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Article

$B(HSO_4)_3$: a Novel and Efficient Solid Acid Catalyst for the Regioselective Conversion of Epoxides to Thiocyanohydrins under Solvent-Free Conditions

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$B(HSO_4)_3$ foi facilmente preparado e usado como um novo e eficiente catalisador ácido sólido, para conversão de epóxidos às correspondentes tiocianohidrinas sob condições livre de solvente, com altos rendimentos. As principais características desta metodologia são o baixo custo do processo, a facilidade de obtenção do catalisador, a versatilidade e alta regiosseletividade do procedimento.

$B(HSO_4)_3$ was easily prepared and used as a novel and efficient solid acid catalyst for conversion of epoxides to the corresponding thiocyanohydrins under solvent-free conditions with high isolated yields. The salient features of this methodology are cheaper process, easy availability of the catalyst, versatility, and high regioselectivity of the procedure.

Keywords: boron sulfonic acid, solid acid, thiocyanohydrin, solvent-free, ring opening of epoxide

Introduction

The importance of minimizing the impact that chemical processing produces on the environment is growing, with an increased appreciation of the need to reduce pollution and depletion of our finite environmental resources. Optimal use of material and energy, and an efficient waste management can be recognized as important factors for environmental protection. To realize this goal, in recent years, significant articles have appeared reporting efficient solvent-free reactions by grinding.[1] This technique has many advantages such as reduced pollution, low cost, process simplicity and easier workup. In addition, from the green and environmental acceptability, recently more attention has been paid to the application of inorganic acidic salts in organic synthesis.[2] Solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal in different chemical processes. Also, wastes and by-products can be minimized or avoided by using solid acids in developing cleaner synthesis routes.

Thiocyanates are important intermediates in agricultural and pharmaceutical chemistry. Synthetic access by epoxide ring opening with thiocyanate anion has been limited by a further reaction to give thiirane.[3] The formation of thiirane from the reaction of epoxide and thiocyanate ion has been explained to occur through the intermediacy of the corresponding β-hydroxy thiocyanate, but this intermediate has not been isolated due to its rapid conversion to the corresponding thiirane.[4] Thus, few methods are reported for the preparation of β-hydroxy thiocyanates,[5-11] but some of these methods are limited to specific epoxides and are not applicable as versatile reagents in the preparation of β-hydroxy thiocyanates and suffer from disadvantages such as long reaction times, low regioselectivity, using of organic solvents, using of expensive catalysts or involve high temperature reaction conditions. Therefore, it seems that there is still a need for development of novel methods that proceed under mild and eco-friendly conditions.

In continuation of our studies on the synthesis of β-hydroxy thiocyanate,[12,13] we describe our successful results that led to an extremely convenient method for the transformation of epoxides into the corresponding β-hydroxy thiocyanates using NH_4SCN and in the presence of $B(HSO_4)_3$ as solid acid catalyst in solvent-free process in high isolated yields.

Results and Discussion

Boron sulfonic acid was easily prepared by addition of chlorosulfonic acid to boric acid under N_2 atmosphere at room temperature. This reaction was easy and clean,

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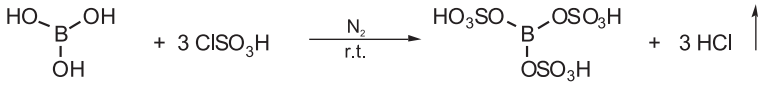
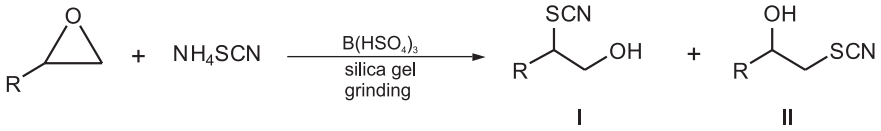


Scheme 1.



Scheme 2.

because HCl gas was evolved from the reaction vessel immediately (Scheme 1).

We examined the catalytic ability of $B(HSO_4)_3$ for conversion of epoxides to corresponding thiocyanohydrins. Therefore, phenyl glycidyl ether (1 mmol) was reacted with ammonium thiocyanate (1.5 mmol) in the presence of $B(HSO_4)_3$ in different solvents and under solvent-free condition. The results in Table 1 were clearly shown that although water was the best solvent among those tested, the best result was obtained under solvent-free conditions. TLC analysis was showed that under solvent free conditions, conversion was completed after 4 minutes and 3-phenoxy-2-hydroxypropyl thiocyanate was produced in 92% isolated yield. According to obtained results, this catalyst acted very efficiently and only 0.3 mmol of the catalyst is enough to convert different epoxides (1 mmol) carrying electron donating or withdrawing groups to their corresponding β-hydroxy thiocyanates in high isolated yields (Scheme 2).

It is noteworthy that no evidence for the formation of thiiranes as by-product of the reactions was observed. It seems that $B(HSO_4)_3$ can be facilitated the ring opening of the epoxides by hydrogen bonding. In addition it, probably stabilize the produced thiocyanohydrins and inhibit their conversion to thiiranes.

As shown in Table 1, in the absence of catalyst, thiirane was produced as only product. Also, in the presence of boric acid as catalyst, reaction time was increased and the mixture of thiocyanohydrin and thiirane were produced.

To ascertain the scope and limitation of the present reaction, several epoxides were examined; these results are summarized in Table 2. Except for the reactions of styrene oxide (entry 1) and 1,2-epoxybutane (entry 7) which produced a small percentage of the other regioisomer, the reactions of the epoxides were found to be highly regioselective and only one isomer was obtained. Also in the case of cyclic epoxides (Table 2, entries 9, 10), *trans* products were obtained. Obviously, the regioselectivity of the ring opening of epoxides is thoroughly dependent on the mechanism of the reaction and particularly on steric and electronic factors. As shown in Table 2, for epoxides carrying electron withdrawing groups, it is the steric factor which predominates and the nucleophilic attack of thiocyanate anion is strongly favored on the primary carbon atom of epoxides. In contrary, for epoxides carrying electron donating groups, the electronic factor predominates and the nucleophilic attack of thiocyanate anion is strongly favored on the secondary carbon atom of epoxides.

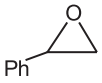
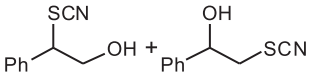
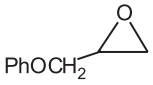
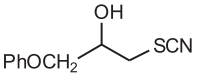
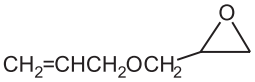
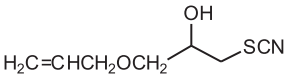
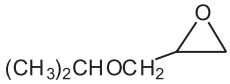
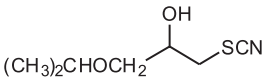
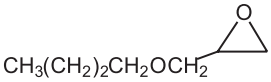
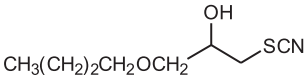
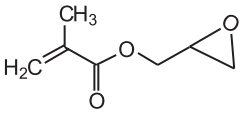
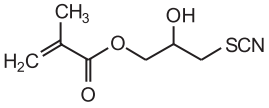
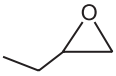
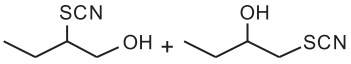
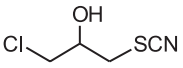
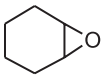
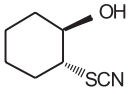
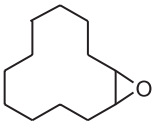
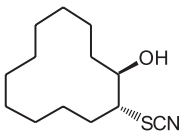
By comparison, numbers of methods for the conversion of epoxides to the corresponding thiocyanohydrins are

Table 1. Consideration of different conditions for thiocyanation of phenyl glycidyl ether

No.	Solvent	NH_4SCN/mmol	$B(HSO_4)_3$/mmol	Condition	time/min	Conversion/(%)	Yields/(%)	
							thiocyanohydrin	thiirane
1	Et_2O	3	0.5	r.t.	240	50	45	-
2	CH_2Cl_2	3	0.5	r.t.	240	60	35	20
3	CH_3CN	3	0.5	r.t.	240	50	45	-
4	H_2O	3	0.5	r.t.	180	100	75	-
5	H_2O	3	0.5	reflux	60	100	50 (30)[a]	-
6	-	1.5	0.3	grinding	4	100	92	-
7	-	1.5	-	grinding	10	100	-	80

[a]Yield in parenthesis refers to produced diol.

Table 2. Conversion of epoxides to thiocyanohydrins by using $B(HSO_4)_3$ under solvent-free conditions

Entry	Substrate	Product(s)[a]	time / min	Yields / (%)
1			4	84:7[b]
2			4	92
3			3	90
4			3	85
5			4	88
6			3	94
7			3	78:5[b]
8			4	85
9			3	89
10			10	45[b]

[a]Products were identified by compared of their physical and spectral data with those of authentic samples. [b]According to GC analysis.

given in Table 3. As shown in Table 3, our procedure has higher regioselectivity and shorter reaction time than other methods.

Conclusions

We describe a novel and efficient method for the synthesis of β-hydroxy thiocyanates by the regioselective ring opening of epoxides with ammonium thiocyanate in the presence of $B(HSO_4)_3$ as a novel catalyst. This method offers several advantages including mild reaction conditions, high conversions, greater regioselectivity, short reaction times, clean reaction profiles, ease of handling and ready availability of the catalyst, which makes it a useful and attractive process for the synthesis of β-hydroxy thiocyanates.

Table 3. Comparison of thiocyanation of styrene oxide with different methods

Entry	Reagents and reaction conditions	Reaction time / min	α attack[a]	β attack[b]	Yield / (%)
1	$B(HSO_4)_3$ / NH_4SCN / solvent-free[c]	4	92	8	91
2	DDQ / NH_4SCN / CH_3CN / reflux[5]	50	89	11	91
3	$Ti(OPr^i)_4$ / NH_4SCN / THF / reflux[7]	240	-	-	30
4	PTC / NH_4SCN / CH_3CN / r.t.[9]	90	90	10	90
5	T(4-OH P)P / NH_4SCN / CH_3CN / reflux[10]	20	-	-	96
6	BABMB / NH_4SCN / CH_3CN / reflux[11]	10	20	80	91
7	$Co^{II}T(p\text{-OHP})P$ / NH_4SCN / N_2 / CH_3CN / reflux[14]	25	17	83	96
8	$[PTPPCl_2]Cl$ / NH_4SCN / N_2 / CH_3CN / reflux[15]	22	20	80	96
9	Selectfluor / NH_4SCN / CH_3CN / r.t.[16]	150	17	83	95
10	$Pd(PPh_3)_4$ / NH_4SCN / N_2 / THF / reflux[12]	120	thiirane		35
11	BABMB / KSCN / CH_3CN / reflux[11]	120	"		10
12	$ZnCl_2$ / KSCN / THF / reflux[17]	180	"		60

[a]Attack of nucleophile on the more substituted carbon of epoxide. [b]Attack of nucleophile on the less substituted carbon of epoxide. [c]Present method.

Experimental

General

Epoxides and other chemicals were purchased from Fluka and Merck in high purity. All of the thiocyanohydrin compounds were prepared by our procedure, and their spectroscopic and physical data were compared with those of authentic samples. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Advanced DPX 400 MHz spectrometer using TMS as internal standard. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates.

Preparation of boron sulfonic acid

A 50 mL suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution (water) and an alkali trap. Boric acid (1.55 g, 25 mmol) was charged in the flask and chlorosulfonic acid (8.74 g, *ca.* 5 mL, 75 mmol) was added dropwise over a period of 1 h at room temperature. HCl evolved immediately. After completion of the addition, the mixture was shaken for 1 h, while the residual HCl was eliminated by suction. Then the mixture was washed with diethyl ether to remove the unreacted chlorosulfonic acid. Finally, a grayish solid material was obtained in 93% yield (7.0 g).

General procedure for the preparation of β-hydroxy thiocyanates

In a mortar, a mixture of epoxide (1 mmol), NH_4SCN (1.5 mmol), $B(HSO_4)_3$ (0.3 mmol) and silica gel (0.5 g) was pulverized for the time specified in the Table 2. The reaction progress was followed by TLC. After completion of the reaction, ethyl acetate was added and the heterogeneous mixture was filtered. Then, the filtrate washed with water (2×10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. After evaporation of solvent under reduced pressure, the desired thiocyanohydrins were obtained in high isolated yields. For styrene oxide and 1,2-epoxybutane, further purification were achieved by preparative TLC or by silica gel column chromatography.

Selected spectroscopic data

*3-Phenoxy-2-hydroxypropyl thiocyanate (**2**)[14]*

IR ν_{max}/cm^{-1}: 2157 (SCN); ^1H-NMR ($CDCl_3$, 400 MHz): δ 3.30 (2H, d, C<u>H</u>$_2$SCN), 3.78 (1H, s, O<u>H</u>), 4.15 (2H, d, OC<u>H</u>$_2$), 4.29 (1H, m, C<u>H</u>OH), 6.95 (2H, m, Ar-<u>H</u>), 7.02 (1H, m, Ar-<u>H</u>), 7.28 (2H, m, Ar-<u>H</u>); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 37.4 (CH_2SCN), 68.1 (CHOH), 69.5 (OCH_2), 113.0 (SCN), 114.6 (*o*-CH), 121.3 (*p*-CH), 129.9 (*m*-CH), 158.5 (C).

*3-Allyloxy-2-hydroxypropyl thiocyanate (**3**)[14]*

IR ν_{max}/cm^{-1}: 2156 (SCN); ^1H-NMR ($CDCl_3$, 400 MHz): δ 3.04 (1H, s, O<u>H</u>), 3.24 (2H, d, C<u>H</u>$_2$SCN), 3.53 (2H, d, OC<u>H</u>$_2$), 4.05 (3H, m, OC<u>H</u>$_2$C<u>H</u>OH), 5.19-5.29 (2H, m,

=C<u>H</u>$_2$), 5.87 (1H, m, =C<u>H</u>); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 37.3 (CH_2SCN), 69.2 (CH_2O), 71.1 (CHOH), 71.6 (OCH_2), 113.1 (SCN), 117.5 (CH_2=), 133.7 (=CH).

*2-Hydroxy-3-thiocyanatopropyl methacrylate (**6**)*[12]

IR ν_{max}/cm^{-1}: 2157 (SCN); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.85 (3H, m, C<u>H</u>$_3$), 3.01-3.18 (2H, d, C<u>H</u>$_2$SCN), 3.40 (1H, m, C<u>H</u>OH), 4.13 (1H, s, O<u>H</u>), 4.15 (2H, d, OC<u>H</u>$_2$), 5.56 (1H, m, =C<u>H</u>$_2$), 6.07 (1H, m, =C<u>H</u>$_2$); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 18.4 (CH_3), 37.3 (CH_2SCN), 66.1 (OCH_2), 68.1 (CHOH), 112.8 (SCN), 126.6 (CH_2=), 135.2 (=CH), 167.1 (C=O).

*2-Hydroxycyclohexyl thiocyanate (**9**)*[9,14]

IR ν_{max}/cm^{-1}: 2152 (SCN); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.21-1.29 (4H, m, C<u>H</u>$_2$C<u>H</u>$_2$CHSCN), 1.69 (2H, m, C<u>H</u>$_2$CH$_2$CHOH), 1.98 (2H, m, C<u>H</u>$_2$CHOH), 3.14 (1H, s, O<u>H</u>), 3.16 (1H, m, C<u>H</u>SCN), 3.34 (1H, m, C<u>H</u>OH). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 23.1 (CH_2CH_2), 25.2 (CH_2CH_2), 30.0 (CH_2CHSCN), 31.4 (CH_2CHOH), 51.5 (CHSCN), 79.1 (CHOH), 110.6 (SCN).

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Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br, as PDF file.

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