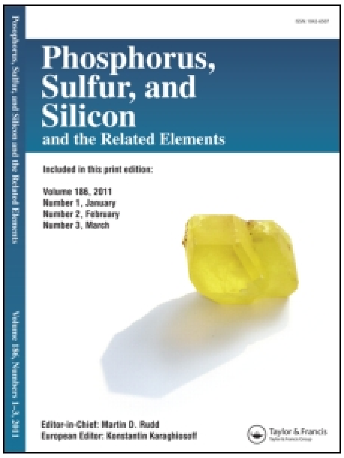


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

DDQ CATALYSES THE CONVERSION OF EPOXIDES TO ß-HYDROXY THIOCYANATES WITH NH_4SCN

Nasser Iranpoor[a]; Gholam Ali Kohmareh[a]
[a] Chemistry Department, Shiraz University, Shiraz, Iran

To cite this Article Iranpoor, Nasser and Kohmareh, Gholam Ali(1999) 'DDQ CATALYSES THE CONVERSION OF EPOXIDES TO ß-HYDROXY THIOCYANATES WITH NH_4SCN', Phosphorus, Sulfur, and Silicon and the Related Elements, 152: 1, 135 — 139

To link to this Article: DOI: 10.1080/10426509908031625

URL: http://dx.doi.org/10.1080/10426509908031625

Phosphorus, Sulfur and Silicon, 1999, Vol. 152, pp. 135-139
Reprints available directly from the publisher
Photocopying permitted by license only

DDQ CATALYSES THE CONVERSION OF EPOXIDES TO ß-HYDROXY THIOCYANATES WITH NH_4SCN

NASSER IRANPOOR* and GHOLAM ALI KOHMAREH

Chemistry Department, Shiraz University, Shiraz 71454, Iran

(Received 04 February, 1999)

2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) catalyses the addition of thiocyante ion to epoxides to afford β-hydroxy thiocyanates in high yields and regioselectivity.

Keywords: 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ); Ammonium thiocyante; Epoxid; β-Hydroxy thiocyanate

INTRODUCTION

Epoxides are important intermediates in organic synthesis[1] and their nucleophilic reactions with different anions[1–7] have been the subject of interest. Among these anions, the reaction of thiocyanate ion and epoxides in the absence or in the presence of a catalyst is a suitable method for the preparation of thiiranes and is widely studied.[8–15] The formation of thiirane 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. We also did not observe the formation of β- hydroxy thiocyanates in the course of our studies for the conversion of epoxides to thiiranes with thiocyante ion in the presence of different catalysts,[13–15] and thiiranes were obtained as the only product. As far as we know, there is only one method reported in the literature for the synthesis of β-hydroxy thiocyanates.[16] In this method, the in situ generated thi-

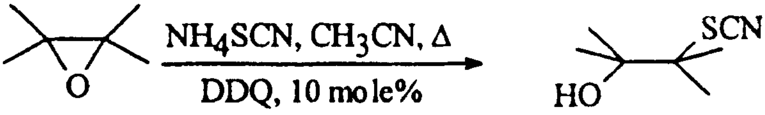
---

* Correspondence Author: (E-mail: iranpoor@chem.susc.ac.ir).

ocyanic acid is added to the epoxide.[16a,b] For this synthesis, it has been reported that the presence of some hydroquinone is required to stabilize the produced β-hydroxy thiocyanate.[16a] This method is limited to the reaction of unsubstituted symmetrical epoxides such as cyclohexene, cyclopentene and ethylene oxides. Their corresponding thiocyanates are obtained in moderate yields.

RESULTS AND DISCUSSION

We have already reported the use of DDQ as catalyst for the alcoholysis of epoxides[17] and thiiranes.[18] In continuation of our investigation on the catalytic activities of DDQ, we studied the possibility of its use as a catalyst for the conversion of epoxides to thiiranes with ammonium thiocyanate, but instead of getting thiiranes, the corresponding β-hydroxy thiocyanates were obtained. In this work we report a novel and efficient method for the addition of thiocyanate ion to the epoxides in the presence of DDQ as catalyst to afford β-hydroxy thiocyanates in high yields (Scheme).

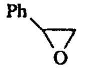
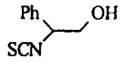
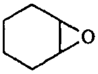
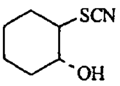
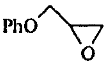
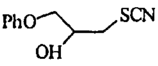
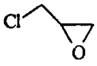
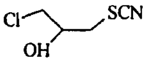
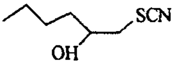
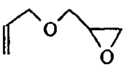
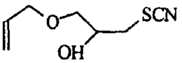


SCHEME

The reactions of different epoxides carrying electron-donating or withdrawing groups with ammonium thiocyanate were performed in refluxing acetonitrile in the presence of 0.1 molar equivalents of DDQ. From these reactions, the corresponding β-hydroxy thiocyanates were obtained in 70 – 90% yield together with the formation of small amounts of the corresponding thiirane (Table I).

Except of the reaction of styrene oxide (Table I, Entry 1) and 1,2-hexene oxide (Table I, Entry 5) which produced 11% and 15% of the other regio isomer respectively, the reaction of other epoxides were found to be highy regiospecific and only one isomer was obtained. In the case of epichloro-

TABLE I Reaction of epoxides with NH_4SCN in refluxing acetonitrile in the presence of 10 mole% of DDQ

Entry	Epoxide	Time (min)	Product	Yield%[a]
1		50		80[b]
2		60		85
3		65		86
4		120		70
5		90		78[b]
6		80		85

[a] Yield refers to isolated product. [b] 11% and 15%of the minor isomer from C_2- attack was also obtained from the reaction of styrene oxide and 1,2-hexene oxide respectively.

hydrine (Table I, Entry 4) where the reaction is relatively slow, 12% of thiirane was also obtained. In other reactions, 3–5% of the corresponding thiiranes was formed which can be easily removed with column chromatography.

The reason for the formation of β-hydroxy thiocyanate instead of thiirane in this reaction is not clear. However as it is reported, that the presence of hydroquinone[16] can stabilize β-hydroxy thiocyanates and inhibit their conversion to thiiranes. In our case, a similar interaction between DDQ and thiocyanate group can stabilize β-hydroxy thiocyanates during the reaction. This interacation is reflected in the UV spectrum of DDQ in the presence of 2-hydroxycyclohexyl thiocyanate.

In conclusion, the simplicity of this new method by using ammonium thiocyanate and DDQ as catalyst, high yield, chemoselectivity and regioselectivity and the possibility of performing the reaction with electron-withdrawing substituted epoxides make this procedure a novel method for the synthesis of alkyl- and functionalized alkyl thiocyanates.

Experimental

Products were characterized by their spectral data. IR spectra were recorded on a Perkin Elmer 781 and Pye Unicam 8725 spectrometers. ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker DPX 250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000EX. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-14A instrument.

Conversion of Cyclohexene Oxide to 2-Hydroxycyclohexyl Thiocyanate

Typical procedure

To a mixture of cyclohexene oxide (1 mmol, 98 mg) and NH_4SCN (3 mmol, 228mg) in acetonitrile (3 ml), DDQ (0.1 mmol, 22.6 mg) was added and the mixture was stirred under reflux condition for 50–120 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 n-hexane for separation of styrene episulfide (4%) followed by using CCl_4/CH_2Cl_2 (1:1) for the separation of 2-hydroxycyclohexyl thiocyanate as a pale yellow viscous liquid (85%), $n^{25}D$ 1.5304 (Lit.[16b] $n^{25}D$ 1.5307).

Selected spectral data: (a) 2-Hydroxycyclohexyl thiocyanate: IR (neat): ν SCN, 2163cm^{-1}; ^{1}H-NMR (DMSO), δ(ppm): 2.95(1H, m), 2.35(1H, m), 2.15 (1H, s), 1.8 (2H, m), 1.65(2H, m), 1.2–1.5(4H, m); ^{13}C-NMR (CCl_4), δ(ppm): 110.0, 72.2, 54.8, 34.9, 32.6, 30.6, 27.1.

(b) 2, Hydroxy, 2-phenyl ethyl thiocyanate: IR (neat): ν SCN, 2160cm^{-1}; ^{1}H-NMR (DMSO), δ(ppm): 7.3 (5h, m), 4.9(1H, dd), 3.95(2H, dd), 3.2(1h, s), ^{13}C-NMR (DMSO), δ(ppm): 137.6, 129.1, 128.6, 126.4, 112.6, 71.3, 63.6.

(c) 3-Allyloxy, 2-hydroxy propyl thiocyanate: IR (neat): ν SCN, 2163cm^{-1}: ^{13}C-NMR (DMSO), δ(ppm): 135.4, 135.0, 116.6, 113.1, 72.5, 71.7, 68.3.

(d) 3-Phenoxy, 2-hydroxy propyl thiocyanate: IR (neat): ν SCN, 2160cm^{-1}, ^{1}H-NMR (DMSO): 7.25(2H, m), 6.85 (3H, m), 4.25(1H, m), 4.0 (2H, m), 3.3(1H, bs), 3.3(1H, dd)), 3.15(1H, dd), ^{13}C-NMR (CCl_4), δ(ppm): 165.6, 137.0, 128.9, 124.6, 119.1, 76.9, 76.1.

Acknowledgements

The authors wish to thank Shiraz University Research Council for partial support of this research.

References

[1] J.G. Smith, *Synthesis* 629, (1984).

[2] N. Iranpoor, F. Kazemi and P. Salehi, *Synthetic Commun.* **27,** 1247 (1997) and the references cited there in.

[3] N. Iranpoor and P. Salehi, *Tetrahedron,* **51,** 909 (1995).

[4] (a) A. Guy, T. Dubuffet, J. Doussot and A. Godefroy-Falguieres, *Synlett* 403 (1991),
(b) A. Guy, J. Doussot, C. Ferroud and A. Godefroy-Falguieres, *Synthesis* 821 (1992).

[5] M. Chini, P. Crotti, and F. Macchia, *Tetrahedron Lett.* **31,** 5641 (1990).

[6] J. A. Ciaccio, C. Stanescu and J. Bontemps, *Tetrahedron Lett.* **33,** 1431 (1992).

[7] M. Chini, P. Crotti, L. Favero and F. Macchia, *Tetrahedron Lett.* **32,** 4775 (1991).

[8] M. Sander, *Chem. Rev.* **66,** 297 (1966).

[9] E. Vedejs, and G. A. Krafft, *Tetrahedron* **38,** 2857 (1982).

[10] K. Kloc, E. Kubicz and J. Mlochowski, *Heterocycles* **22,** 2517 (1984).

[11] K. Jankowski, and R. Harvey, *Synthesis* 627 (1972).

[12] B. Tamami and A. R. Kiasat, *Synthetic Commun.* **26,** 3953 (1996).

[13] N. Iranpoorand F. Kazemi, *Synthesis* 821 (1996).

[14] N. Iranpoor and F. Kazemi, *Tetrahedron* **33,** 11377 (1997).

[15] N. Iranpoor and B. Zeynizadeh, *Synthetic Commun.* **28,** 3913 (1998).

[16] (a) G,Wagner-Jauregg, *Ann.,* ***87,*** 561 (1949),
(b) E. E. van Tamelen, *J. Org. Chem.,* **73,** 3444 (1951).

[17] N. Iranpoor and I. Mohammadpou Baltork, *Tetrahedron Lett.,* **31,** 735 (1990).

[18] N. Iranpoor and J. Owji, *Synthetic Commun.,* **20,** 1047 (1990).