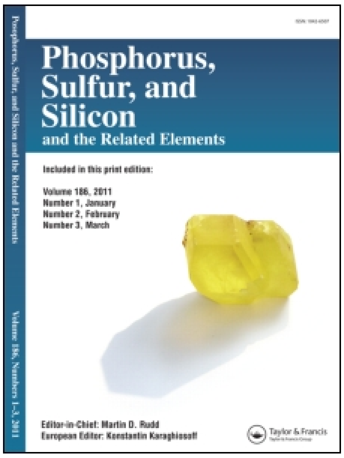

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Facile Conversion of Epoxides to Thiiranes with Ammonium Thiocyanate Catalyzed with Oxalic Acid

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FACILE CONVERSION OF EPOXIDES TO THIIRANES WITH AMMONIUM THIOCYANATE CATALYZED WITH OXALIC ACID

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Epoxids are efficiently converted to the corresponding thiiranes by ammonium thiocyanate (NH_4SCN) in the presence of catalytic amounts of oxalic acid with excellent isolated yields under mild and nonaqueous reaction conditions. This conversion performed under both conventional heating and microwave conditions. Distinct rate enhancement is observed under microwave irradiation.

Keywords: Ammonium thiocyanate; epoxide; microwave irradiation; oxirane; thiirane

Thiiranes are probably the most interesting class of cyclic sulfides both from a theoretical and synthetically point of view.[1] They serve as useful precursors for the synthesis of olefins[2] and other functional group moieties,[3] and so their synthesis is of fundamental interest. Various methods already have been proposed in the literature for the synthesis of these heterocyclices.[4–20] The most efficient route reported so far is based on the conversion of oxiranes into the corresponding thiiranes by an oxygen-sulfur exchange reaction. Sulfur introducing agents such as inorganic thiocyanates,[4,5] thiourea,[5] phosphine sulfides,[6] 3-methylbenzothiazol-2-thione,[7] dimethylthioformamide,[8] silica gel supported KSCN,[9] and polymer supported thiocyanate[10] have been used for this purpose. Most of these reagents suffer from disadvantages such as relatively long reaction times, low yields of the products, increase in pH of the reaction media, requirement of aqueous reaction conditions and drastic reaction conditions required to generate the thiolate ion, so that accurate conditions control is necessary to avoid extensive decomposition and/or polymerization of the formed thiirane.

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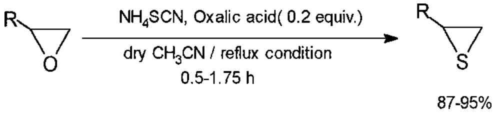
Recently, interest in the development of effective catalysts for the mild conversion of epoxide to thiirane has prompted reports of many catalysts,[11–19] which are effective in accomplishing this transformation.

In continuation of our studies for the conversion of oxiranes to thiiranes,[15–19] we now report conditions whereby various types of thiiranes can be conveniently synthesized in high isolated yields from the corresponding oxiranes under mild nonaqueous reaction conditions by ammonium thiocyanate in the presence of catalytic amounts of oxalic acid.

RESULTS AND DISCUSSION

We examined the catalytic ability of oxalic acid for conversion of epoxides to thiiranes with ammonium thiocyanate in dry acetonitrile under reflux conditions. This catalyst acted very efficiently and it was observed that only 0.2 molar equivalent of the catalyst is required to convert epoxides to their corresponding thiiranes (Eq. 1) in excellent yields within 0.5–1.75 h.

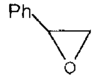
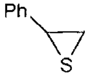
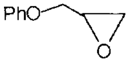
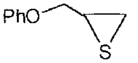
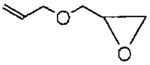
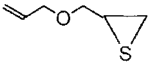
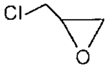
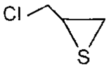
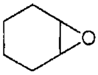
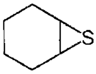


The effects of other solvents such as CCl_4, CH_2Cl_2, n-hexane, and t-butanol also were studied, but in comparison with acetonitrile the reaction times were longer and the yields were considerably lower. With this approach, different types of epoxides are converted to the corresponding thiiranes as exclusive and virtually pure products according to TLC and ^{1}HNMR. The obtained results are summarized in Table I.

The promoting effect of oxalic acid was definitely confirmed by reaction of styrene oxide with ammonium thiocyanate under similar reaction conditions, without adding oxalic acid. It is observed that in the absence of oxalic acid, ammonium thiocyanate was much less efficient and GC and TLC analysis of the reaction mixture show only trace amount of styrene sulfide as product.

Microwave heating and its application in organic chemistry for a variety of reactions have been developed successfully, and in the past few years there have been a tremendous amount of interest in this area. Remarkable decrease in reaction times and, in some cases, clean reaction and better yields have been reported with microwave irradiation.[20–21] Therefore, it seemed interesting to complete this work by studying the reactivity of this catalyst for the conversion of epoxides to their corresponding thiiranes with ammonium thiocyanate in dry acetonitrile under microwave irradiation.

TABLE I Conversion of Epoxides to Thiiranes[a] with NH_4SCN Catalyzed with Oxalic Acid (0.2 eq) in Dry Acetonitrile

			Thermal		Microwave	
Entry	Substrate	Product	Time (min)	Yield%[b]	Time (min)	Yield%[b]
1			80	95	3	93
2			105	93	8	92
3			60	87	5	94
4			45	89	3	90
5			30	90	4	89

[a] Products were identified by comparison of their physical and spectral data with those of authentic samples.
[b] Isolated yield.

As shown in Table I, we have found a distinct rate enhancement under microwave conditions where reactions were completed in just 3–8 min as compared to a few hours (0.5–1.75 h) under conventional heating. The experimental procedure is very simple and involves stirring the solution of oxirane (1 mmol) in acetonitrile (5 ml) with ammonium thiocyanate (2 mmol) and oxalic acid (0.2 mmol) under reflux condition for a few hours or irradiating in a microwave oven for a few minutes.

The advantage of using oxalic acid as catalyst for the synthesis of thiiranes using ammonium thiocyanate is shown by comparing our results with those previously reported in the literature (Table II). Contrary to the previous reports, our procedure, especially under microwave conditions, provides good yields of thiiranes in a comparatively short reaction time.

CONCLUSION

We believe that the present protocols offer mild, simple, and efficient methods for the preparation of thiiranes from oxiranes. In addition, availability of the reagent and catalyst, high yields and short reaction times make this method a useful addition to the present methodologies.

TABLE II Comparison of Some Results Obtained from the Reaction of Epoxides with SCN in the Presence of Oxalic Acid with Those Reported from Other Methods

Method	Styrene Oxide Time/Cond./Yield (min) (%)	Phenyl Glycidyl Ether Time/Cond./Yield (min) (%)	Cyclohexene Oxide Time/Cond./Yield (min) (%)
I	3/MW/95	8/MW/92	4/MW/89
II	80/△/95	105/△/93	30/△/90
III	180/△/72	—	2400/r.t/73
IV	—	—	1200/ /65
V	270/△/93	900/△/85	840/△/82
VI	45/r.t/95	20/r.t/95	30/r.t/92
VII	60/r.t/98	90/△/95	45/△/93

I = The present method (microwave heating).
II = The present method (Conventional heating).
III = SCN^- anion has been used without a catalyst.[4]
IV = Silica gel has been used as catalyst.[9]
V = Polymer supported thiocyanate has been used.[10]
VI = CAN has been used as catalyst.[15]
VII = $RuCl_3$ has been used as catalyst.[6]

EXPERIMENTAL

General

IR spectra were recorded on a Shimadzo 450 spectrophotometer, ^{1}HNMR spectra in $CDCl_3$ on a Bruker Avance DPX instrument (250 MHz). Products were characterized by comparison of their physical data, IR, and ^{1}H NMR spectra with known samples. All yields refer to isolated products. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. Microwave reactions were carried out in Butane made domestic microwave oven operating at 200 watt.

General Procedure for the Conversion of Oxiranes to Thiiranes Under Conventional Heating

In a round-bottom flask (25 ml) equipped with a condenser and a magnetic stirrer, a solution of epoxide (1 mmol) in dry CH_3CN (5 ml) and ammonium thiocyanate (0.152 g, 2 mmol) was prepared. Then, oxalic acid (0.018 g, 0.2 mmol) was added to the solution and the reaction mixture was stirred magnetically under reflux condition for the appropriate time according to Table I. The progress of the reaction was monitored by TLC. To the reaction mixture, 10 ml of water was added and the mixture was extracted with $CHCl_3$ (2 × 10 ml). Evaporation of the solvent followed by chromatography on a short column of silica gel (elut: CCl_4) gave the pure products in 87–95% isolated yields.

General Procedure for the Conversion of Oxiranes to Thiiranes Under Microwave Irradiation

Ammonium thiocyanate (0.152 g, 2 mmol), oxalic acid (0.018 g, 0.2 mmol), and 5 ml of dry CH_3CN were placed in a Pyrex round-bottomed flask (25 ml) equipped with a reflux condenser (reflux condenser was outside the microwave oven). Epoxide (1 mmol) was added to the resulting mixture which was then irradiated in a commercial microwave oven (200 W) for 3–8 min. The progress of the reaction was monitored by TLC. To the reaction mixture, 10 ml of water was added and the mixture was extracted with $CHCl_3$ (2 × 10 ml). Evaporation of the solvent followed by chromatography on a short column of silica-gel (elut: CCl_4) gave the pure products in 89–94% isolated yields.

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