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Boric acid catalysed mild and efficient method for the synthesis of thiiranes from oxiranes

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ABSTRACT

Oxiranes are efficiently converted to the corresponding thiiranes by potassium thiocyanate in the presence of catalytic amounts of $B(OH)_3$ with excellent yield under mild and non-aqueous conditions.

Key words : Boricacid, thiiranes, potassium thiocyanate, oxiranees.

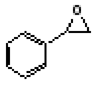
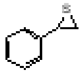
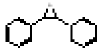
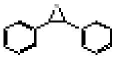
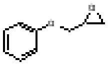
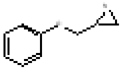
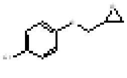
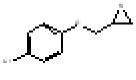
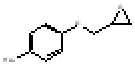
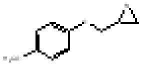
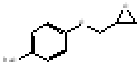
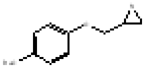
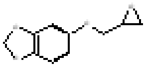
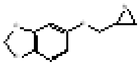
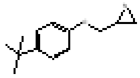
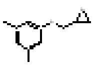
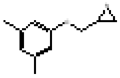
INTRODUCTION

Organic sulphur compounds have become increasingly and important in organic synthesis. Thiiranes are sulphur heterocycles and are used in the pharmaceuticals, polymer, pesticides 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 involves extended reaction times, uses 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 boricacid [$B(OH)_3$] is used as a mild Lewise acid catalyst in various organic transformations and is shown to enhance reaction rates[5] for the hydrolysis of phenylsalicylates[6], and both α- and β-hydroxy imines[7] as well as catalyzing the hydration of β-hydroxynitriles[8]. Organic solutions of boricacid provide a convenient reaction medium to perform the reactins under neutral conditions. Potassium thiocyanate s a transfer agent for sulphur commonly used in the thiiranes synthesisfrom epoxides. Now, We have found that potassium thiocyanate reacts with oxiranes in the presence of catalytic amount of boricacid in the no-aqueous solvent acetonitrile under mild conditions to perform the corresponding thiiranes in excellent yield. In this report, we have describe the synthesis of thiiranes from oxiranes using boricacid.

EXPERIMENTAL

To a stirred solution of epoxide (1 mmol) and potassium thiocyanate (1 mmol) in acetonitrile (3 mL), boric acid (10 mol %) at room temperature for an appropriate time (Table 1). After completion of the reaction as indicated by the TLC, the solvent was removed underreduced pressure and the reaction mixture was extracted with methylenechloride. The obtained organic fractions were dried over Na_2SO_4 and concentrated. The resulting crude product was directly subjected to column chromatography on silica gel and was eluted with a mixture of (ethylacetate:n-hexane 2:8)to afford 2a in 93 % yield.

Table 1: $B(OH)_3$ - Catalyzed Conversion of Oxiranes to Thiiranes

Entry	Epoxides	Time(h)	Product	Yield(%)[b]
1	 1a	1.0	 2a	90
2	 1b	1.0	 2b	87
3	 1c	0.5	 2c	95
4	 1d	0.5	 2d	93
5	 1e	0.70	 2e	88
6	 1f	0.70	 2f	83
7	 1g	1.0	 2g	80
8	 1h	1.0	 2h	76
9	 1i	0.5	 2i	85
10	 1j	1.0	 2j	85
11	 1k	0.70	 2k	83
12	 1l	0.5	 2l	93

[a]Products were characterized by their melting points and IR, NMR spectral analysis [b]yields refer to isolated pure products

RESULTS AND DISCUSSION

The reaction was carried by adding boric acid 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 silica gel and provided product was conformed as 2a and was compared with the literature data (Scheme 1).

Scheme 1

Similarly, a wide range of epoxides reacted smoothly with KCN under similar conditions, giving the products in good yield ranging from 80 to 95% (Table1). As we observed, the electron - releasing groups on the aromatic ring facilitate the formation of thiiranes whereas electron-withdrawing groups do not.

CONCLUSION

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

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