

An efficient synthesis of thiiranes from oxiranes using fluoroboric acid adsorbed on silica gel ($\text{HBF}_4\text{-SiO}_2$) as a catalyst under mild conditions in the absence of solvent

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Received 4 December 2006; received in revised form 26 February 2007; accepted 27 February 2007
Available online 3 March 2007

Abstract

A mild, simple and efficient method for the synthesis of thiiranes from epoxides using catalytic amount of $\text{HBF}_4\text{-SiO}_2$ under solvent-free conditions has been developed. Experimental simplicity, simple work-up procedure and solvent-free reaction condition are important features of the present protocol.

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Keywords: Oxiranes; Thiiranes; $\text{HBF}_4\text{-SiO}_2$; Heterogeneous catalyst; Solvent-free

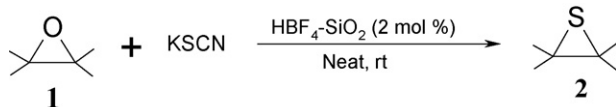
Synthetic chemists continue to explore new methods to carry out chemical transformations. One of these new methods is to run reactions on the surface of solids. Surfaces have properties that are not duplicated in the solution or gas phase, hence entirely new chemistry may occur. Even in the absence of new chemistry, a surface reaction may be more desirable than a solution counterpart, because the reaction is more convenient to run or a higher yield of the product is attained. For these reasons, surface synthetic organic chemistry is a rapidly growing field of study.

Thiiranes, the simplest sulfur heterocycles occurring in nature, are useful from both theoretical and synthetic point of view. They have been used advantageously in the pharmaceuticals, polymer and herbicide industries [1]. Since organic sulfur compounds have become increasingly useful and important in organic synthesis, the development of convenient and practical method for the preparation of thiiranes is desirable. Various methods have been developed for their synthesis. The most common and important method is the transformation of oxiranes into thiiranes with thiourea, thioamides, phosphine sulfide or dimethylthioformamide in the presence of trifluoroacetic acid or using inorganic thiocyanates, polymer-supported thiocyanates,

silica supported KSCN or other related compounds [2]. Usually, CAN [3] and Lewis acids such as, RuCl_3 [4], InBr_3 [5], BiCl_3 [6], $\text{TiO}(\text{CF}_3\text{SO}_3)$ [7], $\text{TiCl}_3(\text{CF}_3\text{SO}_3)$ [8] have been used as catalysts. Polymer-supported Lewis acid catalyst such as poly(4-vinylpyridine)- $\text{Ce}(\text{OTf})_4$ [9], AlCl_3 [10] as well as polymeric co-solvent [11] have been used for this important transformation. More recently, the $[\text{bmim}]\text{PF}_6\text{-H}_2\text{O}$ solvent system [12] and MW [13] irradiation has been used for the conversion of oxiranes to thiiranes. However, long reaction times, high temperature, low yields of the products, use of organic solvents, the use of highly acidic catalyst, difficulties in the separation of the product from the original reactant and catalyst, formation of polymeric byproducts, high catalytic loading and in most of the cases, the use of expensive [14] and unrecoverable catalyst are limitations.

The toxic and volatile nature of many organic solvents, particularly chlorinated hydrocarbons that are widely used in organic synthesis have posed a serious threat to the environment. Consequently, methods that successfully minimize their use are the focus of much attention. In recent years, the use of catalysts immobilized on solid supports has received considerable attention. Such catalysts not only simplify purification process but also help in preventing release of reaction residues into the environment. Thus the solvent less conditions along with supported catalyst provides a protocol for

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achieving environmentally friendly economical organic synthesis. Therefore, in this communication we report HBF₄-SiO₂ [15] catalyzed efficient and convenient synthesis of thiiranes from various oxiranes with potassium thiocyanate in high yields under solvent-free conditions at room temperature (Scheme 1).

Initially, a systematic study was carried out for evaluation for HBF₄-SiO₂ as a catalyst for the reaction of styrene oxide with potassium thiocyanate under various conditions (Table 1). The reaction was very slow in the absence of the catalyst (Table 1, entry 1) and low yields were obtained in presence of only silica as a catalyst (Table 1, entries 2–3). Further, no improvement of the yield was observed in presence of only HBF₄ as a catalyst (Table 1, entries 4–5). Next, we optimized the quantity of the catalyst (HBF₄-SiO₂) at room temperature under solvent-free conditions (Table 1, entries 6–11) and it was observed that the use of just 2 mol% is sufficient to produce an excellent yield of the product (Table 1, entry 9) whereas more than 2 mol% of the catalyst did not improve the results (Table 1, entries 10–11). However, inferior results were obtained in presence of solvents (Table 1, entries 12–15).

A variety of epoxides reacted smoothly with potassium thiocyanate in presence of 2 mol% of HBF₄-SiO₂ at room temperature under solvent-free conditions to furnish the corresponding thiiranes in high yields. The reactions were rapid and in most cases thiirane formation was complete in 10–20 min in excellent yields. The results shown in Table 2 clearly indicate the scope and generality of this protocol as a variety of aliphatic, aromatic and allylic epoxides, including those with electron-withdrawing and electron-donating substituents, underwent smooth conversion into the corresponding thiiranes. The present procedure was efficient for the synthesis of thiiranes from styrene oxide (Table 2, entry a), cyclohexene oxide

(Table 2, entry o), and stilbene oxide (Table 2, entry f) which are otherwise difficult to prepare [16]. Comparison of the results obtained using HBF₄-SiO₂ with recently reported methods indicate the superiority of the present protocol in terms of yield, catalyst loading (2 mol%) and reaction time (Table 3).

It is also important to mention that HBF₄-SiO₂ is a better catalyst than recently reported 2,4,6-trichloro 1,3,5-triazine (cyanuric chloride) [17] because HBF₄-SiO₂ can be recovered and reused at least four times without any appreciable loss of activity whereas 2,4,6-trichloro 1,3,5-triazine was not recovered and reused. The catalyst cyanuric chloride is hazardous as compared to safer HBF₄-SiO₂. In conclusion, we firmly believe that the present methodology compared to most of the reported methods offers a simple and efficient route for the conversion of epoxides to thiiranes with least loading (2 mol%) of the catalyst. In summery, simple work up, inexpensive and easily available catalyst, fast reaction rates, mild reaction conditions, high yields and the relatively clean reactions with no polymeric byproduct make this method an attractive and alternative contribution to the existing methodologies.

1. Experimental Section

The ¹H NMR spectra were recorded in CDCl₃ on 200 MHz using TMS as an internal standard. IR spectra were recorded on Bomem MB 104 IR spectrometer. Column chromatography was performed using Silica gel (100–200 mesh). Chemical shifts are given in ppm with respect to internal TMS, and *J* values are quoted in Hz. Mass spectra were recorded at 70 eV.

1.1. A general experimental procedure for the synthesis of thiirane from oxirane

A mixture of epoxide (1 mmol), potassium thiocyanate (194 mg, 2 mmol) and HBF₄-SiO₂ (40 mg, 2 mol %) was stirred at room temperature for the specified time (Table 1). After completion of the reaction (TLC), diethyl ether (3 × 10 ml) was added in the reaction mixture and the solid catalyst was filtered off. Organic solvent was evaporated to afford almost pure product or if necessary the product was purified by column chromatography (Silica gel: 60–120 mesh, petroleum ether (40–60 °C): ethyl acetate = 9:1). The combined organic layer were dried over anhydrous Na₂SO₄, concentrated *in Vacuo*, and if required, purified by column chromatography (silica gel Merck; 60–120 mesh, petroleum ether: ethyl acetate 9:1) to afford pure product.

1.2. Spectral data of the compounds

(2c): Colour less liquid; IR (neat): 3028, 2940, 1640, 1580, 1240 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ 2.16 (s, 3H), 2.63 (dd, 1H, *J* = 3.6 and 6.2 Hz), 2.86 (dd, 1H, *J* = 3.6 and 4.6 Hz), 3.96 (dd, 1H, *J* = 4.6 and 6.2 Hz), 6.60 (m, 2H); EIMS: *m/z* 140 (M⁺); Anal. Calcd for C₈H₈S: C, 59.96; H, 5.74; S, 22.86. Found: C, 59.80; H, 5.80; S, 22.70.

(2e): Colour less liquid; IR (neat): 3030, 2870, 1640, 1530, 1260, 1140 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ 2.64 (dd, 1H,

Table 1
Reaction of styrene oxide with potassium thiocyanate under various conditions

Entry	Solvent	Catalyst (mol%)	Time min [h]	Yield (%)
1	neat	–	[20]	10
2	neat	silica [50 mg]	[10]	28
3	neat	silica [100 mg]	[10]	45
4	neat	HBF ₄ [1 equi.]	50	55
5	neat	HBF ₄ [2 equi.]	40	65
6	neat	HBF ₄ -SiO ₂ (0.5)	10	65
7	neat	HBF ₄ -SiO ₂ (1.0)	25	80
8	neat	HBF ₄ -SiO ₂ (1.5)	15	88
9	neat	HBF ₄ -SiO ₂ (2)	10	98
10	neat	HBF ₄ -SiO ₂ (2.5)	10	97
11	neat	HBF ₄ -SiO ₂ (3.3)	10	97
12	CH ₂ Cl ₂	HBF ₄ -SiO ₂ (2)	50	60
13	THF	HBF ₄ -SiO ₂ (2)	55	65
14	CH ₃ CN	HBF ₄ -SiO ₂ (2)	45	55
15	CHCl ₃	HBF ₄ -SiO ₂ (2)	40	60

Table 2
 HBF₄-SiO₂ catalyzed conversion of epoxides to thiiranes at room temperature

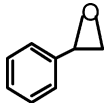
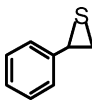
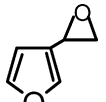
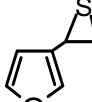
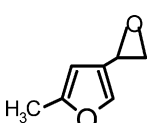
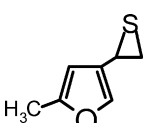
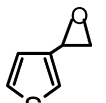
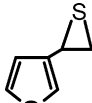
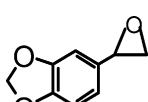
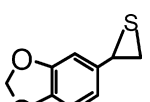
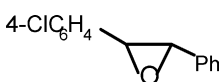
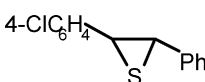
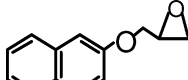
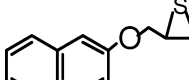
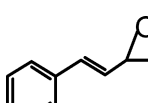
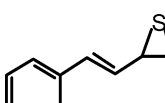
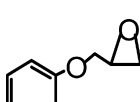
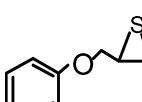





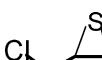
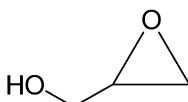
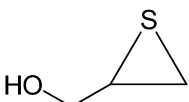
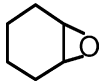
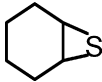
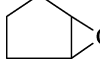

Entry	Substrate	Product	Time (min.)	Yield (%)
a			10	98
b			10	94
c			10	92
d			10	92
e			10	90
f			15	92
g			20	87
h			20	88
I			20	90
j			15	87
k			15	84
l			15	85
m			15	80
n			20	88
o			20	86

Table 3

Preparation of thirane from styrene oxide: a comparative study of reported catalysts with $\text{HBF}_4\text{-SiO}_2$

Entry	Catalyst ^{ref}	Loading (mol %)	Reaction time	Yield (%)
1	Silica gel ^{2f}	–	20–120 h	55–90
2	Dimethylthio foramide ^{2b}	100	3 h	64–95
3	InBr_3 ⁵	5	3–5 h	83–92
4	BiCl_3 ⁶	10	10–35 min.	96–99
5	Poly(4-vinyl pyridine)- $\text{Ce}(\text{OTf})_8$ ⁸	5–10	15–40 min.	85–92
6	Polymeric cosolvent ¹⁰	50 mg	0.5–2 h	80–90
7	$[\text{Bmim}]\text{PF}_6$ ¹¹	100	3–5 h	95–100
8	TiO_2 ^{14a}	5	30–60 min.	89–96
9	Phosphoro- dithioate ^{14b}	100	0.5–3 h	75–93
10	Diethyl phosphite ^{14c}	100	0.5–180 min.	42–83
11	Cyanuric chloride ¹⁷	2	5–20 min.	90–98
12.	$\text{HBF}_4\text{-SiO}_2$	2	10–20 min.	80–98

$J = 4.0$ and 6.0 Hz), 2.78 (dd, 1 H, $J = 4.0$ and 5.6 Hz), 4.05 (dd, 1 H, $J = 5.6$ and 6.0 Hz), 5.9 (s, 2H), 7.3 (m, 3H); EIMS: m/z 180 (M^+); Anal. Calcd for $\text{C}_9\text{H}_8\text{SO}_2$: C, 59.98; H, 4.47; S, 17.78. Found: C, 59.70; H, 4.65; S, 17.58.

(2f): Oil; bp. 75°C , $^1\text{H NMR}$ (200 MHz, CDCl_3) δ : 7.63 (d, 2H, $J = 8.2$ Hz), 7.50 (d, 2 H, $J = 8.2$ Hz), 7.20 (m, 5H), 2.60 (d, 1 H, $J = 6.8$ Hz), 2.35 (d, 1H, $J = 6.8$ Hz); IR (neat) 2920, 1805, 1715, 1450, 1305, 1260, 710 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{ClS}$ (246.5): C, 65.72; H, 4.46; Cl, 14.40; S, 12.98%. Found: C, 65.85; H, 4.55; Cl, 14.28; S, 12.88 %. EIMS: m/z 246.5 [M^+].

(2i): Colour less liquid; IR (neat): 3030, 2940, 1630, 1560, 1260 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 200 MHz): δ 2.33 (dd, 1 H, $J = 4.3$ and 6.4 Hz), 2.61 (dd, 1 H, $J = 4.3$ and 5.0 Hz), 3.28 (m, 1 H), 4.2 (d, 2H, $J = 6$ Hz), 7.25–7.48 (m, 5 H); EIMS: m/z 166 (M^+); Anal. Calcd for $\text{C}_9\text{H}_{10}\text{OS}$: C, 65.02; H, 6.06; S, 19.28. Found: C, 65.35; H, 6.18; S, 19.10.

(2k): Colour less liquid; IR (neat): 2900, 1425, 1230 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 200 MHz): δ 1.1 (t, 3H, $J = 6$ Hz), 1.73 (m, 2H), 2.2 (dd, 1H, $J = 4.0$ and 6.0 Hz), 2.55 (dd, 1H, $J = 4.0$ and 5.0 Hz), 2.9 (m, 1 H); EIMS: m/z 88 (M^+); Anal. Calcd for $\text{C}_4\text{H}_8\text{S}$: C, 54.49; H, 9.14; S, 36.36. Found: C, 54.70; H, 9.20; S, 36.20.

(2n): Colour less liquid; IR (KBr): 2940, 1450, 1230 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 200 MHz): δ 1.10–1.46 (m, 4 H), 1.60–1.80 (m, 2H), 2.0–2.20 (m, 2H), 2.91 (m, 2H); EIMS: m/z 114 (M^+); Anal. Calcd for $\text{C}_6\text{H}_{10}\text{S}$: C, 63.10; H, 8.82; S, 28.07. Found: C, 63.25; H, 8.60; S, 28.20.

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