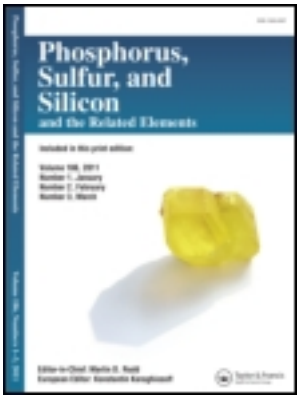

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

A Green Protocol for the Easy Synthesis of Thiiranes from Epoxides Using Thiourea/Silica Gel in the Absence of Solvent

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Published online: 18 Aug 2006.

To cite this article: Nasser Iranpoor , Habib Firouzabadi & Abbas Ali Jafari (2005): A Green Protocol for the Easy Synthesis of Thiiranes from Epoxides Using Thiourea/Silica Gel in the Absence of Solvent, Phosphorus, Sulfur, and Silicon and the Related Elements, 180:8, 1809-1814

To link to this article: http://dx.doi.org/10.1080/104265090889404

Phosphorus, Sulfur, and Silicon, 180:1809–1814, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090889404

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A Green Protocol for the Easy Synthesis of Thiiranes from Epoxides Using Thiourea/Silica Gel in the Absence of Solvent

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The use of thiourea/silica gel provides a green protocol for the easy and high-yielding preparation of thiiranes from different classes of epoxides in the absence of solvent at room temperature. The high stereospecific conversion of (R)(+)-styrene oxide to (S)(+)-styrene sulfide is also reported using this reagent system.

Keywords Epoxide; silica gel; thiirane; thiourea

INTRODUCTION

There are many methods reported in the literature for the preparation of thiiranes.[1,2] The most efficient route reported so far is based on the conversion of epoxides into the corresponding thiiranes by an oxygen–sulfur exchange reaction.[1–8] Thiourea has also been reported as an example of one of these sulfur agents that reacts with epoxides to give thiiranes under wet conditions or in aqueous solvents.[9,10] For example, the reaction of styrene oxide with wet thiourea in the absence of solvent has been reported to afford styrene episulfide in only 45% yield after 10 h. The reaction of epoxides with thiourea in aqueous ethanol is more or less similar to the reaction of epoxides with KSCN,[10] usually with longer reaction times and lower yields, especially in the cases of cyclic epoxides. To overcome the difficulties of long reaction times, low yields and high temperatures of the reactions and the occurrence of side reactions such as polymerization or desulfurization, new methods including

Received July 8, 2004; accepted September 7, 2004.
The authors appreciate the Research Council of Shiraz University and Iran TWAS Chapter Based at ISMO for the support of this work.
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the use of different Lewis acids[11] or use of polymeric reagents,[12] have been employed by us and other groups.

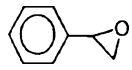
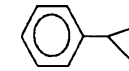
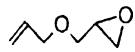
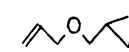
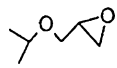
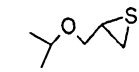
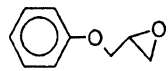
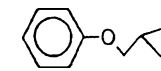
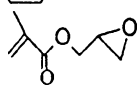
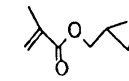
Due to the importance of reducing environmental pollution in chemical reactions, green protocols garner great attention in both laboratory and industrial synthesis.[1] In this respect we now report a green method for the easy and high-yielding synthesis of thiiranes from epoxides using thiourea/silica gel under nonsolvent condition. Due to the absence of solvent in this method and the possibility of applying distillation to the crude mixture, thiiranes can be obtained with high purity and yields and leave only SiO_2 and urea as nonpolluting residues.

RESULTS AND DISCUSSIONS

The use of silica-gel supported KSCN as a source of sulfur in the reaction with epoxides to produce thiiranes suffers from high reaction temperature (90°C) and long reaction times (4.5–18 h).[8] However, when we reacted silica-gel-supported–thiourea with epoxides in the absence of solvent, a quick reaction occurred (3–5 min) and quantitative conversion to thiiranes were observed. For the isolation of thiiranes, vacuum distillation techniques using a bulb-to-bulb system were applied to the crude reaction mixture. For those reactions in which distillation was not possible (e.g., small scale reactions), we also investigated the possibility of using this conversion in solvent or doing solvent work up. Among the solvents used for this study, such as CH_2Cl_2, $CHCl_3$, diethyl ether, THF, acetone, and CH_2Cl_2 was found to be most suitable. In comparison with the reactions under non-solvent conditions, the reactions in CH_2Cl_2 occur slower (0.5–3 h), but the conversion yields are similar to those obtained in the absence of solvent (Table I). The only substrate which produces a higher yield of the product in solution is cyclohexene oxide. The results obtained for conversion of epoxides to thiiranes with thiourea/silica-gel in the absence of solvent and in solution are shown in Table I.

Although the synthesis of thiiranes from starting materials other than epoxides is extensively studied, reports on the preparation of optically active thiiranes are rare.[14] Due to the low yields and low optical purity of the thiiranes obtained by these methods, epoxides have gained favor as alternative starting materials for the preparation of optically active thiiranes. Enantioselective synthesis of (2S,3S)-(+)-*trans*-2,3-epithiosuccinate from its corresponding epoxide in 48% yield has been reported in the presence of triphenylphosphine sulfide and trifluoroacetic acid as a catalyst.[6] The conversion of optically active styrene

TABLE I Reaction of Epoxides (1.0 mmol) with Thiourea/Silica-Gel[a] in the Absence of Solvent, (Method A) and in CH_2Cl_2 (Method B) at Room Temperature

Entry	Epoxide	Method A Time(min)/yield %[b]	Method B Time(min)/yield %[c]	Product
1		5/86	80/95	
2		3/88	40/92	
3		3/80	45/93	
4		5/90	120/95	
5		3/89	30/97	
6		3/88	80/90	
7		5/80	135/94	
8		5/67	190/92	

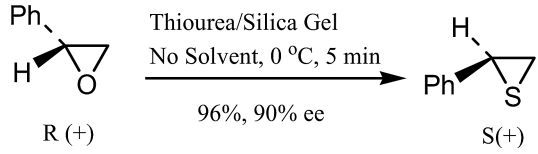
[a] 3 g of thiourea/silica-gel was used.

[b] The conversion yield (gc analysis using internal standard) is quantitative. Isolated yield after distillation.

[c] Isolated yield after column chromatography.

oxide to optically active styrene episulfide using NH_4SCN in the presence of Ru(III) or Ce(IV) as catalysts are also reported by our group.[11a,d]

We observed that using thiourea/silica gel under a solvent-free condition, the conversion of (*R*)-(+)-styrene oxide into (*S*)-(+)-styrene sulfide occurs with high yield and stereospecificity (Scheme 1). When we reacted optically active (*R*)-(+)-styrene oxide with this reagent at 0°C in the absence of solvent, (*S*)-(+)-styrene episulfide was obtained in 96% yield and 90% optical purity.



SCHEME 1

The optical purity of the product was determined by comparison of its optical rotation ($[\alpha]^D = +39.25^\circ$ in *n*-heptane) with that reported for styrene sulfide ($[\alpha]^D = -15.7^\circ$ in *n*-heptane) which is considered to be 35.8% optically pure with the (*R*) configuration.[15]

The reaction of (*R*)-(+)-styrene oxide with thiourea/silica-gel in CH_2Cl_2 at 0°C produces the optically active (S)-(+)-styrene episulfide in 93% yield and in only 70% optical purity after 2 h. This result shows that stereospecificity of the reaction in the absence of solvent is higher. For comparison, the results obtained for the stereospecific conversion of optically active styrene oxide to its episulfide with thiourea/silica gel are compared with other reported methods in the literature (Table II).

In addition to the green nature of this method, the availability of the reagent, simplicity, and mildness of the method; short reaction times; easy work-up; and high yields of the products and high stereospecificity of the reaction are the advantages of this procedure, which makes it very useful in organic synthesis.

Experimental

The products were characterized by comparison of their b.p, IR, ^{1}H and ^{13}C-NMR with those prepared by known procedures. IR spectra were recorded on a Perkin Elmer IR-157 G and a Perkin Elmer 781 spectrometer. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker Avance

TABLE II Stereospecific Preparation of Optical Active (*S*)-(+)-Styrene Sulfide from (*R*)-(+)-Styrene Oxide with Different Reagents[a]

Entry	Catalyst	Reagent	Stereochemistry of Styrene Sulfide	% Yield[b]	% ee[c]
1	$RuCl_3$	NH_4SCN[11a]	(S)	93	78
2	Polymer-SCN	NH_4SCN[11d]	(S)	90	25
3	(P4VP)-Ce(OTf)$_4$	NH_4SCN[11d]	(S)	80	87
4	Ce(IV)	NH_4SCN[11d]	(S)	90	25
5	Ti(IV)	NH_4SCN[11d]	(S)	93	35
6	Non	Thiourea/Silica Gel	(S)	96	90[d]
7	Non	Thiourea/Silica Gel/CH_2Cl_2	(S)	93	70

[a]Optical active (*R*)-(+)-styrene oxide, the product of Merck Company, was used without further purification.

[b]Isolated yield.

[c]The optical purity of the product was determined according to the literature.[15]

[d]The reaction was performed in the absence of solvent. Instead of distillation, the product was extracted in dichloromethane and purified by chromatography on silica gel using ethyl acetate as eluent.

DPX-250. Optical rotation was determined using a Perkin Elmer 241 polarimeter.

Preparation of the Reagent

To a solution of thiourea (0.02 mole, 1.52 g) in acetone, silica gel was added (28.5 g). The mixture was evaporated on a rotary evaporator and dried under vacuum to give a homogeneous solid.

General Procedure

Method A

The mixture of epoxide (1 mmol) and 3 g of thiourea/silica gel were placed in a mortar and were thoroughly mixed for 3–5 min. Monitoring of the reaction with TLC and GC showed the completion of the reaction after this period of time. The mixture was transferred to a bulb-to-bulb distillation system and distilled under reduced pressure. The collecting flask was kept as cool as possible to avoid the loss of product due to its vaporization. The pure products were obtained in 80–90% yield. The reaction mixture can also be worked up by adding solvent, followed by filtration and chromatography. The products were known compounds and were identified by comparison of their phycical and spectral data with those of known samples.[11c]

Method B

To a solution of epoxides (1.0 mmol) in CH_2Cl_2 (15 mL), thiourea/ silica gel (3 g) was added and the reaction mixture was stirred at room temperature for 0.5–3 h. The reaction was monitored with GC or TLC. After completion of the reaction, the mixture was filtered. The organic layer was washed with water (20 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by chromatography on a short column of silica gel afforded the pure episulfide in 90–97% yield.

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