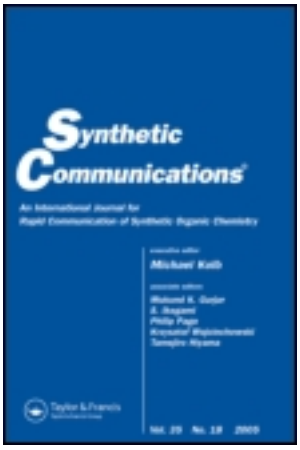

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Titanium Dioxide as a Mild and Efficient Catalyst for Conversion of Epoxides to Thiiranes

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ABSTRACT

Titanium dioxide (TiO_2) efficiently catalyze the reaction of a variety of epoxides with ammonium thiocyanate in refluxing acetonitrile to afford the corresponding thiirane in high to excellent yields.

Key Words: Titanium dioxide; Catalysis; Epoxide; Thiirane; Ammonium thiocyanate.

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INTRODUCTION

The most general procedure for the synthesis of thiiranes is the conversion of epoxides by an oxygen–sulfur exchange reaction. Sulfur introducing reagents, such as inorganic thiocyanates,[1–3] thiourea,[3,4] phosphine sulfide,[5] 3-methyl benzothiazole-2-thione,[6] dimethylthioformamide,[7] silica-gel supported KSCN,[8] and polymer supported thiocyanate,[9] have been used for this purpose. Very recently, conversion of epoxides to thiiranes in the presence of one electron transfer and the Lewis acid catalysts such as ceric ammonium nitrate,[10] ruthenium trichloride,[11] and metalloporphyrins,[12–14] have also been reported.

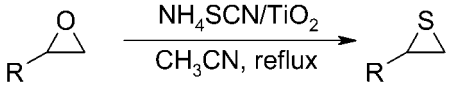
However, some of these methods suffer from disadvantages such as long reaction times, low yields of the products, formation of polymeric by-products, requirement for aqueous reaction conditions, and presence of sulfuric and trifluoroacetic acids.

There are a few methods that used from the Ti(IV) compounds in conversion of epoxides to thiiranes,[15] but these Ti(IV) compounds are expensive reagents. Therefore, we decided to use from titanium dioxide in this transformation. In our studies, we found that titanium dioxide can act as an efficient catalyst for conversion of various epoxides to thiiranes with ammonium thiocyanate in refluxing acetonitrile (Sch. 1).

The reaction of styrene oxide as a model substrate with ammonium thiocyanate in the presence of titanium dioxide was studied in refluxing acetonitrile for 30 min without polymerization (Table 1, entry 1). Different types of aliphatic as well as cyclic epoxides including those with electron-withdrawing substituents were also converted to their thiiranes performed in refluxing acetonitrile and in the presence of only 0.05 M eq. of TiO_2 (Table 1, entries 2–7).

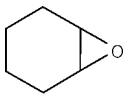
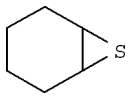
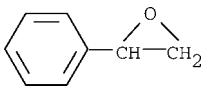
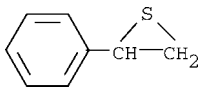
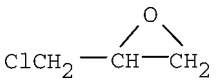
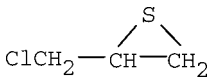
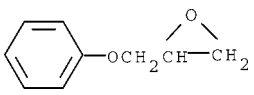
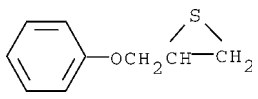
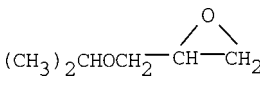
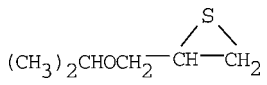
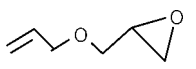
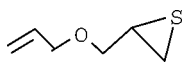
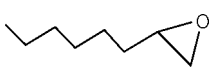
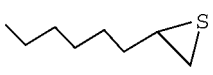
The effects of other solvents such as acetone, chloroform, dichloromethane, carbon tetrachloride, and *n*-hexane were also investigated. In comparison with acetonitrile, the reaction times were longer and the yields of thiiranes were considerably lower in all other solvents. Control experiments carried out on the epoxides showed that in the absence of the catalyst, no conversion of epoxides to thiiranes compounds takes place at short reaction times.

In conclusion, titanium dioxide (TiO_2) and ammonium thiocyanate can act as a mild and as efficient catalytic system for conversion of epoxides to



Scheme 1.

Table 1. Conversion of epoxides to thiiranes in the presence of TiO_2 at reflux.[a]

Entry	Substrate	Product	Yield (%);[b,c] t (min)	BP (°C)/Torr found (reported)
1			89; 30	53–55.5 (71.5–73.5/21)[16]
2			92; 30	84–86 (87–88/4)[8]
3			91; 60	54/28 (55/28)[17]
4			96; 40	104–106/7 (113/13)[7]
5			95; 40	54.5–56/11 (54/11)[18]
6			94; 30	76–78/8 (78–79/8)[7]
7			92; 30	83.5–85/5 (83/5)[19]

[a]The ratios of epoxide : ammonium thiocyanate : TiO_2 were 1 : 2 : 0.05, respectively, and all reactions were performed in CH_3CN as solvent.
[b]All products were identified by comparison of their physical and spectral data with those of authentic samples.
[c]Yields refer to isolated yields.

thiiranes. High yields, short reaction times, stability, and easy work-up make this method a suitable procedure for conversion of epoxides to thiiranes.

EXPERIMENTAL

All chemicals used were of reagent grade.

General Procedure for Conversion of Epoxides to Thiiranes

In a typical experiment, a solution of epoxide (1 mmol) in CH_3CN (5 mL) was prepared. Ammonium thiocyanate (0.152 g, 2 mmol) and TiO_2 (4 mg, 0.05 mmol) were added to this solution, and the reaction mixture was stirred magnetically under reflux conditions. After completion of the reaction (monitored by GC), the mixture was directly passed through a short column of silica gel [eluent: 1/1 (hexane/ethyl acetate)] to remove the catalyst. The eluent was evaporated under reduced pressure and the crude product was obtained in 89–96% yields without any polymerization by-products. Distillation of the product from one experiment with 5 mmol of styrene epoxide under reduced pressure resulted the corresponding thiirane in 92% yield.

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