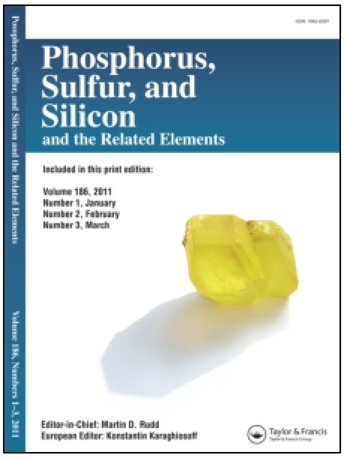

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Green Protocol for Solvent-Free Conversion of Epoxides to Thiiranes with Dowex-50WX8-Supported Thiourea

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To cite this Article Zeynizadeh, Behzad and Yeghaneh, Samal(2009) 'A Green Protocol for Solvent-Free Conversion of Epoxides to Thiiranes with Dowex-50WX8-Supported Thiourea', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 2, 362 — 368
To link to this Article: DOI: 10.1080/10426500802157515
URL: http://dx.doi.org/10.1080/10426500802157515

Phosphorus, Sulfur, and Silicon, 184:362–368, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802157515

A Green Protocol for Solvent-Free Conversion of Epoxides to Thiiranes with Dowex-50WX8–Supported Thiourea

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Structurally different epoxides were efficiently converted to the corresponding thiiranes by Dowex-50WX8–supported thiourea under solvent-free conditions. The reactions were carried out either in an oil bath or under microwave irradiation to give the thiiranes in 75–98% yields within 30 sec–120 min.

Keywords Dowex-50WX8; epoxide; microwave; solvent-free; thiirane; thiourea

INTRODUCTION

Epoxides are small molecules with numerous synthetic applications. They are able to react with various nucleophiles, and their potential to undergo regioselective ring opening reactions makes them highly useful precursors for the synthesis of organic compounds.[1] Thiirane is the simplest heterocyclic ring system carrying a sulfur atom in the ring and it is found in naturally occurring compounds, herbicides, pesticides, polymeric compounds, pharmaceuticals, and in many other manmade chemicals.[2] Transformation of epoxides to thiiranes by an oxygen–sulfur exchange reaction is a useful reaction and has been achieved with various methods using sulfur transfer agents.[3–27] However, some of these methods often suffer from one or more disadvantages, such as low yields of the products, long reaction times, difficult workup procedures, use of expensive reagents, formation of polymeric byproducts, and the need for aqueous reaction conditions.

Currently, increasing attention is being focused on green chemistry in organic synthesis, using environmentally benign reagents and conditions, particularly solvent-free reactions. Working without solvents has

Received 23 March 2008; accepted 24 April 2008.
We acknowledge the financial support of this work by the research council of Urmia University.
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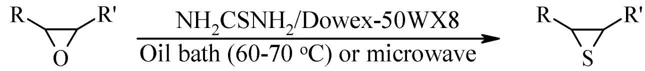
the advantage of a simpler process and smaller plants, and eliminates the energy costs of removal, recycling, and eventual disposal of waste solvents.[28]

As a part of our research program on the synthesis of thiiranes, in this article we wish to report the efficient conversion of epoxides to the corresponding thiiranes by Dowex-50WX8–supported thiourea under solvent-free conditions either in an oil bath (60–70°C) or under microwave irradiation (Scheme 1).



SCHEME 1

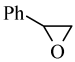
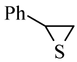
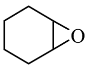
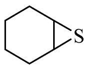
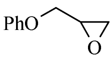
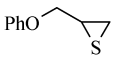
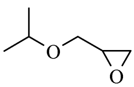
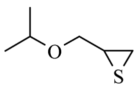
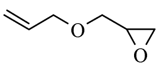
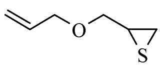
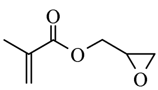
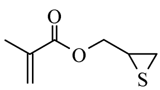
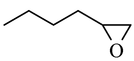
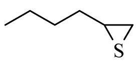
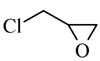
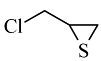
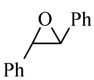
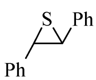
RESULTS AND DISCUSSION

In recent years, the use of reagents/catalysts immobilized on solid supports has received considerable attention, and numerous reviews and papers have demonstrated their importance. Reagents supported on organic polymers or on the surface of inorganic materials have distinguishing characteristics such as simplicity of purification process, recyclability, selectivity, and an increase of the stability of air- or moisture-sensitive reagents/catalysts.[29]

Although thiourea has been one of the most widely used reagents for the conversion of epoxides to thiiranes,[30] it suffers from various disadvantages such as low reactivity, the need for aqueous or alcoholic conditions, long reaction times, low yields, and in some cases desulfuration of the resulting thiiranes to olefins.[5] Among the outlined strategies, a survey of the literature shows that the transformation of epoxides to thiiranes with thiourea under solid supported and solvent-free conditions has been reported only for silica-gel–supported thiourea.[6] This method provides a green protocol for the preparation of thiiranes from epoxides; however, it suffers from low to moderate yields (67–89%).

In the course of our investigations in green protocols for the preparation of thiiranes from epoxides, we found that thiourea supported on Dowex-50WX8, an easily available anionic exchange resin, promotes the conversion of epoxides to the corresponding thiiranes under solvent-free conditions. The optimized experimental conditions showed that the reaction of styrene oxide (1 mmol) with thiourea (3 mmol) supported on Dowex-50WX8 (0.5 g) proceeded efficiently in an oil bath at 60–70°C. The epoxide was converted to the corresponding thiirane in 93% yield within 60 min. The capability of this synthetic method was further investigated by reacting activated, deactivated, and cyclic

TABLE I Conversion of Epoxides to Thiiranes with $(NH_2)_2CS$/Dowex-50WX8 System[a]

			Oil bath[b]		Microwave[c]	
Epoxide	Thiirane		Time (min)	Yield (%)[d]	Time (sec)	Yield (%)[d]
		(**1**)	60	93	90	96
		(**2**)	60	85	90	90
		(**3**)	20	91	90	93
		(**4**)	20	95	30	95
		(**5**)	30	96	30	98
		(**6**)	60	93	60	96
		(**7**)	15	94	60	94
		(**8**)	120	75	120	78
		(**9**)	50	97	60	98

[a] All reactions were carried out with 1 mmol of epoxide and Dowex-50WX8 (0.5 g) supported thiourea (3 mmol) at solvent-free conditions.
[b] Temperature of oil bath was 60–70°C.
[c] Microwave irradiation was carried out with 40% power amplitude (400 W).
[d] Yields refer to isolated pure products.

epoxides with Dowex-50WX8–supported thiourea under the optimized conditions. Table I shows the general trend and the versatility of this synthetic method. All reactions were carried out efficiently to give the thiiranes in 75–98% yields within 15–120 min.

Microwave heating and its application in organic synthesis has been developed successfully, and in the past few years there has been a tremendous amount of interest in this area. Remarkable decrease in reaction times and, in most cases, clean reaction and better yields have been reported after applying microwave irradiation.[31] We investigated the solvent-free conversion of epoxides to thiiranes with Dowex-50WX8–supported thiourea under microwave irradiation. The experiments showed that the irradiation of a mixture of styrene oxide (1 mmol) and Dowex-50WX8 (0.5 g)–supported thiourea (3 mmol) with microwave (40% power amplitude, 400 W) resulted in a complete reaction within 90 sec with 96% yield. This result encouraged us to perform the same reaction with the examined epoxides at the optimized conditions. The results of this investigation are summarized in Table I. As becomes evident from Table I, there is a distinct rate enhancement under microwave conditions with better yields (78–98%): the reactions are completed within 30–120 sec as compared to 15–120 min under conventional heating.

In conclusion, we have shown that structurally different epoxides are easily and efficiently converted to the corresponding thiiranes with Dowex-50WX8–supported thiourea under solvent-free conditions. The reactions can be carried out under conventional heating or microwave irradiation. We believe that the present protocols offer a mild, simple, and efficient method for the preparation of thiiranes from epoxides. In addition, availability of the reagents, high yields of thiiranes, and short reaction times, as well as the advantages of solvent-free conditions make these methods useful additions to the present methodologies.

EXPERIMENTAL

All reagents and substrates were purchased from commercial sources with the best quality and were used without further purification. Irradiation with microwave was carried out with Yousch domestic microwave oven (overall power 1000 W). IR and ^{1}H NMR spectra were recorded with a Thermo Nicolet Nexus 670 FT-IR spectrophotometer and a 300 MHz Bruker spectrometer, respectively. The products were characterized by their ^{1}H NMR and IR spectra and by comparison with the reported data in the literature. All yields refer to isolated pure products. TLC (silica gel 60 F_{254} aluminum sheet) was applied for the purity determination of substrates and products and for reaction monitoring.

Preparation of Dowex-50WX8–Supported Thiourea

To a round-bottomed flask charged with finely grinded Dowex-50WX8 (0.5 g), thiourea (0.228 g, 3 mmol) and water (2 mL) were added. The mixture was stirred for 5 min at room temperature. Evaporation of the solvent under microwave irradiation (1000 W) gave Dowex-50WX8–supported thiourea in quantitative yield.

Conversion of Epoxides to Thiiranes with Dowex-50WX8–Supported Thiourea Under Solvent-Free Conditions: General Procedure

In an experimental tube, the epoxide (1 mmol) and Dowex-50WX8 (0.5 g)–supported thiourea (0.228, 3 mmol) were well mixed. The tube was heated in an oil bath (60–70°C) or irradiated with microwave (40% power amplitude, 400 W) for the appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was washed with ethyl acetate followed by filtration. Evaporation of the solvent and flash column chromatography of the resulting crude product afforded the pure liquid episulfide in 93–96% yield.

Epithiostyrene (Styrene Episulfide) (1)

^{1}H NMR ($CDCl_3$): δ = 7.36–7.26 (m, 5H), 3.93 (t, J = 6.2 Hz, 1H), 2.90 (dd, J = 1.5, 6.6 Hz, 1H), 2.68 (dd, J = 1.5, 5.7 Hz, 1H).

7-Thia-bicyclo[3.1.0] Heptane (Cyclohexeneepisulfide) (2)

^{1}H NMR ($CDCl_3$): δ = 3.13–3.05 (m, 2H), 2.00–1.85 (m, 2H), 1.85–1.71 (m, 2H), 1.48–1.31 (m, 2H), 1.28–1.11 (m, 2H).

Phenoxymethyl Thiirane (3-Phenoxypropylene Sulfide) (3)

^{1}H NMR ($CDCl_3$): δ = 7.39–7.22 (m, 2H), 7.05–6.87 (m, 3H), 4.24 (dd, J = 3.3, 11.1 Hz, 1H), 3.96 (dd, J = 5.7, 11.1 Hz, 1H), 3.40–3.30 (m, 1H), 2.91 (t, J = 4.5 Hz, 1H), 2.76 (dd, J = 2.5, 4.8 Hz, 1H).

Isopropoxymethyl Thiirane (3-Isopropoxypropylene Sulfide) (4)

^{1}H NMR ($CDCl_3$): δ = 3.72–3.62 (m, 2H), 3.40 (dd, J = 6.9, 10.5 Hz, 1H), 3.12–3.03 (m, 1H), 2.54 (d, J = 5.7 Hz, 1H), 2.23 (dd, J = 1.2, 5.4 Hz, 1H), 1.91 (dd, J = 3.3, 6.0 Hz, 6H).

Allyloxymethyl Thiirane (3-Allyloxypropylene Sulfide) (5)

^{1}H NMR ($CDCl_3$): δ = 6.01–5.84 (m, 1H), 5.29 (ddd, J = 1.5, 3.3, 17.4 Hz, 1H), 5.21 (dd, J = 1.2, 10.2 Hz, 1H), 4.05 (dt, J = 1.2, 5.7 Hz, 2H), 3.65 (dd, J = 5.7, 10.8, Hz, 1H), 3.46 (dd, J = 6.6, 10.5 Hz, 1H), 3.14–3.04 (m, 1H), 2.53 (d, J = 6.3 Hz, 1H), 2.22 (dd, J = 1.2, 5.4 Hz, 1H).

Methacrylatomethyl Thiirane (3-Methacrylpropylene Sulfide) (6)

^{1}H NMR ($CDCl_3$): $\delta = 6.15$ (d, $J = 0.9$ Hz, 1H), 5.63–5.57 (m, 1H), 4.31–4.14 (m, 2H), 3.22–3.12 (m, 1H), 2.54 (dd, $J = 0.6$, 6.0 Hz, 1H), 2.30 (dd, $J = 1.5$, 5.1 Hz, 1H), 1.95 (s, 3H).

Butyl Episulfide (Butyl Thiirane) (7)

^{1}H NMR ($CDCl_3$): $\delta = 3.13$–3.04 (m, 1H), 2.53 (d, $J = 6.0$, 1H), 2.22 (d, $J = 5.1$, 1H), 1.67–1.51 (m, 4H), 1.46–1.32 (m, 2H), 0.93 (t, $J = 7.3$, 3H).

Chloromethyl Thiirane (Epithiochlorohydrine) (8)

^{1}H NMR ($CDCl_3$): $\delta = 3.67$ (dd, $J = 5.8$, 10.9 Hz, 1H), 3.49 (dd, $J =$ 6.8, 10.7 Hz, 1H), 3.15–3.03 (m, 1H), 2.54 (dd, $J = 1.3$, 5.7 Hz, 1H), 2.24 (dd, $J = 1.4$, 5.1, Hz, 1H).

trans-Stilben Episulfide (9)

^{1}H NMR ($CDCl_3$): $\delta = 7.35$ (s, 10H), 3.94 (s, 2H).

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