

Schiff-Base Metal(II) Complexes as New Catalysts in the Efficient, Mild and Regioselective Conversion of 1,2-Epoxyethanes to 2-Hydroxyethyl Thiocyanates with Ammonium Thiocyanate

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A convenient and efficient procedure for the ring-opening of 1,2- epoxyethanes with ammonium thiocyanate in the presence of some Schiff-base complexes of metal(II) is described. The cleavage of the oxirane ring is found to proceed regioselectively under mild reaction conditions. Thus, several 2-hydroxyethyl thiocyanates, useful intermediates toward biological-active molecules, are easily obtained in very good yields.

Thiocyanates are important intermediates in agricultural and pharmaceutical chemistry. 2-Hydroxyethyl thiocyanates represent an interesting subclass having multiple modes of reactivity. Synthetic access by oxirane ring opening with thiocyanate has been limited by a further reaction to give thiiranes.[1,2] There are two methods reported in the literature for the synthesis of 2-hydroxyethyl thiocyanates. In one method, 2-hydroxyethyl thiocyanates are prepared by the opening of a cyclic sulfate with NH_4SCN to form the corresponding β-sulfate, which is hydrolyzed to the 2-hydroxyethyl thiocyanates. A second method employs an addition to the 1,2-epoxyethanes of thiocyanic acid generated in situ at low temperature.[3] For these syntheses, it has been reported that the presence of some hydroquinone or DDQ is required to stabilize the produced 2-hydroxyethyl thiocyanates, and to inhibit its conversion to thiirane.[4] Although reagents, such as $Ti(O\text{-}^iPr)_4$[5], $Ph_3P(SCN)_2$[6], $TiCl_3$(or $ZnCl_2$)[7], $Pd(PPh_3)_4$[8] and TMSNCS (Cat. TBAF),[9] are useful, they are limited to specific oxiranes, and are not applicable as versatile reagents in the preparation of 2-hydroxyethyl thiocyanates.[9]

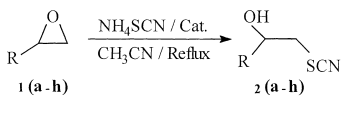
In conjunction with ongoing work in our laboratory on the synthesis and complex formation of Schiff base-metal complexes with different molecules,[10] we found that these complexes efficiently catalyzed the addition of ammonium thiocyanate to oxiranes to form 2-hydroxyethyl thiocyanates. Here, we report on the reaction of some oxiranes with ammonium thiocyanate in the presence of catalytic amounts of Schiff-base complexes of metal(II) wherein high yields are produced with regioselectivity under mild reaction conditions.

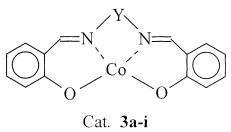
Result and Discussion

Metal(II)-salen complexes have been recognized as being among the most promising catalysts for various reactions. These complexes show wide applicability, and are now used as catalysts for a variety of enantioselective reactions, such as oxidation,[11] aziridination,[12] cyclopropanation,[13] the Diels–Alder reaction,[14] the addition of TMSCN to aldehydes,[15] the Strecker reaction,[16] and the conversion of 1,2-epoxyethanes to 2-haloethanols with molecular halogen.[10] Metal(II)-salen complexes can be readily synthesized from metal salts and salen ligands, which are prepared by simply mixing 1 mol of ethylenediamine and 2 mol of salicylaldehyde.

In this study, reactions of styrene oxide with ammonium thiocyanate in the presence of some Schiff-base (SB) complexes of Co(II) were carried out. In order to examine the effects of ligands on the catalyst in the reaction, nine kinds of ligands were employed (Scheme 1). It should be noted that the Schiff-bases of complexes **2e–i** behave as donor doubly-bidentate ligands, and form dinuclear complexes (SB–M, 2:2) with metal(II) ions.[17–19]

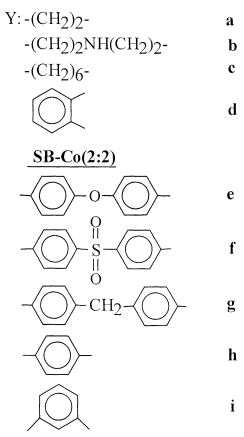
To a mixture of styrene oxide and ammonium thiocyanate in acetonitrile was added a solution of a catalyst in dichloromethane; the mixture was stirred under reflux conditions. Regarding the complex catalyst, a 0.01 molar amount of sty-





Cat. **3a-i**

R **1(a-h)**		2-Hydroxyethyl thiocyanate **2(a-h)**
Ph	**a**	**a**
$PhOCH_2$	**b**	**b**
Cyclohexane-1,2-diyl	**c**	**c**
i-$PrOCH_2$	**d**	**d**
CH_2=$CHCH_2OCH_2$	**e**	**e**
$ClCH_2$	**f**	**f**
$CH_3(CH_2)_5$	**g**	**g**
Indan-1,2-diyl	**h**	**h**



Scheme 1.

Table 1. Reaction of Styrene Oxide with Ammonium Thiocyanate in the Presence of Various Co(II)-Schiff Base Complexes as Catalysts in CH_3CN under Reflux Condition

Entry	Catalyst	Time/min	Yield/%[a)]
1	**3a**	35	93
2	**3b**	45	80
3	**3c**	50	70
4	**3d**	50	85
5	**3e**	25	95
6	**3f**	45	90
7	**3g**	60	90
8	**3h**	55	75
9	**3i**	50	83
10[b)]	—	190	—[c)]

a) Determined by GC.
b) In the presence of excess of NH_4SCN
c) A 35% of the corresponding thiirane was obtained.

rene oxide was used. The reaction product was 2-hydroxy-2-phenylethyl thiocyanate (**2a**), and the yield was determined by GLC and TLC analyses. The results of the reactions of styrene oxide with thiocyanate ion in the presence of the above-mentioned catalysts are summarized in Table 1. In each case, cleavage of the oxirane ring occurred and upon a work-up, the corresponding 2-hydroxyethyl thiocyanate was obtained. Two-valent metal salen complexes are well-know to be oxidized to their three-valent complexes upon exposure to oxygen.[20] In order to find whether a three-valent metal-salen complex is also formed in the reactions under our studies, the Co(II)-salen complex was exposed to an excess amount of ammonium thiocyanate for an appropriate time. Oxidation did not occur and the Co(II)-salen complex was isolated intact. It therefore seems that the formation of three-valent metal salen complexes under this condition is improbable. A comparison of the electronic absorption spectra of the recovered Co(II)-salen complex for a reaction with Co(II)-salen before the reaction and Co(III)-salen was also in accord with the above discussion. The catalysts were easily recovered and could be reused several times.

A comparison of the cleavage of the styrene oxide with ammonium thiocyanate in the absence of a catalyst is given in entry 10 of Table 1. As shown in Table 1, the yields of thiocyanation with this new methodology were quite good, and the reaction time was very short. Without a catalyst, the reaction required a much longer time; moreover, undesirable thiirane-formation predominated. In these reactions, 3–10% of the corresponding thiiranes was also formed, which could be easily isolated by column chromatography. It is of great importance that the reaction is largely affected by the various ligands of the complexes. The use of catalysts **3a** and **3e** was most effective, and the reactions were completed within 35 and 25 min, respectively (Table 1, entries 1 and 5). In the presence of other catalysts (**3b**, **3c**, **3d**, and **3f–i**) the reaction times for thiocyanation were in the rang 45–60 min. On the other hand, because first-row transition metal(II) complexes of simple Schiff bases are known to be sparingly soluble in common organic solvents, the difference in the activity between the complexes used in this study may instead be attributed to their own solubility, or their adducts with ammonium thiocyanate in refluxed acetonitrile.

Table 2. Reaction Times and the Yields of 2-Hydroxy-2-phenylethyl Thiocyanate in the Reactions of Styrene Oxide and Ammonium Thiocyanate in the Presence of Various Metal(II)-Salen Complexes

Entry	Cat. M(II)-Salen	Time/min	Yield/%[a)]
1	Co(II)	35	93
2	Ni(II)	75	80
3	Mn(II)	50	90
4	Zn(II)	80	75
5	Cu(II)	100	80
6	Fe(II)	150	60

a) Determined by GC.

Table 3. Thiocyanative Cleavage of Styrene Oxide in the Presence of 0.01 mol Catalyst **3e** in Various Solvents

Entry	Solvent	Time/min	Yield/%[a)]
1	CH_3CN	25	95
2	THF	50	80
3	CH_3COCH_3	70	60
4	EtOH	35	45
5	$CHCl_3$	120	< 20
6	C_6H_6	120	< 15
7	DMF	120	< 15

a) Determined by GC.

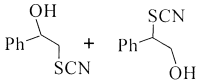
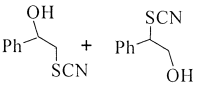
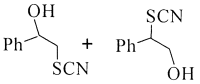
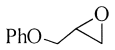
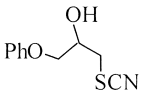
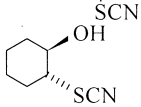
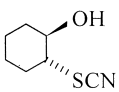
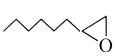
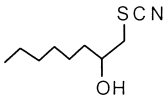
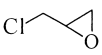
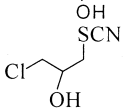
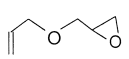
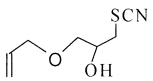
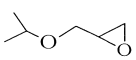
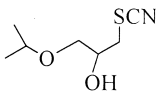
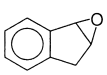
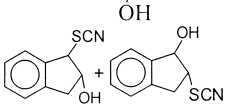
Next, we studied the catalytic effect of the first-row transition metal(II) with the ligand of *N*,*N*′-disalicylideneethylenediamine (or H_2salen) on the formation of 2-hydroxy-2-phenylethyl thiocyanate (**2a**). In all of the used catalysts, ring opening with a thiocyanato group of styrene oxide was carried out; the corresponding results are summarized in Table 2. Among the catalysts examined, the use of Co(II)-salen gave the best results in the yields and reaction rates.

The results of a ring opening of styrene oxide with ammonium thiocyanate by catalyst **3e** in various aprotic solvents are reported in Table 3. We found that these reactions appeared to be largely dependent on the nature of the solvent.

To ascertain the scope and limitation of the present reaction, several oxiranes were examined using catalyst **3e**; these results are summarized in Table 4. By comparison, a number of methods[5–8] for the conversion of oxiranes to the corresponding 2-hydroxyethyl thiocyanates are given in entries 2–5 and 8 (Table 4). In all of the cases listed, the yields increased and the regioselectivities were also enhanced. The optimum amount of the catalyst was found to be 0.01 equiv vs oxiranes. However, other factors can exert a controlling influence, such as (1) the steric hindrance of oxiranes, (2) the nature of the solvent, and (3) electron-donating or withdrawing groups bonded to the oxiranes. Each one can have a pronounced effect on the observed ratio of 2-hydroxyethyl thiocyanate isomers and the overall yield.

As shown in Table 4 (entry7), in which only the trans isomer is given, the reactions are completely *anti* stereoselective. As for the regioselectivity, an attack of the nucleophile preferentially occurs at the less-substituted oxirane carbon. An *anti*-

Table 4. Reaction of Epoxides with NH_4SCN in the Presence of the Representative Catalyst

Entry	Oxirane	Catalyst (0.01 mol amt.)	Reaction Conditions	Product(s)	Reaction time/min	Yield/%[a)]
1		3e	NH_4SCN/CH_3CN Reflux/N_2		25	95 (4:1)
2		$Pd(PPh_3)_4$[8]	NH_4SCN/N_2 THF/Reflux		120	35
3		$Ti(O\text{-}^iPr)_4$[5]	NH_4SCN THF/Reflux		240	30
4		$ZnCl_2$[7]	KSCN THF/Reflux		180	60
5		DDQ[4b]	NH_4SCN/CH_3CN Reflux		50	91 (1:8)
6		3e	NH_4SCN/CH_3CN Reflux/N_2		25	92
7		3e	NH_4SCN/CH_3CN Reflux/N_2		30	93
8		H_2Q[3a]	$KSCN/H_3PO_4$ H_2O/Et_2O		—	48[b)]
9		3e	NH_4SCN/CH_3CN Reflux/N_2		55	85
10		3e	NH_4SCN/CH_3CN Reflux/N_2		50	75
11		3e	NH_4SCN/CH_3CN Reflux/N_2		40	85
12		3e	NH_4SCN/CH_3CN Reflux/N_2		45	83
13		3e	NH_4SCN/CH_3CN Reflux/N_2		45	93 (1:4)

a) Determined by GC. b) Hydroquinone has been used to stabilize 2-hydroxycyclohexyl thiocyanate (see Ref. 3a).

Markovnikov-type[21] regioselectivity is generally observed in these reactions, except for the reactions of styrene oxide (Table 4, entry1) and indene oxide (Table 4, entry13), which produced 17% and 20% of other regioisomer, respectively, the reaction of other oxiranes were found to be highly regioselective, and only one isomer was obtained. The above-mentioned regiochemical mode can be viewed as occurring via a nucleophilic attack by a thiocyanate ion on the less sterically hindered oxirane carbon. This mechanism closely resembles the S_N2 model for an aliphatic nucleophilic displacement.

We have already reported on the related reaction of oxiranes and ammonium thiocyanate to 2-hydroxyethyl thiocyanates using macrocyclic diamides as catalysts. In that paper, we suggest that the conversion of 1,2-epoxyethane to 2-hydroxyethyl thiocyanate occurs according to the following four-step mechanism. The first step involves the formation of a molecular complex between macrocycle and NH_4SCN in which thiocyanate ion (SCN^-) exists as a contact ion pair. In the second step, this complex is further decomposed to release the SCN^- ion into the solution. Therefore, in this way, the SCN^- ion is produced as a nucleophilic species in the presence of a suitable macrocycle and, in the third step, this ion participates in the ring-opening reaction of oxiranes. Finally, in step (4) the catalyst is reproduced and is used in the first step again.[22]

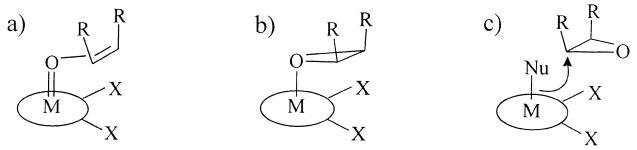
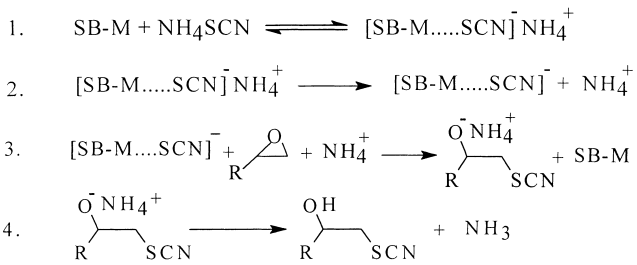


Fig. 1.



Scheme 2.

Given that salen complexes are remarkably effective for the epoxidation of simple olefins,[23] it has been considered whether similar systems could be useful in oxirane ring-opening reactions. Thus, the elements of the stereochemical interaction between the substrate and the ligand in olefin oxidation (Fig. 1a)[24] might apply to oxirane activation by a metal-(salen) complex (e.g., Figs. 1, b or c).[25]

Based on our previous studies[10] and other work[26] on the ring opening of oxirane with different nucleophiles in the presence of some Schiff base-metal complexes, a general mechanism was suggested for ring-opening with a thiocyanato group of oxiranes, as Shown in Scheme 2.

The use of catalysts **3a** and **3e** resulted in the highest reaction yield in the series (Table 1). This was most probably due to the formation of the most stable complexes between NH_4SCN and catalysts **3a** and **3e** (i.e. the largest number catalyst sites). In order to obtain a clue about the stability of the 1:1 complexes of ammonium thiocyanate with all of the catalysts tested, a spectrophotometric procedure in an acetonitrile solution was performed.[27] Sample absorption spectra of **3e** in the presence of increasing concentrations of NH_4SCN are

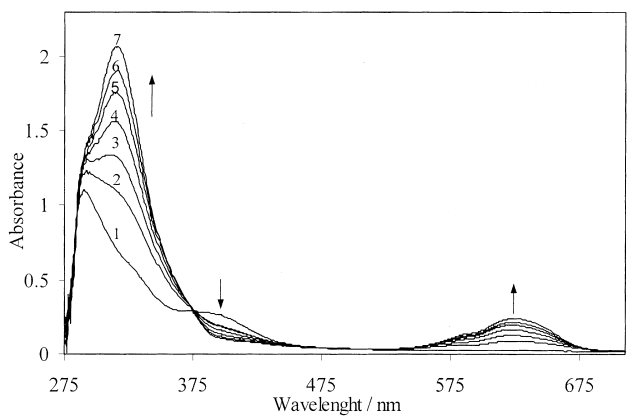


Fig. 2. Absorption spectra of catalyst **3e** (8×10^{-4} M) in the presence of different concentrations of NH_4SCN at 25 °C in acetonitril: (1) 0, (2) 1.5×10^{-4}, (3) 2.5×10^{-4}, (4) 3.5×10^{-4}, (5) 4.5×10^{-4}, (6) 5.5×10^{-4}, (7) 7.5×10^{-4} M.

Table 5. The Formation Constants K (mol^{-1} dm^3) for Complexation of SCN^- with Some Co(II)-Schiff Bases at 25C° in Acetonitril Solution

Catalyst	K
3a	$1.74(\pm0.1) \times 10^3$
3d	$1(\pm0.06) \times 10^3$
3e	$2.5(\pm0.11) \times 10^3$
3f	$3.7(\pm0.2) \times 10^2$
3g	$1.53(\pm0.1) \times 10^2$

shown in Fig. 2; the resulting stability constants are summarized in Table 5. Figure 2 shows that the addition of a reagent results in an increasing absorbance of **3e** at 315 and 625 nm, while decreasing the intensity of the 400 nm bands. The observation of a clear isosbestic point in the spectra supports the occurrence of a simple 1:1 complexation in solution. The data given in Table 1 clearly indicate the formation of the most stable complexes between ammonium thiocyanate and **3a** and **3e** in the series. This obviously supports the increased reaction yield with these two catalysts as well as the predominance of the mechanism (Scheme 2) in solution.

Moreover, based on the experimental results, it can be concluded that the reaction rate in the present reaction should be affected not only by complexation of NH_4SCN with M(II)-Schiff base complexes, but also by dissociation of the SCN^- anion from the adduct and the solubility of M(II)-Schiff base complex or the adduct in acetonitrile.

It is noteworthy that the operation is quite simple and the reaction conditions are sufficiently mild to operate several sensitive functionalities, and that the salen catalysts can be recycled and reusable.

Experimental

General. Some 1,2-epoxyethanes and other chemical materials were purchased from Fluka and Merck in high purity. The Schiff-base complexes were prepared by reported procedures, and their spectroscopic and physical data were compared with the literature.[17,19,28]

General Procedure for the Conversion of 1,2-Epoxyethanes to 2-Hydroxyethyl Thiocyanate Using Schiff-Base Complexes of Metal(II) as a Catalyst. To a mixture of 1,2-epoxyethanes (10 mmol) and NH_4SCN (10 mmol, 0.76 g) in acetonitrile (30 mL), a solution of catalyst (0.1 mmol) in CH_2Cl_2 (5 mL) was added, and the mixture was stirred under reflux for 25–150 min (in the case of Fe, Co, Mn, metals, under nitrogen atmosphere). The reaction was monitored by TLC or GC. After completion of the reaction, the mixture was filtered and the solvent was evaporated. Chromatography of the crude product was performed on a column of silica gel eluted first with hexane for the separation of thiirane, followed by using C_6H_{14}/CH_2Cl_2 (1:1) for the separation of 2-hydroxyethyl thiocyanate as a pale-yellow liquid. Then, the Schiff base metal(II) complex was recovered by elution with methanol.

Selected Spectral Data for 2-Hydroxyethyl Thiocyanates.[4,6,9]

(a) 2-Hydroxy-2-phenylethyl Thiocyanate: IR (neat) ν(SCN) 2160 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 7.3(5H, m), 5.0 (1H, dd), 3.1–3.3 (2H, m), 2.4–2.9 (1H, brs). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 135.8, 129.5, 128.3, 126.2, 113.0, 72.9, 42.4.

(b) 3-Phenoxy-2-hydroxypropyl Thiocyanate: IR (neat)

ν(SCN) 2163 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 7.27 (2H, m), 6.92 (3H, m), 5.0 (1H, m), 4.2 (2H, d), 3.64 (2H, d). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 158.0, 130.0, 122.0, 115.1, 114.9, 78.2, 67.2, 33.6.

(c) 2-Hydroxycyclohexyl Thiocyanate: IR (neat) ν(SCN) 2165 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.95 (1H, m), 2.35 (1H, m), 2.15 (1H, s), 1.80 (2H, m), 1.65 (2H, m), 1.20–1.50 (4H, m). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 110.0, 72.0, 55.0, 34.5, 32.5, 30.5, 27.0.

(d) 2-Hydroxy-3-isopropoxypropyl Thiocyanate: IR (neat) ν(SCN) 2170 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.74 (1H, m), 3.57 (3H, m), 3.33 (2H, d), 3.17 (1H, brs), 1.1 (6H, d, J = 6 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 114.5, 79.4, 73.2, 67.6, 38.2, 23.0, 22.0.

(e) 3-Allyloxy-2-hydroxypropyl Thiocyanate: IR (neat) ν(SCN) 2158 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 5.81 (1H, m), 5.1–5.25 (2H, m), 4.7 (1H, brs), 3.98 (3H, m), 3.6 (2H, d), 3.36 (2H, d). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 134.2, 118.0, 117.0, 80.2, 72.9, 69.2, 32.5.

(f) 3-Chloro-2-hydroxypropyl Thiocyanate: IR (neat) ν(SCN) 2168 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 4.1 (1H, m), 3.7 (4H, m), 2.64 (1H, brs). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 117.8, 71.2, 46.1, 43.4.

(g) 2-Hydroxyoctyl Thiocyanate: IR (neat) ν(SCN) 2162 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.91 (1H, m), 3.15 (1H, dd, J = 13, J = 3.5 Hz), 2.95 (1H, dd, J = 13, 7.5 Hz), 2.69 (1H, brs), 1.2–1.6 (10H, m), 0.88 (3H, m). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 113.2, 70.6, 41.5, 36.3, 32.0, 29.4, 25.8, 22.9, 14.4.

(h) 2-Hydroxy-1-indanyl Thiocyanate: IR (neat) ν(SCN) 2160 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 7.2–7.5 (4H, m), 5.0 (1H, d), 4.8 (1H, m), 3.55 (2H, d), 3.2–3.5 (1H, brs). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 139.0, 130.0, 128.0, 126.0, 124.0, 120.0, 112.4, 83.7, 50.1, 39.4.

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