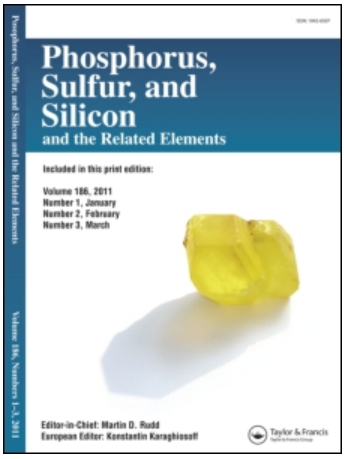


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Novel Method for the Synthesis of *N*-Sulfonylaldimines by ZnO as a Recyclable Neutral Catalyst Under Solvent-Free Conditions

Mona Hosseini-Sarvari[a]; Hashem Sharghi[a]
[a] Department of Chemistry, College of Science, Shiraz University, Shiraz, I.R., Iran

To cite this Article Hosseini-Sarvari, Mona and Sharghi, Hashem(2007) 'A Novel Method for the Synthesis of *N*-Sulfonylaldimines by ZnO as a Recyclable Neutral Catalyst Under Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 9, 2125 — 2130
To link to this Article: DOI: 10.1080/10426500701372355
URL: http://dx.doi.org/10.1080/10426500701372355

Phosphorus, Sulfur, and Silicon, 182:2125–2130, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701372355

Taylor & Francis
Taylor & Francis Group

A Novel Method for the Synthesis of *N*-Sulfonylaldimines by ZnO as a Recyclable Neutral Catalyst Under Solvent-Free Conditions

Mona Hosseini-Sarvari
Hashem Sharghi
Department of Chemistry, College of Science, Shiraz University, Shiraz, I.R. Iran

ZnO acts as an effective catalyst for the rapid synthesis of a range of N-*sulfonylaldimines from aromatic aldehydes and sulfonamides under solvent free conditions. The ZnO powder can be reused up to three times after simple washing with distilled water and ethyl acetate.*

Keywords aldehyde; *N*-sulfonylaldimines; solvent-free conditions; ZnO

INTRODUCTION

The sulfonyl moiety has proven to be a powerful activating group of imine derivatives. As a consequence, *N*-sulfonylimines have been increasing in importance because they are one of the few types of electron-deficient imines that are stable enough to be isolated but reactive enough to undergo addition reactions. *N*-Sulfonylimines continue to attract the attention of chemists as versatile synthetic intermediates. As electron deficient imines, they find application in inverse electron demand Diels-Alder chemistry,[1–4] stable and reactive alkenes in ene reactions,[5] aza-aldehyde equivalents in addition reactions,[6] and valuable precursors for the preparation of optically active 2-imidazolines.[7]

There are several methods available for the preparation of *N*-sulfonylimines namely via the rearrangement of oxime *O*-sulfinates,[8] Lewis acid catalyzed reactions of sulfonamides with aldehydes precursors,[9,10] the addition of *N*-sulfinyl sulfonamides to aldehydes in the presence of boron-trifluoride etherate,[11] the utilization of in

Received November 30, 2006; accepted February 26, 2007.
We gratefully acknowledge the support of this work by the Shiraz University Research Council.
Address correspondence to Mona Hosseini-Sarvari, Department of Chemistry, College of Science, Shiraz University, Shiraz 71454, Iran. E-mail: hossaini@susc.ac.ir

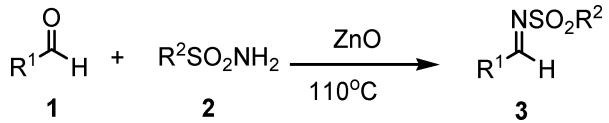
situ generated *N*, *N*′-ditosyltellurodiimide from tellurium metal and chloramine T,[12] using tetraethyl orthosilicate,[13] halogen-mediated conversion of *N*-(trimethylsilyl)imines in the presence of corresponding sulfonyl chloride,[14] or solvent-free synthesis using micromave irradiation.[15] Some of the reported methods suffer from drawbacks like long reaction times, unsatisfactory yields, expensive and hazardous reagents, and a cumbersome experimental protocol. Therefore, it seems highly desirable to find a simple, efficient, economical, and inexpensive protocol for *N*−sulfonylimines synthesis.

In the light of stringent and growing environmental regulations, the chemical industry needs to re-examine the most important synthetic processes and to develop more eco-compatible synthetic methodologies.[16] To this purpose heterogeneous catalysis plays a fundamental role, mainly due to its economic and environmental advantages (i.e., minimum execution time, low corrosion, waste minimization, recycling of the catalyst, easy transport, and disposal of the catalyst).[17]Another important goal in green chemistry is represented by the elimination of volatile organic solvents, in fact solvent-free organic reactions make syntheses simpler, save energy, and prevent solvent waste, hazards, and toxicity.[18]

Of course the combination of heterogeneous catalysis with the use of solvent less conditions represent a suitable way toward the so-called ideal synthesis.[19] Since the revision of fundamental synthetic reactions under solvent free conditions (SFC) has been the subject of our research in recent years,[20] we have recently examined the catalytic activity of zinc oxide (ZnO) in organic synthesis.[21]

RESULTS AND DISCUSSION

ZnO is a non-toxic, inexpensive and non-hydroscopic white powder. It is an important material with a wide ranging application as catalyst for a number of organic syntheses. So, we wish to report here some efficient ZnO mediated preparations of *N*-sulfonylimines under solvent-free conditions by conventional heating in an oil bath (Scheme 1). Furthermore, ZnO can be reused up to three times. In light of this and after several trials; we found that ZnO accelerated the synthesis of *N*-sulfonylimines



SCHEME 1

TABLE I Reaction of *p*-Toluenebenzenesulfonamide (1 mmol) with Benzaldehyde (1 mmol) in Different Reaction Conditions

Entry	Conditions	Time (h.)	Yield[a] %
1	ZnO (1 mmol)/r.t.	8	0
2	ZnO (1 mmol) /80°C	8	50
3	ZnO (1 mmol) /110°C	3	92
4	ZnO (0.5 mmol)/110°C	3	75
5	ZnO (1 mmol) /reflux/CH_3CN	8	Trace
6	MgO (1 mmol)/110°C	8	75
7	Al_2O_3 (1 mmol)/110°C	8	50
8	$CaCl_2$ (1 mmol)/110°C	8	50
9	K_2CO_3 (1 mmol)/110°C	8	50
10	No catalyst/110–150°C	24	0

[a]Isolated yields.

significantly. Results of various optimization studies are listed in Table I, from which we conclude that the best condition is as shown in entry 3.

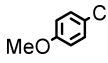
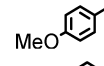
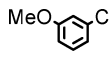
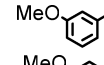
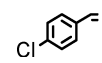
The generality of the scope of the reaction can be deduced from the results summarized in Table II. We were pleased to find that when a diverse range of aromatic aldehydes in the presence of ZnO was heated with sulfonamides in an oil bath at 110°C, the corresponding *N*-sulfonylimines were obtained in a high state of purity, and in good yield.

According to Table II, aromatic aldehydes containing both electron withdrawing and -donating substitutions (entries 2–9) afforded the corresponding *N*-sulfonylimines in high yields. Mention must be made here that the conversion rate of *p*-toluenesulfonamide with arylaldehydes was a little higher than benzensulfonamide. In the case of ketones the overall yields are not as high as those obtained from the aldehydes (entries 13, 14).

Furthermore, the catalytic activity of the recovered catalyst (ZnO) was examined. The yields of *N*-phenylmethylidenebenzenesulfonamide 3a (entry 1, Table 2) in 2nd and 3rd uses of the catalyst were almost the same as that in the 1st use. In every case almost >70% of the ZnO was easily recovered from the reaction mixture by simple washing with distilled water and ethyl acetate.

In conclusion, we have described a novel and highly efficient solvent-free protocol for the synthesis of *N*-sulfonylimines using non-toxic and inexpensive ZnO powder. Our method is superior to other existing methods as: *i*) there is no need of toxic and waste producing Lewis acids; *ii*) work-up is simple; *iii*) the reaction procedure is not requiring specialized equipment; *iv*) zinc oxide powder can be re-used; and *v*) SFC.

TABLE II ZnO (1 mmol) Catalyzed the Preparation of *N*-Sulfonylaldimines in SFC

Entry	Aldehyde	Sulfonylamide	Products	Time (h)	Yields[a] %
1		 **2a**	 **3a**	4	90
		 **2b**	 **3b**	3	92
2		**2a**	 **3c**	4	87
		2b	 **3d**	3	90
3		**2a**	 **3e**	4.5	88
		2b	 **3f**	3	92
4		**2a**	 **3g**	5	61
		2b	 **3h**	4.5	63
5		**2a**	 **3i**	4.5	62
		2b	 **3j**	3.5	69
6		**2a**	 **3k**	4.5	65
		2b	 **3l**	3	73
7		**2a**	 **3m**	3	90
		2b	 **3n**	2	90
8		**2a**	 **3o**	4	73
		2b	 **3p**	3	75
9		**2a**	 **3s**	7.5	62
		2b	 **3t**	6	64
10		**2b**	 **3u**	6	32
11		**2b**	 **3v**	2	90
12		**2b**	 **3w**	4	74
13		**2b**	 **3x**	5	20
14	PhCOPh	**2b**	—	8	0

[a]Yields are the isolated compounds.

EXPERIMENTAL

Starting materials were obtained from the Fluka Company. Melting points were determined by a Buchi 510 apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer spectrometer. Proton NMR spectra were recorded on a Bruker Advance DPX FT 250 MHz instrument.

General Procedure

ZnO (dry powder, 1 mmol, and 0.08 g), an aldehyde (1 mmol), and sulfonamide (1 mmol) were mixed together and the reaction mixture was heated in an oil bath at 110°C and stirred with a mechanical stirrer. The reaction mixture was became very sticky and needed to be stirred very thoroughly. The progress of the reaction monitored by TLC. After the reaction was complete, ethyl acetate was added to the reaction mixture, and zinc oxide (ZnO) was removed by filtration. After removal of the solvent, the product was obtained. This was further purified by recrystallization with a suitable solvent (ether). The structure of the products was confirmed by NMR, IR, and comparison with authentic samples obtained commercially or prepared by reported methods.

REFERENCES AND NOTES

[1] D. L Borger and S. N. Weinreb, *Hetero Diels-Alder Methodology in Organic Synthesis* (Academic Press, San Diego, 1987).
[2] R. Albrecht and G. Kresze, *Chem. Ber.*, **97,** 490 (1964).
[3] D. L. Boger, W. L. Corbett, T. T. Curran, and A. M. Kasper, *J. Am. Chem. Soc.*, **113,** 1713 (1991).
[4] M. D. Alexander, R. E. Anderson, J. Sisko, and S. M. Weinreb, *J. Org. Chem.*, **55,** 2563 (1990).
[5] (a) D. M. Tschaen, E. Turos, and S. M. Weinreb, *J. Org. Chem.,* **49,** 5058 (1984); (b) M. J. Melnick, A. J. Freyer, and S. M. Weinreb, *Tetrahedron Lett.,* **29,** 3891 (1988).
[6] J. Sisko and S. M. Weinreb, *J. Org. Chem.,* **55,** 393 (1990).
[7] X.-T. Zhou, Y. -R. Lin, L. -X. Dai, J. Sun, L.-J. Xia, and M.-H. Tang, *J. Org. Chem.,* **64,** 1331 (1999).
[8] D. L. Borger and W. L. Corbett, *J. Org. Chem.*, **57,** 4777 (1992).
[9] W. B. Jennings and C. J. Lovely, *Tetrahedron*, **47,** 5561 (1991).
[10] (a) R. Albrecht, G. Kresze, and B. Mlaker, *Chem. Ber.,* **97,** 483 (1964); (b) Z. Li, X. Ren, P. Wei, H. Wan, Y. Shi, and P. Ouyang, *Green Chem.*, **8,** 433 (2006).
[11] (a) A. K. McFarlane, G. Thomas, and A. Whiting, *Tetrahedron Lett.,* **34,** 2379 (1993); (b) J. L. G. Ruano, J. Aleman, M. B. Cid, and A. Parra, *Organic Lett.*, **7,** 179 (2005).
[12] B. M. Trost and C. Marrs, *J. Org. Chem.*, **56,** 6468 (1991).
[13] B. E. Love, P. S. Raje, and T. C. Williams, *Synlett*, 493 (1994).
[14] G. I. G. George, C. B. Harriman, and S. C. Peterson, *J. Org. Chem.*, **60,** 7366 (1995).
[15] A. Vass, J. Dudas, and R. S. Varma, *Tetrahedron Lett.,* **40,** 4951 (1999).

[16] (a) A. Corma, *Chem. Rev.,* **95**, 559 (1995); (b) R. A. Sheldon, *CHEMTECH*, **21,** 566 (1991); (c) I. W. C. E. Arends, R. A. Scheldon, M. Wallan, and U. Sxhunchardt, *Angew. Chem. Int. Ed. Engl.,* **36,** 1145 (1997); (d) J. H. Clark and D. J. Macquarrie, *Chem. Soc. Rev.*, **25,** 303 (1996).
[17] R. Sheldon and A. Dakka, *J. Catal. Today*, **19,** 215 (1994).
[18] K. Tanka, *Solvent Free Organic Synthesis* (Wiley-VCH, Weinhein, 2003).
[19] P. A. Wender, S. L. Handy, and D. L. Wright, *Chem. Ind.,* 765 (1997).
[20] (a) H. Sharghi and M. Hosseini-Sarvari, *Synlett*, 99 (2001); (b) H. Sharghi and M. Hosseini-Sarvari, *Tetrahedron*, **58,** 10323 (2002); (c) H. Sharghi, and M. Hosseini-Sarvari, *Synthesis*, 243 (2003).
[21] (a) M. Hosseini-Sarvari and H. Sharghi, *J. Org. Chem*., **69**, 6953 (2004); (b) M. Hosseini-Sarvari, H. Sharghi, *Synthesis*, 1057 (2002); (c) M. Hosseini-Sarvari, *Synthesis*, 787 (2005); (d) M. Hosseini-Sarvari, H. Sharghi, *Tetrahedron*, **61,** 10903 (2005); (e) M. Hosseini-Sarvari and H. Sharghi, *J. Org. Chem.*, **71**, 6652 (2006).