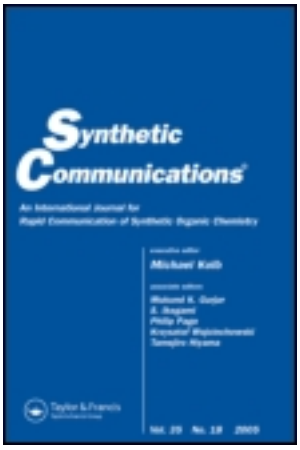

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Conversion of Oxiranes to Thiiranes Catalyzed with Silica Gel-Supported Aluminium Chloride

K. Parvanak Borujeni [a]
[a] College of Sciences, Shahrekord University, Shahrekord, Iran
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Conversion of Oxiranes to Thiiranes Catalyzed with Silica Gel–Supported Aluminium Chloride

K. Parvanak Borujeni
College of Sciences, Shahrekord University, Shahrekord, Iran

Abstract: Silica gel–supported aluminium chloride, SiO_2-$AlCl_3$, catalysizes the efficient conversion of different oxiranes to their corresponding thiiranes in the presence of thiourea under nonaqueous conditions.

Keywords: Aluminium chloride, oxirane, silica gel, thiirane

INTRODUCTION

Various procedures have been reported for the preparation of thiiranes,[1] and the most general one has been the conversion of oxiranes to thiiranes through their reactions with thiourea[2,3] or inorganic thiocyanates[4,5] in water or other aqueous solvents. Also, several different Lewis acids, such as Ce(IV) as ceric ammonium nitrate (CAN),[6] Ru(III) as ruthenium trichloride ($RuCl_3$),[7] $BiCl_3$,[8] $TiO(CF_3CO_2)_2$,[9] and $TiCl_3(CF_3SO_3)$,[9] have been used as catalysts for the conversion of epoxides to thiiranes. However, some of these methods suffer from drawbacks such as tedious workup, aqueous and/or alcoholic media, low yields, rapid increase of pH during the reaction, the presence of trifluroacetic acid, formation of the polymeric by-products, and in, some cases, expensive and unreusable catalysts. Thus, it seems that convenient and general methods for this purpose, especially by heterogeneous catalysts, are still in demand.

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Address correspondence to K. Parvanak Borujeni, College of Sciences, Shahrekord University, Shahrekord, Iran. Fax: 0098-381-4424419; E-mail: parvanak-ka@sci.sku.ac.ir

In continuation of our recent work on the use of heterogeneous catalysts,[10–13] we described the preparation and application of silica gel–supported aluminium chloride, (SiO_2-$AlCl_3$), as an efficient and chemoselective heterogeneous catalyst for dithioacetalization.[12] Along this line, in this article a simple and efficient method for conversion of oxiranes to their corresponding thiiranes is described by reaction with thiourea in the presence of a catalytic amount of SiO_2-$AlCl_3$ is described (Scheme 1).

RESULTS AND DISCUSSION

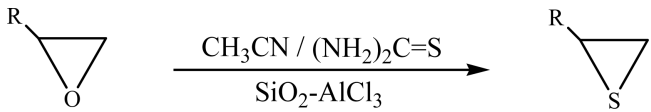
SiO_2-$AlCl_3$ was prepared by reacting silica gel with aluminium chloride in refluxing carbon tetrachloride. Using this solid acid catalyst, different kinds of epoxides were converted to their corresponding thiiranes with thiourea in acetonitrile (Table 1). The effects of other solvents such as acetone and *tert*-butanol were also studied, but in comparison with CH_3CN the reaction times were longer and the yields were found to be considerably lower. The reactions proceed in a clean manner and the conditions employed are both simple and convenient. The optimum molar ratio of catalyst to epoxide was found to be 0.2 : 1.

The present method has the following advantages: the reagents are readily available, the procedure is simple, the reaction times are short, it can be performed with a wide range of epoxides under mild conditions, and the yield of thiiranes is high. Most important, the workup is reduced to mere filtration and evaporation of the solvent. The performance of reactions in non-aqueous media can be ideal for substrates containing water-sensitive groups. The catalyst can be prepared easily with cheap starting materials and is reusable.

EXPERIMENTAL

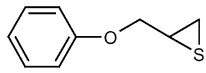
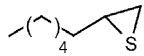
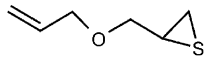
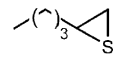
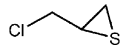
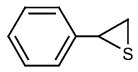
Material and Techniques

Starting materials were obtained from Fluka Company. Products were characterized by comparison of their physical and spectral data with those of known samples. Gas chromatography was recorded on Shimadzu GC 14-A. IR spectra were recorded on a Perkin-Elmer 781 spectrometer. ^1H and



Scheme 1.

Table 1. Conversion of oxiranes to thiiranes with thiourea catalyzed by SiO_2-$AlCl_3$[a]

Entry	Thiirane	Time (hr)	Yield (%)[b]	Bp (°C)/Torr	
				Found	Reported
1		1.5	95	103.5–104.5/7	103–104/7[14]
2		1.0	94	79–81/5	81–82/5[14]
3		1.8	93	78.5–80/8	78–79/8[14]
4		1.9	95	48–50/1	49–51/1[6]
5		2.0	92	59–60/30	60–62/30[8]
6		1.4	85	86–89/5	86/5[14]
7		1.1	91	71.5–70.5/70	72–73/70[6]
8		1.3	89	54–56.5/7	55–56/7[8]

[a]The molar ratio of epoxide/thiourea/cat. is 1 : 2 : 0.2.

[b]Yields refer to pure isolated products. All thiiranes are known compounds and were characterized by comparison of their physical and spectral data with those of the authentic samples.

^{13}C NMR spectra were recorded on a Bruker Advance DPX FT 250 MHz instrument.

Preparation of SiO_2-$AlCl_3$

This catalyst was prepared as reported in the literature.[13,15] The loading of aluminium chloride determined was 1.3 mmol/gr.[16]

Conversion of Epoxides to Thiiranes: General Procedure

SiO_2-$AlCl_3$ (0.2 mmol) was added to a mixture of epoxide (1 mmol) and thiourea (2 mmol) in acetonitrile (10 ml), and the reaction mixture was stirred magnetically at 45°C. Progress of the reaction was followed by TLC and GC. Upon completion of the reaction, the solvent was evaporated and

diethyl ether (2 × 20 ml) was added to the residue and filtered. The filtrate was washed with water (2 × 20 ml) and the organic layer dried with anhydrous Na_2SO_4 to obtain the pure products in 85–95% yields after evaporation of the solvent. The spent catalyst from different experiments was washed with diethyl ether and used again without further drying.

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