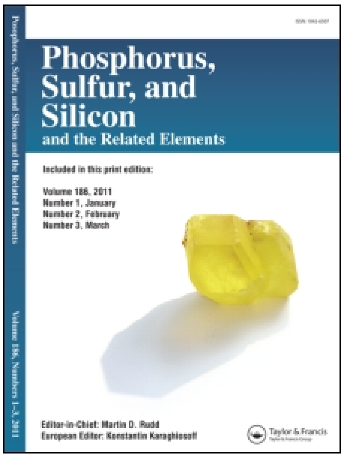


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Silica Chloride-Catalyzed Synthesis of Thiiranes from Oxiranes Under Solvent-Free Conditions

Liqiang Wu[a]; Limin Yang[a]; Lizhen Fang[a]; Chunguang Yang[a]; Fulin Yan[a]
[a] School of Pharmacy, Xinxiang Medical University, Xinxiang, Henan, China

To cite this Article Wu, Liqiang , Yang, Limin , Fang, Lizhen , Yang, Chunguang and Yan, Fulin(2010) 'Silica Chloride-Catalyzed Synthesis of Thiiranes from Oxiranes Under Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 10, 2159 — 2164

To link to this Article: DOI: 10.1080/10426500903544298

URL: http://dx.doi.org/10.1080/10426500903544298

Phosphorus, Sulfur, and Silicon, 185:2159–2164, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903544298

SILICA CHLORIDE–CATALYZED SYNTHESIS OF THIIRANES FROM OXIRANES UNDER SOLVENT-FREE CONDITIONS

Liqiang Wu, Limin Yang, Lizhen Fang, Chunguang Yang, and Fulin Yan
School of Pharmacy, Xinxiang Medical University, Xinxiang, Henan, China

A mild, simple, and efficient method for the synthesis of thiiranes from epoxides using a catalytic amount of silica chloride under solvent-free conditions has been developed. Experimental simplicity, simple work-up procedure, and solvent-free reaction conditions are important features of the present protocol.

Keywords Oxirane; silica chloride; solvent-free; thiirane

INTRODUCTION

Thiiranes are sulfur heterocycles that are used in the pharmaceutical, polymer, pesticide, and herbicide industries[1] and have played an important role in various synthetic transformations.[2] Various methods have been developed for the preparation of these compounds. The most common and important method is the transformation of oxiranes into thiiranes with thiourea,[3] inorganic thiocyanates,[4] Dowex-50WX8–supported thiourea,[5] and polymer-supported thiocyanates.[6] Along with each sulfurated reagent, a protic acid such as Mg(HSO$_4$)$_2$,[3g] oxalic acid,[4k] or SiO$_2$-HBF$_4$[4d] or a Lewis acid such as NH$_4$Cl,[3a] Al(DS)$_3$·3H$_2$O,[3b] SiO$_2$-AlCl$_3$,[3c] LiBF$_4$,[3h] RuCl$_3$,[3i] SbCl$_3$,[3j] Montmorillonite K-10,[3k] I$_2$,[4a] LiClO$_4$,[4b] Sn^{IV}(TPP)(BF$_4$)$_2$,[4c] 2,4,6-trichloro-1,3,5-triazine,[4f] TiO$_2$,[4g] Sn^{IV}(TPP)(OTf)$_2$,[4h] InBr$_3$,[4l] Bi(TFA)$_3$,[4m] Bi(OTf)$_3$,[4m] BiCl$_3$,[4n] TiO(CF$_3$CO$_2$)$_2$[4o], and TiCl$_3$(CF$_3$SO$_3$)[4o] is employed. Recently, ionic liquid[7] and MW irradiation[8] have also been applied to the conversion of oxiranes into thiiranes. However, long reaction times, high temperature, low yields of the products, use of organic solvents, use of highly acidic catalyst, difficulties in the separation of the product from the original reactant and catalyst, formation of polymeric byproducts, high catalytic loading, and, in most of the cases, the use of expensive and unrecoverable catalyst are all limitations of these methods.

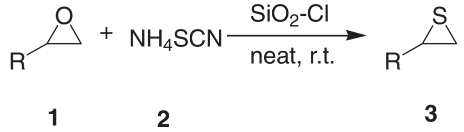
Silica chloride (SiO$_2$-Cl), which is easily prepared from silica gel and thionyl chloride, is a good solid acid in terms of convenience, low cost, easy production, and insolubility in all organic solvents. Due to its insolubility in organic solvents, excellent in situ proton

Received 10 October 2009; accepted 7 December 2009.

We are pleased to acknowledge the financial support from Xinxiang Medical University.

Address correspondence to Liqiang Wu, School of Pharmacy, Xinxiang Medical University, Xinxiang, Henan 453003, China. E-mail: wliq1974@sohu.com

generation, and its acceptance of different nucleophiles, it can be used for different purposes in organic chemistry, such as SiO_2-Cl–catalyzed protection of carbonyl compounds[9a]; acetylation of alcohols[9b]; synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes,[9c] 1,8-dioxo-octahydroxanthenes,[9c] and 2-aminothiazoles[9d]; and SiO_2-Cl as a starting material for the preparation of other silica-bonded reagents.[9e] In this article, we report a simple, efficient, and environmentally benign synthesis of thiiranes under solvent-free conditions in the presence of SiO_2-Cl (see Scheme 1).



Scheme 1

RESULTS AND DISCUSSION

Initially, a systematic study was carried out for evaluation for SiO_2-Cl as a catalyst for the reaction of styrene oxide with ammonium thiocyanate under various conditions (Table I). The reaction was slow in the absence of the catalyst (Table I, entry 1), and low yields were obtained in presence of only SiO_2 as a catalyst (Table I, entries 2–4). Further, improvement of the yield was observed in the presence of SiO_2-Cl as a catalyst (Table I, entries 5). Next, we optimized the quantity of the catalyst (SiO_2-Cl) at room temperature under solvent-free conditions (Table I, entries 5–10), and it was observed that the use of just 100 mg/mmol of SiO_2-Cl was sufficient to produce an excellent yield of the product (Table I, entry 7), whereas more than 100 mg/mmol of the catalyst did not improve the results (Table I, entries 8–10). However, inferior results were obtained in the presence of solvents (Table I, entries 11–13).

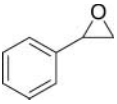
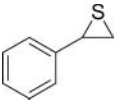
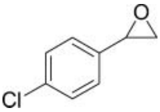
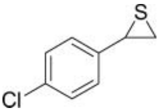
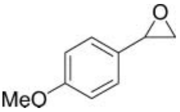
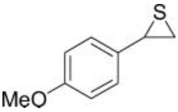
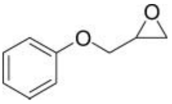
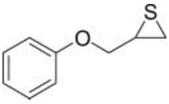
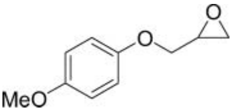
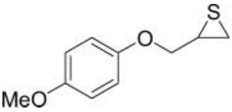
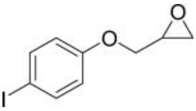
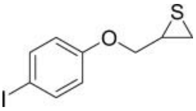
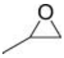
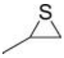
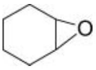
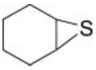
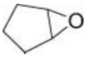
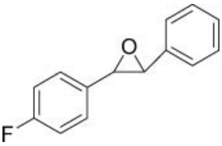
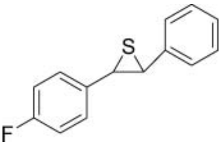
Table I Reaction of styrene oxide with ammonium thiocyanate under various conditions[a]

Entry	Solvent	Catalyst (mg/mmol)	Time (min)	Yield (%)[b]
1	Neat	—	360	< 5
2	Neat	SiO_2 (20 mg)	240	12
3	Neat	SiO_2 (50 mg)	240	19
4	Neat	SiO_2 (100 mg)	240	31
5	Neat	SiO_2-Cl (50 mg)	60	62
6	Neat	SiO_2-Cl (75 mg)	45	76
7	Neat	SiO_2-Cl (100 mg)	30	96
8	Neat	SiO_2-Cl (125mg)	30	96
9	Neat	SiO_2-Cl (150 mg)	30	95
10	Neat	SiO_2-Cl (175mg)	30	94
11	THF	SiO_2-Cl (100 mg)	45	68
12	$CHCl_3$	SiO_2-Cl (100 mg)	45	56
13	CH_3CN	SiO_2-Cl (100 mg)	45	64

[a] Reaction conditions: 2-phenyloxirane (1 mmol); ammonium thiocyanate (1.2 mmol); room temperature.
[b] Isolated yield.

Based on the optimized reaction conditions, a range of thiiranes was synthesized by the reaction of oxiranes (**1**, 1 mmol) with ammonium thiocyanate (**2**, 1.2 mmol) under solvent-free conditions. The reaction proceeded at room temperature within 1 h in excellent yields after the addition of SiO_2-Cl (100 mg/mmol) as catalyst (see Table II). In these

Table II SiO_2-Cl catalyzed conversion of epoxides to thiiranes at room temperature[a]

Entry	Epoxide	Product	Time (min)	Yield (%)[b]	Reference
a			45	96 (89, 79, 71)[c]	10
b			45	98	11
c			45	92	11
d			30	91	4a
e			30	94	4a
f			30	89	
g			30	92	4p
h			30	90	4p
i			60	94	10
j			60	92	10
k			60	87	

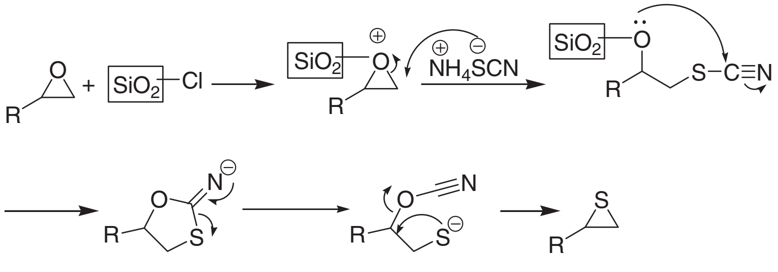
[a] Reaction conditions: epoxide (1 mmol); ammonium thiocyanate (1.2 mmol); SiO_2-Cl (100 mg); room temperature; neat.

[b] Isolated yield.

[c] Yields after three times of catalyst recovery.

experiments, the catalyst was isolated by filtration and could be run up to three times (recycling) without significant loss of activity.

The plausible mechanism of the reaction is shown in Scheme 2. The Si-Cl bond of SiO_2-Cl is labile and can give rise to Lewis acid centers on silica, so SiO_2-Cl can act as a catalyst for the activation of epoxide.[4a]



Scheme 2

CONCLUSION

In conclusion, this article clearly demonstrates the synthesis of thiiranes from oxiranes using a catalytic amount of SiO_2-Cl (100 mg/mmol). It is a valid alternative to the existing methods. The important features of the present method are mild and solvent-free reaction conditions, fast reaction rates, high yields of the products, relatively clean reactions, and an inexpensive and easily available catalyst with low loading.

EXPERIMENTAL

NMR spectra were determined on Bruker AV-400 spectrometer at room temperature using TMS as internal standard; coupling constants (*J*) were measured in Hz. Elemental analyses were performed by a Vario-III elemental analyzer. Melting points were determined on a XT-4 binocular microscope and were uncorrected. SiO_2-Cl was prepared according to the literature.[9e] Commercially available reagents were used throughout without further purification unless otherwise stated,

Typical Procedure: Preparation of Thiiranes

A mixture of epoxide (1 mmol), ammonium thiocyanate (1.2 mmol), and SiO_2-Cl (100 mg) was stirred at room temperature for the specified time (Table I). After completion of the reaction (TLC), diethyl ether (2 × 10 mL) was added in the reaction mixture, and the solid catalyst was filtered off. The solvent was evaporated, and the crude product was purified by column chromatography (petroleum ether:ethyl acetate = 9:1) to afford the pure product **3**. All products were characterized by comparison of their physical data and ^{1}H NMR, ^{13}C NMR data with those of authentic samples.[4a,4p,10,11] The spectral data of some new thiiranes are given below:

2-((4-Iodophenoxy)methyl)thiirane (3f)

Oil, ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.20$–6.79 (m, 4H, ArH), 4.10–3.90 (m, 2H, OCH_2), 3.26–3.22 (m, 1H, CH), 2.55–2.26 (m, 2H, CH_2S). ^{13}C NMR ($CDCl_3$, 100 MHz):

$\delta = 155.4$, 130.1, 124.9, 117.6, 74.8, 32.2, 22.8. Anal. calcd. for C_9H_9IOS: C 37.00, H 3.11, S 10.98; found C 37.18, H 3.02, S 11.09.

2-(4-Fluorophenyl)-3-phenylthiirane (3k)

Oil, ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.70$ (d, $J = 8.4$ Hz, 2H, ArH), 7.58 (d, $J = 8.4$ Hz, 2H, ArH), 7.26–7.18 (m, 5H, ArH), 2.71 (d, $J = 7.2$ Hz, 1H, CH), 2.42 (d, $J = 7.2$ Hz, 1H, CH). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 159.6$, 138.2, 135.2, 130.8, 130.7, 128.5, 128.3, 125.9, 115.6, 115.5, 45.6. Anal. calcd. for $C_{14}H_{11}FS$: C 73.01, H 4.81, S 13.92; found C 73.14, H 4.96, S 13.76.

REFERENCES

1. D. C. Ditter, A. R. Katritzky, and C. W. Rees, *Thiiranes and Thiiranes in Comprehensive Hetrocyclic Chemistry* (Pergamon, NewYork, 1984), vol. 7, pp. 132–182.
2. N. Iranpoor, B. Tamami, and K. Niknam, *Can. J. Chem.*, **75,** 1913 (1997).
3. (a) B. Zeynizadeh and S. Yeghaneh, *Phosphorus, Sulfur, and Silicon*, **183,** 2280 (2008); (b) H. Firouzabadi, N. Iranpoor, and A. Khoshnood, *J. Mol. Catal. A: Chem.*, **274,** 109 (2007); (c) K. Parvanak Borujeni, *Synth. Commun.*, **35,** 2575 (2005); (d) N. Iranpoor, H. Firouzabadi, and A. Jafari, *Phosphorus, Sulfur, and Silicon*, **180,** 1809 (2005); (e) A. Kiasat, F. Kazemi, and M. Jardi, *Phosphorus, Sulfur, and Silicon*, **179,** 1841 (2004); (f) K. Surendra, N. S. Krishnaveni, and K. R. Rao, *Tetrahedron Lett.*, **45,** 6523 (2004); (g) P. Salehi, M. M. Khodaei, M. A. Zolfigol, and A. Keyvan, *Synth. Commun.*, **33,** 3041 (2003); (h) F. Kazemi, A. R. Kiasat, and S. Ebrahimi, *Synth. Commun.*, **33,** 595 (2003); (i) F. Kazemi, A. R. Kiasat, and S. Ebrahimi, *Phosphorus, Sulfur, and Silicon*, **176,** 135 (2001); (j) I. Mohammadpoor-Baltork and A. R. Khosropoor, *Asian Chem. Lett.*, **2,** 123 (1998); (k) I. Mohammadpoor-Baltork and H. Aliyan, *J. Chem. Res. (S)*, 122 (2000).
4. (a) J. S. Yadav, B. V. S. Reddy, S. Sengupta, M. K. Gupta, G. Baishya, S. J. Harshavardhana, and U. Dash, *Monatsh. Chem.*, **139,** 1363 (2008); (b) C. S. Reddy and S. Nagavani, *Heteroatom Chem.*, **19,** 97 (2008); (c) M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, and S. A. Taghavi, *Catal. Commun.*, **8,** 2087 (2007); (d) B. P. Bandgar, A. V. Patil, V. T. Kamble, and J. V. Totre, *J. Mol. Catal. A: Chem.*, **273,** 114 (2007); (e) B. Das, V. S. Reddy, and M. Krishnaiah, *Tetrahedron Lett.*, **47,** 8471 (2006); (f) B. P. Bandgar, N. S. Joshi, and V. T. Kamble, *Tetrahedron Lett.*, **47,** 4775 (2006); (g) B. Yadollahi, S. Tangestaninejad, and M. H. Habibi, *Synth. Commun.*, **34,** 2823 (2004); (h) M. Moghadam, S. Tangestaninejad, V. Mirkhani, and R. Shaibani, *Tetrahedron*, **60,** 6105 (2004); (i) N. S. Krishnaveni, K. Surendra, M. Somi Reddy, Y. V. D. Nageswar, and K. Rama Rao, *Adv. Synth. Catal.*, **346,** 395 (2004); (j) B.Tamami and M. Kolahdoozan, *Tetrahedron Lett.*, **45,** 1535 (2004); (k) F. Kazemi and A. R. Kiasat, *Phosphorus, Sulfur, and Silicon*, **178,** 1333 (2003); (l) J. S. Yadav, B. V. S. Reddy, and G. Baishya, *Synlett*, 396 (2003); (m) I. Mohammadpoor-Baltork and A. R. Khosropour, *Molecules*, **6,** 996 (2001); (n) I. Mohammadpoor-Baltork and H. Aliyan, *Synth. Commun.*, **28,** 3943 (1998); (o) N. Iranpoor and B. Zeynizadeh, *Synth. Commun.*, **28,** 3913 (1998); (p) N. Iranpoor and F. Kazemi, *Synthesis*, 821 (1996).
5. B. Zeynizadeh and S. Yeghaneh, *Phosphorus, Sulfur, and Silicon*, **184,** 362 (2009).
6. B. Tamami and A. R. Kiasat, *Synth. Commun.*, **26,** 3953 (1996).
7. J. S. Yadav, B. V. S. Reddy, C. S. Reddy, and K. Rajasekhar,*J. Org. Chem.*, **68,** 2525 (2003).
8. B. Kaboudin and H. Norouzi, *Synthesis*, 2035 (2004).
9. (a) Y. Kamitori, M. Hojo, R. Masuda, T. Kimura, and T. Yoshida, *J. Org. Chem.*, **51,** 1427 (1986); (b) H. Firouzabadi, N. Iranpoor, and H. Hazarkhani, *Phosphorus, Sulfur, and Silicon*, **176,** 165 (2001); (c) L. Q. Wu, C. G. Yang, L. M. Yang, and L. J. Yang, *Phosphorus, Sulfur, and Silicon*, **185,** 903, (2010); (d) H. Karade, M. Sathe, and M P. Kaushik, *Catal.Commun.*, **8,** 741 (2007);

(e) P. Salehi, M. A. Zolfigol, F. Shirini, and M. Baghbanzadeh, *Curr. Org. Chem.*, **10,** 2171 (2006).
10. T. Takido, Y. Kobayashi, and K. Itabashi, *Synthesis*, 779 (1986).
11. M. O. Brimeyer, A. Mehrota, S. Quici, A. Nigam, and S. L. Regen, *J. Org. Chem.*, **45,** 4254 (1980).