoxime sulfonate for binding to the surface of silica gel using *ab initio* 6-31G is demonstrated. As is shown in Figure 1, it is supposed that the hydrogen bonding between hydroxyl groups on silica surface and negative oxygens of sulfonate direct the approach of *Z*- or *E*-*O*-acetophenoxime sulfonate to the electrophilic center of silicon. To witness this claim, the charges of heteroatoms in both *Z*- and *E*-*O*-acetophenoxime sulfonate were calculated, and the data are depicted in Table VII. As is indicated in Table VII, the oxygen of the sulfonyl moiety has the most negative values, and it is assumed that maximum interaction between these oxygens and the silica surface can happen. However,

Table VII Calculated charges of heteroatoms in *Z*- and *E*-*O*- acetophenoxime sulfonate using AM1 calculations



	Charge[a]				
Isomer	N(1)	O(2)	O(3)	O(4)	S(5)
E-isomer	0.08292	−0.66618	−0.97670	−1.00095	3.12114
Z-isomer	0.08599	−0.69705	−0.98678	−0.98369	3.11724

[a]Charges in Mulliken unit.

comparing the geometrical differences between two isomers is a good indication that the *E*-isomer has more room for approaching the silica surface than *Z*-isomer does.

CONCLUSIONS

A facile and highly efficient method for Beckmann rearrangement of ketoximes into *N*-substituted amides using *N*-(*p*-toluenesulfonyl)imidazole (TsIm) is described. This methodology is highly efficient and regioselective for various structurally diverse ketoximes including symmetrical and unsymmetrical as well as cyclic oximes. In this experiment, SiO_2 as a mild Lewis acid catalyst affects the ease of reaction as well as regioselectivity. Several quantum mechanical reasons were discussed for rationalizing the effect of SiO_2 in this BR.

EXPERIMENTAL

All chemicals were purchased from Fluka or Merck chemical companies except for TsIm[17a] and some of the oximes,[20] which were prepared according to published methods. Solvents were purified and dried according to reported methods[25] and stored over 3Å molecular sieves. The progress of the reactions was followed with TLC using silica gel SILG/UV 254 plates. Silica gel 60, 0.063–0.200 mm (70–230 mesh ASTM) was used for column chromatography. IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H NMR (250 MHz) and ^{13}C NMR (62.5 MHz) were run on a Brüker Avance DPX-250 FT-NMR spectrometer; δ in parts per million, J in hertz. Mass spectra were recorded on a Shimadzu GCeMS-QP 1000 EX apparatus. Microanalyses were performed on a Perkin Elmer 240-B microanalyzer. Melting points (mp) were recorded on a Büchi 510 apparatus in open capillary tubes and are uncorrected.

GENERAL PROCEDURE FOR THE BECKMANN REARRANGEMENT OF KETOXIMES INTO AMIDES

To a double-necked round bottom flask (100 mL) equipped with a condenser, a mixture of ketoxime (0.01 mol), freshly prepared TsIm[17a] (0.012 mol), SiO_2 (1 g), and Cs_2CO_3 (0.01 mol) in DMF (20 mL) was added. The mixture was refluxed, and in most cases, darkening occurred. Reflux was continued until TLC monitoring indicated no further improvement in the conversion (Table V). The catalyst was filtered off, and the filtrate was evaporated under vacuum to remove the solvent. The remaining foam was dissolved in $CHCl_3$ (100 mL) and subsequently washed with water (2 × 100 mL). The organic layer was dried (Na_2SO_4) and evaporated. The crude product was purified by column chromatography on silica gel and eluted with a mixture of *n*-hexane/EtOAc.

REFERENCES

1. (a) M. Negwer and H.-G. Scharnow, *Organic-Chemical Drugs and Their Synonyms*, 8th ed. (Wiley-VCH, Weinheim, Germany, 2001), p. 4254 (b) G. W. A. Milne, *CRC Handbook of Pesticides* (CRC Press, Boca Raton, FL, 1995); (c) A. Greenberg, C. M. Breneman, and J. F. Liebman, *The Amide Linkage Structural Significance in Chemistry, Biochemistry, and Materials Science* (Wiley-Interscience, New York, 2002).
2. (a) J. March, *Advanced Organic Chemistry*, 4th ed. (John Wiley & Sons (Asia) Ltd., Singapore, 2005); (b) G. Tennant, In *Comprehensive Organic Chemistry*, D. Barton, D. W. Ollis, and

I. O. Sutherland, Eds. (Pergamon Press, Oxford, UK, 1979), vol. 2, p. 528 (c) R. C. Larock, *Comprehensive Organic Transformations*, 2nd ed. (VCH, New York, 1999); (d) K. N. Moruoka and H. Yamamoto, In *Comprehensive Organic Chemistry*, B. M. Trost, I. Fleming, and E. Winterfeld, Eds. (Pergamon Press, Oxford, UK, 1991), vol. 6, p. 381.

3. (a) E. Beckmann, *Ber.*, **19,** 988 (1886); (b) B. Jones, *Chem. Rev.*, **35,** 335 (1944); (c) A. H. Blatt, *Chem. Rev.*, **12,** 215 (1933); (d) L. G. Donaruma and W. Z. Heldt, *Org. React.*, **11,** 1 (1960).
4. (a) L. De Luca, G. Giacomelli, and A. Porcheddu, *J. Org. Chem.*, **67,** 6272 (2002); (b) Y. Furuya, K. Ishihara, and H. Yamamoto, *J. Am. Chem. Soc.*, **127,** 11240 (2005).
5. S. Chandrasekhar and K. Gopalaiah, *Tetrahedron Lett.*, **44,** 755 (2003).
6. S. Chandrasekhar and K. Gopalaiah, *Tetrahedron Lett.*, **43,** 2455 (2002).
7. M. Arisawa and M. Yamaguchi, *Org. Lett.*, **3,** 311 (2001).
8. B. Wang, Y. Gu, C. Luo, T. Yang, L. Yang, and J. Suo, *Tetrahedron Lett.*, **45,** 3369 (2004).
9. R. Anilkumar and S. Chandrasekhar, *Tetrahedron Lett.*, **41,** 5427 (2000).
10. Y. Izumi, *Chem. Lett.*, **19,** 2171 (1990).
11. (a) D. Li, F. Shi, S. Guo, and Y. Deng, *Tetrahedron Lett.*, **46,** 671 (2005); (b) M. A. Kira and Y. M. Shaker, *Egypt. J. Chem.*, **6,** 551 (1973).
12. (a) Y. Ikushima, K. Hatakeda, O. Sato, T.Yokoyama, and M. Arai, *J. Am. Chem. Soc.*, **122,** 1908 (2000); (b) O.Sato, Y. Ikushima, and T.Yokoyama, *J. Org. Chem.*, **63,** 9100 (1998); (c) M. Boero, T. Ikeshoji, C. C. Liew, K. Terakura, and M. Parrinello, *J. Am. Chem. Soc.*, **126,** 6280 (2004); (d) Y. Ikushima, O. Sato, M. Sato, K. Hatakeda, and M. Arai, *Chem. Eng. Sci.*, **58,** 935 (2003).
13. (a) J. Peng and Y. Deng, *Tetrahedron Lett.*, **42,** 403 (2001); (b) R. X. Ren, L. D. Zueva, and W. Ou, *Tetrahedron Lett.*, **42,** 8441 (2001); (c) J. Gui, Y. Deng, Z. Hu, and Z. Sun, *Tetrahedron Lett.*, **45,** 2681 (2004).
14. (a) Y. Ishihada, S. Sasatani, K. Maruoka, and H. Yamamoto, *Tetrahedron Lett*., **24,** 3255 (1983); (b) A.Costa, R. Mestres, and J. M. Riego, *Synth. Commun.*, **12,** 1003 (1982); (c) W. Z. Heldt, *J. Am. Chem. Soc.*, **80,** 5880 (1958); (d) R. P. Frutos and D. M. Spero, *Tetrahedron Lett.*, **39,** 2475 (1998); (e) C. A. Grob, H. P. Fischer, W. Raudenbusch, and J. Zergeny, *Helv. Chim. Acta*, **47,** 1003 (1964); (f) J. C. Craig and A. R. Naik,*J. Am. Chem. Soc.*, **84,** 3410 (1962); (g) B. S. Lee, S. Chu, I. Y. Lee, B.-S. Lee, C. E. Song, and D. Y. Chi, *Bull. Korean Chem. Soc.*, **21,** 860 (2000).
15. (a) T. A. Geissman and A. Armen, *J. Am. Chem. Soc.*, **77,** 1623 (1955); (b) D. J. Cram and M. J. Hatch, *J. Am. Chem. Soc.*, **75,** 33 (1953); (c) P. Oxley and W. F. Short, *J. Chem. Soc.*, 1514 (1948); (d) K. Maruoka, T. Miyazaki, M. Ando, Y. Matsumura, S. Sakane, K. Hattori, and H. Yamamoto, *J. Am. Chem. Soc.*, **105,** 2831 (1983).
16. (a) R. F. Brown, N. M. V. Gulick, and G. H. Schmid, *J. Am. Chem. Soc.*, **77,** 1094 (1955); (b) R. K. Hill and O. T. Chortyk, *J. Am. Chem. Soc.*, **84,** 1064 (1962).
17. (a) M. N. Soltani Rad, S. Behrouz, and A. Khalafi-Nezhad, *Tetrahedron Lett.*, **48,** 3445 (2007); (b) M. N. Soltani Rad, A. Khalafi-Nezhad, S. Behrouz, and M. A. Faghihi, *Tetrahedron Lett.*, **48,** 6779 (2007); (c) M. N. Soltani Rad, S. Behrouz, M. A. Faghihi, and A. Khalafi-Nezhad, *Tetrahedron Lett.*, **49,** 1115 (2008); (d) M. N. Soltani Rad, A. Khalafi-Nezhad, S. Behrouz, M. A. Faghihi, A. Zare, and A. Parhami, *Tetrahedron*, **64,** 1778 (2008).
18. (a) F. Matloubi Moghaddam, A. A. Rastegar Rad, and H. Zali-Boinee, *Synth. Commun*., **34,** 2071 (2004); (b) M. K. Dongare, V. V. Bhagwat, C. V. Ramana, and M. K. Gurjar, *Tetrahedron Lett.*, **45,** 4759 (2004); (c) H. Eshghi and Z. Gordi, *Synth. Commun*., **33,** 2971 (2003); (d) B. M. Khadikar and D. J. Upadhyaya, *Synth. Commun.*, **32,** 1867 (2002).
19. The reusability of SiO_2 was checked by elaborating the recycled SiO_2 for ten reactions without remarkable losses in reactivity.
20. J. S. Buck and W. S. Ide, *Org. Syn. Coll. Vol. II*, 622 (1943).
21. (a) S. Yamabe, N. Tsuchida, and S. Yamazaki, *J. Org. Chem.*, **70,** 10638 (2005); (b) M. T. Nguyen, G. Raspoet, and L. G. Vanquickenborne, *J. Am. Chem. Soc.*, **119,** 2552 (1997); (c) W. Z. Heldt, *J. Org. Chem.*, **26,** 1695 (1961).

22. The separation of *E*- and *Z*-oximes was achieved following a procedure in the literature: J. H. Paul, U.S. Patent, 4158015 (1979); *Chem. Abstr.*, **91,** P107810v (1979) and also visit http//www.freepatentsonline.com/4158015.html.
23. To endorse such interconversion, AM1 calculation indicated that the barrier energy is 4.0505 Kcal/mol for conversion of *Z*- and *E*-acetophenoxime to each other. Also see E. D. Raczyńska, T. M. Krygowski, J. E. Zachara, B. Ośmiałowski, and R. Gawinecki, *J. Phys. Org. Chem.*, **18,** 892 (2005).
24. A. Hinchliffe, *Molecular Modeling for Beginners* (John Wiley & Sons, Ltd., Chichester, England, 2005).
25. A. I. Vogel, *Practical Organic Chemistry* (Longmans, Green, London, England, 1954), Chapter 2, pp. 161–176.