

# SYNLETT Spotlight 282

## Synthetic Utility of *N*-Sulfonylimines

Compiled by Davender Kumar Shukla



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Davender Kumar Shukla was born in 1979 at Pratapgarh, Uttar Pradesh, India. He received his M.Sc. degree in 2003. Presently he is working as a university research fellow towards his Ph.D. degree under the supervision of Dr. Arif Ali Khan at Guru Gobind Singh Indraprastha University, Delhi, India. His research work is focused on metal ion catalyzed organic synthesis and the synthesis of new range of *N*-sulfonylimines and their applications in organic synthesis.

Department of Chemistry, University School of Basic & Applied Sciences, Guru Gobind Singh Indraprastha University, Kashmere Gate, Delhi-110403, India.  
E-mail: dev.shukla@rediffmail.com

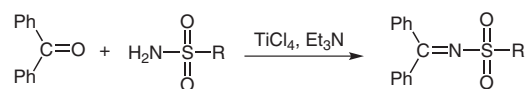
### Introduction:

Analogous to carbon–carbon and carbon–oxygen double bonds, carbon–nitrogen double bond has been an active site of study in recent times. The reactivity of the carbon–nitrogen double bond lies in between that of the carbonyl and olefinic functions. The carbon–nitrogen double bond has an additional lone pair of electrons which leads to its distinctive properties from carbon–carbon double bond.

*N*-Sulfonylimine<sup>1</sup> (also known as sulfonylimine) is one such good example of azomethenic carbon–nitrogen double bond. *N*-Sulfonylimines are useful precursors for the synthesis of important synthetic intermediates such as oxaziridines<sup>2</sup> and aziridines<sup>3</sup> as well as for the synthesis of compounds of medicinal importance.<sup>4–5</sup> *N*-Sulfonylimines also serves as heterodienes and heterodienophiles in [4+2] cycloadditions.<sup>6</sup>

### Preparation:

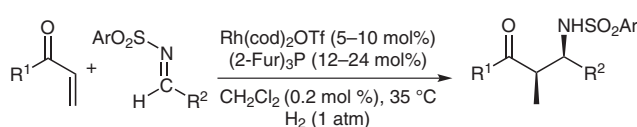
*N*-Sulfonylimines can be synthesised by direct condensation of primary sulfonamides with aldehydes or ketones in the presence of some dehydrating agents (TiCl<sub>4</sub>, 4 Å molecular sieve, MgSO<sub>4</sub>, AlCl<sub>3</sub>).<sup>2,7–9</sup> However, only few methods are reported for the preparation of *N*-Sulfonylimines of enolizable and sterically hindered ketones. Such reactions involve the in situ generation of oxime *O*-sulfinyl derivatives<sup>10</sup> and their subsequent homolytic rearrangement to sulfonylimines. Recently, a simple method has been reported which involves the condensation of simple as well as hindered ketones with 4-toluenesulfonamides in the presence of TiCl<sub>4</sub> and Et<sub>3</sub>N.<sup>11</sup>



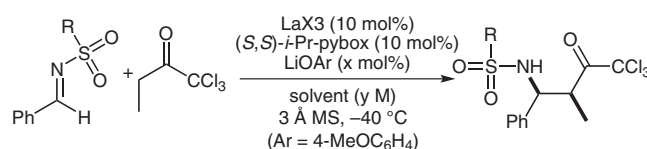
Scheme 1

### Abstracts

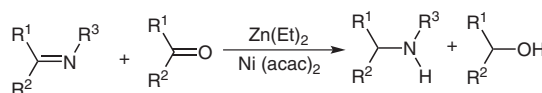
(A) Catalytic hydrogenation of methyl vinyl ketone and ethyl vinyl ketone in the presence of *N*-(2-nitrophenylsulfonyl)imines at ambient pressure with tri-2-furylphosphine ligand rhodium catalysts produces the mannich product with moderate to good *syn*-diastereoselectivity.<sup>12</sup>



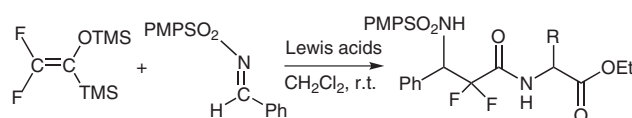
(B) Direct asymmetric mannich-type reaction of *N*-sulfonylimines with trichloromethylketone in the presence of lanthanum aryloxide and Pybox gives β-amino carbonyl compounds.<sup>13</sup>



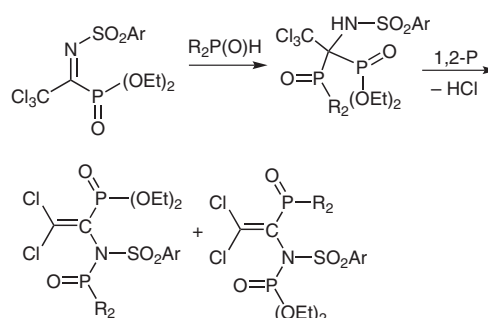
(C) Selective reduction of electronically deficient imines in the presence of ketones, Et<sub>3</sub>Zn, and Ni(acac)<sub>2</sub> produces respective amines in moderate to good yields.<sup>14</sup>



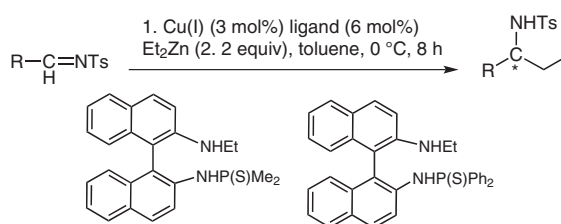
(D) The catalytic mannich reaction of 1,1-difluoro-2-trialkyl(aryl)-silyl-2-trimethylsilyloxyethenes with sulfonylimines gives  $\alpha,\alpha$ -difluoro- $\beta$ -amino acid derivatives.<sup>15</sup>



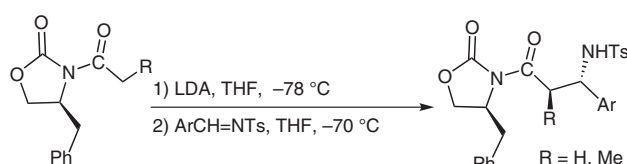
(E) The reaction of phosphorylated *N*-sulfonylimines with hydrophosphoryl agents involve the C–N transfer of phosphoryl group and produce aza-Perkow products.<sup>16</sup>



(F) In the presence of a catalytic amount of chiral diaminothio-phosphoramidate the asymmetric addition of diethyl zinc to *N*-sulfonylimines can be achieved in moderate to good yield ee (63–93%).<sup>17</sup>



(G) The nucleophilic addition of chiral lithium enolates of (*S*)-(-)-4-benzyl-2-oxazolidinone acetamide with *N*-tosylarylaldehyde imines gives  $\beta$ -aryl- $\beta$ -amino acid derivatives in good to excellent diastereoselectivity.<sup>18</sup>



## References

- (1) Ruano, J. L. G.; Alemán, J.; Cid, M. B.; Parra, A. *Org. Lett.* **2005**, 7, 179.
- (2) Davis, F. A.; Lamendola, J. F. Jr.; Nadir, U.; Kluger, E. W.; Sedergran, T. C.; Panunto, T. W.; Billmers, R.; Jenkins, R. Jr.; Turchi, I. J.; Watson, W. H.; Chen, J. S.; Kimura, M. *J. Am. Chem. Soc.* **1980**, 102, 2000.
- (3) Zhou, Y.-G.; Li, A.-H.; Hou, X.-L.; Dai, L.-X. *Tetrahedron Lett.* **1997**, 38, 7225.
- (4) Zhou, X.-T.; Lin, Y.-R.; Dai, L.-X.; Sun, J.; Xia, L.-J.; Tang, M.-H. *J. Org. Chem.* **1999**, 64, 1331.
- (5) Hayashi, T.; Kishi, E.; Soloshonok, V. A.; Uozumi, Y. *Tetrahedron Lett.* **1996**, 37, 4969.
- (6) Boger, D. L.; Weinreb, S. M. *Hetero Diels–Alder Methodology in Organic Synthesis*, In *Organic Chemistry*, Vol. 47; Wasserman, H. H., Ed.; Academic Press: New York, **1987**, 36.
- (7) Boger, D. L.; Corbett, W. L.; Curran, T. T.; Kasper, A. M. *J. Am. Chem. Soc.* **1991**, 113, 1713.
- (8) Jennings, W. B.; Lovely, C. J. *Tetrahedron Lett.* **1988**, 29, 3725.
- (9) Davis, F. A.; Zhou, P.; Lal, G. S. *Tetrahedron Lett.* **1990**, 31, 1653.
- (10) Boger, D. L.; Corbett, W. L. *J. Org. Chem.* **1992**, 57, 4777.
- (11) Ram, R. N.; Khan, A. A. *Synth. Commun.* **2001**, 31, 841.
- (12) Garner, S. A.; Krische, M. J. *J. Org. Chem.* **2007**, 72, 5843.
- (13) Morimoto, H.; Lu, G.; Aoyama, N.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2007**, 129, 9588.
- (14) Xiao, X.; Wang, H.; Huang, Z.; Yang, J.; Bian, X.; Qin, Y. *Org. Lett.* **2006**, 8, 139.
- (15) Chungh, W. J.; Omote, M.; Welch, J. T. *J. Org. Chem.* **2005**, 70, 7784.
- (16) Rassukana, Y. V.; Onys'ko, P. P.; Davydova, K. O.; Sinita, A. D. *Tetrahedron Lett.* **2004**, 45, 3899.
- (17) Shi, M.; Zhang, W. *Tetrahedron Asymmetry* **2003**, 14, 3407.
- (18) Ma, Z.; Zhao, Y.; Jiang, N.; Jin, X.; Wang, J. *Tetrahedron Lett.* **2002**, 43, 3209.