

## **Bi(TFA)<sub>3</sub> and Bi(OTf)<sub>3</sub> Catalyzed Conversions of Epoxides to Thiiranes with Ammonium Thiocyanate and Thiourea under Non-Aqueous Conditions**

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*Received: 30 July 2001; in revised form 10 October 2001 / Accepted: 23 October 2001 / Published: 30 November 2001*

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**Abstract:** Various epoxides are converted to their corresponding thiiranes in excellent yields with ammonium thiocyanate and thiourea under non-aqueous conditions in the presence of catalytic amounts of Bi(TFA)<sub>3</sub> and Bi(OTf)<sub>3</sub>.

**Keywords:** Bi (III) salts, Epoxides, Lewis acids, Thiiranes.

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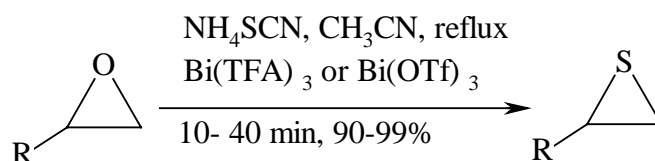
### **Introduction**

Epoxides are important intermediates in organic synthesis. One of the most important reactions of these compounds is the conversion to their corresponding thiiranes by an oxygen-sulfur exchange process. Many methods have already been reported in the literature for this purpose [1-11]. 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 by-products and the need for aqueous reaction conditions, therefore, the introduction of new, efficient methods for this transformation is a desirable objective. Recently we have reported the bismuth (III) chloride catalyzed conversion of epoxides to thiiranes in the presence of ammonium thiocyanate [12], but in the presence of thiourea this catalyst is not effective. As a continuation of our studies on catalysis by Bi(III) salts [13], we now report that Bi(TFA)<sub>3</sub> or Bi(OTf)<sub>3</sub> can act as efficient catalysts for the conversion of epoxides to their corresponding thiiranes in the presence of both ammonium thiocyanate and thiourea.

## Results and Discussion

The reactions of various epoxides with  $\text{NH}_4\text{SCN}$  were performed in the presence of 0.05 molar equivalent of  $\text{Bi}(\text{TFA})_3$  or 0.02 molar equivalent of  $\text{Bi}(\text{OTf})_3$  in refluxing acetonitrile to afford the corresponding thiiranes in excellent yields (Scheme 1, Table 1). The substrates used (cyclohexene and styrene oxides, epichlorohydrin, glycidyl phenyl ether, glycidyl isopropyl ether, allyl glycidyl ether and 1,2-epoxyoctane) were selected as examples of aliphatic, cyclic, activated and deactivated epoxides.

**Scheme 1**



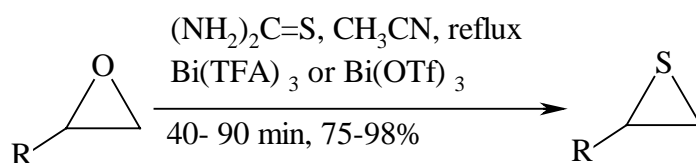
**Table 1.** Conversion of Epoxides to Thiiranes with  $\text{NH}_4\text{SCN}$  Catalyzed by  $\text{Bi}(\text{TFA})_3$  or  $\text{Bi}(\text{OTf})_3$  in Refluxing  $\text{CH}_3\text{CN}$

Epoxide	$\text{Bi}(\text{TFA})_3$		$\text{Bi}(\text{OTf})_3$	
	Yield% <sup>a</sup>	Cat./epoxide (Time, Min)	Yield% <sup>a</sup>	Cat./epoxide (Time, Min)
	96	0.05(30)	99	0.02(15)
	94	0.05(20)	98	0.02(15)
	94	0.05(35)	99	0.02(25)
	90	0.05(40)	93	0.02(10)
	95	0.05(15)	97	0.02(10)
	92	0.05(15)	99	0.02(10)
	92	0.05(20)	98	0.02(10)

<sup>a</sup> All products were identified by comparison of their physical and spectral data with those of authentic samples. <sup>b</sup> Isolated yields.

Although the methodology has not been tested on 1,1-disubstituted, trisubstituted or tetrasubstituted epoxides at this time, based on our experience with mono- and 1,2-disubstituted ones we have no reason to believe it will not work equally well with those substrates too. We have also investigated the catalytic abilities of these two catalysts for the conversion of epoxides to thiiranes with thiourea as sulfur-introducing reagent (Scheme 2). In comparison with ammonium thiocyanate, thiourea is a less reactive and more stable sulfurating agent and further its handling is easier. Therefore, the proposed method based on using thiourea can be considered as a practical and useful achievement in synthesis of thiiranes from epoxides.

Scheme 2.

Table 2. Conversion of Epoxides to Thiiranes with  $(\text{NH}_2)_2\text{C}=\text{S}$ 

Epoxide	$\text{Bi}(\text{TFA})_3$		$\text{Bi}(\text{OTf})_3$	
	Yield% <sup>a</sup>	Cat./epoxide(Time, Min)	Yield% <sup>a</sup>	Cat./epoxide(Time, Min)
	92	0.1 (60)	95	0.05 (40)
	90	0.1 (75)	92	0.05 (60)
	80	0.15 (70)	90	0.07 (60)
	75	0.15 (75)	88	0.07 (70)
	90	0.15 (60)	98	0.07 (60)
	85	0.15 (90)	92	0.07 (90)
	77	0.15 (75)	93	0.07 (60)

<sup>a</sup> All products were identified by comparison of their physical and spectral data with those of authentic samples. <sup>b</sup> Isolated yields.

As shown in Table 2, different classes of epoxides reacted with thiourea in the presence of 0.05-0.15 molar equivalent of the catalysts in refluxing acetonitrile and the corresponding thiiranes were obtained in high yields. In contrast, the conversion of epoxides to thiiranes with thiourea under wet (solvent free) conditions or in aqueous ethanol suffers from long reaction times and low yields of the products [2]. It is also worth mentioning that while in an aqueous medium the pH must be controlled to avoid polymerization of the thiiranes, in this method, since the reactions occur under non-aqueous conditions, no polymerization was observed and thiiranes were obtained in excellent yields. The experimental results also show that Bi(OTf)<sub>3</sub> is more reactive than Bi(TFA)<sub>3</sub> in these reactions.

## Conclusions

We have shown that Bi(TFA)<sub>3</sub> or Bi(OTf)<sub>3</sub> can be used as efficient catalysts for the conversion of epoxides to thiiranes with ammonium thiocyanate and thiourea. Noteworthy advantages of this method are the high yields of the products, short reaction times, easy workup, stability, availability, and non-toxicity of the catalysts.

## Experimental

### General

All products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples. Yields refer to isolated products. IR spectra were run on a Philips PU9716 spectrophotometer. <sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker AM 80 MHz spectrometer using TMS as an internal standard. GC analysis was performed using a column of 15% Carbowax 20M Chromosorb-W 60-80 mesh on a Shimadzu 16A GC equipped with a FID. Bi(TFA)<sub>3</sub> and Bi(OTf)<sub>3</sub> were prepared according to described procedures [14].

### General Procedure for the Conversion of Epoxides to Thiiranes

A solution of epoxide (1 mmol) and NH<sub>4</sub>SCN or thiourea (2 mmol) in CH<sub>3</sub>CN (5 mL) was prepared in a round-bottomed flask (25 mL) equipped with a condenser and a magnetic stirrer, Bi(TFA)<sub>3</sub> or Bi(OTf)<sub>3</sub> (0.02-0.15 mmol) were added to the solution and the reaction mixture was stirred magnetically under reflux conditions for 10-90 min. The progress of the reaction was monitored by GLC. After completion of the reaction, the solvent was evaporated and H<sub>2</sub>O (10 mL) was added. The mixture was extracted with CHCl<sub>3</sub> (2 × 10 mL) and the organic solution was dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the crude product was purified on a short column of silica-gel (4:1 *n*-hexane/EtOAc as eluent) to afford the pure thiiranes in 75-99% yields (Tables 1 and 2).

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*Sample Availability:* Samples are available from MDPI.

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