PAPER

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Metalloporphyrins as new catalysts in the mild, efficient and regioselective conversion of epoxides to β-hydroxy thiocyanates with NH_4SCN

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The regioselective cleavage of 1,2-epoxyethanes to 2-hydroxyethyl thiocyanates with ammonium thiocyanates in the presence of some metalloporphyrins has been studied. The epoxides were subject to cleavage by NH_4SCN in the presence of these catalysts under mild reaction conditions in various aprotic solvents. In this study, reagents and conditions have been discovered with which the individual β-hydroxy thiocyanates (useful intermediates toward biological active molecules) can be synthesized in high yield and with greater than 90% regioselectivity.

Introduction

Epoxides are among the most useful synthetic intermediates towards the synthesis of many biologically active compounds[1] and a large variety of reagents are known for the ring opening of these compounds.[2] The reaction of epoxides with thiocyanate ion has been widely studied and it is a suitable method for the preparation of thiiranes.[3,4] 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, but this intermediate has not been isolated due to its rapid conversion to the corresponding thiirane.

Thiocyanates are important intermediates in agricultural and pharmaceutical chemistry. 2-Hydroxyethyl thiocyanates represent an interesting subclass having multiple modes of reactivity. 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 employed the addition to the 1,2-epoxyethanes of thiocyanic acid generated *in situ* at low temperature.[5] 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.[6,7] Although reagents such as $Ti(O^iPr)_4$,[8] $Ph_3P(SCN)_2$,[9] $TiCl_3$(or $ZnCl_2$),[10] $Pd(PPh_3)_4$,[11] TMSNCS (Cat. TBAF)[12] and PTC[13] are useful, they are limited to specific oxiranes and are not applicable as versatile reagents in the preparation of 2-hydroxyethyl thiocyanates.[12]

In conjunction with ongoing work in our laboratory on the new synthesis of *meso*-tetraarylporphyrins[14] and complex formation of metalloporphyrins with different molecules,[15a] 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 metalloporphyrins wherein high yields are produced with regioselectivity under mild reaction conditions. The efficiency of this process and the stability of the catalyst under the reaction conditions enabled us to understand the pathway of this reaction.

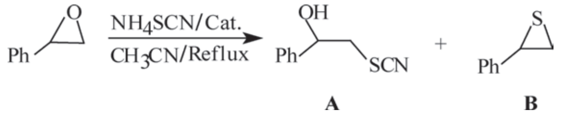
Results and discussion

Metalloporphyrins have been the subject of many studies because these complexes show wide applicability and are now used as the catalysts for a variety of photosensitizers,[16] solar-energy conversion,[17] redox catalysts,[18] hydroxylation and epoxidation of hydrocarbon compounds,[19] aziridination of olefins,[20] oxidation of sulfides to sulfones,[21] hydroxylation of aromatic compounds,[22] asymmetric carbon–hydrogen bond formation,[23] oxidative carbonylation of amines,[24] silylation of hydroxyl groups,[25] and ring opening of epoxides.[15]

Recently we reported new methodologies for synthesis of *meso*-tetraarylporphyrins in good to excellent yields.[14] Then metallation of the porphyrin ligands was achieved by the general method of Adler, Longo *et al.*[26] We disclose here several critical findings that have emerged from this investigation, including the effect of the central metal and groups at the *para* positions of the four phenyls around the porphyrin ring on the catalytic properties of porphyrin in these reaction conditions and the identification of the initially formed intermediate in the ring-opening reaction.

In this study, reactions of styrene oxide with ammonium thiocyanate in the presence of some metal complexes of tetraphenylporphyrin $M^{II}TPP$ and $M^{III}(TPP)Cl$ [M = Co(II), Ni(II), Cu(II), Zn(II), Mn(III), Fe (III) and Co(III) and TPP = tetraphetetraphenylporphyrin dianion] were carried out to examine the effects of the central metal on the catalytic properties of porphyrin in these reaction conditions. To a mixture of styrene oxide (10 mmol) and ammonium thiocyanate (10 mmol) 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 conditions. The reaction product was 2-hydroxy-2-phenylethyl thiocyanate (**2a**) and the yield was determined by GLC and TLC analyses. The results 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. Notably, the yield of thiocyanohydrin is controlled by the variation of catalysts. With $Co^{II}TPP$ the yield of thiocyanohydrin (**A**) is 85% and that of thiirane (**B**) 6% while with other metals the yield of **A** decreases from 70% with NiTPP to 40% with ZnTPP while in the same time, the yield of **B** increases from 16% to 47%. The use of $Co^{II}TPP$ catalyst was most effective, and the reaction was completed in 40 min (entry

Table 1 Reaction times and yields of 2-hydroxy-2-phenylethyl thiocyanate (**A**) and styrene episulfide (**B**) in the reactions of styrene oxide (10 mmol) and ammonium thiocyanate (10 mmol) in the presence of various metallotetraphenylporphyrins (0.1 mmol) in refluxing CH$_3$CN (30 mL)



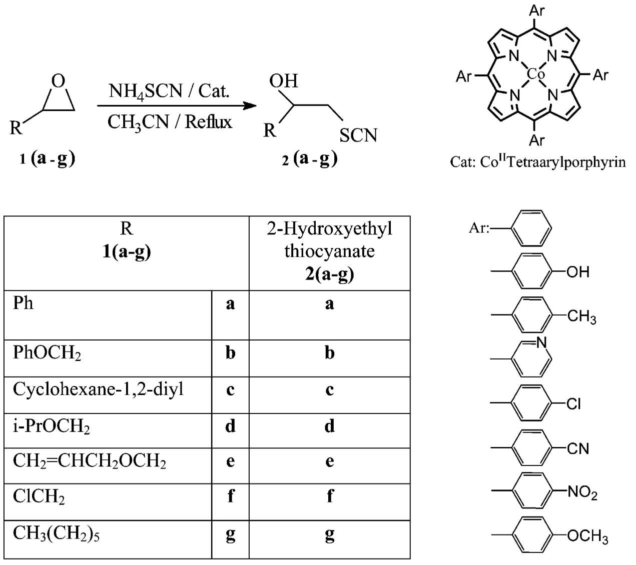
Entry	Catalyst	Time/min	% Yield of **A**[a]	% Yield of **B**
1	Co$^{\mathrm{II}}$TPP	40	85	6
2	Ni$^{\mathrm{II}}$TPP	65	70	16
3	Mn$^{\mathrm{III}}$TPPCl	80	58	30
4	Zn$^{\mathrm{II}}$TPP	120	40	47
5	Cu$^{\mathrm{II}}$TPP	100	53	34
6	Fe$^{\mathrm{III}}$TPPCl	110	50	38
7	Co$^{\mathrm{III}}$TPPCl	90	60	28
8[b]	–	180	–	38

[a] Determined by GC. [b] In the presence of excess of NH$_4$SCN without any catalyst (see ref. 4*f*).

1 in Table 1). In the presence of other catalysts the reaction times for thiocyanation were longer, and the yield of thiocyanohydrin was low. On the other hand, because first-row transition metal complexes of simple tetraarylporphyrins are known to be soluble in common organic solvents, the difference in the activity between the complexes used in this study may instead be attributed to their adducts with ammonium thiocyanate and epoxide in refluxing acetonitrile. A comparison of the cleavage of the styrene oxide with NH$_4$SCN in the absence of a catalyst is given in entry 8 of Table 1. Without a catalyst, the reaction required a much longer time; moreover, undesirable thiirane formation predominated.

Two-valent metalloporphyrin complexes are well-know to be oxidized to their three-valent complexes upon exposure to oxygen.[27] In order to determine whether a three-valent metalloporphyrin complex is also formed in our reactions under study, the Co$^{\mathrm{II}}$TPP complex was exposed to an excess amount of ammonium thiocyanate for an appropriate time. Oxidation did not occur and the Co$^{\mathrm{II}}$-porphyrin complex was isolated intact. It therefore seems that the formation of three-valent cobalt-porphyrin complexes under these conditions is improbable. A comparison of electronic absorption spectra of the recovered Co$^{\mathrm{II}}$TPP complex from a reaction with Co$^{\mathrm{II}}$TPP before the reaction and Co$^{\mathrm{III}}$-tetraphenylporphyrin was also in accord with the above discussion. The catalysts were easily recovered and could be reused several times.

Moreover, due to the conjugation effect, either electron-donating or electron-withdrawing groups at the *para* positions of the four phenyls around the porphyrin ring at the positions 5, 10, 15, and 20 strongly influence the catalytic activities of metalloporphyrins. To obtain information on the catalytic activities, eight kinds of cobalt$^{\mathrm{II}}$-porphyrin catalysts were also examined in the formation of 2-hydroxy-2-phenylethyl thiocyanate (**2a**; Scheme 1). In all of the used catalysts, ring opening of styrene oxide with a thiocyanato group was carried out and the corresponding results are summarized in Table 2. Their catalytic activities were in the sequence of Co$^{\mathrm{II}}$T(*p*-OHP)P > Co$^{\mathrm{II}}$T(*p*-OCH$_3$P)P > Co$^{\mathrm{II}}$T(*p*-ClP)P > Co$^{\mathrm{II}}$T(*p*-CH$_3$P) > Co$^{\mathrm{II}}$TPP > Co$^{\mathrm{II}}$T(*p*-NO$_2$P)P > Co$^{\mathrm{II}}$T(3-Py)P > Co$^{\mathrm{II}}$T(*p*-CNP)P. Rotation of phenyl rings in metal complexes of substituted tetraphenylporphyrins, in comparison to free porphyrins, causes the overlap between the π-systems of the phenyl rings and porphyrin.[28] On the other hand, the main electronic effect of a metal coordinated to a porphyrin is the conjugation of its p$_\pi$ orbital with the π-electrons of the porphyrin ring.[29] Thus, according to the results from Table 1, it seems that the observed trend for Co$^{\mathrm{II}}$T(*p*-ClP)P and Co$^{\mathrm{II}}$TPP correlate with better π-donation of (*p*-Cl)phenyl relative to phenyl. Among the catalysts examined, the use of Co$^{\mathrm{II}}$-tetrakis *para*-hydroxyphenylporphyrin [Co$^{\mathrm{II}}$T(*p*-OHP)P] gave the best results in yield and reaction rate. These results can probably be explained by adduct formation with ammonium thiocyanate and epoxide in refluxed acetonitrile. In these reactions, 3–8% of the corresponding thiiranes was also formed, which could be easily isolated by column chromatography.



R 1(a-g)		2-Hydroxyethyl thiocyanate 2(a-g)
Ph	**a**	**a**
PhOCH$_2$	**b**	**b**
Cyclohexane-1,2-diyl	**c**	**c**
i-PrOCH$_2$	**d**	**d**
CH$_2$=CHCH$_2$OCH$_2$	**e**	**e**
ClCH$_2$	**f**	**f**
CH$_3$(CH$_2$)$_5$	**g**	**g**

Scheme 1

The results of the ring opening of styrene oxide with ammonium thiocyanate by Co$^{\mathrm{II}}$T(*p*-OHP)P 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 and CH$_3$CN is the best solvent for these reaction conditions (entry 1 in Table 3).

To ascertain the scope and limitation of the present reaction, several oxiranes were examined using Co$^{\mathrm{II}}$T(*p*-OHP)P as catalyst; these results are summarized in Table 4. By comparison, a numbers of methods[8–11] for the conversion of oxiranes to the corresponding 2-hydroxyethyl thiocyanates are given in entries 2–5 and 8 of Table 4. In all of the cases listed, the yields increased and the regioselectivities were also enhanced. The optimum amount of the Co$^{\mathrm{II}}$T(*p*-OHP)P as catalyst was found to be 0.01 equiv. *vs.* the oxirane in refluxing acetonitrile.

As shown in entry 7 in Table 4, in which only the *trans* isomer is given, the reactions are completely *anti* stereoselective.

Table 2 Reaction of styrene oxide (10 mmol) with ammonium thiocyanate (10 mmol) in the presence of various Co(II)-tetraarylporphyrins (0.1 mmol) as catalysts in CH$_3$CN (30 mL) under refluxing conditions

Entry	Catalyst	Time/min	% Yield[a]
1	Co$^{\mathrm{II}}$TPP	40	85
2	Co$^{\mathrm{II}}$T(*p*-OHP)P	25	96
3	Co$^{\mathrm{II}}$T(*p*-MeP)P	35	87
4	Co$^{\mathrm{II}}$T(3-Py)P	70	70
5	Co$^{\mathrm{II}}$T(*p*-ClP)P	35	90
6	Co$^{\mathrm{II}}$T(*p*-CNP)P	75	65
7	Co$^{\mathrm{II}}$T(*p*-NO$_2$P)P	60	80
8	Co$^{\mathrm{II}}$T(*p*-OMeP)P	30	92

[a] Determined by GC.

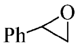
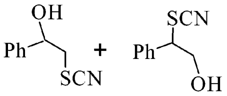
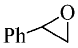
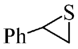
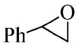
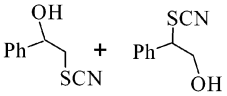
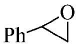
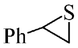
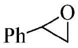
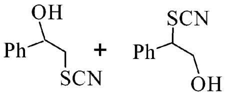
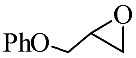
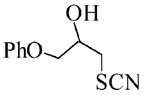
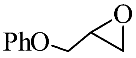
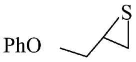
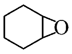
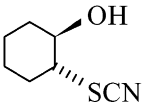
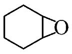
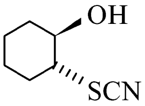
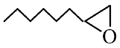
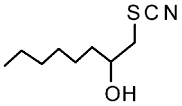
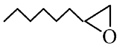
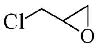
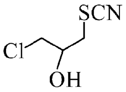
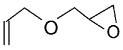
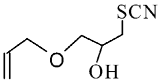
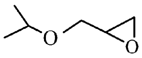
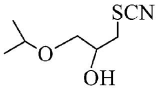
Table 3 Thiocyanate mediated cleavage of styrene oxide in the presence of 0.01 mol Co^{II}T(*p*-OHP)P as catalyst in various solvents

Entry	Solvent	Time/min	% Yield[a]
1	CH_3CN	25	96
2	CH_3COCH_3	65	70
3	$CHCl_3$	120	40
4	Et_2O	50	30
5	THF	60	75
6	C_6H_6	100	15
7	DMF	120	10
8	*t*-BuOH	70	25

[a] Determined by GC.

As for the regioselectivity, an attack of the nucleophile preferentially occurs at the less-substituted oxirane carbon. An *anti*-Markovnikov-type[27] regioselectivity is generally observed in these reactions, except for the reactions of styrene oxide (entry 1 in Table 4), which produced 18% of the other regioisomer; the reactions 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. The mechanism of nucleophile transfer from nucleophile-metal intermediates to organic substrates has stimulated great interest as a result of its relevance to a wide range of important synthetic and biological catalytic pathways.[30]

Table 4 Reaction of epoxides with NH_4SCN in the presence of the represented catalyst

Entry	Oxirane	Catalyst	Reaction conditions	Product(s)	Reaction time/min	% Yield[a]
1		Co^{II}T(*p*-OHP)P[b]	NH_4SCN/CH_3CN reflux/N_2		25	96 (5:1)
2		$Pd(PPh_3)_4$[11]	NH_4SCN/N_2 THF/reflux		120	35
3		Ti(O–^{i}Pr)$_4$[8]	NH_4SCN THF/reflux		240	30
4		$ZnCl_2$[10]	KSCN THF/reflux		180	60
5		DDQ[7]	NH_4SCN/CH_3CN reflux		50	91 (1:8)
6		Co^{II}T(*p*-OHP)P[b]	NH_4SCN/CH_3CN reflux/N_2		30	91
7		Oxalic acid[4f]	NH_4SCN/CH_3CN reflux		105	93
8		Co^{II}T(*p*-OHP)P[b]	NH_4SCN/CH_3CN reflux/N_2		30	94
9		H_2Q[5a]	$KSCN/H_3PO_4$ H_2O/Et_2O		—	48[c]
10		Co^{II}T(*p*-OHP)P[b]	NH_4SCN/CH_3CN reflux/N_2		50	86
11		$Bi(TFA)_3$[4g]	$(NH_2)_2CS/CH_3CN$ reflux		75	77
12		Co^{II}T(*p*-OHP)P[b]	NH_4SCN/CH_3CN reflux/N_2		45	78
13		Co^{II}T(*p*-OHP)P[b]	NH_4SCN/CH_3CN reflux/N_2		40	82
14		Co^{II}T(*p*-OHP)P[b]	NH_4SCN/CH_3CN reflux/N_2		45	85

[a] Determined by GC. [b] 0.01 equiv. *vs*. epoxide. [c] Hydroquinone has been used to stabilize 2-hydroxycyclohexyl thiocyanate (see ref. 5*a*).

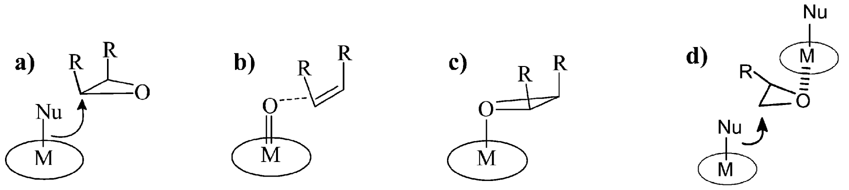


Fig. 1 (a) Nucleophilic delivery. (b) Olefin epoxidation. (c) Lewis acid activation. (d) Catalyst activation of both nucleophile and electrophile.

Given that metalloporphyrin complexes are remarkably effective for the epoxidation of simple olefins,[18,19] 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. 1(c)][18,19] might apply to oxirane activation by a metalloporphyrin complex [*e.g.*, Figs. 1(a) or (b) or (d)].[31,32]

Previously Jacobsen *et al.*[32g] reported a mechanistic proposal for the ring opening of *meso* epoxides with TMS-N_3 catalysed by a (salen)Cr complex involving simultaneous activation of epoxide and azide by two different catalyst molecules. The observation of spectroscopic and regioselectivity data in this work shows that ring opening of epoxide with NH_4SCN in the presence of Co^{II}T(*p*-OHP)P also can be accomplished according to the above mechanism [Fig. 1(d)].

Based on our previous studies[15,33] and other works[32] on the ring opening of oxirane with different nucleophiles in the presence of some metalloporphyrin complexes, a general mechanism is suggested for ring opening with the thiocyanato group of oxiranes, as shown in Scheme 2. While the participation of a metal thiocyanate as the catalytically active species suggests that the mechanism of epoxide ring opening involves thiocyanate delivery from the catalyst, epoxide activation by the Co(II)-porphyrin catalyst is possible, either with or without SCN^- dissociation. It suggests that it can act in either manner. We propose a mechanism involving catalyst activation of both nucleophile and electrophile.

The use of Co^{II}T(*p*-OHP)P as catalyst resulted in the highest reaction yield in the series (Table 2). This is most probably due to the formation of the most stable complexes between NH_4SCN and this catalyst (*i.e.*, the largest number of 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.[34] Sample absorption spectra of Co^{II}T(*p*-OHP)P in the presence of increasing concentration of NH_4SCN are shown in Fig. 2; the resulting stability constants are summarized in Table 5. Fig. 2 shows that the addition of a reagent results in a considerable decreasing absorbance of Co^{II}T(*p*-OHP)P at 532 nm, with an increasing absorbance of 554 nm, accompanied by the creation of a new absorption band at 595 nm. The observation of a clear isobestic point in the spectra supports the occurrence of a simple 1:1 complexation in solution. The data given in Table 5 clearly indicate the formation of the most stable complexes between ammonium thiocyanate and Co^{II}T(*p*-OHP)P in the series. UV-Vis spectra of Co^{II}TPP in the presence of increasing concentration of styrene oxide results in decreasing absorbance of Co^{II}TPP at 410 nm, with an increasing absorbance at 437 nm and an isobestic point at 417 nm (Fig. 3). These obviously support the increased reaction yield with this catalyst as well as the predominance of the proposed 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 metalloporphyrin complexes, but also by dissociation of the SCN^- anion from the adduct and simultaneous activation of epoxide and thiocyanate by two different catalyst molecules.

It is noteworthy that the procedure is quite simple and the reaction conditions are sufficiently mild to work with several sensitive functionalities, and that the metalloporphyrin catalysts can be recycled and reusable.

The critical features of the catalytic mechanism for Co(II)-porphyrin-catalyzed ring opening of epoxides by NH_4SCN have thus been elucidated and reveal an important design principle for this and almost certainly many other, nucleophile-electrophile reactions.

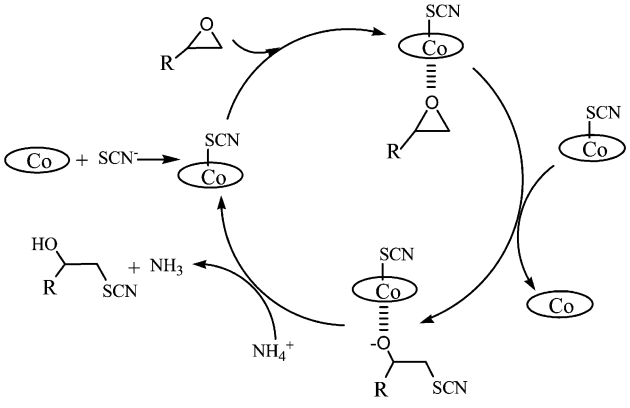
Experimental

General

The metalloporphyrin complexes were prepared by reported procedures, and their spectroscopic and physical data were compared with the literature.[18,19,26] Some 1,2-epoxyethanes and other chemical materials were purchased from Fluka and Merck in high purity.

General procedure for the conversion of 1,2-epoxyethanes to 2-hydroxyethyl thiocyanates using metalloporphyrin complexes as catalyst

To a mixture of the 1,2-epoxyethane (10 mmol) and NH_4SCN (10 mmol, 0.76 g) in acetonitrile (30 mL), a solution of catalyst



Scheme 2

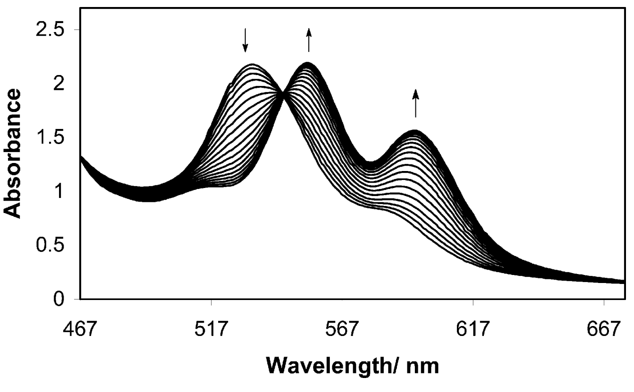


Fig. 2 Absorption spectra of Co^{II}T(*p*-OHP)P as catalyst (3×10^{-4} M) in the presence of different concentrations of NH_4SCN at 25 °C in acetonitrile.

Table 5 The formation constants K for complexation of SCN^- with some Co(II)-tetraarylporphyrins at 25 °C

Catalyst	K/mol^{-1} dm^3
Co^{II}TPP	5.1(±0.1) × 10^2
Co^{II}T(*p*-OHP)P	3.1(±0.05) × 10^3
Co^{II}T(3-Py)P	1. 9(±0.1) × 10^1
Co^{II}T(*p*-ClP)P	8.5(±0.15) × 10^2
Co^{II}T(*p*-NO$_2$P)P	4(±0.2) × 10^2

(0.1 mmol) in CH_2Cl_2 (5 mL) was added and the mixture was stirred under reflux for 20–170 min (in the case of Fe, Co, Mn, Ni, Cu, and Zn 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 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 metalloporphyrin complex was recovered by elution with chloroform–ethyl acetate.

2-Hydroxy-2-phenylethyl thiocyanate (2a)[7,12]. IR (neat): ν SCN (2160 cm^{-1}); ^{1}HNMR (CDCl$_3$, 250 MHz) $\delta = 7.3$ (5H, m), 5.0 (1H, dd), 3.1–3.3 (2H, m), 2.4–2.9 (1H, br s). ^{13}CNMR (CDCl$_3$, 62.9 MHz) $\delta = 135.8$, 129.5, 128.3, 126.2, 113.0, 72.9, 42.4.

3-Phenoxy-2-hydroxypropyl thiocyanate (2b)[7]. IR (neat): ν SCN (2163 cm^{-1}); ^{1}HNMR (CDCl$_3$, 250 MHz) $\delta = 7.27$ (2H, m), 6.92 (3H, m), 5.0 (1H, m), 4.2 (2H, d), 3.64 (2H, d). ^{13}CNMR (CDCl$_3$, 62.9 MHz) $\delta = 158.0$, 130.0, 122.0, 115.1, 114.9, 78.2, 67.2, 33.6.

2-Hydroxycyclohexyl thiocyanate (2c)[7,9]. IR (neat): ν SCN (2165 cm^{-1}); ^{1}HNMR (CDCl$_3$, 250 MHz) $\delta = 2.95$ (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}CNMR (CDCl$_3$, 62.9 MHz) $\delta = 110.0$, 72.0, 55.0, 34.5, 32.5, 30.5, 27.0.

2-Hydroxy-3-isopropoxypropyl thiocyanate (2d)[33b]. IR (neat): ν SCN (2170 cm^{-1}); ^{1}HNMR (CDCl$_3$, 250 MHz) $\delta =$ 3.74 (1H, m), 3.57 (3H, m), 3.33 (2H, d), 3.17 (1H, br s), 1.1 (6H, d, $J = 6$ Hz). ^{13}CNMR (CDCl$_3$, 62.9 MHz) $\delta =$ 114.5, 79.4, 73.2, 67.6, 38.2, 23.0, 22.0.

3-Allyloxy-2-hydroxypropyl thiocyanate (2e)[7]. IR (neat): ν SCN (2158 cm^{-1}); ^{1}HNMR (CDCl$_3$, 250 MHz) $\delta = 5.81$ (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}CNMR (CDCl$_3$, 62.9 MHz) $\delta = 134.2$, 118.0, 117.0, 80.2, 72.9, 69.2, 32.5.

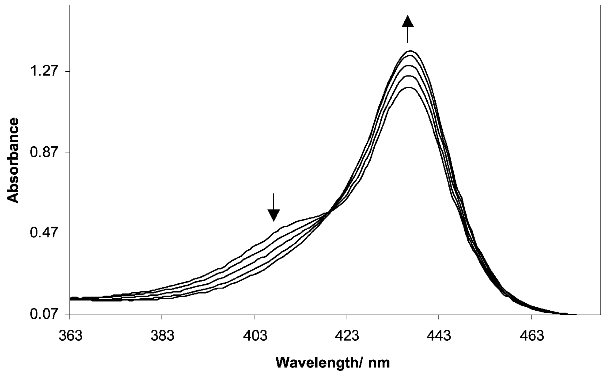


Fig. 3 Absorption spectra of Co^{II}TPP as catalyst (2×10^{-5} M) in the presence of different concentrations of styrene oxide at 25 °C in CHCl$_3$.

3-Chloro-2-hydroxypropyl thiocyanate (2f). IR (neat): ν SCN (2168 cm^{-1}); ^{1}HNMR (CDCl$_3$, 250 MHz) $\delta = 4.1$ (1H, m), 3.7 (4H, m), 2.64 (1H, br s). ^{13}CNMR (CDCl$_3$, 62.9 MHz) $\delta = 117.8$, 71.2, 46.1, 43.4.

2-Hydroxyoctyl thiocyanate (2g). IR (neat): ν SCN (2162 cm^{-1}); ^{1}HNMR (CDCl$_3$, 250 MHz) $\delta = 3.91$ (1H, m), 3.15 (1H, dd, $J = 13$, $J = 3.5$ Hz), 2.95 (1H, dd, $J = 13$, $J = 7.5$ Hz), 2.69 (1H, br s), 1.2–1.6 (10H, m), 0.88 (3H, m). ^{13}CNMR (CDCl$_3$, 62.9 MHz) $\delta = 113.2$, 70.6, 41.5, 36.3, 32.0, 29.4, 25.8, 22.9, 14.4.

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References

1 (*a*) I. Erden, in *Comprehensive Heterocyclic Chemistry*, ed. A. Pawa, Pergamon Press, Oxford, 2nd edn., 1996; (*b*) M. Bartok and K. L. Lang, in *The Chemistry of Heterocyclic Compounds*, eds. A. Weissberger and E. C. Taylor, Wiley, New York, 1985, vol. 42, Part 3, p. 1; (*c*) E. J. Corey, S. Shibata and R. K. Bakshi, *J. Org. Chem.*, 1988, **53**, 2861; (*d*) N. Finney, *Chem. Biol.*, 1998, **4**, R73.

2 (*a*) C. Bonini and G. Righi, *Synthesis*, 1994, 225; (*b*) N. Iranpoor and I. M. Baltork, *Synth. Commun.*, 1990, **20**, 2789; (*c*) M. Shimizu, A. Yoshida and T. Fujisawa, *Synlett*, 1992, 204; (*d*) J. G. Smith, *Synthesis*, 1984, 629.

3 (*a*) M. Sander, *Chem. Rev.*, 1966, **66**, 297; (*b*) K. Jankowski and R. Harvey, *Synthesis*, 1972, 627; (*c*) E. Vedejs and G. A. Krafft, *Tetrahedron*, 1982, **38**, 2857; (*d*) K. Kloc, E. Kubicz and J. Mlochowski, *Heterocycles*, 1984, **22**, 2517.

4 (*a*) B. Tamami and A. R. Kiasat, *Synth. Commun.*, 1996, **26**, 3953; (*b*) N. Iranpoor and F. Kazemi, *Synthesis*, 1996, 821; (*c*) N. Iranpoor and F. Kazemi, *Tetrahedron*, 1997, **33**, 11 377; (*d*) N. Iranpoor and B. Zeynizadeh, *Synth. Commun.*, 1998, **28**, 3943; (*e*) S. Tangestaninejad and V. Mirkhani, *J. Chem. Res., Synop.*, 1999, 370; (*f*) F. Kazemi and A. R. Kiasat, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2003, **178**, 1333; (*g*) I. Mohammadpoor-Baltork and A. R. Khosropour, *Molecules*, 2001, **6**, 996; (*h*) V. Mirkhani, S. Tangestaninejad and L. Alipanah, *Synth. Commun.*, 2002, **32**, 621.

5 (*a*) E. E. van Tamelen, *J. Am. Chem. Soc.*, 1951, **73**, 3444; (*b*) Y. Gao and K. B. Sharpless, *J. Am. Chem. Soc.*, 1988, **110**, 7538; (*c*) K. Kawashima and T. Ishiguro, *Chem. Pharm. Bull.*, 1978, **26**, 951; (*d*) S. A. Vasileva and F. Minnigulov, *Khim. Geterotsikl. Soedin.*, 1997, **8**, 1061.

6 G. Wagner-Jaurgg, *Justus Liebigs Ann. Chem.*, 1948, **561**, 87.

7 N. Iranpoor and G. A. Kohmareh, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1999, **152**, 135.

8 C. Najera and J. M. Sansano, *Tetrahedron*, 1991, **47**, 5193.

9 Y. Tamura, T. Kawasaki and Y. Kita, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1577.

10 A. Olszewski-Ortar, P. Gros and Y. Fort, *Tetrahedron Lett.*, 1997, **38**, 8699.

11 B. M. Choudary, S. Shobha and M. L. Kantam, *Synth. Commun.*, 1990, **20**, 2313.

12 Y. Tanabe, K. Mori and Y. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, 1997, 671.

13 B. Tamami and H. Mahdavi, *Tetrahedron Lett.*, 2002, **43**, 6225.

14 (*a*) H. Sharghi and A. Hasani Nejad, *Helv. Chim. Acta*, 2003, **86**, 408; (*b*) H. Sharghi and A. Hasani Nejad, *J. Chem. Res., Synop.*, 2003, 87; (*c*) H. Sharghi and A. Hasani Nejad, *Tetrahedron*, 2004, **60**, 1863.

15 (*a*) H. Sharghi and H. Naeimi, *J. Chem. Res., Synop.*, 1999, 370; (*b*) A. Robert, O. Dechy-Cabavet, J. Cazelles and B. Meunier, *Acc. Chem. Res.*, 2002, **35**, 167; (*c*) D. Takeuchi, Y. Watanabe, T. Ada and S. Inoue, *Macromolecules*, 1995, **28**, 651; (*d*) T. Aida, *Prog. Polym. Sci.*, 1994, **19**, 469.

16 E. D. Sternberg, D. Dolphin and C. Bruckner, *Tetrahedron*, 1998, **54**, 4151.

17 D. Mauzerall and F. T. Hong, in *Porphyrins and Metalloporphyrins*, ed. K. M. Smith, Elsevier Publishing Company, Amesterdam, Oxford, New York, 1975, p. 701.

18 (*a*) D. Mansuy, *Coord. Chem. Rev.*, 1993, **125**, 129; (*b*) J. Bernadou and A. S. Fabiano, *J. Am. Chem. Soc.*, 1994, **116**, 9375; (*c*) J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, 1983, **105**, 6243; (*d*) J. Lee, J. A. Hunt and T. J. Groves, *J. Am. Chem. Soc.*, 1998, **120**, 6053; (*e*) T. Hirotaka, I. Taketo and Y. Tohru, *Synlett.*, 2003, **4**, 576.

19 (*a*) B. Meunier, E. Guilmet, M. E. De Garvalho and R. Poilblanc, *J. Am. Chem. Soc.*, 1984, **106**, 6668; (*b*) T. G. Traylor, K. W. Hill, W. P. Fann, S. Tsuchiya and B. E. Dunlap, *J. Am. Chem. Soc.*, 1992, **114**, 1308; (*c*) C. L. Hill and C. Schardt, *J. Am. Chem. Soc.*, 1980, **102**, 6375; (*d*) R. Breslow, X. Zhang and Y. Huang, *J. Am. Chem. Soc.*, 1997, **119**, 4535.

20 J. P. Mahy, G. Bedi, P. Battioni and D. Mansuy, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1517.

21 J. H. Ramsben, R. S. Drago and R. Riely, *J. Am. Chem. Soc.*, 1989, **111**, 3958.

22 M. N. Carrier, C. Scheer, P. Gourine, J. F. Bartoli, P. Battioni and D. Mansuy, *Tetrahedron Lett.*, 1990, **31**, 6645.

23 R. Noyori and H. Takaya, *Acc. Chem. Res.*, 1990, **23**, 345.

24 T. W. Leung and B. D. Dombex, *J. Chem. Soc., Chem. Commun.*, 1992, 205.

25 H. Firouzabadi, A. R. Sardarian, Z. Khayat, B. Karimi and S. Tangestaninejad, *Synth. Commun.*, 1997, **27**, 2709.

26 (*a*) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Golldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476; (*b*) A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *Inorg. Nucl. Chem.*, 1970, **32**, 2443.

27 P. B. D. De Lamare and R. Bolton, *Electrophilic Addition to Unsaturated Systems*, Elsevier Scientific, Amsterdam, 1996, p. 132.

28 (*a*) S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, 1975, **97**, 3660; (*b*) M. Meot-Net and A. D. Adler, *J. Am. Chem. Soc.*, 1975, **97**, 5107.

29 (*a*) M. Gouterman, *J. Chem. Phys.*, 1959, **30**, 1139; (*b*) K. S. Suslick and R. A. Watson, *New. J. Chem.*, 1992, **16**, 633.

30 (*a*) *Cytochrome p-450. Structure, Mechanism, and Biochemistry*, ed. P. R. Ortiz de Montellano, Plenum, New York, 2nd edn., 1996; (*b*) M. K. Stern and J. T. Groves, in *Manganese Redox Enzymes*, ed. V. L. Pecoraro, VCH, New York, 1992, ch. 11; (*c*) K. A. Jorgensen, *Chem. Rev.*, 1989, **89**, 431; (*d*) R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401.

31 B. Steiger and F. C. Anson, *Inorg. Chem.*, 2000, **39**, 4579.

32 For discussions, see: (*a*) B. Hansen, L. Leighton and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1996, **118**, 10 924; (*b*) S. Cai, S. Licoccia and F. Ann Walker, *Inorg. Chem.*, 2001, **40**, 5795; (*c*) E. N. Jacobsen, F. Kakiuchi and M. Tokunaga, *Tetrahedron Lett.*, 1997, **38**, 773; (*d*) M. H. Wu and E. N. Jacobsen, *J. Org. Chem.*, 1998, **63**, 5252; (*e*) J. Ready and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1999, **121**, 6086; (*f*) J. Ready and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2001, **123**, 2687; (*g*) L. E. Martinez, J. L. Leighton, D. H. Carsten and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1995, **117**, 5897.

33 (*a*) H. Sharghi and H. Naeimi, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 1525; (*b*) H. Sharghi, M. A. Nasseri and K. Niknam, *J. Org. Chem.*, 2001, **66**, 7287.

34 J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. Trav. Chim.*, 1952, **71**, 1104.