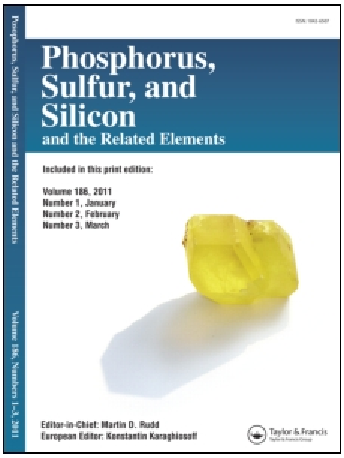

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Efficient Conversion of Oxiranes to Thiiranes with Thiourea Catalyzed with Ruthenium Trichloride and Alumina

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To cite this Article Kazemi, Foad , Kiasat, Ali Reza and Ebrahimi, Shahriar(2001) 'Efficient Conversion of Oxiranes to Thiiranes with Thiourea Catalyzed with Ruthenium Trichloride and Alumina', Phosphorus, Sulfur, and Silicon and the Related Elements, 176: 1, 135 — 140

To link to this Article: DOI: 10.1080/10426500108055110

URL: http://dx.doi.org/10.1080/10426500108055110

Phosphorus, Sulfur and Silicon, 2001, Vol. 176, pp. 135–140
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1042-6507/01 $12.00 + .00

EFFICIENT CONVERSION OF OXIRANES TO THIIRANES WITH THIOUREA CATALYZED WITH RUTHENIUM TRICHLORIDE AND ALUMINA

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Oxiranes are efficiently converted to the corresponding thiiranes by thiourea in the presence of catalytic amounts of Ru(III) with excellent yields under mild and nonaqueous conditions. It is proved that the presence of Woelm chromatographic alumina in reaction media increases the rate of reactions.

Keywords: Oxirane; ruthenium trichloride; thiirane; thiourea

INTRODUCTION

Since episulfides serve as useful precursors for the synthesis of olefins[1] and other functional group moieties,[2] their synthesis are of fundamental interest. There are many methods reported in the literature for this conversion,[3–10] and the most general one involves application of oxiranes as convenient starting materials and inorganic thiocyanates or thiourea as sulfur introducing reagents.[7–14]

Application of thiourea as sulfurating agent for this conversion was reported under wet conditions (solvent free) or in aqueous ethanol,[7] but the reactions suffer from long reaction times, low yield, and occurrence of desulfuration of obtained episulfide to olefin in some cases. Recently, application of poly(4-vinyl pyridine)-Ce(OTf)$_4$[12] and tin(IV) meso-tetraphenylporphyrin[13] as catalysts for this conversion was reported.

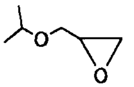
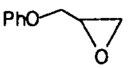
The continuation of our studies on application of Ru(III) as commercially available anhydrous ruthenium trichloride in organic synthesis[10,15,16] and its successful application in the synthesis of thiiranes using ammonium thiocyanate,[10] prompted us to explore the potential of this Lewis acid for the conversion of oxiranes to thiiranes using thiourea. Now we report on an improved, efficient, and easy synthesis of thiiranes from oxiranes under mild nonaqueous conditions in excellent yields in the presence of alumina and catalytic amounts of anhydrous $RuCl_3$.

RESULTS AND DISCUSSION

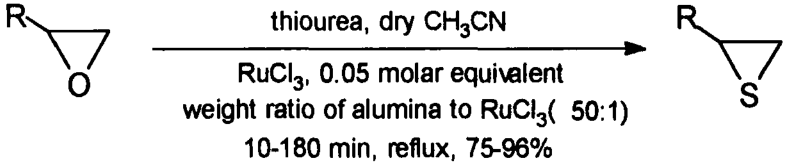
Different solvents such as t-butanol, diethyl ether, acetonitrile, CH_2Cl_2, and CCl_4 were used for transformation of oxiranes to the corresponding thiiranes. Among these solvents acetonitrile was found to be most suitable. Although, transformation of styrene oxide to styrene sulfide using thiourea and a catalytic amount of anhydrous $RuCl_3$ (0.05 molar equivalent) in dry CH_3CN was relatively successful after 1 h and 90% yield, the conversion of other epoxides under the same conditions was not successful. Increasing the amount of the $RuCl_3$ catalyst did not improve the reaction efficiently.

The use of alumina as catalyst and reagent in organic synthesis is increasingly widespread due to improved efficiency of many surface bound reagent.[17] We found that Woelm chromatographic alumina dramatically accelerates thiirane synthesis in the present method (Table I). Therefore, conversion of several oxiranes to corresponding thiiranes

TABLE I Conversion of Oxirranes to Thiiranes Using Thiourea[a] in Refluxing CH_3CN with Different Amounts of $RuCl_3$ and Alumina

Entry	Substrate	$RuCl_3$ (molar equivalent)	Alumina (g)	$Al_2O_3/RuCl_3$ (w/w)	Time (min)	Conversion %[b]
1		0	0	—	180	0
		0	0.8	—	180	trace
		0.01	0.05	25	80	trace
		0.01	0.105	50	90	20
		0.02	0.21	50	120	100
		0.05	0	—	180	20
		0.05	0.21	20	60	70
		0.05	0.42	40	40	85
		0.05	0.52	50	10	100
		0.05	0.78	75	8	100
2		0	0	—	180	0
		0.05	0	—	180	40
		0.02	0.21	50	110	100
		0.03	0.31	50	90	100
		0.04	0.42	50	70	100
		0.05	0.52	50	20	100

[a] Molar ratio of thiourea to epoxide was 2:1.
[b] GC yield.



SCHEME 1

was performed with different amount of $RuCl_3$ and Al_2O_3 in order to find the most adequate condition for this transformation. The mole ratio 2:1:0.05 of thiourea, substrate, and $RuCl_3$, respectively, and weight ratio 50:1 of alumina to $RuCl_3$ were found to be optimal conditions (Table I).

Different types of oxiranes (except cyclooctene oxide) carrying activated and deactivated groups are converted to the corresponding thiiranes as exclusive and virtually pure products according to TLC and ^{1}HNMR in considerably short times and excellent yields. The results are shown in Table II.

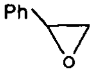
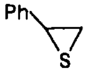
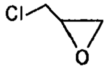
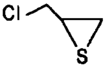
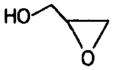
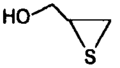
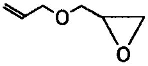
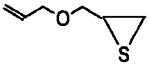
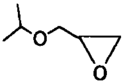
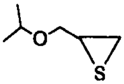
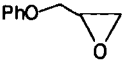
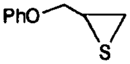
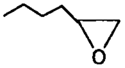
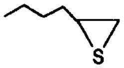
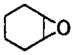
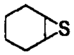
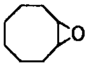
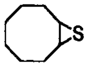
Under similar conditions when styrene oxide was reacted with thiourea in the absence of $RuCl_3$ and alumina, GC and TLC analysis of the reaction mixture did not show formation of any product after 3 h.

In reports where an aqueous solvent has been used, control of pH is important to obtain a high yield of episulfides without polymerization.[3] Our procedure provides excellent yields of thiiranes in a comparatively very short time, without formation of any polymeric by product, and with no water required as cosolvent. The advantage of using alumina and anhydrous $RuCl_3$ as catalyst for the synthesis of thiiranes using thiourea is shown by comparing our results with those previously reported in the literature (Table III). For example, conversion of cyclooctene oxide to cyclooctene sulfide is very difficult and only a few reports are available in the literature for this transformation.[3,7] Contrary to the previous reports, our procedure provides a good yield of cyclooctene sulfide in comparatively short reaction time.

CONCLUSION

We believe that the present methodology offers a mild, simple, and efficient method for the preparation of thiiranes from oxiranes. In addition, availability of the reagent, easy work-up, high yields, and short reaction times make this method a useful addition to the present methodologies.

TABLE II Conversion of Epoxides to Thiiranes[a] with Thiourea Catalyzed with $RuCl_3$/Alumina (50:1 w/w) in Refluxing Acetonitrile

Entry	Substrate	Product	Time (min)	Yield %[b]
1			15	95
2			10	94
3			30	96
4			10	92
5			10	96
6			20	94
7			15	93
8			15	96
9			180	75

[a] Products were identified by comparison of their physical and spectral data with those of authentic samples.

[b] Isolated yield.

EXPERIMENTAL

General

Products were characterized by comparison of their physical data with those of authentic samples. All yields refer to isolated products. IR spectra were recorded on a Shimadzo 450 spectrophotometer. ^{1}HNMR spectra were recorded on a Bruke Avance DPX instrument (250 MHZ). Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX. Melting points were determined in open capillaries with a Galen-Kamp melting point apparatus. TLC accomplished the purity determination of the substrates and reactions monitoring on silica gel polygram SILG/UV 254 plates.

TABLE III Comparison of Some Results Obtained from the Reaction of Epoxides with Thiourea in the Presence of $RuCl_3$ and Alumina with Those Reported from Other Methods

	Time/temp/yield (h)/(°C)/(%)			
Method	Styrene oxide	Phenyl glycidyl ether	Cyclohexene oxide	Cyclooctene oxide
A[a]	0.25/85/95	0.33/85/94	0.25/85/96	3/85/75
B[b]	NR	NR	32/15/40	NR
C[c]	1.3/85/85	5/85/92	1.8/85/55	—
D[d]	10/r.t/45	—	—	—
E[e]	18/r.t/98	—	—	20/rt/60
F[f]	0.75/85/95	0.75/85/95	0.75/85/93	—

[a] The present method.
[b] The thiourea has been used without a catalyst in aqueous solvent.[3]
[c] $TiO(TFA)_2$ has been used as catalyst.[14]
[d] The thiourea has been used without catalyst in ethanol.[7]
[e] The thiourea has been used without catalyst in solvent free condition.[7]
[f] Sn (IV) (tpp) $(ClO_4)_2$ has been used as catalyst.[13]

General Procedure for the Conversion of Oxiranes to Thiiranes

In a round-bottom flask (25 ml) equipped with a condenser and a magnetic stirrer, a solution of epoxide (1 mmol) in dry CH_3CN (5 ml) and thiourea (2 mmol) was prepared. Anhydrous $RuCl_3$ (0.0103 g, 0.05 mmol) and alumina (0.52 g) were then added to the solution and the reaction mixture was stirred magnetically under reflux condition for the appropriate time according to Table II. The progress of the reaction was monitored by TLC. To the reaction mixture, 20 ml of water was added and the mixture was extracted with $CHCl_3$ (3 × 10 ml). The organic layer was dried with anhydrous Na_2SO_4 after washing with 20 ml of water. Evaporation of the solvent followed by chromatography on a short column of silica-gel (elut: CCl_4) gave the pure products in 75–96% isolated yields.

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