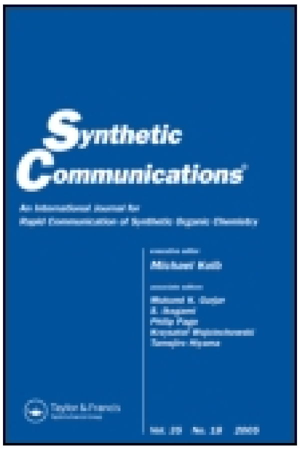

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Synthesis of Thiiranes from Oxiranes Using Cross-Linked Polystyrene Supported Aluminium Chloride as a Catalyst

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ABSTRACT

A simple and efficient method for conversion of oxiranes to their corresponding thiiranes using thiourea catalyzed with cross-linked polystyrene supported aluminium chloride, (Ps-$AlCl_3$), under non-aqueous condition is described.

Key Words: Oxiranes; Thiirane; Aluminium chloride; Cross-linked polystyrene.

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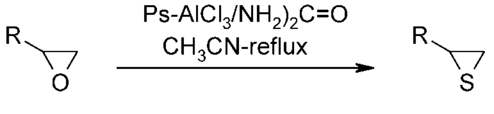
INTRODUCTION

The generation of hybrid catalysts which combine the attributes of homogeneous catalysts with the experimental ease of heterogeneous catalysts has lured many workers into this area of research.[1,2] Among such heterogeneous catalysts, a large number of polymer supported polymeric Lewis acids have been prepared by immobilization of the catalysts on polymers via coordination or covalent bonds.[3] Such polymer catalysts are as active and selective as their homogeneous counterparts while having the distinguishing characteristics of being easily separable from reaction media, recyclability and selectivity in various organic reactions. The most frequently used polymeric support is polystyrene; its hydrophobic nature protects the water-sensitive Lewis acids from hydrolysis by atmospheric moisture until it is placed in an appropriate solvents where it can be used in a reaction medium.[4–10]

There are many methods reported in the literature for preparation of thiirans,[11,12] and the most general one has been the conversion of oxiranes to thiiranes. For this purpose several sulfured agents such as thiourea,[13,14] inorganic thiocyanats,[15] phosphin sulfides,[16,17] silica gel-supported KSCN,[18] dimethylthioformamide,[19] and low hydrate KSCN-liquid heterogeneous mediums,[20] have been used. Also, several different Lewis acids such as, Ce(IV) as ceric ammonium nitrate (CAN),[21] Ru(III) as ruthenium trichloride($RuCl_3$),[22] $BiCl_3$,[23] $TiO(CF_3CO2)_2$,[24] and $TiCl_3(CF_3SO_3)$,[24] have been used as catalysts for the conversion of epoxides to thiiranes. However, some of these methods suffer from drawbacks such as, aqueous and/or alcoholic medium has to be used, low yield, rapid increase of pH during the reaction, reaction to be carried out in the presence of trifluroacetic acid, difficulty in separation of the product from the original reactant and catalysts, and formation of the polymeric by-products, and in some cases, use of expensive and unreuseable catalysts. Thus, it seems that convenient and general methods for this purpose especially by heterogeneous catalysts are still being demanded.

Recently we reported,[25,26] polymer-supported thiocyanate as a reagent and poly(vinylpyridine)-$Ce(OTF)_4$ as a catalyst for synthesis of thiiranes from oxiranes. Both these polymeric systems could overcome many drawbacks in the synthesis of thiiranes. As part of our general program to investigate the reactions of the polymer supported reagents and catalysts, herein we report



Scheme 1.

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that polystyrene supported aluminium chloride can act as an efficient polymeric catalyst for the conversion of various epoxides to thiranes using thiourea under mild non-aqueous condition (Sch. 1).

RESULT AND DISCUSSION

Ps-$AlCl_3$ was prepared by addition of anhydrous $AlCl_3$ to polystyrene [8% Divinylbenzene] in carbon disulfide under reflux condition.[4] Using this polymeric catalyst, different kinds of epoxides were converted to their corresponding thiiranes with thiourea as sulfurating agent (Table 1). Reactions were carried out in refluxing acetonitrile which proved to be the solvent of choice among other organic solvents. The reactions proceed in clean manner and the conditions employed are both simple and convenient. The optimum molar ratio of the polymeric catalyst to epoxide was found to be 0.3 : 1.

In conclusion, we believe that Ps-$AlCl_3$ is an effective and convenient catalyst for conversion of epoxides to thiranes with high yields, mild reaction condition, and easy work-up procedure. 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.

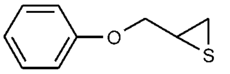
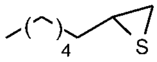
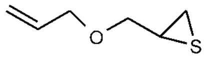
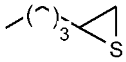
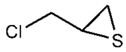
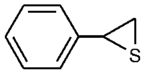
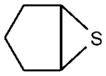
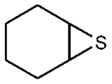
EXPERIMENTAL

Starting materials were obtained from Fluka Company. Polystyrene (8% divinylbenzene) was obtained from Iran Polymer Institute. Products were characterized by comparison of their physical data with those of known samples. Gas chromatography was recorded on Shimadzu GC. 14-A. IR spectra recorded on Perkin–Elmer 781 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker Advance DPX FT 250 MHz instrument.

Preparation of Ps-$AlCl_3$

This catalyst was prepared using crosslinked polystyrene [8% Divinylbenzene] as reported in the literature.[4] The chloride content of Ps-$AlCl_3$ was 5.28%.[29]

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

				B.p(°C)/torr	
Entry	Thiirane[b]	Time (hr)	Yield (%)[c]	Found	Reported
1		2.1	98	104.5–105.5/7	103–104/7[19]
2		1.6	93	80.5–81.5/5	83/5[27]
3		2.7	93	77.5–78.7/8	78–79/8[19]
4		2	95	48.7–51.5/1	43/0.16[28]
5		2.5	90	59.7–60.5/30	55/28[28]
6		1.5	85	85.5–86.7/5	85–86/5[21]
7		1.2	92	71.5–72/70	72–73/70[21]
8		1.3	85	54.5–56.5/7	55–56/7[23]

[a] The molar ratio of epoxide/thiourea/Cat. is: 1 : 2 : 0.3.

[b] All products were identified by comparison of their IR, ^1H and ^{13}C NMR spectra with those of the authentic samples.[19]

[c] Isolated yield.

Conversion of Epoxides to Thiiranes: General Procedure

In a round-bottomed flask (25 mL) equipped with a condenser and a magnetic stirrer a solution of epoxide (1 mmol) in acetonitrile (10 mL) was prepared. Thiourea (2 mmol) and Ps-$AlCl_3$ (0.3 mmol) were added to the solution and the reaction mixture was stirred magnetically under reflux condition. Progress of the reaction was followed by TLC and GC. On completion of the reaction, solvent was evaporated and ether (2 × 20 mL) was added to the residue and filtered. The filtrate was washed with water (2 × 20 mL). The organic layer was passed through a short pad of silica gel and dried with anhydrous Na_2SO_4 to obtain the pure products in 85–98%

yields after evaporation of solvent. The spent polymeric catalyst from different experiments was washed with water, then with ether and dried overnight in vacuum oven and reused.

ACKNOWLEDGMENT

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