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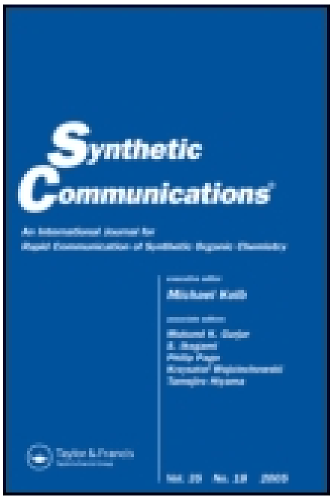

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MILD, EFFICIENT, AND CONVENIENT CONVERSION OF OXIRANES TO THIIRANES WITH AMMONIUM THIOCYANATE AND THIOUREA IN THE PRESENCE OF CERIUM(IV) POLYOXOMETALLATE

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SYNTHETIC COMMUNICATIONS, 32(4), 621–626 (2002)

MILD, EFFICIENT, AND CONVENIENT CONVERSION OF OXIRANES TO THIIRANES WITH AMMONIUM THIOCYANATE AND THIOUREA IN THE PRESENCE OF CERIUM(IV) POLYOXOMETALLATE

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ABSTRACT

Selective conversion of various oxiranes to the corresponding thiiranes in the presence of ammonium thiocyanate and thiourea can be effectively carried out by ammonium decatungestocerate(IV) icosahydrate, $(NH_4)_8[CeW_{10}O_{36}]\cdot 20H_2O$.

Many methods have been already reported in the literature for the preparation of thiiranes.[1,2] The most general one is based on the conversion of oxiranes to their corresponding thiiranes by an oxygen–sulfur exchange reaction. Various sulfurating reagents such as inorganic thiocyanate,[1–4] thiourea,[4–6] phosphine sulfide,[7,8] dimethylthioformamide,[9] 3-methylbenzothiazole-2-thione,[10] silica-gel supported KSCN,[11] and polymer supported

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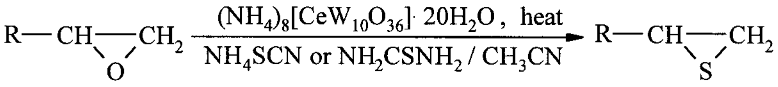
thiocyanate[12] have also been reported for this purpose. In general, all of these reagents suffer from at least one of the following disadvantages: long reaction times, low yields of the products, pH increase of the reaction mixture, formation of polymeric by-products, tedious work-up, requirement for aqueous reaction conditions, and presence of sulfuric and trifluoroacetic acids. Therefore, there is a need to develop and introduce new methods and reagents for the conversion of oxiranes to thiiranes. Recently, conversion of oxiranes to thiiranes with ammonium thiocyanate or thiourea in the presence of ruthenium(III) chloride,[13] bismuth(III) chloride,[14] iron(III) tetrakis-(pentafluorophenyl)porphyrin[15] and tin(IV) *meso*-tetraphenylporphyrin[16] as Lewis acids and ceric ammonium nitrate[17] as a one-electron transfer catalyst have been reported. The chemistry of Ce(IV) oxidation of organic compounds is dominated by radical and radical cations.[17–22] Since the fate of these radical intermediates and the nature of the oxidation can affect the type of the organic products, new Ce(IV) reagents were synthesized and applied for different types of transformations.[18–23] The application of some polyoxometallates as perfect outer-sphere one-electron oxidizing agents for different functional group transformations have been investigated.[24–28]

In this paper, we wish to report that $(NH_4)_8[CeW_{10}O_{36}]\cdot 20H_2O$ can act as a mild and highly effective one-electron transfer heterogeneous catalyst for regio and stereoselective conversion of oxiranes to thiiranes with ammonium thiocyanate and thiourea (Scheme 1).



Scheme 1.

At first, we examined the reaction of epichlorohydrin as a model substrate with ammonium thiocyanate and thiourea in the presence of $(NH_4)_8[CeW_{10}O_{36}]\cdot 20H_2O$ (0.04 molar equivalents) as a catalyst in different refluxing solvents such as dichloromethane, chloroform, carbon tetrachloride, *n*-hexane and acetonitrile. Compared to acetonitrile, longer reaction times and lower yields were observed in all of the other solvents. The results of our study are summarized in Table 1. It is worth mentioning that in cases where an aqueous solvent is used, control of pH is important in order to obtain high yields and to avoid polymerization of thiiranes. In this method, no water is required and thiiranes are obtained in excellent yields without any polymerization.

Table 1. Conversion of Oxiranes to Thiiranes with Different Refluxing Solvents/ $(NH_4)SCN$ or NH_2CSNH_2

		Yield%[a,b] (Time/h)	
Entry	Solvents	NH_4SCN	NH_2CSNH_2
1	Acetonitrile	98 (0.5)	95 (1)
2	Dichloromethane	31 (0.5)	27 (1)
3	Chloroform	17 (0.5)	15 (1)
4	Carbon tetrachloride	46 (0.5)	40 (1)
5	*n*-Hexane	38 (0.5)	36 (1)

[a] The product was characterization by comparison with known sample.
[b] Yields refer to product.

As shown in Table 2, different aliphatic and cyclic oxiranes react rapidly with ammonium thiocyanate and thiourea in the presence of 0.04 molar equivalents of ammonium decatungestocerate(IV) icosahydrate, $(NH_4)_8[CeW_{10}O_{36}]\cdot 20H_2O$, in refluxing acetonitrile affording the corresponding thiiranes in excellent yields. It is important to note that in the absence of catalyst, thiocyanate and thiourea were much less efficient in conversion of oxiranes to thiiranes in refluxing acetonitrile.

In conclusion, we have shown that $(NH_4)_8[CeW_{10}O_{36}]\cdot 20H_2O$ is a mild and convenient catalyst for the efficient conversion of oxiranes to thiiranes in the presence of ammonium thiocyanate and thiourea. In addition, high yields, short reaction times and easy work-up make this method a useful and important addition to the modern organic synthetic methodologies.

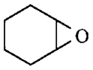
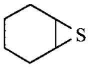
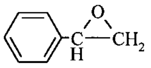
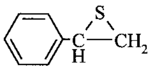
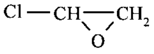
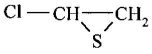
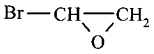
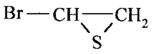
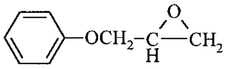
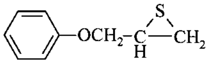
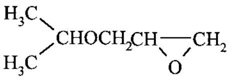
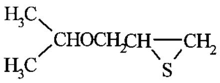
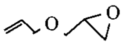
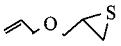
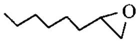
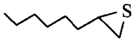
EXPERIMENTAL

All chemicals used were reagent grade. The ammonium decatungestocerate(IV) icosahydrate was prepared according to the literature.[29,30] Products were characterized by comparison of their physical data, IR and NMR spectra with those of authentic samples.[9,18,31,32]

General Procedure for the Conversion of Epichlorohydrin to Thiiranes in Different Refluxing Solvents

A mixture of epichlorohydrin (1 mmol), ammonium thiocyanate (0.152 g, 2 mmol) or thiourea (0.152 g, 2 mmol) and $(NH_4)_8[CeW_{10}O_{36}]\cdot 20H_2O$ (0.04 mmol) in different solvents (5 ml) was stirred under reflux

Table 2. Conversion of Oxiranes to Thiiranes with Ammonium Decatungestocerate (IV)/$(NH_4)SCN$ or NH_2CSNH_2 in Refluxing CH_3CN

			Yield (%)[a,b] (Time/h)	
Entry	Substrate	Product	NH_4SCN	NH_2CSNH_2
1			96(3.5)	86(2)
2			94(3)	98(1.5)
3	 $\mathrm{Cl{-}\underset{O}{CH{-}CH_2}}$	 $\mathrm{Cl{-}\underset{S}{CH{-}CH_2}}$	98(0.5)	95(1)
4	 $\mathrm{Br{-}\underset{O}{CH{-}CH_2}}$	 $\mathrm{Br{-}\underset{S}{CH{-}CH_2}}$	94(0.5)	94(1)
5			88(1)	96(1)
6			98(1)	96(1)
7			98(1)	95(1)
8			94(1.5)	81(1.5)

[a] All products were identified by comparison of their physical and spectral data with those of authentic samples.

[b] Yields refer to isolated products.

conditions. The progress of the reaction was monitored by GLC. The catalyst was removed by a silica-gel column (1 : 1 hexane–ethyl acetate). Evaporation of the solvent, followed by chromatography on silica-gel gave the product in 15–98% yields (Table 1).

General Procedure for the Conversion of Oxiranes to Thiiranes with Ammonium Thiocyanate

$(NH_4)_8[CeW_{10}O_{36}]\cdot 20H_2O$ (0.04 mmol) was added to a solution of oxirane (1 mmol) and ammonium thiocyanate (0.152 g, 2 mmol) in acetonitrile

(5 ml). The mixture was stirred for a specified time and reflux according to Table 2. The progress of the reaction was monitored by GLC. After completion of the reaction, the mixture was passed through a silica-gel column (1 : 1 hexane–ethyl acetate) to remove the catalyst. The eluate was concentrated under reduced pressure and chromatographed on a silica-gel column to give a pure product in 88–98% yields, without any polymerization by-products.

General Procedure for the Conversion of Oxiranes to Thiiranes with Thiourea

In a round-bottomed flask (25 ml) equipped with a condenser and magnetic stirrer, a solution of oxirane (1 mmol) in CH_3CN (5 ml) was prepared. Thiourea (0.152 g, 2 mmol) and $(NH_4)_8[CeW_{10}O_{36}]\cdot 20H_2O$ (0.04 mmol) were added to this solution and the mixture was stirred magnetically under reflux conditions. After completion of the reaction (monitored by GLC), the mixture was directly passed through a short column of silica-gel (1 : 1 hexane–ethyl acetate) to remove the catalyst. The eluate was evaporated under reduced pressure and the crude product was obtained in a quantitative yield. Distillation of the product under reduced pressure, afforded the corresponding thiirane in 81–98% yields, without any polymerization by-products.

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