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EFFICIENT CONVERSION OF EPOXIDES TO THIIRANES WITH THIOUREA CATALYZED BY TIN(IV) PORPHYRIN

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Abstract: Conversion of various epoxides to the corresponding thiiranes is achieved by thiourea in the presence of tin(IV) *meso*-tetraphenylporphyrin with excellent yields under non-aqueous conditions.

Various methods have been reported for preparation of thiiranes using epoxides as convenient starting materials. Sulfur introducing reagents such as inorganic thiocyanates,[1-3] thiourea,[3,4] phosphine sulfide,[5] 3-methylbenzothiazol-2-thione,[6] dimethylthioformamide,[7] silica-gel supported KSCN[8] and polymer supported thiocyanate[9] have been used for this purpose. However, as usual for every reagent, these methods suffer from disadvantage such as, relatively long reaction times, low yields of the products, formation of polymeric by-products and requirement for aqueous reaction conditions. Recently, conversion of epoxides to thiiranes in the presence of efficient catalysts such as ceric ammonium nitrate[10] and ruthenium trichloride[11] have been reported.

The successful applications of metalloporphyrins as mild Lewis acid catalysts,[12-15] prompted us to explore the potential of these complexes as catalysts for conversion of epoxides to thiiranes. We found that $Sn(IV)(tpp)(ClO_4)_2$ can act

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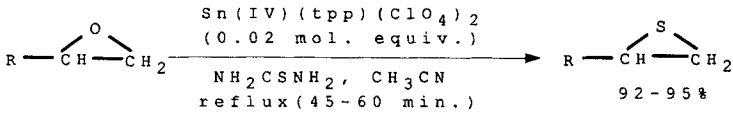
as an efficient catalyst for conversion of various epoxides to thiiranes with thiourea in refluxing acetonitrile (Scheme 1).



Scheme 1

The reaction of styrene oxide as a model substrate with thiourea in the presence of 0.02 molar equivalents of different metalloporphyrin complexes were studied in refluxing acetonitrile for 45 min.The catalytic activities in the reaction appear to be in order: $Sn(tpp)(ClO_4)_2$ (95%) >> $Fe(tpp)ClO_4$ (41%) > $Mn(tpp)ClO_4$ (6%) > $Sn(tpp)Cl_2$ (5%) > Fe(tpp)Cl (4%) > Mn(tpp)Cl (2%) > Cu(tpp) (1%).

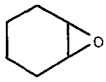
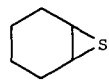
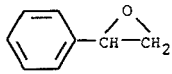
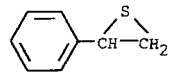
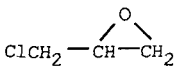
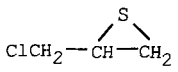
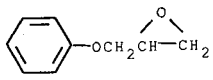
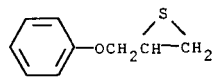
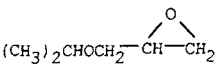
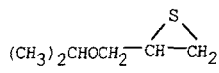
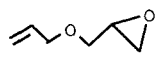
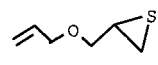
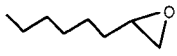
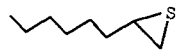
Reactions of different aliphatic and cyclic epoxides including those with electron-withdrawing substituents were also performed in refluxing acetonitrile and in the presence of only 0.02 molar equivalent of $Sn(IV)(tpp)(ClO_4)_2$. Table 1 summarizes the results obtained for conversion of different epoxides to their corresponding thiiranes.

The effect of other solvents such as acetone, dichloromethane, chloroform and carbon tetrachloride were also investigated. Compared to acetonitrile solvent, the reaction times were longer and the yields of thiiranes were considerably lower in all of the other solvents.

In the absence of tin(IV) tetraphenylporphyrin catalyst, thiourea was much less efficient in conversion of epoxides to thiiranes in refluxing acetonitrile.

In conclusion, $Sn(IV)(tpp)(ClO_4)_2$/thiourea as a mild and efficient catalytic system expands the scope of utilization of metalloporphyrins in useful organic transformations.

Table 1. Conversion of epoxides to thiiranes with $Sn(IV)(tpp)(ClO_4)_2/NH_2CSNH_2$ in refluxing CH_3CN.

Substrate	Product	Yield %[a,b] (t/min)	Bp(°C) / Torr Found(Reported)
		93(45)	53-54/7(54-55/7)[10]
		95(45)	84-85/5(85-86/5)[10]
		93(60)	59-60/30(60-61/30)[10]
		95(45)	104-106/7(103-104/7)[10]
		93(60)	55-56/11(54/11)[16]
		94(45)	76-78/8(78-79/8)[7]
		92(60)	83-85/5(83/5)[17]

a: All products were identified by comparison of their physical and spectral data with those of authentic samples.
b: Yields refer to isolated products.

Experimental

All chemicals used were reagent grade. The tetraphenylporphyrin was prepared and metallated according to the literature.[18,19] $Sn(IV)(tpp)(ClO_4)_2$, $Fe(tpp)ClO_4$ and $Mn(tpp)ClO_4$ prepared as described by Arnold[20] and Suda.[13]

General procedure for conversion of epoxides to thiiranes

In a round-bottomed flask (25 mL) equipped with a condenser and magnetic stirrer, a solution of epoxide (1 mmol) in CH_3CN (5 mL) was prepared. Thiourea

(0.152 g, 2 mmol) and Sn(IV)(tpp)(ClO_4)$_2$ (0.019 g, 0.02 mmol) were added to this solution and the reaction mixture was stirred magnetically under reflux conditions. After completion of the reaction (monitored by GLC), the mixture was directly passed through a short column of silica-gel (1:1 hexane-ethyl acetate) to remove the catalyst. The eluate was evaporated under reduced pressure and the crude product was obtained in a quantitative yield. Distillation of the product under reduced pressure resulted the corresponding thiirane in 92-95% yields without any polymerization by-products.

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