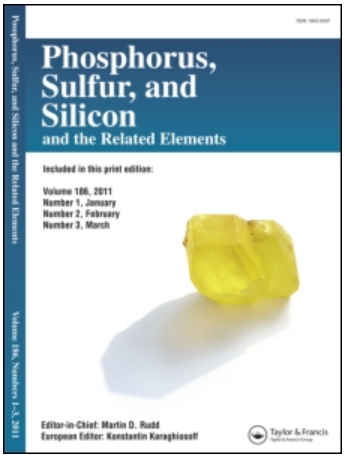

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Ali Reza Kiasat[a]; Foad Kazemi[a]; Mehdi Fallah Mehr Jardi[a]
[a] Chemistry Department, College of Science, Shahid Charman University, Ahvaz, Iran

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SOLVENT-FREE CONVERSION OF OXIRANES TO THIIRANES WITH THIOUREA

Ali Reza Kiasat, Foad Kazemi, and Mehdi Fallah Mehr Jardi
Chemistry Department, College of Science, Shahid Charman University, Ahvaz 6137-4-3169, Iran

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A simple and efficient method for the conversion of various oxiranes to the corresponding thiiranes using thiourea under solvent free conditions is described.

Keywords: Oxirane; solvent free; thiirane; thiourea

INTRODUCTION

In organic syntheses and reactions, increasing attention is being focused on green chemistry, using environmentally benign reagents and conditions, particularly solvent-free procedures,[1] which often lead to clean, eco-friendly, and highly efficient procedures involving simplified workups.[2] Reactions under dry conditions were originally developed in the late 1980s[3] and offer several advantages.[4] The absence of solvent reduces the risk of hazardous explosion when the reaction takes place in a closed vessel. Moreover, aprotic dipolar solvents with high boiling points are expensive and are difficult to remove from reaction mixtures.

As the most interesting class of cyclic sulfides, thiiranes serve as useful precursors for the synthesis of olefins by phosphite- or phosphite-mediated desulfurizations and other functional group moieties,[6] and so their synthesis is of fundamental interest. A variety of synthetic methods exist to prepare thiiranes;[7–14] one of the most intriguing routes involves the reaction of epoxides with inorganic thiocyanates or thiourea as sulfurintroducing reagents.[11–18]

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Address correspondence to Ali Reza Kiasat, Chemistry Department, College of Science, Shahid Charman University, Ahvaz 6137-4-3169, Iran.

In comparison with ammonium thiocyanate, thiourea is a less-reactive and more-stable sulfurating agent and its handling is easier.[19] Therefore, application of oxiranes as convenient starting materials and thiourea as sulfurating agent can be considered as a practical and useful achievement in the synthesis of thiiranes. Conversion of oxiranes to thiiranes with thiourea was previously reported under wet conditions or in aqueous ethanol,[11] but the reactions suffer from long reaction times, low yield, and the occurrence of desulfuration of obtained episulfide to olefin in some cases. Recently, application of poly (4-vinylpyridine)-Ce(OTf)$_4$,[16] tin(IV) mesotetraphenylporphyrin,[17] TiO(CF$_3$CO$_2$)$_2$,[18] TiCl$_3$(CF$_3$SO$_3$),[18] Bi(TFA),[19] and RuCl$_3$[20] as catalysts for this conversion was reported.

RESULTS AND DISCUSSION

In continuation of our ongoing program to develop synthetic protocols for the conversion of oxiranes to thiiranes,[12–14,21–23] we report here conditions whereby various types of thiiranes can be conveniently synthesized from the corresponding oxiranes under mild nonaqueous reaction conditions by thiourea under solvent-free conditions (Figure 1).

The substrates used (cyclohexene and styrene oxides, glycidyl phenyl ether, glycidyl isopropyl ether, and allyl glycidyl ether) were selected as examples of aliphatic, cyclic, activated, and deactivated epoxides. With this approach these substrates are converted to the corresponding thiiranes as exclusive and virtually pure products according to TLC and ^{1}H NMR. The obtained results are summarized in Table I.

In reports where an aqueous solvent has been used, control of pH is important to obtain high yields of thiiranes without polymerization.[5] Our procedure provides good yields of thiiranes in comparatively short time, without formation of any polymeric by-product.

We reasoned that the mechanism of the reaction involves a SN$_2$-type nucleophilic attack of the thiourea on the epoxide, Furthermore, if this reasoning was valid and the reaction rate was second order, then increasing the concentration of each reactant should result in an increase of the rate of reaction. Thus the reaction was carried out neat with a

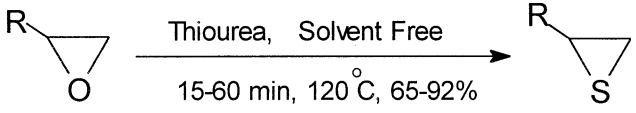
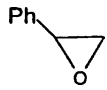
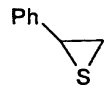
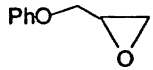
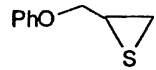
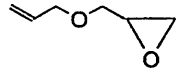
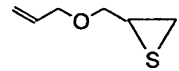
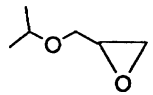
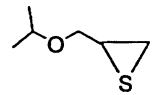
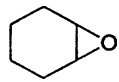
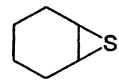


FIGURE 1

TABLE I Conversion of Epoxides to Thiiranes[a] with Thiourea Under Solvent-Free Condition

Entry	Substrate	Product	Time (min)	Yield %[b]
1			15	65
2			15	84
3			60	77
4			60	80
5			25	92

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

variety of epoxides, and to our satisfaction the neat reactions were fast and clean, typically affording the episulfides in good yields (Table I).

CONCLUSION

In conclusion, this efficient method can be applied for conversion of different classes of epoxides carrying activated and deactivated groups into their corresponding thiiranes. Short times, simple workup, and mild reaction conditions make this method a useful addition to the present methodologies.

EXPERIMENTAL

General

Products were characterized by comparison of their physical data with those of authentic samples. All yields refer to isolated products. TLC accomplished the purity determination of the substrates and reactions monitoring on silica gel polygram SILG/UV 254 plates.

General Procedure for the Conversion of Oxiranes to Thiiranes

A stirred mixture of epoxide (1 mmol) and thiourea (2 mmol) was heated at 120°C with a constant temperature bath for the appropriate time, as shown in Table I. The progress of the reaction was monitored by TLC. The mixture was cooled to room temperature, and CCl_4 (20 ml) was added to the mixture and filtered. Evaporation of the solvent under reduced pressure gave the pure products in 65–92% isolated yields.

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