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Fast, Efficient and Regioselective Conversion of Epoxides to β-Hydroxy Thiocyanates with NH_4SCN/Zeolite Molecular Sieve 4 Å under Solvent-Free Conditions

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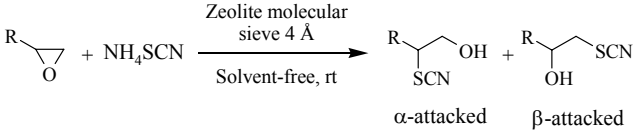
Solvent-free conversion of various epoxides to their corresponding β-hydroxy thiocyanates was carried out successfully with NH_4SCN/zeolite molecular sieve 4 Å system at room temperature. The reactions were completed within 2 - 7 min to give thiocyanohydrins with perfect regioselectivity and isolated yields. Moreover, the zeolite can be reused for several times without losing its activity.

Key Words: Epoxide, Zeolite molecular sieve 4 Å, β-Hydroxy thiocyanate, NH_4SCN

Introduction

Epoxides (oxiranes) are one of the most useful synthetic intermediates in organic synthesis[1] and a vast variety of protocols have been developed for regioselective ring opening of these compounds.[2] Nucleophilic ring opening of epoxides with thiocyanate ion usually gives thiiranes and numerous articles exhibit the importance of this synthetic method.[3] It is explained that the formation of thiiranes from the reaction of epoxides with thiocyanate ion has been occurred through the intermediacy of the corresponding β-hydroxy thiocyanates; however, this intermediate has not been isolated due to its rapid conversion to the corresponding thiirane. Literature review shows that hydroquinone,[4] HSCN,[5] DDQ,[6] $Ti(O^iPr)_4$,[7] $Ph_3P(SCN)_2$,[8] $TiCl_3$,[9] $ZnCl_2$,[9] $Pd(PPh_3)_4$,[10] TMSNCS/TBAF,[11] poly[*N*-(2-aminoethyl) acrylamido]trimethyl ammonium chloride (PTC),[12] $GaCl_3$,[13] selectfluor,[14] metalloporphyrins,[15] dichloro(5,10,15,20-tetraphenylporphyrin) phosphorus (V) chloride $[P(TPP)Cl_2]Cl$,[16] tetraarylporphyrins,[17] PEG-SO_3H,[18] thioxanthenone-fused azacrown ethers,[19] silica sulfuric acid,[20] Dowex-50X8,[21] 2,6-bis[2-(*o*-aminophenoxy)methyl]-4-bromo-1-methoxybenzene (BABMB),[22] phenol-containing macrocyclic diamides,[23] 2-phenyl-2-(2-pyridyl)imidazolidine (PPI),[24] $B(HSO_4)_3$[25] and $Al(HSO_4)_3/SiO_2$[26] are the reagents which stabilize the produced β-hydroxy thiocyanate and therefore inhibit from the conversion to thiirane. In contrast to above mentioned protocols, it was also reported that conversion of epoxides to β-hydroxy thiocyanates can be achieved with high quantities of NH_4SCN in the absence of any catalyst.[27]

Though the reported methods are useful for preparation of β-hydroxy thiocyanates from epoxides, however, some of these protocols suffer from disadvantages such as long reaction times, use of volatile organic solvents and expensive reagents, low regioselectivity and high temperature reaction conditions. Thus, the development and introduction of convenient methods which use green and mild reaction conditions are practically concerned and still in demand. Herein, we wish to introduce zeolite molecular sieve 4 Å as a reusable promoter for fast, efficient and perfect regioselective conversion of various epoxides to their corresponding β-hydroxy thiocyanates under solvent-free conditions at room temperature (Scheme 1).



Scheme 1

Results and Discussion

Zeolite molecular sieves are crystalline and highly porous materials which belong to the class of aluminosilicates. These crystals are characterized by a three-dimensional pore system with pores of precisely defined diameter. These micropores are of molecular sizes and give zeolites, adsorption, catalytic and ion exchange properties of paramount importance in the chemical industries. Moreover, interests are growing on the study of new zeolite applications related to all branches of science and technology.[28] On the other hand; one of the most urgent challenges for organic chemists is the definition of more economical and environmental friendly processes. To realize this goal, in these last years an ever increasing interests have been aimed to solvent-free organic synthesis.[29] In fact, avoiding the use of volatile, often flammable, expensive and toxic solvents strongly reduce the waste production and many fundamental processes have been proved to be achievable through efficient procedures with high simplicity of set-up and work-up.

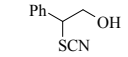
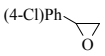
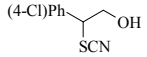
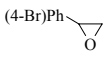
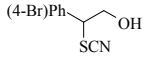
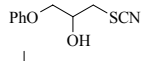
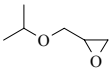
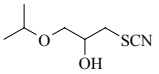
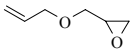
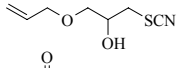
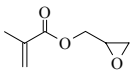
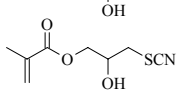
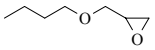
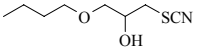
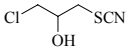
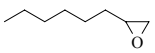
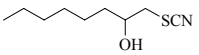
Along the outlined strategies, a survey showed that the capability of zeolite molecular sieve 4 Å for regioselective conversion of epoxides to β-hydroxy thiocyanates with NH_4SCN has not been investigated yet. We therefore decided to study the titled reaction with NH_4SCN/zeolite molecular sieve 4 Å under mild and eco-friendly conditions. Molar ratio of the reactants and reaction conditions were optimized by the reaction of styrene oxide, NH_4SCN and zeolite molecular sieve 4 Å under different conditions (Table 1). The results exhibited in view points of selectivity, time and mild reaction conditions, using 1 mmol styrene oxide, 2 mmol NH_4SCN and 0.3 g molecular sieve 4 Å at room temperature and under solvent-free conditions was the optimum for selective conversion of styrene

Table 1. Zeolite-catalyzed reaction of styrene oxide with NH_4SCN under different conditions[a]

Entry	Molar ratio	Zeolite (g)	Condition	Time (min)	α-attacked (%)	β-attacked (%)	Thiirane (%)	Epoxide[b] (%)
1	Epoxide/NH_4SCN (1:2)	-	CH_3CN/reflux	120	25	5	0	70
2	Epoxide/NH_4SCN (1:2)	0.2	CH_3CN/reflux	60	80	10	10	0
3	Epoxide/NH_4SCN (1:2)	0.2	THF/reflux	60	75	10	15	0
4	Epoxide/NH_4SCN (1:2)	0.2	MeOH/reflux	40	10	0	90	0
5	Epoxide/NH_4SCN (1:2)	-	Solvent-free/rt	60	5	5	0	90
6	Epoxide/NH_4SCN (1:2)	0.2	Solvent-free/rt	10	100	0	0	0
7	Epoxide/NH_4SCN (1:2)	0.3	Solvent-free/rt	5	100	0	0	0
8	Epoxide/NH_4SCN (1:2)	0.5	Solvent-free/rt	3	100	0	0	0

[a]All reactions were carried out with 1 mmol of styrene oxide. [b]Yield of recovered styrene oxide.

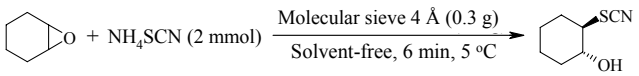
Table 2. Conversion of epoxides to β-hydroxy thiocyanates with NH_4SCN/zeolite molecular sieve 4[a]

Entry	Epoxide (**a**)	β-Hydroxy thiocyanate (**b**)	Molar ratio Epoxide/Thiourea	Time (min)	Yield (%)[b]	Ref.
1			1:2	5	98	15, 21
2			1:2	7	97	13
3			1:2	7	97	13
4			1:2	7	98	15, 21
5			1:2	3	94	15, 21
6			1:2	6	93	15, 21
7			1:2	2	95	21
8			1:2	2	92	21
9			1:2	2	75	15
10			1:2	4	90	13, 15
11[c]			1:2	6	85	15, 21

[a]All reactions were carried out in the presence of zeolite molecular sieve 4 Å (0.3 g) under solvent-free conditions at room temperature. [b]Isolated yields. [c]This reaction was carried out at 5 °C.

oxide to 2-hydroxy-1-phenylethyl thiocyanate (α-attacked product) in excellent yield (Table 1, entry 7).

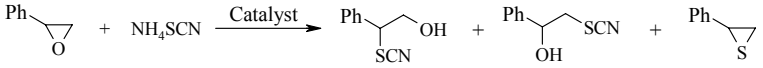
The suitability and scope of this synthetic protocol was further examined by solvent-free reaction of different types of substituted epoxides bearing electron donating and withdrawing groups with NH_4SCN/zeolite molecular sieve 4 Å under the optimized conditions. All epoxides were easily and efficiently converted to their corresponding β-hydroxy thiocyanates in excellent yields and regioselectivity. The reactions were completed within 2-7 min without formation of any side-product thiirane (Table 2). As seen, the zeolite catalyzed ring opening of epoxides with thiocyanate ion took place rapidly at room temperature except cyclohexene oxide which has been carried out at 5 °C, because at the elevated temperature, the minor formation of thiirane can be observed as a side-product (Table 2, entry 11). We also observed that nucleophilic ring opening of



Scheme 2

aryl substituted epoxides by thiocyanate ion was carried out exactly on more-hindered carbon (α-position) of the epoxide ring; however, alkylated epoxides performed the reaction from less-hindered one (β-position). This observation could be explained by stabilization of partially positive charge on the aryl substituted carbon of the epoxide through complexation of the oxygen with aluminates and silicates of the zeolite. In the case of alkylated epoxides predominance of steric factor relative to stabilization of partially positive charge is supposed to play a role in this transformation. Moreover, nucleophilic attack of

Table 3. Comparison of the reaction of styrene oxide with thiocyanate ion in the presence of different catalysts



(**1**) (**2**) (**3**)

Entry	Catalyst	Conditions	Product	Time (min)	Yield (%)	Ref.
1	ZMS-4	NH_4SCN/solvent-free/rt	1	5	98	a
2	Selectfluor	NH_4SCN/CH_3CN/rt	1+2	150	95 (16:84)	14
3	Dowex-50WX8	NH_4SCN/SiO_2/solvent-free/rt	1+2	6	89 (90:10)	21
4	$ZnCl_2$	KSCN/THF/reflux	3	180	60	9
5	$Ti(O^iPr)_4$	NH_4SCN/THF/reflux	1+2	240	30	7
6	BABMB	NH_4SCN/CH_3CN/reflux	1+2	10	91 (20:80)	22
7	BABMB	$KSCN/CH_3CN$/reflux	3	120	10	22
8	PTC	NH_4SCN/CH_3CN/rt	1+2	90	90 (90:10)	12
9	$[P(TPP)Cl_2]Cl$	NH_4SCN/CH_3CN/reflux/N_2	1+2	22	96 (20:80)	16
10	DDQ	NH_4SCN/CH_3CN/reflux	1+2	50	91 (89:11)	6
11	$Pd(PPh_3)_4$	NH_4SCN/THF/reflux/N_2	3	120	35	10
12	$GaCl_3$	NH_4SCN/H_2O/rt	1	18	92	13
13	Silica sulfuric acid	NH_4SCN/SiO_2/solvent-free/rt	1+2	5	70 (96:4)	20
14	PEG-SO_3H	NH_4SCN/H_2O/rt	1+2	60	84 (5:95)	18b
15	PEG-SO_3H	NH_4SCN/CH_2Cl_2/rt	1+2	60	83 (96:4)	18a
16	$CO^{II}T(4\text{-}OHP)P$	NH_4SCN/CH_3CN/reflux/N_2	1+2	25	96 (17:83)	15
17	T(4-OHP)P	NH_4SCN/CH_3CN/reflux	1+2	20	96	17
18	$B(HSO_4)_3$	NH_4SCN/SiO_2/solvent-free/rt	1+2	4	91 (92:8)	25
19	PPI	NH_4SCN/CH_3CN/reflux	1+2	45	95 (17:83)	24

[a]The present method.

thiocyanate ion on cyclohexene oxide in the presence of zeolite molecular sieve 4 Å produced *rac-trans*-2-hydroxycyclohexyl thiocyanate which is in agreement with the reported data in literature (Scheme 2).

It is noteworthy under the examined conditions, the formation of thiirane as a side-product was not observed in all reactions. In addition the zeolite can be reused in this transformation. Recovering of the zeolite from the reaction mixture and then activation in a heating oven, gave the catalyst which has been used for several times for conversion of styrene oxide to 2-hydroxy-1-phenylethyl thiocyanate without losing its activity.

The regioselectivity and advantages of NH_4SCN/zeolite molecular sieve 4 Å system were highlighted by comparison of conversion of styrene oxide to β-hydroxy thiocyanates with those of reported in literature (Table 3). A case study shows that in view points of reusability of the catalyst, solvent-free conditions, short reaction times, perfect regioselectivity and efficiency, our protocol is more efficient than the others.

In summary, we have shown that zeolite molecular sieve 4 Å is a highly efficient promoter for solvent-free conversion of various epoxides to their corresponding β-hydroxy thiocyanates in high yields and regioselectivity. The reactions were carried out within 2 - 7 min at room temperature. This protocol offer several advantages including mild reaction conditions, perfect selectivity, short reaction times, clean reaction profile, easy work-up procedure, environmentally benign, and use of inexpensive and commercially available reagents which introduce the present method as a mild, easy, efficient and general method for the preparation of β-hydroxy thiocyanates.

Experimental

All reagents and substrates were purchased from commercial sources with the best quality and they were used without further purification. IR and $^1H/^{13}C$ NMR spectra were recorded on Thermo Nicolet Nexus 670 FT-IR and 300 MHz Bruker Avance spectrometers, respectively. The products were characterized by their spectra data and comparison with the reported data in literature. All yields refer to isolated pure products. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

A Typical Procedure for Solvent-free Conversion of Styrene Oxide to 2-Hydroxy-1-phenylethyl Thiocyanate with NH_4SCN/Zeolite Molecular Sieve 4 Å System. A mixture of styrene oxide (0.12 g, 1 mmol), NH_4SCN (0.152 g, 2 mmol) and zeolite molecular sieve 4 Å (0.3 g) was thoroughly ground in a mortar for 5 min at room temperature. The progress of the reaction was monitored by TLC using *n*-hexane:EtOAc (5:2) as an eluent. After completion of the reaction, the mixture was washed with CH_2Cl_2 (2 × 8 mL) and the combined washing solvents was evaporated under reduced pressure to give 2-hydroxy-1-phenylethyl thiocyanate in high purity and 98% isolated yield (0.176 g) (Table 2, entry 1).

A Typical Procedure for Solvent-free Conversion of Cyclohexene Oxide to *rac-trans*-2-Hydroxycyclohexyl Thiocyanate with NH_4SCN/Zeolite Molecular Sieve 4 Å System. A mixture of cyclohexene oxide (0.098 g, 1 mmol), NH_4SCN (0.152 g, 2 mmol) and zeolite molecular sieve 4 Å (0.3 g) was thoroughly ground in a mortar putted in a ice-water bath (5 ^oC) for 6 min.

Completion of the reaction was monitored by TLC using *n*-hexane:EtOAc (5:2) as an eluent. Then, the mixture was washed with CH_2Cl_2 (2 × 8 mL) and the combined washing solvents was evaporated under reduced pressure to give pure *rac-trans*-2-hydroxycyclohexyl thiocyanate in 85% isolated yield (0.134 g) (Table 2, entry 11).

Spectral data for compounds **(1-11)b** are as the followings:

2-Hydroxy-1-phenylethyl Thiocyanate (1a): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46-7.33 (m, 5H), 4.52 (t, *J* = 6.6 Hz, 1H), 4.19 (d, *J* = 6.6 Hz, 2H), 2.16 (bs, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 135.35, 129.44, 129.34, 127.90, 111.11, 64.95, 54.75; IR (ν_{max}/cm^{-1}, neat) 3428, 3031, 2918, 2849, 2153, 1658, 1454, 1063, 760, 699.

1-(4-Chlorophenyl)-2-hydroxyethyl Thiocyanate (2b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36-7.34 (m, 4H), 4.46 (t, *J* = 6.6 Hz, 1H), 4.12 (d, *J* = 6.6 Hz, 2H), 2.38 (bs, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 135.16, 133.92, 129.41, 129.11, 112.01, 64.42, 53.99; IR (ν_{max}/cm^{-1}, neat) 3440, 2938, 2153, 1495, 1415, 1179, 1101, 1071, 830.

1-(4-Bromophenyl)-2-hydroxyethyl Thiocyanate (3b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58-7.56 (m, 2H), 7.27-7.25 (m, 2H), 4.44 (t, *J* = 6.6 Hz, 1H), 4.21 (d, *J* = 6.6 Hz, 2H), 2.56 (bs, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 134.51, 132.44, 129.61, 123.41, 110.55, 64.43, 54.17; IR (ν_{max}/cm^{-1}, neat) 3431, 2935, 2885, 2152, 1490, 1424, 1071, 1011, 834.

2-Hydroxy-3-phenoxypropyl Thiocyanate (4b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38-7.21 (m, 2H), 7.04-6.97 (m, 1H), 6.94-6.85 (m, 2H), 4.38-4.24 (m, 1H), 4.09 (d, *J* = 4.5 Hz, 2H), 3.61 (bs, 1H), 3.32 (dd, *J* = 4.2, 13.2 Hz, 1H), 3.19 (dd, *J* = 7.2, 13.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 157.96, 129.7, 121.73, 114.57, 112.45, 69.43, 68.88, 37.23; IR (ν_{max}/cm^{-1}, neat) 3448, 3063, 2929, 2877, 2156, 1636, 1598, 1496, 1243, 1173, 1046, 911, 733, 648.

2-Hydroxy-3-isopropoxypropyl Thiocyanate (5b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.1-4.0 (m, 1H), 3.7-3.63 (m, 1H), 3.58 (dd, *J* = 4.2, 9.6 Hz, 1H), 3.50 (dd, *J* = 5.4, 9.6 Hz, 1H), 3.18 (dd, *J* = 4.9, 13.2 Hz, 1H), 3.09 (dd, *J* = 7.2, 13.2 Hz, 1H), 2.77 (bs, 1H), 1.18 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 112.49, 76.6, 72.58, 69.36, 37.29, 21.96; IR (ν_{max}/cm^{-1}, neat) 3448, 2974, 2917, 2156, 1636, 1469, 1382, 1128, 1092, 913, 734.

3-Allyloxy-2-hydroxypropyl Thiocyanate (6b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.97-5.8 (m, 1H), 5.35-5.2 (m, 2H), 4.15-4.07 (m, 1H), 4.04 (d, *J* = 5.7 Hz, 2H), 3.63-3.51 (m, 2H), 3.19 (dd, *J* = 4.5, 13.2 Hz, 1H), 3.08 (dd, *J* = 7.2, 13.2 Hz, 1H), 2.88 (bs, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 133.88, 117.93, 112.45, 72.44, 71.45, 69.137, 37.23; IR (ν_{max}/cm^{-1}, neat) 3450, 2916, 2862, 2156, 1644, 1421, 1110, 995, 911, 733, 648.

2-Hydroxy-3-thiocyanatopropyl Methacrylate (7b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.15 (s, 1H), 5.67-5.59 (m, 1H), 4.29 (d, *J* = 4.5 Hz, 2H), 4.24-4.15 (m, 1H), 3.32 (bs, 1H), 3.20 (dd, *J* = 4.2, 13.5 Hz, 1H), 3.06 (dd, *J* = 7.5, 13.5 Hz, 1H), 1.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 167.36, 135.51, 126.87, 112.29, 68.49, 66.26, 37.33, 18.24; IR (ν_{max}/cm^{-1}, neat) 3472, 2957, 2928, 2156, 1720, 1637, 1454, 1296, 1165, 1106, 1018, 946, 814.

3-Butoxy-2-hydroxypropyl Thiocyanate (8b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.14-4.01 (m, 1H), 3.62-3.42 (m, 4H), 3.18 (dd, *J* = 4.8, 13.2 Hz, 1H), 3.08 (dd, *J* = 7.2, 13.2 Hz, 1H), 2.80 (bs, 1H), 1.54-1.47 (m, 2H), 1.45-1.28 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 112.48, 72.02, 71.51, 69.12, 37.27, 31.54, 19.22, 13.85; IR (ν_{max}/cm^{-1}, neat) 3453, 2958, 2872, 2156, 1637, 1464, 1120, 738.

3-Chloro-2-hydroxypropyl Thiocyanate (9b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.26-4.18 (m, 1H), 3.79-3.68 (m, 2H), 3.24 (dd, *J* = 4.6, 13.8 Hz, 1H), 3.12 (dd, *J* = 7.2, 13.8 Hz, 1H), 2.73 (bs, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 112.01, 69.82, 47.10, 37.31; IR (ν_{max}/cm^{-1}, neat) 3431, 2956, 2917, 2849, 2157, 1634, 1429, 1073, 735.

2-Hydroxyoctyl Thiocyanate (10b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.99-3.83 (m, 1H), 3.18 (dd, *J* = 3.5, 13.5 Hz, 1H), 2.93 (dd, *J* = 8.1, 13.2 Hz, 1H), 2.11 (bs, 1H), 1.70-1.52 (m, 2H), 1.42-1.18 (m, 8H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 112.12, 70.33, 41.14, 35.95, 31.64, 29.04, 25.42, 22.52, 14.01; IR (ν_{max}/cm^{-1}, neat) 3436, 2930, 2855, 2155, 1718, 1634, 1464, 1048, 724.

2-Hydroxycyclohexyl Thiocyanate (11b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.65-3.55 (m, 1H), 2.96-2.87 (m, 1H), 2.36 (bs, 1H), 2.31-2.14 (m, 2H), 1.84-1.66 (m, 4H), 1.47-1.39 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 111.01, 72.68, 55.30, 35.01, 32.78, 25.91, 24.01; IR (ν_{max}/cm^{-1}, neat) 3422, 2936, 2859, 2151, 1637, 1449, 1068, 958, 865, 719.

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