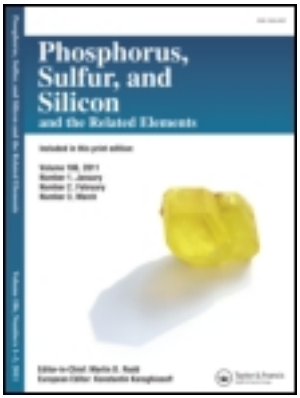

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DICHLORO (5,10,15,20-TETRAPHENYLPORPHYRIN) PHOSPHORUS(V) CHLORIDE AS A NEW CATALYST FOR CONVERSION OF 1,2-EPOXYETHANES TO 2-HYDROXYETHYL THIOCYANATES WITH AMMONIUM THIOCYANATE

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DICHLORO (5,10,15,20-TETRAPHENYLPORPHYRIN) PHOSPHORUS(V) CHLORIDE AS A NEW CATALYST FOR CONVERSION OF 1,2-EPOXYETHANES TO 2-HYDROXYETHYL THIOCYANATES WITH AMMONIUM THIOCYANATE

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

Keywords: Epoxide; porphyrin; thiocyanohydrine

INTRODUCTION

Epoxides or oxirans are versatile intermediates in organic synthesis, and a large variety of reagents are known for the ring opening of these compounds.[1,2] The reaction of thiocyanate ion with epoxides has been widely studied. Synthetic access by oxirane ring opening with thiocyanate ion has been limited by a further reaction to give thiiranes.[3,4] There are two methods reported in the literature for the synthesis of 2-hydroxyethyl thiocyanates. In one method, 2-hydroxyethyl thiocyanates are prepared by opening a cyclic sulfate with NH_4SCN to form the corresponding β-sulfate, which is hydrolyzed to the 2-hydroxyethyl thiocyanates. A second method employs the addition of thiocyanic acid

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generated in situ at low temperature[5] to the 1,2-epoxyethanes. 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 inhibit its conversion to thiirane.[6] Although the reagents, such as Ph_3P $(SCN)_2$,[7] Pd $(PPh_3)_4$,[8] Ti $(O\text{-}iPr)_4$,[9] TMSNCS (Cat. TBAF),[10] and $TiCl_3$ (or $ZnCl_2$),[11] are useful, they are limited to specific oxiranes and are not applicable as versatile reagents in preparation of 2-hydroxyethyl thiocyanates.[10]

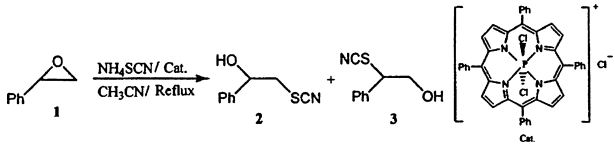
RESULT AND DISCUSSION

Although metalloporphyrins have been recognized as one of the most promising catalysts for various reactions,[12] a literature survey shows that less attention has been paid to the use of nonmetal porphyrins as new catalysts in organic synthesis. Phosphorus(V)porphyrin, with a central six-coordinated phosphorus, is both a unique nonmetal porphyrin[13] and an unusual hypervalent compound with a large π-electron system.[14] The electrochemical behavior, redox chemistry, photochemistry, and structure of phosphorus porphyrins have been reported,[15] and new conducting materials and chemotherapeutic agents have been found.[16]

In conjunction with the ongoing work in our laboratory on the new synthesis of meso-tetraarylporphyrins,[17] complex formation of metalloporphyrins with different molecules,[18] and anion-selective membrane electrodes based on phosphorus(V)porphyrins,[19] we found that phosphorus (V) tetraphenylporphyrin ($[P(TPP)Cl_2]Cl$) efficiently catalyzed the addition of ammonium thiocyanate to oxiranes to form 2-hydroxyethyl thiocyanates with regioselectivity under mild reaction conditions. The results of the reaction of styrene oxide with thiocyanate ion in the presence of the $[P(TPP)Cl_2]Cl$ in various solvents are summarized in Table I. The reaction product was 2-hydroxy-2-phenylethyl thiocyanate, and the yield was determined by GLC and thin layer chromatography (TLC) analyses. We found out that the reaction appeared to be largely dependent on the nature of solvent, and CH_3CN was the best solvent for this reaction. The optimum amount of the catalyst was found to be 0.01 equiv versus epoxides.

As shown in Table I, yield of thiocyanation with this new methodology is quite good and the reaction time is very short. However, the cleavage of the styrene oxide with ammonium thiocyanate in CH_3CN in the absence of catalyst was checked. Without the catalyst, the reaction required a much longer time. Moreover, undesirable thiirane-formation predominated.[20]

TABLE I Thiocyanative Cleavage of Styrene Oxide with NH_4SCN in the Presence of 0.01 mol $[P(TPP)Cl_2]Cl$ in Various Solvents under Reflux Conditions



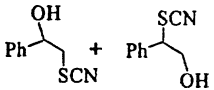
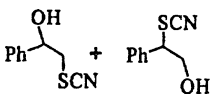
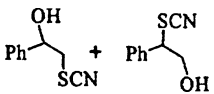
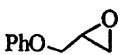
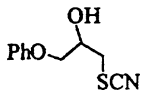
Entry	Solvent	Time (min)	Yield of **2** (%)[a]	Yield of **3** (%)[a]
1	CH_3CN	22	80	18
2	CH_3COCH_3	120	8	2
3	$CHCl_3$	100	12	3
4	THF	60	45	10
5	C_6H_6	100	5	Trace
6	DMF	120	10	2
7	DMSO	80	16	5

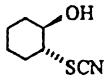
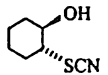
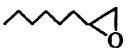
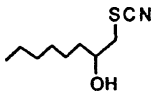
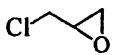
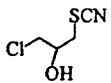
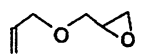
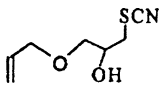
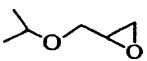
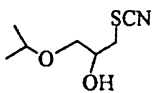
[a]Determined by GC.

To ascertain the scope and limitation of the present reaction, several oxiranes were examined using this catalyst, and these results are summarized in Table II. In these reactions the corresponding thiiranes that also formed (2–7%) could be easily isolated by column chromatography. By comparison, numbers of methods[7–10] for the conversion of oxiranes to the corresponding 2-hydroxyethyl thiocyanates are given in entries 2–5 and 8 (Table II). In all cases listed, when the oxirans were allowed to react with ammonium thiocyanate in the presence of $[P(TPP)Cl_2]Cl$, the yields were increased and regioselectivities were also enhanced. Except for the reactions of styrene oxide (Table II, entry 1) which produces a smal1 percentage (18%) of the other regioisomer, the reaction of other oxiranes was found to be highly regioselective, and only one isomer was obtained. Also in the case of cyclohexene oxide (Table II, entry 7) *trans* product was obtained. As for the regioselectivity, an attack of the nucleophile preferentially occurs at the less-substituted oxirane carbon. 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 use of phosphorus porphyrin catalyst resulted in the highest yield of thiocyanohydrine (Table II). This was most probably due to the formation of the most stable complexes between NH_4SCN and phosphorus porphyrin (i.e., the largest number catalyst sites). In order to obtain a clue about the stability of complexes of ammonium thiocyanate with phosphorus-porphyrin catalyst, a spectrophotometric procedure in an acetonitrile solution was performed.[21] Sample absorption spectra of

TABLE II Reaction of Epoxides with NH_4SCN in the Presence of the Representative Catalyst

Entry	Oxirane	Catalyst (0.01 mol.)	Reaction conditions	Product(s)	Reaction time (min)	Yield (%)[a]
1		$[PTPPCl_2]Cl$	NH_4SCN/CH_3CN Reflux/N_2		22	96 (4:1)
2		$Pd(PPh_3)_4$[8]	NH_4SCN/N_2 THF/Reflux		120	35
3		$Ti(O\text{-}^iPr)_4$[9]	NH_4SCN THF/Reflux		240	30
4		$ZnCl_2$[11]	KSCN THF/Reflux		180	60
5		DDQ[6b]	NH_4SCN/CH_3CN Reflux		50	91 (1:8)
6		$[PTPPCl_2]Cl$	NH_4SCN/CH_3CN Reflux/N_2		30	93

7		$[PTPPCl_2]Cl$	NH_4SCN/CH_3CN Reflux/N_2		20	92
8		H_2Q[5a]	$KSCN/H_3PO_4$ H_2O/Et_2O		—	48[b]
9		$[PTPPCl_2]Cl$	NH_4SCN/CH_3CN Reflux/N_2		40	88
10		$[PTPPCl_2]Cl$	NH_4SCN/CH_3CN Reflux/N_2		35	80
11		$[PTPPCl_2]Cl$	NH_4SCN/CH_3CN Reflux/N_2		40	80
12		$[PTPPCl_2]Cl$	NH_4SCN/CH_3CN Reflux/N_2		45	78

[a]Isolated Yield.
[b]Hydroquinone has been used to stabilize 2-hydroxycyclohexyl thiocyanate (see Tamelen[5a]).

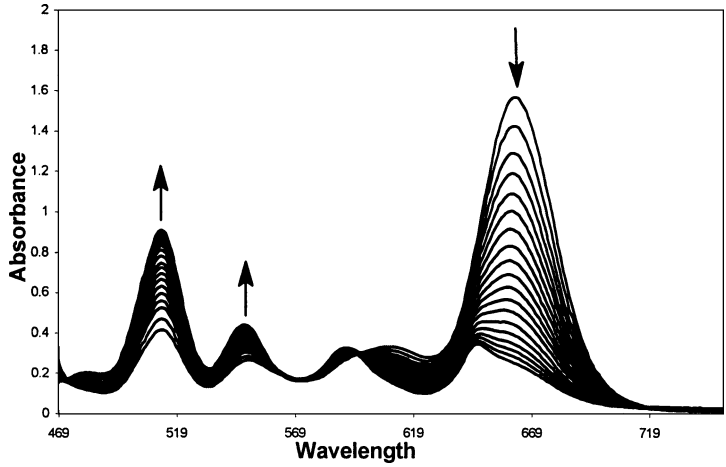


FIGURE 1 Absorption spectra of $[P(TPP)Cl_2]Cl$ as catalyst (5×10^{-4} M) in the presence of different concentrations of NH_4SCN at 25°C in acetonitril.

$[P(TPP)Cl_2]Cl$ in the presence of increasing concentration of NH_4SCN is shown in Figure 1.

Figure 1 shows that the addition of reagent will result in the increasing absorbance of $[P(TPP)Cl_2]Cl$ at 513 and 549 nm, and it will decreasing the intensity of 663 nm bands.

The observation of a clear isosbestic point in the spectra supports the occurrence of a simple complexation in solution. This obviously supports the increased reaction yield with this catalyst. Based on the experimental results, it can be concluded that the reaction rate should be affected not only by complexation of NH_4SCN with phosphorus-porphyrin but also by dissociation of the SCN^- anion from the adduct. It is noteworthy that the operation is quite simple and the reaction conditions are sufficiently mild to operate several sensitive functionalities.

The critical features of the catalytic mechanism for phosphorus(V)-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, nocleophile-electrophile reactions.

EXPERIMENTAL

General

Some 1,2-epoxyethanes and other chemical materials were purchased from Fluka and Merck in high purity. The phosphorus(V)tetraphenylporphyrin was prepared by reported procedures, and their spectroscopic

and physical data were compared with the literature.[13–17] All of the thiocyanohydrin compounds were prepared by our procedure, and their spectroscopic, and physical data were compared with the literature.[6,7,11,20] NMR spectra were recorded in $CDCl_3$ on a Brucker Advanced Dpx-250 (^{1}H NMR 250 MHz and ^{13}C NMR 62.9 MHz) spectrophotometer using TMS as internal standard. UV-vis spectra were obtained with a Philips PU8750 spectrometer. GC spectra were recorded on a Shimadzu GC-14A. Infrared spectra were recorded on a Perkin Elmer IR-157G and a Perkin Elmer 781 spectrometer.

General Procedure for Conversion of 1,2-Epoxyethanes to 2-hydroxyethyl Thiocyanate Using Phosphorus(V)tetraphenylporphyrin as Catalyst

A solution of catalyst (0.1 mmol) in CH_2Cl_2 (5 ml) was added to a mixture of 1,2-epoxyethanes (10 mmol) and NH_4SCN (10 mmol, 0.76 g) in acetonitrile (30 ml), and the mixture was stirred under reflux for 20–60 min. 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, then followed by using C_6H_{12}/CH_2Cl_2 (1:1) for the separation of 2-hydroxyethyl thiocyanate as a pale yellow liquid.

Selected Spectral Data for 2-Hydroxyethyl Thiocyanates[6,7,10,20]

(a) 2-Hydroxy-2-phenylethyl Thiocyanate

IR (neat): ν SCN (2160 cm^{-1}). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 7.3$ (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}). ^{1}H 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}). ^{1}H 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): $\delta = 3.74$ (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): $\delta = 114.5$, 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): $\delta = 5.81$ (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}C NMR ($CDCl_3$, 62.9 MHz): $\delta = 134.2$, 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): $\delta = 4.1$ (1H, m), 3.7 (4H, m), 2.64 (1H, brs). ^{13}C NMR ($CDCl_3$, 62.9 MHz): $\delta =$ 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): $\delta = 3.91$ (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, brs), 1.2–1.6 (10H, m), 0.88 (3H, m). ^{13}C NMR ($CDCl_3$, 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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