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Stereospecific Formation of S(-) Styrene Sulfide: Efficient Conversion of Epoxides to Thiiranes Catalysed with Ru(III)

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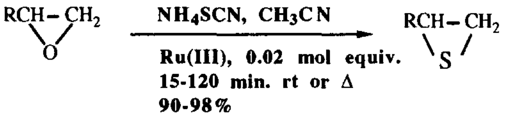
***ABSTRACT*: Ru(III) catalysis the efficient conversion of different epoxides to their corresponding thiiranes in the presence of ammonium thiocyanate in exellent yields. Stereospecific conversion of R(+) styrene oxide to S(-) styrene sulfide was achieved in high optical purity.** © 1997 Elsevier Science Ltd.

There are many methods reported in the literature for preparation of thiiranes.[1,2] The reaction of epoxides with inorganic thiocyanate or thiourea in water or in aqueous solvents have been considered as the most convenient route for the preparation of thiiranes .[1,2,3] By these methods, the yield of thiiranes such as cyclohexene and styrene sulfides as well as those of higher thiiranes is not satisfactory.[4,5] In addition, the increase in pH of the reaction, difficulty in separation of the product from the reaction mixture and formation of polymeric by-product are other drawbacks of these methods. The reactions of phosphine sulfide[6], 3-methylbenzothiazol-2-thione[7] and dimethylthioformamide[8] with epoxides have been also reported but these reactions occur in the presence of trifluoroacetic acid. Modified methods such as the use of silica gel - supported KSCN[9] or low hydrated KSCN-liquid herogeneous mediums[10] have been also reported. But as it is reported even in these systems the presence of traces of water is necessary and in the case of silica gel-supported KSCN, the reaction suffers from high temperature (90 °C) and long reactions time (13-528 hours). Very recently the reaction of polymer supported thiocyanate with epoxides has been studied under nonaqueous conditions.[11] The reactions have been reported in refluxing cyclohexane (4.5-18 hours) and in the presence of 5-8 molar equivalents of the polymeric reagent.

In the course of our studies on the nucleophilic ring opening reaction of epoxides with Ce(IV) salts[12], we found that Ce(IV) as ceric ammonium nitrate (CAN) can efficiently catalyse the conversion of epoxides to thiiranes in the presence of ammonium thiocyanate in t. butanol.[13] In continuation of our studies for conversion of epoxides to thiiranes and especially for stereospecific conversion of optically active styrene oxide to the corresponding optically active sulfide through the reaction with thiocyanate, we found that Ru(III) as ruthenium trichloride can act as an efficient catalyst for the conversion of various epoxides to thiiranes in acetonitrile in excellent yields **(Scheme 1)**.

Scheme 1



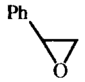
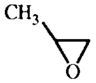
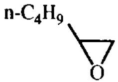
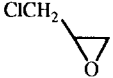
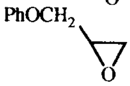
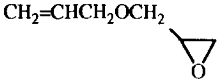
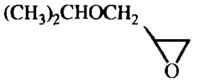
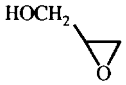
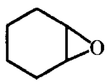
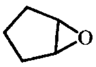
In reports where an aqueous solvent has been used, control of pH is important to obtain a high yield of thiiranes without polymerization.[1] In this method, no water is required as the co-solvent and the reactions occur quickly, in excellent yields and without any polymerization.

The reaction of styrene oxide with NH_4SCN and in the presence of 0.02 molar equivalents of Ru(III) as anhydrous ruthenium trichloride was studied in different solvents such as acetone, t. butanol and acetonitrile. The best solvent for this reaction was found to be acetonitrile. In this solvent, the reaction was finished after one hour at room temperature and gc analysis showed the quantitative formation of styrene sulfide. The reaction was also scaled up without any decrease in the yield of the product.

Reactions of different aliphatic and cyclic epoxides including those with electron-withdrawing substituents were also performed in acetonitrile and in the presence of only 0.02 molar equivalent of Ru(III) at room temperature or under reflux conditions. Table 1 summarizes the results obtained for the conversion of different epoxides to their corresponding thiiranes.

In order to study the effect of other Lewis acids for these transformation, various metal halides were reacted with styrene oxide in the presence of 3 molar equivalents of NH_4SCN in acetonitrile.

Table 1. Conversion of Epoxides to Thiiranes Using 0.02 Equimolar Amount of Ru(III) in Acetonitrile.

Entry	Epoxide	Mole Ratio of SCN$^-$/Epoxide	Time/Temp. min. (°C)	Yield%[a]
1		3	60/(25 °C)	98
2		3	75/(25 °C)	100[b]
3		3	15/(25 °C)	99
4		3	120/(25 °C)	95
5		3	90/(80 °C)	95
6		3	30/(80 °C)	96
7		3	15/(25 °C)	94
8		3	60/(80 °C)	96
9		3	45/(80 °C)	93
10		3	15/(80 °C)	95

[a] Yields refer to isolated products.
[b] G.C yield.

Among the Lewis acids which were studied, $AlCl_3$, $SnCl_2$ and $CrCl_3$ gave moderate yield of styrene sulfide. Table 2 shows the results obtained from this study.

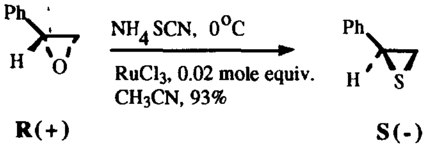
Table 2. Reaction of styrene oxide with 0.02 molar equivalents of various Lewis acids at room temperature.

Entry	Metal Halide[1]	Time (h)	Yield % of Styrene Sulfide[1]
1	Ru(III)	1	100
2	Al(III)	3	70
3	Sn(II)	3	58
4	Mn(II)	3	60
5	Zn(II)	3	18
6	Fe(III)	5	5
7	Fe(II)	5	0
8	Co(II)	5	0
9	Cu(II)	5	0
10	Ti(IV)	5	5

[1] GC yields.

Although there are various methods for preparation of thiiranes, the reported results on preparation of optically pure thiiranes are rare.[14a] In another interesting approach, addition of lithium salt of 2-methylthiothiazoline to benzaldehyde was carried out at -100 °C in the presence of lithium salt of (2S,2'S)-2-hydroxymethyl-1-[(1-alkyl-2-pyrrolidinyl)methyl]pyrrolidines as chiral ligand.[14b] With this method, chiral styrene sulfide was obtained in 50% yield and only in 20% optical purity. Therefore, stereospecific conversion of epoxides to thiiranes in the presence of sulfur transfer agents could be considered as a good alternative method. Very recently, enantioselective synthesis of diethyl (+)-(2S,3S)-trans-2,3-epithiosuccinate from its corresponding optical active epoxide in 48% yield has been reported using triphenyl phosphine sulfide and trifluoroacetic acid as catalyst.[15] We observed that under our conditions (scheme 2), 0.02 molar equivalents of Ru(III) can convert R(+) styrene oxide to S(-) styrene sulfide[16] in quantitative yield and 78% optical purity.[17]

Scheme 2



The optical purity of the product was determined on the basis of the reported rotation for optically active styrene sulfide and also its reduction to the corresponding optically active 1-phenylethanethiol.[14,16] The ability of other Lewis acids for the specific conversion of R(+) styrene oxide to optically active styrene sulfide was also studied. Among those Lewis acids which are reported in Table 2, only $AlCl_3$ converted R(+) styrene oxide to S(-) styrene sulfide in only 65% yield and optical purity of 51%.

The present method has the following advantages: The reagents are readily available, the procedure is simple and the reactions time are relatively short, the reactions can be performed with a wide range of epoxides under mild conditions and the yield of thiiranes is excellent. In addition, this method can be considered as an alternative method for the enantioselective synthesis of thiiranes.

Experimental

Products were characterized by comparison of their physical data IR, NMR and mass spectra with those prepared accordance with literature procedures. Infrared spectra were recorded on a Perkin Elmer IR-157 G and a Perkin Elmer 781 spectrometer. NMR spectra were recorded on a Bruker Avance DPX250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX . The optical rotation was determined using a Perkin-Elmer 241 polarimeter.The purity determination of the substrates and reactions monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-10A instrument with a flame ionization detector using a column of 15% carbowax 20M chromosorb-w acid washed 60-80 mesh.

General Procedure for the Conversion of Epoxides to Thiiranes:

To a mixture of epoxide (10 mmol) and ammonium thiocyanate (30 mmol) in acetonitrile (30 mL), was added anhydrous ruthenium chloride (0.2 mmol) and stirred at room temperature or under reflux condition for the appropriate time according to **Table** 1. The reaction was monitored by GLC. The solvent was evaporated. Chloroform (2x20 mL) was added to the residue and filtered. The combined organic solution was evaporated. The crude product was obtained in quantitative yield. Distillation of the product under reduced pressure gave the corresponding thiirane in 90-95% yield.

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17. Optical active R(+) styrene oxide, the product of Merck Company was used without further purification. The optical purity of the product was determined by the comparison of the observed optical rotation in heptane with the reported rotation in the literature, $[\alpha]^D = -43.85°$ (heptane).[14b,16] In addition, the optical rotation of obtained (-)-1-phenylethanethiol from reduction of optically active styrene sulfide was compared with the reported rotation for the (+) isomer in the literature[14a], $[\alpha]^D = +108°$.

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