Heteroatom Chemistry
Volume 19, Number 1, 2008

$LiClO_4$ Catalyzed Mild and Efficient Method for the Synthesis of Thiiranes from Oxiranes

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Received 26 June 2006; revised 26 October 2006

ABSTRACT: *Oxiranes are efficiently converted to the corresponding thiiranes by potassium thiocyanate in the presence of catalytic amounts of $LiClO_4$ with excellent yields under mild and nonaqueous conditions.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:97–99, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20376

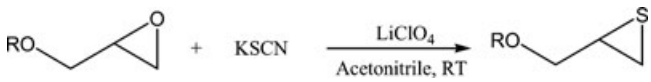
INTRODUCTION

Organic sulfur compounds have become increasingly useful and important in organic synthesis. Thiiranes are sulfur heterocycles and are used in the pharmaceutical, polymer, pesticide, and herbicide industries [1]. Particularly, thiiranes have played an important role in various synthetic transformations [2]. Epoxides are the most convenient starting materials for preparation of simple thiiranes because of their ease of formation, wide reactivity, and ability to undergo regioselective ring-opening reactions, contributing largely to their synthetic value [3]. A variety of methods have been reported to produce thiiranes from oxiranes [4]. Many of these procedures involve extended reaction times, use of expensive reagents, and high-temperature reaction conditions. Therefore, there is still a scope to find potential alternative procedures, especially low cost, low toxic, and operable under mild conditions that are in high demand. In this regard, $LiClO_4$ is used as a mild Lewis acid catalyst in various organic transformations and is shown to enhance reaction rates [5]. Organic solutions of lithium perchlorate provide a convenient reaction medium to perform the reactions under neutral conditions. Potassium thiocyanate is a transfer agent for sulfur, commonly used in the thiiranes synthesis from epoxides. Now, we have found that potassium thiocyanate reacts with oxiranes, in the presence of catalytic amount of lithium perchlorate in the nonaqueous solvent acetonitrile under mild conditions, to form the corresponding thiiranes in excellent yield. In this report, we describe the synthesis of thiiranes from oxiranes using lithium perchlorate.

RESULTS AND DISCUSSION

The reaction was carried out by adding lithium perchlorate to a mixture of styrene oxide and potassium thiocyanate in acetonitrile at room temperature. After the mixture was stirred at room temperature for 1-2 h, TLC showed the disappearance of starting materials. After work up, the crude product was subjected to column chromatography over silicagel and provided the product in 90% yield. By the spectroscopic data, the product was confirmed as **2a** and was compared with the literature data (Scheme 1).

Similarly, a wide range of epoxides reacted smoothly with KSCN under similar conditions, giving the products in good yield ranging from 80 to



SCHEME 1

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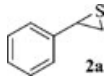
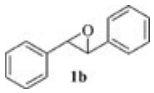
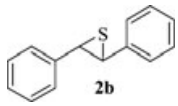
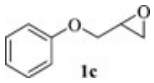
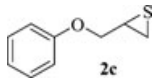
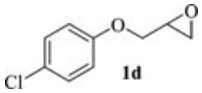
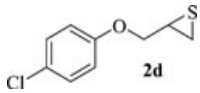
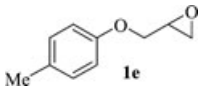
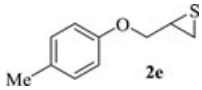
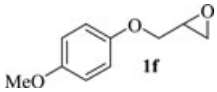
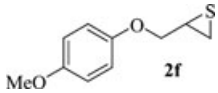
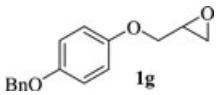
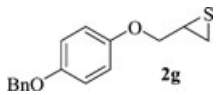
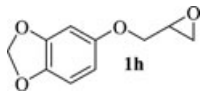
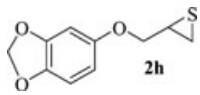
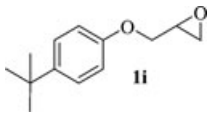
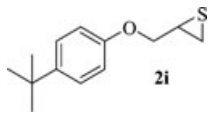
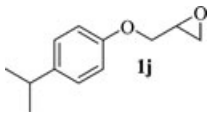
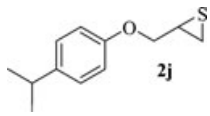
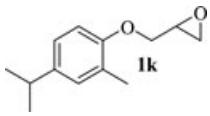
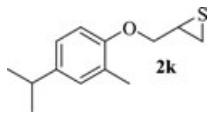
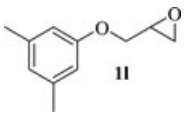
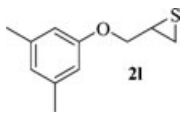
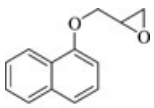
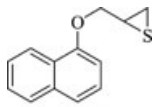
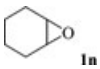
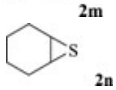
TABLE 1 $LiClO_4$-Catalyzed Conversion of Oxiranes to Thiiranes

Entry	*Epoxides*	*Products*[a]	*Time (h)*	*Yield (%)*[b]
1	 1a	 2a	1	90
2	 1b	 2b	1	85
3	 1c	 2c	0.5	95
4	 1d	 2d	0.5	90
5	 1e	 2e	0.75	85
6	 1f	 2f	0.75	78
7	 1g	 2g	1	75
8	 1h	 2h	1	72
9	 1i	 2i	0.5	80
10	 1j	 2j	1	83
11	 1k	 2k	0.75	80
12	 1l	 2l	0.5	92
13	 1m	 2m	0.75	85
14	 1n	 2n	1	82

[a]All the products were characterized by ^1H NMR and mass spectroscopy.
[b]Yieds are isolated after column chromatography.

95% (Table 1). As we observed, the electron-releasing groups on the aromatic ring facilitate the formation of thiiranes whereas electron-withdrawing groups do not.

CONCLUSION

In summary, we have described a simple and highly efficient protocol for the preparation of thiirane derivatives through the reaction between epoxides

and potassium thiocyanate using lithium perchlorate. The attractive features of this process are mild reaction conditions, inexpensive reagents, short reaction times, and cleaner reactions with improved yields, which make it a useful process for the synthesis of thiiranes.

EXPERIMENTAL

General Procedure

To a stirred solution of epoxide (1 mmol) and potassium thiocyanate (1 mmol) in acetonitrile (3 mL), lithium perchlorate (10 mol%) at room temperature was added. The reaction was stirred at the same temperature for an appropriate time (see Table 1). After completion of the reaction, as indicated by the TLC, the solvent was removed under reduced pressure and the reaction mixture was extracted with methylene chloride. The combined organic fractions were dried over Na_2SO_4 and concentrated. The resulting crude product was directly subjected to column chromatography on silicagel and was eluted with a mixture of (ethylacetate-hexane, 2:8) to afford **2a** in 90% yield.

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