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Iron(III) 5,10,15,20-Tetrakis (pentafluorophenyl)porphyrin as an Efficient Catalyst for Conversion of Epoxides to Thiiranes[†]

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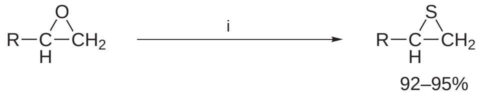
Iron(III) 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, Fe(TF$_5$PP)Cl, is a new catalyst for the conversion of epoxides to the corresponding thiiranes in the presence of ammonium thiocyanate in excellent yields.

Although metalloporphyrins are widely used as redox catalysts[1–6] there have been few studies on their catalytic activity as Lewis acids. The catalytic role of iron and manganese tetraphenylporphyrins as mild Lewis acids have been investigated in several reactions such as rearrangement of oxaziridines,[7,8] isomerization of epoxides[9] and silylation of hydroxyl groups.[10,11] Recently the use of ruthenium trichloride in the reaction of thiocyanate with epoxides was reported.[12] The catalytic activity is considered due to the high electrophilic nature of the central ruthenium ion. Here, we report that such catalytic activity can be observed with an iron porphyrin if an electron deficient porphyrin is used as the ligand.

As shown in Table 1, different aliphatic and cyclic epoxides react rapidly with ammonium thiocyante in the presence of 0.02 molar equivalents of iron(III) 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin chloride, Fe(TF$_5$PP)Cl, in refluxing acetonitrile affording the corresponding thiiranes (Scheme 1).



Scheme 1 *Reagents and conditions*: i, Fe(TF$_5$PP)Cl (0.02 mol equiv.), NH$_4$SCN, MeCN, reflux, 15–25 min.

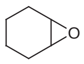
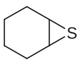
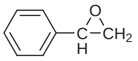
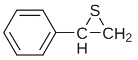
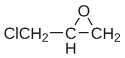
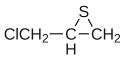
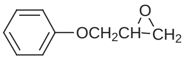
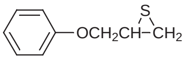
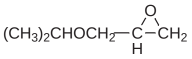
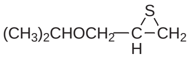
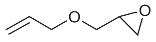
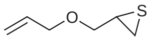
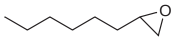
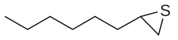
The reaction of styrene oxide with ammonium thiocyanate in the presence of Fe(TF$_5$PP)Cl under reflux was completed in 20 min giving styrene sulfide in 92% isolated yield, without polymerization. By contrast, iron(III) tetraphenylporphyrin chloride, Fe(TPP)Cl was not efficient for this reaction and only 7% yield was obtained under the same reaction conditions. Therefore, the electron-withdrawing character of the perfluorophenyl substituents of the ligand strongly raises the electrophilic nature of the central iron ion.

The effect of other solvents such as acetone, dichloromethane, chloroform and carbon tetrachloride was also studied. Compared to acetonitrile, longer reaction times and considerably lower yields were observed.

Control experiments carried out on the epoxides showed that, in the absence of the catalyst, no conversion of epoxides to thiirane compounds occurs over short reaction times.

Conversion of epoxides to thiiranes using thiourea as another sulfur-introducing reagent has also been reported under wet conditions (solvent free) or in aqueous ethanol in the absence of catalyst.[13] For example, the reaction of styrene oxide with wet thiourea has been reported to afford styrene episulfide in 45% yield after 10 h. The reaction of cyclic epoxides with thiourea in aqueous ethanol suffers from the drawback of long reaction times and low yields.[13]

Table 1 Conversion of epoxides to thiiranes with Fe(TF$_5$PP)Cl/NH$_4$SCN in refluxing MeCN

Entry	Substrate	Product	*t*/min	Yield(%)[a,b]
1			15	95
2			20	92
3			25	95
4			15	95
5			20	95
6			20	94
7			15	95

[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 of reagent grade. 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin was prepared and metallated according to the literature.[14,15]

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 MeCN (5 mL) was prepared. Ammonium thiocyanate (0.152 g, 2 mmol) and Fe(TF$_5$PP)Cl (0.021 g, 0.02 mmol) were added to the resulting solution and the reaction mixture stirred magnetically under reflux. 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 quantitative yield. Distillation of the product under reduced pressure resulted in the corresponding thiirane in 92–95% yield, without any polymerization by-products.

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[†] This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

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