Some Versatile and Efficient Methods for the Regioselective Ring Opening of Epoxides to Corresponding β-Hydroxy Thiocyanates

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ABSTRACT

In this review, was reported some methods for the preparation of â-hydroxy thiocyanates, which are considered as an important class of compounds often used as key intermediates in agricultural and pharmaceutical chemistry.

**Key words**: Regioselectivity, Ring opening, Thiocyanohydrin, Epoxide, β-Hydroxythiocyanate, Solid phase, Liquid phase.

INTRODUCTION

β-hydroxy thiocyanates play an important role in the realm of organic chemistry, such as biological, pharmaceutical and agricultural chemistry[1]. In the recent decade, these compounds were prepared by the reaction of different epoxides with NH_4SCN in the presence of various catalysts and different condition.

Epoxides or oxiranes are useful and important synthetic intermediates in organic synthesis.[2]Their inherent polarity and high angle strain of three-membered ring make them susceptible to react with a wide variety of reagents, including reducing agents, oxidizing agents, electrophiles, nucleophiles, acids, and bases[3-4]. The ring opening of epoxides with different nucleophiles is an attractive subject in organic transformations[5].

Between these nucleophiles, the reaction of thiocyanate ion with epoxides, in the absence or in the presence of catalyst is a widely studied and suitable method for the preparation of thiiranes[6-13]. The formation of thiiranes from the reaction of epoxides and thiocyanate ion has been proposed to occur through the intermediacy of the corresponding β-hydroxy thiocyanate (I) (Scheme 1), but this intermediate has not been isolated due to its rapid conversion to the corresponding thiirane[11-14].
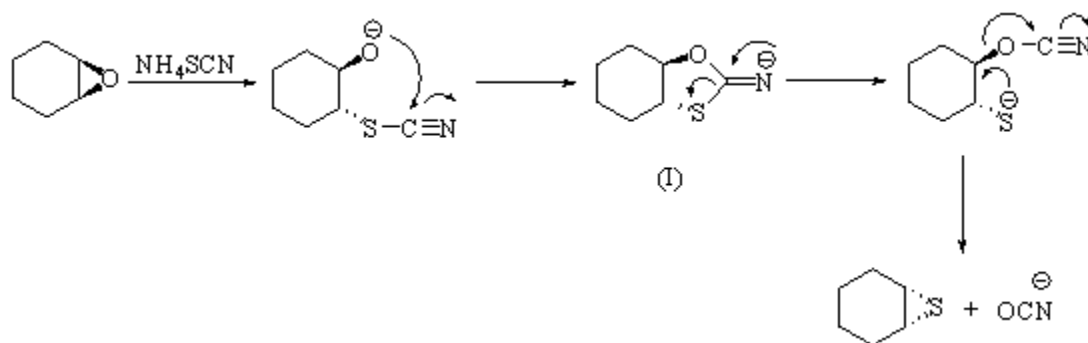
Scheme 1: Reaction of epoxides with NH₄SCN

There are two methods reported in the literature for the synthesis of β-hydroxy thiocyanates. In the first method, thiocyanohydrins were prepared by the opening of a cyclic sulfate with NH_4SCN to form the corresponding β-sulfate, which is hydrolyzed to the thiocyanohydrines. (Scheme 2)
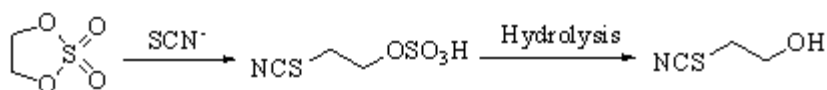
Scheme 2: Reaction of a cyclic sulfate with NH₄SCN

The second method employed the addition of thiocyanic acid generated in situ to the epoxide at low temperature .[15-18] (Scheme 3)


Scheme 3: Reaction of epoxides with thiocyanic acid

In this review, we report some novel and efficient methods for the regioselective ring-opening of epoxides to corresponding β-hydroxy thiocyanates. Various epoxides and β-hydroxy thiocyanates are shown in following table. (Table1)

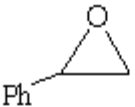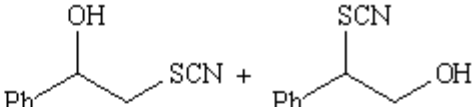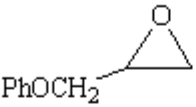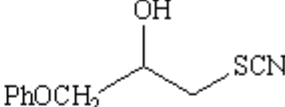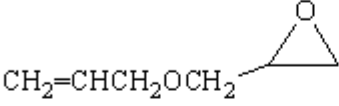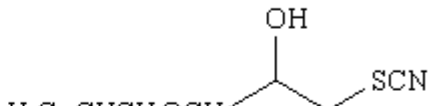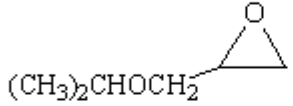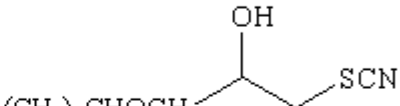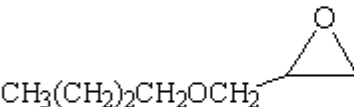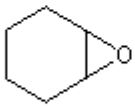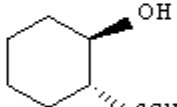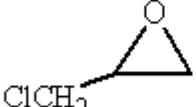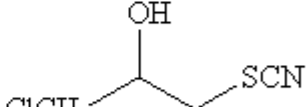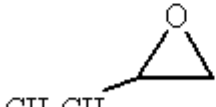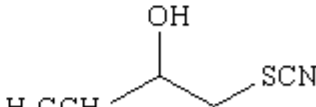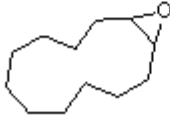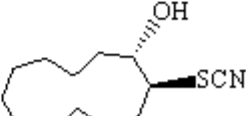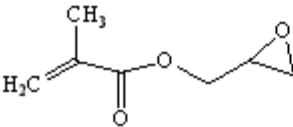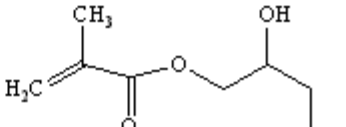It was found that, epoxides carrying electron-donating groups, it is the electronic factor that predominates, and the thiocyanate ion attacks, predominantly at the secondary carbon atom of the epoxide ring (II), a fact that is reasonably well established. In contrast, in epoxides carrying electron withdrawing groups, it is the steric factor in that predominates and the nucleophilic attack of thiocyanate ion is strongly favored on the less substituted carbon of epoxides (I) (Scheme 4).
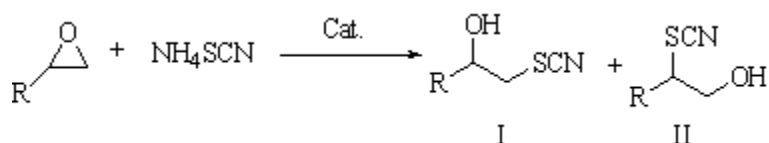
Scheme 4: Regioselective ring opening epoxides to corresponding β-hydroxy thiocyanates

Table 1: Various epoxides and β-hydroxy thiocyanates

No.	Substrate	Products
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		

In the case of cyclohexene oxide, the stereochemistry of the ring-opened product was found to be trans. (Scheme 5)
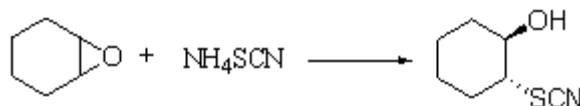
Scheme 5: Stereoselectivity in ring opening of cyclohexene oxide

Reaction in liquid phase
Use of phenol-containing macrocyclic diamides as catalyst

Initially, in 2001, the regioselective ring-opening reactions of some epoxides with ammonium thiocyanate in the presence of a series of new phenol-containing macrocyclic diamides and also dibenzo-18-crown-6-, 18-crown-6-, benzo-15-crown-5-, and pyridine-containing macrocyclic diamide was studied[19](Scheme 6)

dibenzo-18-crown-6

18-crown-6

Cat:

benzo-15-crown-5

pyridine-containing macrocyclic diamide
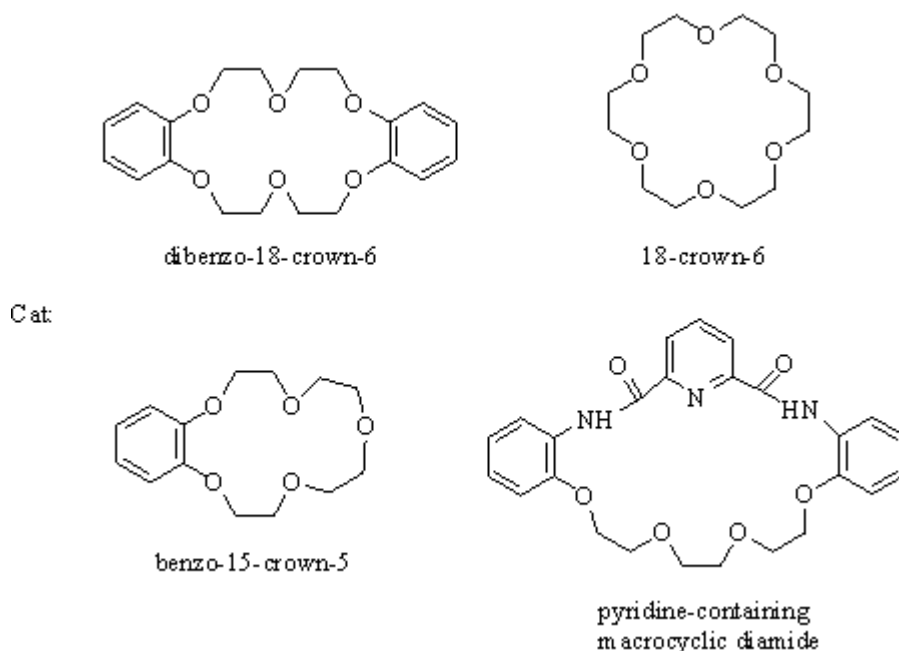
Scheme 6: Various macrocyclic catalysts

The epoxides were subject to cleavage by NH_4SCN in the presence of these catalysts under mild reaction conditions in various aprotic solvents. Thiocyanation reactions proceed very cleanly employing CH_3CN, while those performed in Et_2O and CH_2Cl_2 led to a lower yield of the thiocyanohydrin. (Scheme 7)
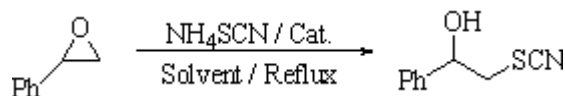
Scheme 7: Reaction of epoxide with NH₄SCN

Four-step mechanism was proposed for this reaction (Scheme 8): The first step involves the formation of a 1:1 molecular complex between macrocycle and NH$_4$SCN in which thiocyanate ion (SCN$^-$) exist as a contact ion pair:

Macrocycle + NH$_4$SCN $\leftrightarrow$ [Macrocycle....NH$_4^+$] SCN$^-$
...(1)
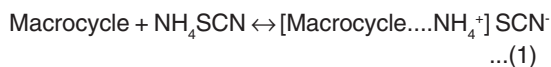
In the second step, this complex is further

decomposed to release SCN$^-$ ion into solution as:

(Macrocycle....NH$_4^+$)SCN$^-$ $\leftrightarrow$ [Macrocycle....NH$_4^+$] + SCN$^-$ ...(2)

Therefore, in this way, 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 epoxides

reaction of epoxide:

(3)
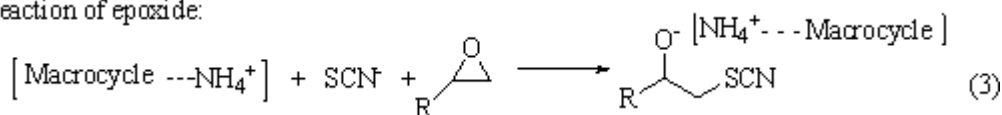
Finally, the catalyst is regenerated in step 4

(4)
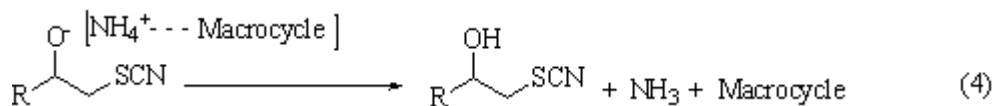
These steps occur continuously until all of the epoxides and ammonium thiocyanate are consumed, and after workup, the catalyst can be recovered easily.

Use of poly[N-(2 aminoethyl) acrylamido] trimethyl ammonium chloride as phase-transfer catalysts

In 2002, Tamami and coworker used

poly[*N*-(2-aminoethyl)acrylamido]trimethyl ammonium chloride resin (quaternized amino functionalized cross-linked polyacrylamide) as an efficient heterogeneous polymeric PTC, for regioselective ring opening of epoxides by thiocyanate ion to give corresponding thiocyanohydrins.[20] (Scheme 9)
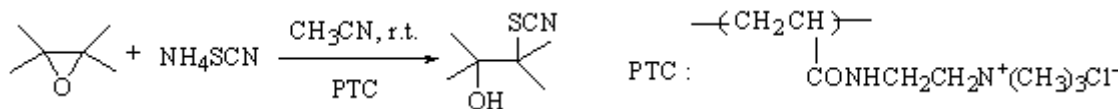
Scheme 9: Ring opening of epoxide in the peresence of PTC as catalyst

Phase-transfer catalysts (PTCs) facilitate reactions between water-soluble reagents and organic soluble substrates. The most important PTCs, which have been used widely in organic reactions, are quaternary ammonium and phosphonium salts, crown ethers, and cryptands.[21-24] During the last few years much interest has been focused on the applications of functionalized

polymers as PTCs[25-28] because they provide ease of separation of the catalyst and isolation of the product. Polyacrylamide cross-linked with divinylbenzene (2%) was prepared by free radical solution polymerization of the monomer mixture in ethanol using benzoyl peroxide as an initiator. Poly[*N*-(2 aminoethyl)acrylamide] was obtained by the transamidation reaction of cross-linked

polyacrylamide with excess ethylene–diamine. Poly [*N*- (2-aminoethyl) acrylamido] trimethyl ammonium chloride was prepared by the reaction of poly [*N*-(2-aminoethyl) acrylamide] with an excess of methyl iodide in DMF at room temperature and subsequent exchange of the iodide anion with chloride.[29-30]

The reactions were carried out in wet tetrahydroforan, chloroform, dichloromethane, ethyl acetate, acetonitrile and water. The best solvent was acetonitrile.

The poly [*N*-(2-aminoethyl)acrylamido] trimethyl ammonium chloride resin in this transformation acts both as a catalyst for nucleophilic ring opening reactions as well as being a phase-transfer agent. It seems that this polymeric catalyst carrying the nucleophile has an activating effect on the epoxy substrate, and the reaction proceeds smoothly in the vicinity of the catalyst. Probably, the ring opening of the epoxide is facilitated by hydrogen bonding between the oxygen of the epoxide and the amidic hydrogen of the polymer.

Use of meso-tetraarylporpherins as catalyst

In 2004, Sharghi and coworker used meso-tetraarylporpherins as a catalyst for the synthesis of several 2-hydroxyethyl thiocyanates.[31] (Scheme 10)
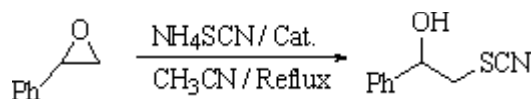
Scheme 10: Use of meso-tetraarylporpherins as catalyst for preparation of thiocyanohydrin

They synthesed meso-tetraarylporphyrins from pyrrole and aryl aldehydes in the presence of PCl$_5$, at room temperature using air as an oxidant. Pyrrole and the desired arylaldehyde in the presence of PCl$_5$ react to form tetraarylporphyrins in one pot without the need of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an oxidant. Under these reaction conditions tetraarylporphyrins are formed in 28–65% yield (Scheme 11).
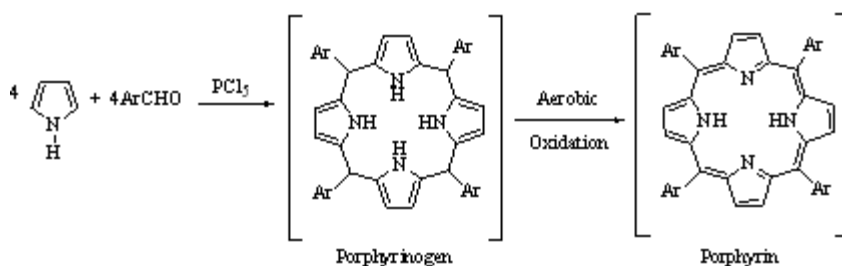
Scheme 11: Preparation of tetraarylporphyrins

Five meso-tetraarylporphyrins (tetraphenyl porphyrin [TPP], 5,10,15,20-tetrakis(4 hydroxyphenyl)- porphyrin [T(4-OH P)P], 5,10,15,20-tetrakis(4-methylphenyl) porphyrin [T(4-Me P)P], 5,10,15,20-tetrakis- (4 chlorophenyl) porphyrin [T(4-Cl P)P] and 5,10,15, 20-tetrakis(4-nitrophenyl)porphyrin [T(4-NO$_2$P)P]) that were synthesized according to above method were used as catalyst. T(4-OHP)P was the most effective catalyst and the reaction was completed in 20 min. In the presence of other derivatives TPP as catalysts, the reaction times for thiocyanation are in the range of 35–50 min. In these reactions a 3–5% of the corresponding thiiranes was also formed, which could easily isolated by column chromatography.

Use of 2,6-bis[2-(o-aminophenoxy)methyl]-4-bromo-1-methoxybenzene (BABMB) as catalyst

In 2003, conversion of epoxides in to 2-hydroxyethyl thiocyanates with NH_4SCN in the presence of 2,6-bis[2-(o- aminophenoxy) methyl] - 4-bromo – 1 - methoxybenzene (BABMB) as a catalyst was described.[32] (Scheme 12)
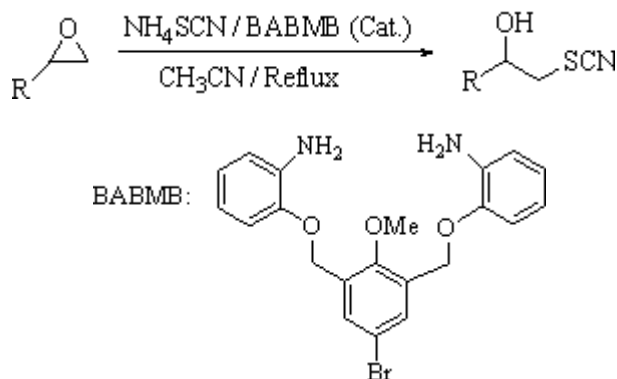
Scheme 12: Ring opening of epoxide in the peresence of BABMB as catalyst

The properties of cyclic crown ethers are approximated by acyclic neutral ligands (podands). Variation of the endo-polarophilicity/exo-lipophilicity balance, complex stability, ion selectivity can often be accomplished more easily, with greater versatility, and at less expense with acyclic polyether than with their cyclic counterparts: complexation and decomplexation are generally faster in an acyclic system and the pesudocavity usually has greater conformational flexibility.[33]The research group found that podand diamino {2,6-bis[2-(o-aminophenoxy)methyl]-4-bromo-1-methoxybenzene (BABMB) efficiently catalyzed the addition of ammonium thiocyanates to epoxide to form 2-hydroxyethyl thiocyanates.

In comparison with previous methods,[19] BABMB is less expensive, have fewer steps needed for the preparation, and has a higher overall yield.

Use of phosphorous (v) tetraphenylporphyrin as catalyst

Sharghi and his groups also described a convenient and efficient procedure for the cleavage of the oxirane rings with ammonium thiocyanates in the presence of phosphorous (v) tetraphenylporphyrin[34] (Scheme 13). Phosphorous (v) porphyrin, with central six-coordinated phosphorus, is both a unique nonmetal porphyrin,[35] and an unusual hypervalent compound with a large ï-electron system.[36-38]
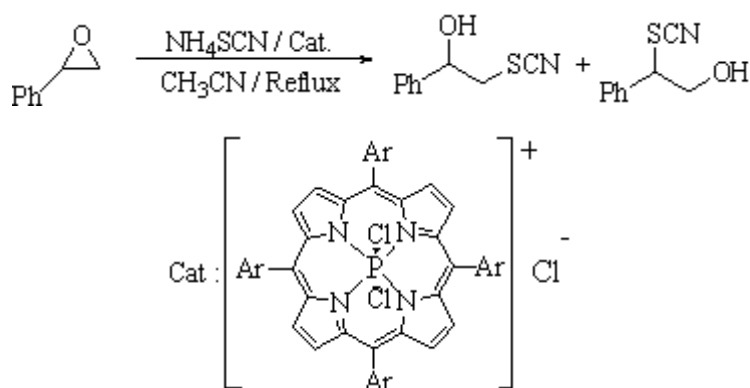
Scheme 13: Reaction of epoxide with NH_4SCN

The results of the reaction of styrene oxide with thiocyanates ion in the presence of the [P(TPP)Cl$_2$]Cl in various solvents are summarized in Table 2.

Table 2: The reaction of styrene oxide with thiocyanates ion in the presence of the [P(TPP)Cl$_2$]Cl in various solvents

Entry	Solvent	Time (min)	Yield of 2 (%)	Yield of 3 (%)
1	CH$_3$CN	22	80	18
2	CH$_3$COCH$_3$	120	8	2
3	CHCl$_3$	100	12	3
4	THF	60	45	10
5	C$_6$H$_6$	100	5	Trace
6	DMF	120	10	2
7	DMSO	80	16	5

The research group found out that the reaction appeared to be largely dependent on the nature of solvent, and CH$_3$CN was the best solvent for this reaction. The cleavage of the styrene oxide with ammonium thiocyanates in CH$_3$CN in the absence of catalyst was checked. Without the catalyst, the reaction required a much longer time. Moreover, undesirable thiirane-formation predominated.[19]

The use of phosphorus porphyrin catalyst resulted in the highest yield of thiocyanohydrin. This was most probably due to the formation of the most stable complexes between NH$_4$SCN and phosphorus porphyrin (i.e., the largest number catalyst sites).

The mechanism of the recent three methods is described in four steps: (Scheme 14)
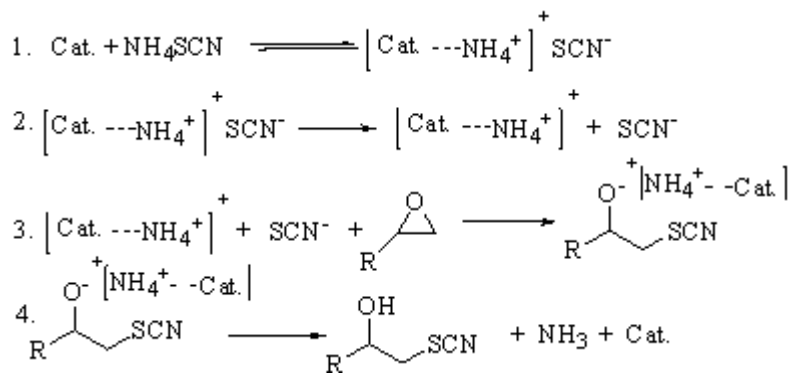
Scheme 14: The mechanism of the recent three methods

Use of Metalloporphyrins as catalyst

Metalloporphyrins have been the subject of many studies because these complexes show wide applicability and were used as the catalyst for a variety of photosensitizers,[39] solar-energy conversion ,[40] redox catalyst,[41-45] hydroxylation and epoxidation of hydrocarbon compounds,[46-49] aziridation of olefins,[50] oxidation of sulfides to sulfones,[51] hydroxylation of aromatic compounds,[52] asymmetric carbon-hydrogen bond formation,[53] oxidative carbonylation of amines,[54] silylation of hydroxyl groups,[55] and ring opening of epoxides.[56-59]

In connection with this trend, Sharghi and coworkers reported the regioselective cleavage of 1,2-epoxyethanes to 2-hydroxyetheyl thiocyanates

with ammonium thiocyanates in the presence of some metal complexes of tetraphenylporphyrins M ^{II} TPP and M^{III}(TPP)Cl [M = Co(II), Ni(II), Cu(II), Zn(II), Mn(II) , Fe(III) and Co(III) and TPP = tetraphenylporphyrin dianion]. The use of Co^{II}T(p-

OHP)P as a catalyst resulted in the highest reaction yield. This is most probably due to the formation of the most stable complexes between NH$_4$SCN and this catalyst.[60] (Scheme 15)
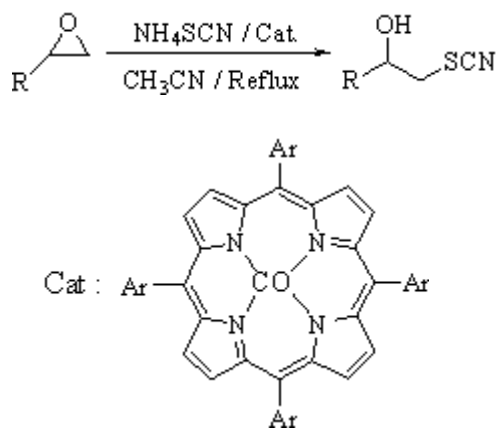
Scheme 15: Use of Metalloporphyrins as catalyst for regioselective ring opening of epoxide

UV-Vis spectral data obviously support the increased reaction yield using this catalyst as well as the predominance of the proposed mechanism in solution (Scheme16).
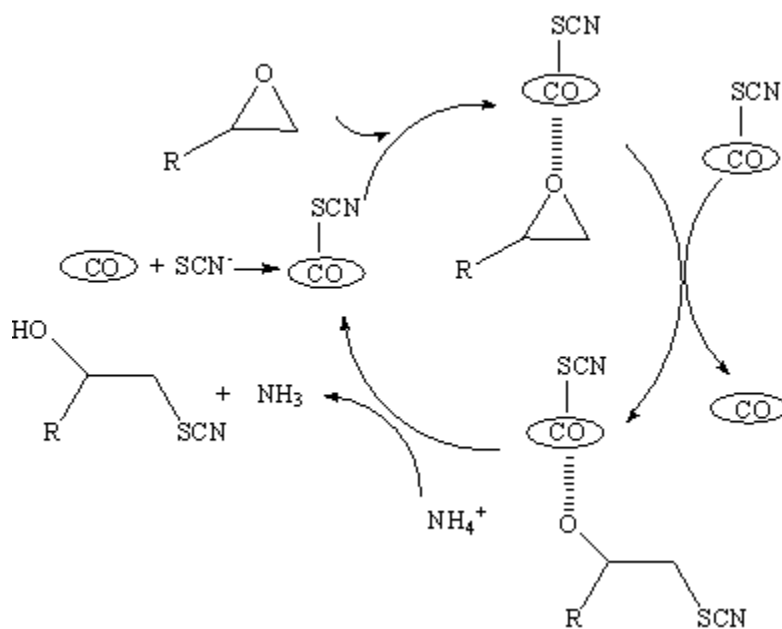
Scheme 16: The proposed reaction mechanism

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 metalloporphyrin complexes, but also by dissociation of the SCN⁻ anion from the adduct and simultaneous activation of epoxide and thiocyanates by two different catalyst molecules.

Use of Selectfluore™ as catalyst

In 2004, it was reported the use of Selectfluore™ as a novel and efficient catalyst for the preparation of β-hydroxy thiocyanates by a regioselective ring opening of epoxides with ammonium thiocyanate under mild conditions.[61] (Scheme 17)
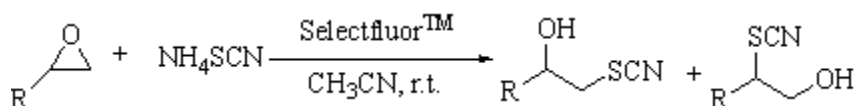
Scheme 17: Use of Selectfluore™ as catalyst for preparation of thiocyanohydrin

Selectfluore™ has been introduced commercially as a user-friendly electrophilic fluorinating agent. Selectfluore™ is readily available at low cost and is easy to handle and also retains its activity even in the presence of amines.[62-63]

The reactivity of several epoxides with ammonium thiocyanate was examined using various Lewis acids such as $CeCl_3.7H_2O$, YCl_3, $TaCl_5$, $InCl_3$, $InBr_3$, $In(OTf)_3$, $Bi(OTf)_3$ and $Sc(OTf)_3$. In most of these cases, thiiranes were obtained exclusively and no β-hydroxy thiocyanate was isolated.

In this reaction selectfluore™ employed as an efficient lewis acid catalyst, and β-hydroxy thiocyanate as the only product.

Use of poly(ethylene glycol)-bound sulfonic acid (PEG-SO_3H) in CH_2Cl_2

Kiasat and coworker have began their studies on the synthesis of β-hydroxy thiocyanates since 2008. Initially they described an efficient and simple method for the transformation of epoxides to the corresponding β-hydroxy thiocyanates using NH_4SCN in the presence of a catalytic amount of poly(ethylene glycol)-bound sulfonic acid, PEG-SO_3H, in high isolated yields.[64] (Scheme 18)
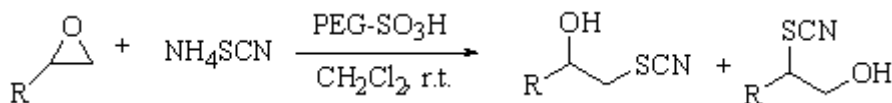
Scheme 18: Regioselective ring opening of epoxide in the presence of PEG-SO_3H

Soluble polymeric supports offer certain advantages over insoluble polymers in terms of ease of analysis and monitoring and, most importantly, the establishment of homogeneous conditions, which are most conducive to bimolecular processes.[65] Polyethylene glycol (PEG) and its derivatives are known to be inexpensive, thermally stable, recoverable, toxicologically innocuous, and environmentally benign media for chemical reactions, [66] as well as having almost negligible vapor pressure.

PEG-SO_3H was prepared[67] by simple mixing of PEG-6000 and chlorosulfonic acid in CH_2Cl_2 (Scheme 19). The reaction is very clean, and the polymeric phase-transfer catalyst can be easily precipitated in ether. The preparation of polymeric catalyst was confirmed by ¹HNMR spectroscopy that the appearance of singlets at 12.85 ppm is due to the proton of SO_3H and d 4.23 ppm for methylene protons in polymer backbone.

$$HO \rightarrow CH_2CH_2O \overset{}{\underset{n}{\rightarrow}} H + ClSO_3H \xrightarrow[\text{Stirr}]{0°C - r.t.} HO_3SO \rightarrow CH_2CH_2O \overset{}{\underset{n}{\rightarrow}} SO_3H$$
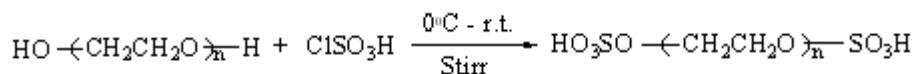
Scheme 19: Preparation of poly(ethylene glycol)-bound sulfonic acid

The efficiency of PEG-SO$_3$H in the conversion of epoxides to β-hydroxy thiocyanates was definitely confirmed by the reaction of styrene oxide with NH$_4$SCN under similar reaction conditions, without adding PEG-SO$_3$H. In this case, the reaction did not complete after 5 h, and only a little thiirane was obtained. Furthermore, this reaction was examined in the presence of PEG instead of PEG-SO$_3$H. TLC analysis showed that the reaction did not complete after 5 h and only a trace amount of β-hydroxy thiocyanate was obtained. Any attempts to prepare thiocyanohydrin by ring opening of styrene oxide with thiocyanate anion in the presence of PEG and sulfuric acid were not successful, and polymerization reaction was occurred. It seems that this polymeric catalyst forms a complex with cation, much like crown ethers, and this complex causes the anion to be activated. In addition, polymeric catalyst probably can be facilitated the ring opening of the epoxide by hydrogen bonding as shown in Scheme 20.
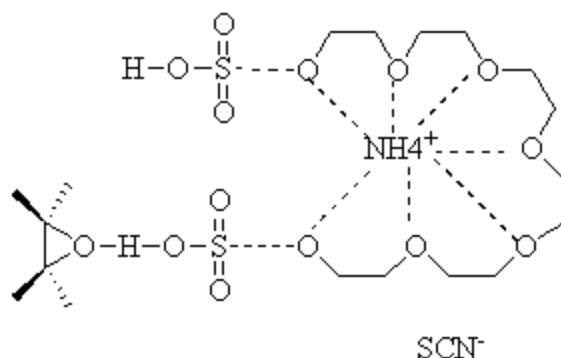
Scheme 20: Anion activation by PEG-SO$_3$H

Compared to some previously reported methods with major or minor drawbacks, several noteworthy features of this reagent are apparent, such as easily workup procedure, operational simplicities, and use of inexpensive reagent.

Use of poly(ethylene glycol)-bound sulfonic acid (PEG-SO$_3$H) in water

In order to develop green chemistry method by using water as a reaction medium,[68-69] kiasat and coworker examined the catalytic ability of PEG-SO$_3$H for conversion of epoxides to β-hydroxy thiocyanates with ammonium thiocyanate in water at room temperature.[70] (Scheme 21)
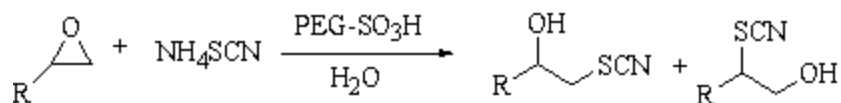
Scheme 21: Preparation of thiocyanohydrin in the presence of PEG-SO$_3$H

This catalyst acted very efficiently, and it was observed that only 0.1 M equivalent of the catalyst is enough to convert different epoxides carrying electrondonating or withdrawing groups to their corresponding β-hydroxy thiocyanates in high isolated yields within 1 h. It is noteworthy that no evidence for the formation of thiirane as by-product of the reaction was observed.

The efficiency of PEG-SO$_3$H as an acidic phase transfer catalyst in the conversion of epoxides to β-hydroxy thiocyanates was definitely confirmed by reaction of styrene oxide with NH$_4$SCN under similar reaction conditions and in the presence of tetrabutylammonium bromide (TBAB) as a nonacidic phase transfer catalyst, or silica sulfuric acid (SSA) and Dowex resin SO$_3$H as a solid acid catalyst. As shown in Table 3, in these cases, the reaction did not complete after 5 h, and was contaminated by diol and thiirane formation. It is worthy to note that attempts for preparation of thiocyanohydrin by ring opening of styrene oxide with thiocyanate anion in the presence of dilute H$_2$SO$_4$ were not successful and the polymerization reaction was occurred. Unfortunately, the use of recycled PEG-SO$_3$H shows a loss in its activity as the yield of ring opening of cyclohexene oxide dropped to a low value (48%).

Table 3: Reaction of styrene oxide with NH$_4$SCN in water

Entry	Catalyst	Time (h)	Result
1	-	5	Not completed (diol + thiirane)
2	TBAB (0.5g)	5	Not completed (diol + thiocyanohydrin)
3	SSA (0.5g)	5	Not completed (diol + thiocyanohydrin)
4	Dowex resin SO$_3$H (0.5g)	5	Not completed (diol + thiocyanohydrin)
5	PEG-SO$_3$H (0.5g)	1	Completed (only thiocyanohydrin)
6	H$_2$SO$_4$	1	Polymerization reaction

SSA: Silica sulfuric acid.

TBAB: Tetrabutyl ammonium bromide.

Use of α,α',α''-N-hexakis(triethyl-ammoniummethylene chloride)-melamine as phase-transfer catalyst

They also decided to apply a multi-site phase-transfer catalyst containing the maximum possible number of active sites for the preparation of β-hydroxythiocyanates by a regioselective ring opening of epoxides with ammonium thiocyanatein in water.[71] (Scheme 22)
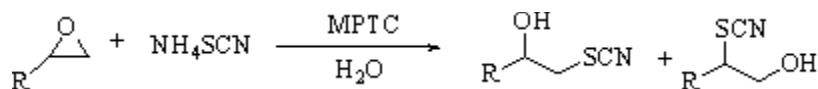
Scheme 22: Regioselective ring opening of epoxide in the presence of MPTC

In 2004, a report by Balakrishnan[72] outlined the preparation of an efficient multi-site phase-transfer catalyst, α,α',α''-N-hexakis(triethyl ammoniummethylene chloride)-melamine. They found that this MPTC catalyst have higher activity than the commercially available single-site phase-transfer catalyst in the alkylation of phenylacetonitrile with 1-bromobutane. Scheme (23) describes the three-step process for the facile preparation of α,α',α''-N hexakis (triethylammoniummethylene chloride)-melamine using inexpensive starting materials.
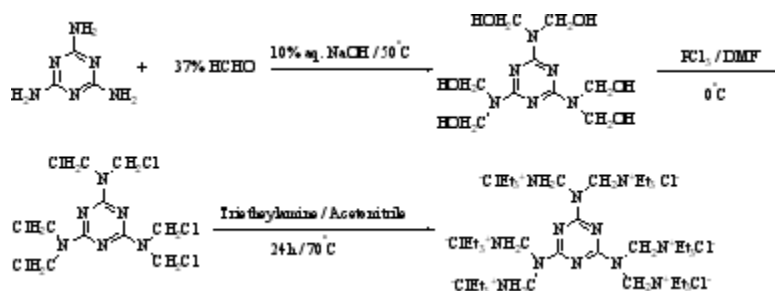
Scheme 23: Preparation of MPTC

In this research, initially, ring opening of phenyl glycidyl ether with NH$_4$SCN was investigated in the presence of α,α,α3 –N- hexakis (triethylammonium-methylene chloride)-melamine in various solvents. TLC analysis of the reaction mixture was clearly shown that in organic solvents and under reflux conditions the reaction did not complete even after 5 h and contaminated by thiirane. Interestingly, the best result was obtained in water as the reaction media. This is not only due to short reaction time and high yield of the obtained β- hydroxythiocyanate, but also due to inhabitation effect of water in the conversion of β-hydroxythiocyanate to the corresponding thiiranes. The obtained results are summarized in Table 4.

Table 4: Efficiency of solvents on the thiocyanation of epoxides.

Entry	Solvent (5mL)	Time (min)	Results
1	CH$_2$Cl$_2$	300	Not completed
2	n-C$_6$H$_{14}$	300	Not completed
3	CH$_3$CN	300	Not completed
4	PEG-400	45	Completed (only thiirane)
5	H$_2$O	15	Completed (only thiocyanohydrin)

The efficiency of α,α',α''-N hexakis (triethylammoniummethylenechloride) - melamine as a multi-site phase transfer catalyst in the conversion of epoxides to β-hydroxythiocyanates in water was definitely confirmed by the reaction of styrene oxide with NH$_4$SCN under similar reaction conditions. This reaction was in the presence of tetrabutylammonium bromide (TBAB) as a single site phase-transfer catalyst, β-podants and polyethylene glycol as an alternative to cyclic crown ethers and cryptands and Dowex resin SO$_3$H as a solid acid catalyst. As shown in Table 5, in these cases, the reaction did not complete after 5 h, and contaminated by diol and thiirane formation.

Table 5: Reaction of styrene oxide with NH$_4$SCN in water under reflux condition

Entry	Catalyst	Time (h)	Result
1	Without catalyst	5	Not completed (diol + thiirane)
2	TBAB (0.5 g)	5	Not completed (diol + thiocyanohydrin)
3	SSA (0.5 g)	5	Not completed (diol + thiocyanohydrin)
4	Dowex resin SO$_3$H (0.5 g)	5	Not completed (diol + thiocyanohydrin)
5	B[PEG-OH]$_3$ (0.5 g)	2	completed (diol + thiirane)
6	MPTC (0.2 mmol)	20 min	Completed (only thiocyanohydrin)

SSA: Silica sulfuric acid.   TBAB: tetrabutyl ammonium bromide.

MPTC: α,α',α' -N-hexakis(triethylammoniummethylene chloride)- melamine.

It should be pointed out that in the absence of catalyst, the reaction was sluggish and a considerable amount of starting material was recovered unchanged and the reaction media was contaminated by diol and thiirane.

Use of N-Thiocyanatosuccinimide (NTS) as reagent

Eventually in 2010, Mokhtari and coworker reported the use of in situ generated N-thiocyanatosuccinimide with NH_4SCN in liquid phase and offer an efficient reagent system for the conversion of epoxides to their corresponding thiocyanohydrines in good to high yields.[73] (Scheme 24)
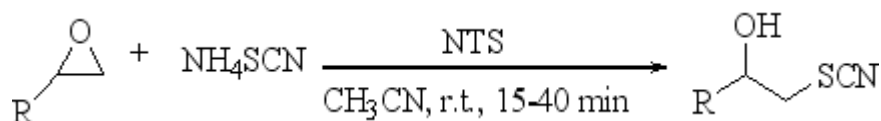
Scheme 24: Use of NTS as catalyst for preparation of thiocyanohydrin

They examined the catalytic ability of $B(HSO_4)_3$ for the conversion of epoxides to corresponding thiocyanohydrins. Therefore, phenyl glycidyl ether was reacted with ammonium thiocyanates in the presence of $B(HSO_4)_3$ in different solvents and under solvent-free condition. The N-Thiocyanatosuccinimide (NTS) is reactive electrophilic sulfur compound which can be simply prepared by the reaction of thiocyanate anion with N-halosuccinimide.[74] Despite the usefulness and high reactivity of NTS there are few reports on the applications of this reagent in organic synthesis including thiocyanation of electron-rich aromatic compounds,[75] ring-expansion thiocyanation of 1,3-dithiolanes and 1,3-dithiones,[76] and a-thiocyantion of N-acyl imides.[77]

Addition of ammonium thiocyanate to an acetonitrile solution of NBS gave NTS in 15 min. Reaction of epoxide with this reagent in the presence of NH_4SCN gave the corresponding thiocyanohydrine.

The following mechanism was suggested for this reaction (Scheme 25).
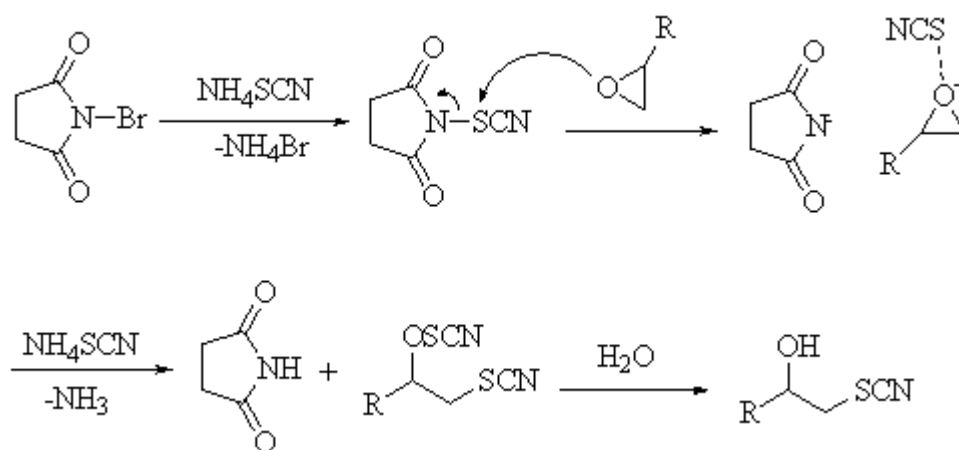
Scheme 25: Proposed reaction mechanism

Reaction in solid phase

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 been appeared to report efficient solvent-free reactions by grinding.[78-80] 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.[81-86] 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.

Use of B(HSO$_4$)$_3$ as solid acid catalyst

In connection with this trend and in continuation of their studies on the synthesis of β-hydroxy thiocyanate, kiasat and coworker described their successful results that led to an extremely convenient method for the transformation of epoxides into the corresponding β-hydroxy thiocyanates using NH$_4$SCN and in the presence of B(HSO$_4$)$_3$ as solid acid catalyst in solvent-free process in high isolated yields.[87] (Scheme 26)
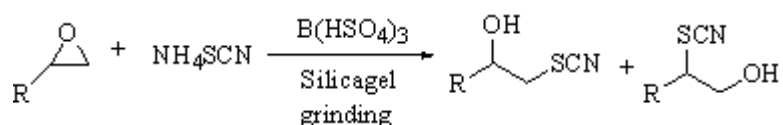

Scheme 26: Preparation of thiocyanohydrin in the presence of B(HSO$_4$)$_3$

Boron sulfonic acid was easily prepared by the addition of chlorosulfonic acid to boric acid under N$_2$ atmosphere at room temperature. This

reaction was easy and clean, because HCl gas was evolved from the reaction vessel immediately (Scheme 27).
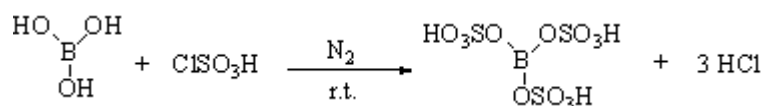
Scheme 27: Preparation of B(HSO$_4$)$_3$

Best result was obtained under solvent-free conditions. The results in Table 6 were clearly shown that although water was the best solvent among those tested. The best result was obtained under solvent-free conditions.

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. 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.

By comparison, numbers of previous methods for the conversion of epoxides to the corresponding thiocyanohydrins are given in Table7. As shown this Table, the recent procedure has higher regioselectivity and shorter reaction time than other methods.

Table 6: Consideration of different conditions for thiocyanation of phenyl glycidyl ether

No.	Solvent	$NH_4SCN/$ mmol	$B(HSO_4)_3$ /mmol	Condition	Time/ min	Conversion	Yield (%) thiocya- nohydrin	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 preparation refers to produced diol.

Table 7: Comparison of thiocyanation of styrene oxide with different methods

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

Use of Dowex as reusable eco-friendly catalyst

In 2008, a convenient and efficient procedure for the regioselective ring opening of epoxides in the presence of Dowex (strongly acidic cationic exchange resin), as reusable eco-friendly catalyst under solvent free conditions was described by kiasat and coworker.[88]

Dowex has been used as an efficient solid acid catalyst in organic synthesis. [89-91]Recently, they have reported the use of Dowex polymer in the protection of carbonyl compounds.[92]In conjunction with the ongoing work on the new methods for the preparation of β-hydroxy thiocyanates, [64, 70] they found that Dowex polymer in the presence of silica gel efficiently catalyzed the addition of ammonium thiocyanate to epoxides to form β-hydroxy thiocyanates with high regioselectivity under solvent free conditions (Scheme 28).
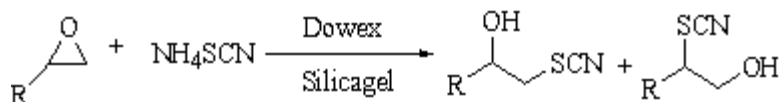
Scheme 28: Regioselectivity in ring opening of epoxides by NH₄SCN

It is notable that no evidence for the formation of thiirane as by-product of the reaction was observed, and the products were obtained in pure form without further purification.

The effect of acidic polymeric catalyst was definitely confirmed by the reaction of styrene oxide with ammonium thiocyanate. In the absence of polymeric catalyst, thiirane was produced as the only product.
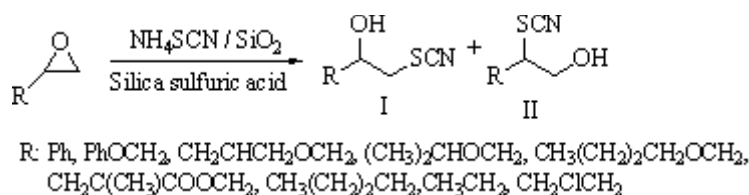
It is worthy to note that the polymeric catalyst can be reused several times without loss of activity. The catalyst (mixture of Dowex and silica gel) recovered by filtering and washing with water and methanol, and then it was reused four times. The catalyst did not show any loss in its activity.

Use of silica sulfuric acid as heterogeneous catalyst

Kiasat and coworker, keeping in mind these facts as well as reports about the successful application of silica sulfuric acid as a stable and efficient heterogeneous catalyst in organic synthesis.[93]This prompted them to explore the potential of this inorganic solid acid as a catalyst for the ring opening of epoxides. They described their successful results that led to an extremely convenient method for the transformation of epoxides into the corresponding β-hydroxy thiocyanate using NH_4SCN supported on silica gel and in the presence of silica sulfuric acid as a catalyst solvent-free process in high isolated yields.[94] (Scheme 29)

R: Ph, $PhOCH_2$, $CH_2CHCH_2OCH_2$, $(CH_3)_2CHOCH_2$, $CH_3(CH_2)_2CH_2OCH_2$, $CH_2C(CH_3)COOCH_2$, $CH_3(CH_2)_2CH_2$, CH_3CH_2, CH_2ClCH_2

Scheme 29: Use of silica sulfuric acid as catalyst for preparation of thiocyanohydrin

Silica sulfuric acid was easily prepared[70] by reaction of silica gel with chlorosulfonic acid. The reaction is very clean, not requiring any work-up procedure because the evolved HCl gas can be removed from the reaction vessel immediately.

NH_4SCN supported on silica gel was prepared by simply co-grinding NH_4SCN with silica gel in an agate mortar. In this simple and efficient method the starting epoxides (1 mmol) were converted to the corresponding β-hydroxy thiocyanates in the presence of supported NH_4SCN on silica gel and silica sulfuric acid.

The inhabitation effect of silica sulfuric acid for the conversion of β-hydroxy thiocyanate to thiirane was definitely confirmed by the reaction of

styrene oxide with NH_4SCN supported on silica gel under similar reaction conditions, without adding silica sulfuric acid. In this case thiirane was obtained exclusively and no β-hydroxy thiocyanate was isolated.

Use of $Al(HSO_4)_3/SiO_2$ as efficient and powerful solid acid catalysts

In 2010, metal hydrogen sulfates and phosphates/silica gel have been studied as an efficient and powerful solid acid catalyst in the ring opening of epoxides with thiocyanate anion.[95] The most significant result was obtained by $Al(HSO_4)_3/SiO_2$ which afforded the corresponding β-hydroxy thiocyanates under mild reaction conditions and in very short reaction times (Scheme 30).
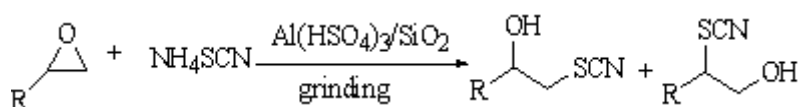
Scheme 30: Regioselective ring opening of epoxide in the presence of $Al(HSO_4)_3/SiO_2$

Metal hydrogen sulfates and phosphates were easily prepared from the corresponding anhydrous metal chlorides and sulfuric or phosphoric acid, respectively.[78,96]The reactions were very clean and did not require a work-up procedure because HCl evolves as a by-product from the reaction vessel immediately (Scheme 31).

$$MCl_n + n\,H_2SO_4 \longrightarrow M\,(HSO_4)_n + n\,HCl$$

$$MCl_n + n\,H_3PO_4 \longrightarrow M\,(H_2PO_4)_n + n\,HCl$$
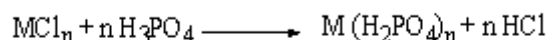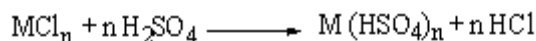
Cat I : Al (HSO$_4$)$_3$; Cat II : Mg(HSO$_4$)$_2$;Cat III : Zn (HSO$_4$)$_2$

Cat IV : Al (H$_2$PO$_4$)$_3$;Cat V : Mg(H$_2$PO$_4$)$_2$; Cat VI : Zn(H$_2$PO$_4$)$_2$

Scheme 31: Preparation of metal hydrogen sulfates

Initially Kiasat and coworker attempted to investigate the possible catalytic properties of these solid acids (I–VI) with simpler systems such as phenyl glycidyl ether with NH$_4$SCN. Under solvent-free conditions, comparative results led them to introduce Al(HSO$_4$)$_3$/SiO$_2$ as the most effective system (Table 8).

Table 8: Comparison of catalytic ability of catalysts

No.	Catalyst	Time (min)	Product
1	Al(HSO$_4$)$_3$/SiO$_2$	5	Thiocyanohydrine
2	Al(H$_2$PO$_4$)$_3$/SiO$_2$	10	Thiocyanohydrine
3	Mg(HSO$_4$)$_2$/SiO$_2$	10	Thiocyanohydrine
4	Mg(H$_2$PO$_4$)$_2$/SiO$_2$	10	(thiocyanohydrin + thiirane)
5	Zn(HSO$_4$)$_2$/SiO$_2$	10	Thiocyanohydrine
6	Zn(H$_2$PO$_4$)$_2$/SiO$_2$	10	Thiocyanohydrine

Use of melamine sulfonic acid (MSA) as catalyst

This research group in continuation of their research reported the regioselective ring opening of epoxides with thiocyanate anion in the presence of melamine sulfonic acid (MSA) as a catalyst at room temperature under solvent-free conditions.[97] (Scheme 32)
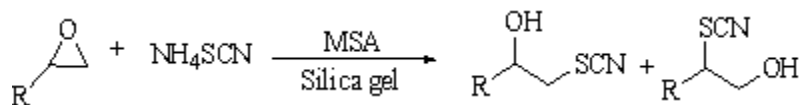
Scheme 32: Ring opening of epoxides to the thiocyanohydrins

As described in (Scheme 33), MSA, a novel and efficient solid acid, was easily prepared by the addition of chlorosulfonic acid to melamine under an N$_2$ atmosphere at room temperature. The reaction was very easy and clean, because the evolved HCl gas can be removed from the reaction vessel immediately. This solid acid was not soluble in water or common polar or nonpolar organic solvents.
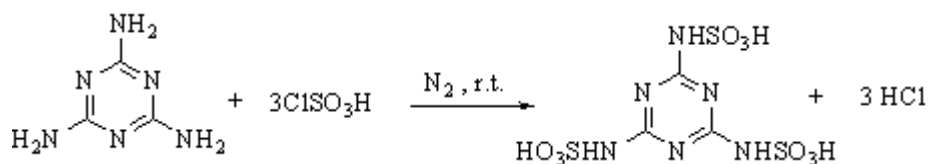
Scheme 33: Preparation of MSA

To ascertain the possible catalytic property of this solid acid, the reaction of 2, 3-epoxypropyl phenyl ether with NH_4SCN in the presence of a catalytic amount of melamine sulfonic acid was studied under solvent-free conditions. This reaction was completed after 3 min and the corresponding thiocyanohydrin was obtained, whereas in the absence of catalyst, this reaction was completed after 10 min and the corresponding thiirane was obtained as the only product (Scheme 34).
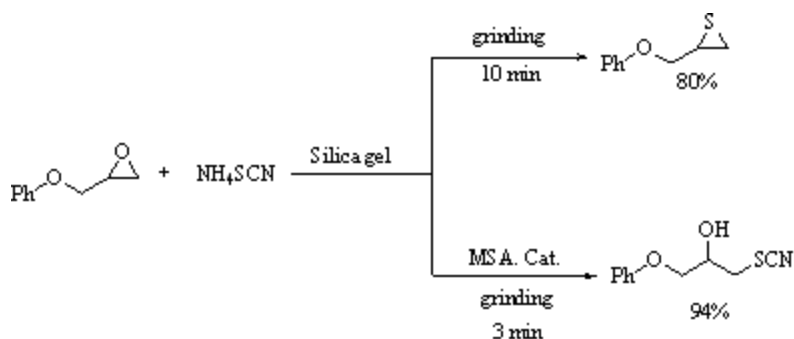
Scheme 34: Ring opening of 2,3-epoxypropyl phenyl ether with and without catalyst

The results of the ring opening of 2,3-epoxypropyl phenyl ether in the presence of MSA using various solvents are summarized in Table 9. The results clearly show that although this reaction proceeded in refluxing acetonitrile, the best result was obtained under solvent-free conditions. The MSA can be stabilized the produced β-hydroxy thiocyanate under solvent-free conditions and without using silica gel, the presence of silica gel for facile grinding of reaction media is necessary.

Table 9: Solvent optimization in the ring opening of 2,3-epoxypropyl phenyl ether (1 mmol) by NH_4SCN (1.5 mmol) in the presence of MSA (0.3 mmol)

No.	Solvent	Time (h)	Result
1	CH_2Cl_2	6	No reaction
2	CH_2Cl_2/ reflux	6	Thiocyanohydrin (60%)
3	H_2O / r.t.	6	Thiocyanohydrin (40%)
4	H_2O/ reflux	1	Thiocyanohydrin + thiirane
5	CH_3CN/ r.t.	6	Thiocyanohydrin (45%)
6	CH_3CN/ reflux	3	Thiocyanohydrin (85%)
7	PEG/r.t.	6	Thiocyanohydrin + thiirane
8	-/ silica gel (0.5 g)	3 mim	Thiocyanohydrin (94%)

By comparison, the obtained results for the conversion of 2,3-epoxypropyl phenyl ether to the corresponding thiocyanohydrin in the presence of acidic catalysts are given in Table 10. As shown in this table, MSA has greater efficiency and shorter reaction time than other catalysts.

Table 10: Comparison of catalytic ability of acidic catalysts in the thiocyanation of 2,3-epoxypropyl phenyl ether under solvent-free condition

No.	Catalyst	Time (min)	Yield (%)
1	MSA	3	94
2	SSA	10	88
3	Dowex	8	85
4	PEG-SO_3H	5	-
5	$B(HSO_4)_3$	4	92
6	$Mg(HSO_4)_2$	10	85
7	$Zn(HSO_4)_2$	10	89
8	$Al(HSO_4)_3$	5	91

They recently reported the synthesis of thiocyanohydrins in the presence of poly(ethylene glycol) (PEG)-SO_3H as an acidic phase-transfer catalyst.[64,70] Unfortunately, the use of recycled PEG-SO_3H resulted in a substantial loss of its activity as the yield of products dropped to a low value. The most ideal synthetic methodology could be defined as a system wherein 100% atom economy is preserved, the catalyst is recycled, and the excess of reagent remains throughout in the medium and does not lose activity for several runs. In this procedure, ring opening of epoxides with NH_4SCN in the presence of catalyst furnished the corresponding thiocyanohydrins in excellent yields. The catalyst, the additional ammonium thiocyanate, and silica gel were conveniently separated from the reaction mixture by simple filtration. The mixture was reused three consecutive times with only a slight variation in the yields of the corresponding products.

The facile nucleophilic ring opening of epoxides with ammonium thiocyanate in the atom economical method is described in (Scheme 35).
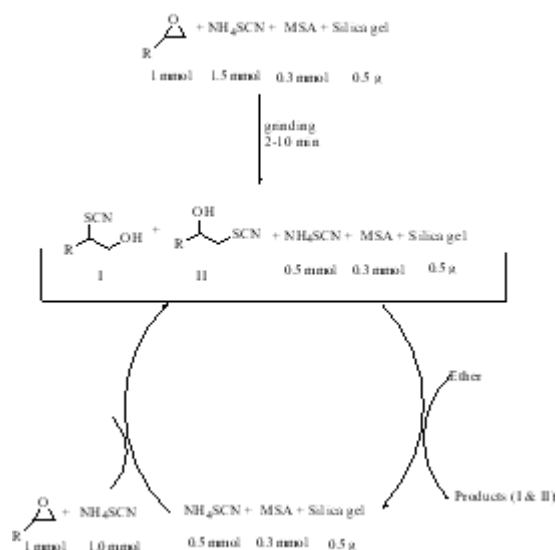
Scheme 35: Facile nucleophilic ring opening of epoxides in the atom economical method

CONCLUSION

In this review, we reported some methods for preparation of β-hydroxy thiocyanates in the liquid and solid phase. By comparing the results, we realized that the reaction in solid phase and use of solid acid as a catalyst is better. Advantages of This method are environmental friendliness, short reaction times, simplicity in the operation catalyst, the low cost of catalyst, high regioselectivity and stereoselectivity, and excellent yields of products. These advantages make this process as an attractive alternative to current methodologies.

ACKNOWLEDGMENTS

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