

Efficient conversion of epoxides to episulfides with thiourea catalysed with cerium(IV)[†]

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Efficient conversion of epoxides into episulfides with thiourea in the presence of ceric ammonium nitrate (CAN) as catalyst and under mild and non-aqueous conditions is reported; this conversion was performed under both conventional heating and microwave conditions and distinct rate enhancement was observed under microwave irradiation.

Keywords: epoxides, episulfides, thiourea, cerium(IV)

Episulfides, a most interesting class of cyclic sulfides, serve as useful precursors for the synthesis of olefins,¹ by phosphine or phosphite mediated desulfurizations, and other functional group moieties² and so their synthesis is of fundamental interest. There are many methods reported in the literature for synthesis of these heterocycles³⁻¹⁰ and the most general one involves oxiranes as convenient starting materials and inorganic thiocyanates or thiourea as sulfur introducing reagents.⁷⁻¹⁵

Application of oxiranes as convenient starting materials and thiourea as the sulfur introducing agent for this conversion was reported under wet conditions (solvent free) or in aqueous ethanol⁷, but the reactions suffer from long reaction times, low yield and the occurrence of the desulfuration of obtained episulfide to olefin in some cases. Recently, application of poly(4-vinylpyridine)-Ce(OTf)₄,¹² tin(IV) mesotetraphenylporphyrin,¹³ TiO(CF₃CO₂)₂,¹⁴ TiCl₃(CF₃SO₃)¹⁴ and RuCl₃¹⁵ as catalysts for this conversion has been reported.

In continuation of our ongoing programme to develop synthetic protocols for the conversion of epoxides into episulfides,^{8-10, 15-17} we now wish to report conditions whereby various types of thiranes can be conveniently synthesised from the corresponding oxiranes under mild non-aqueous reaction conditions by thiourea in the presence of catalytic amounts of cerium(IV), as ceric ammonium nitrate (CAN), in high isolated yields.

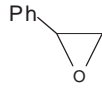

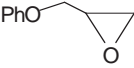
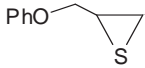
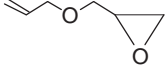
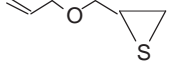
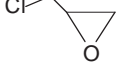
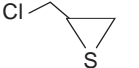


The reaction of styrene oxide with thiourea in the presence of 0.2 molar equivalents of CAN was studied in different solvents such as CCl₄, CH₂Cl₂, *n*-hexane, *t*-butanol and acetonitrile. The best solvent for this conversion was found to be acetonitrile. In this solvent, the reaction was complete after 1.7 hours under reflux conditions and GC analysis showed the quantitative formation of styrene sulfide. Under similar conditions, when styrene oxide was reacted with thiourea in the absence of the catalyst, GC and TLC analysis of the reaction mixture did not show the formation of any product after 2h.

With this approach, different types of epoxides are converted into the corresponding thiranes as exclusive and virtually pure products according to TLC and ¹HNMR analysis. The results obtained are summarised in Table 1.

In reports where an aqueous solvent has been used, control of pH is important to obtain a high yield of episulfides without polymerisation.³ Our procedure provides an excellent yield of episulfides in a comparatively very short time, without formation of any polymeric by product and no water is required as co-solvent.

The wide applicability of microwave irradiation¹⁸ in organic reaction enhancement encouraged us to carry out the reactions under microwave irradiation. We have observed a distinct rate enhancement under microwave conditions where reactions were completed in just 2-7 min as compared to the few hours

Table 1 Conversion of epoxides to episulfides^a with thiourea catalyzed with CAN (0.2 eq) in dry acetonitrile

Entry	Substrate	Product	Thermal		Microwave		Bp/°C/Torr Found (reported)
			Time/min	Yield% ^b	Time/min	Yield% ^b	
1			100	93	4	93	85-87/5(85-86/5) ¹³
2			150	89	7	94	104-105/8(113/13) ⁹
3			80	95	3	90	77-78/8(78-79/8) ⁹
4			60	90	3	92	59-60/30(60-61/30) ¹³
5			45	86	5	89	52-54/7(54-55/7) ¹³

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

^a Products were identified by comparison of their physical and spectral data with those of authentic samples.

^b Isolated yield.

(0.75–2.5 h) required under conventional heating (Table 1). The experimental procedure is very simple and involves stirring the solution of oxirane (1mmol) in acetonitrile (5 ml) with thiourea (2 mmol) and CAN (0.2 mmol) under reflux condition for a few hours or irradiating in a microwave oven for few minutes.

Although the exact mechanism of the reaction is not clear, on the basis of our previous observations on the reaction of Ce(IV) with epoxides and especially thiiranes and a recent report on the use of Ce(IV) as CAN for deprotection of the *tert*-butoxycarbonyl group, the possibility of one electron transfer reaction between epoxide and Ce(IV) cannot be ruled out.¹⁹

The advantage of using CAN as catalyst for the synthesis of thiiranes using thiourea is shown by comparing our results with those previously reported in the literature (Table 2). Contrary to the previous reports, our procedure, especially under microwave conditions, provides good yield of thiiranes in comparatively short reaction times.

In conclusion this catalytic method can be applied for conversion of different classes of epoxides into their corresponding episulfides. Excellent yields, short times, simple work-up and mild reaction conditions make this method a useful addition to the present methodologies.

Table 2 Comparison of some results obtained from the reaction of epoxides with thiourea in the presence of CAN with those reported from other methods

method	Styrene oxide	Phenyl glycidyl ether	Cyclohexene oxide
	Time/Cond./Yield /min %	Time/Cond./Yield /min %	Time/Cond./Yield /min %
I	4/MW/93	7/MW/94	5/MW/89
II	100/Δ/95	150/Δ/89	45/Δ/86
III	NR	NR	1920/r:t/40
IV	80/Δ/85	300/Δ/92	108/Δ/55
V	600/r:t/45	—	—
VI	1080/r:t/98	—	—
VII	45/Δ/95	45/Δ/95	45/Δ/93

- I. The present method (microwave (MW) heating).
 - II. The present method (Conventional heating).
 - III. The thiourea has been used without catalyst in aqueous solvent.³
 - IV. TiO (TFA)₂ has been used as catalyst.¹⁴
 - V. The thiourea has been used without catalyst in ethanol.⁷
 - VI. The thiourea has been used without catalyst in solvent free condition.⁷
 - VII. Sn(IV)(Tpp)(ClO₄)₂ has been used as catalyst.¹³
- NR = no reaction

Experimental

IR spectra were recorded on a Shimadzo 450 spectrophotometer, ¹H NMR spectra in CDCl₃ on a Bruker Avance DPX instrument (250 MHz). Products were characterised by comparison of their physical data, IR and ¹H 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 a Butane made domestic microwave oven operating at 200 W.

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 CH₃CN (5 ml) and thiourea (0.152 g, 2 mmol) was prepared. Then, CAN (0.110 g, 0.2 mmol) was added to the solution and the reaction mixture was stirred magnetically under reflux conditions for the appropriate time according to Table 1. 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 CHCl₃ (2 × 10 ml). Evaporation of the solvent followed by chromatography on a short column of silica gel (eluent: *n*-hexane) to give the pure products in 86–95 % isolated yields.

General procedure for the conversion of oxiranes to thiiranes under microwave irradiation: Thiourea (0.152 g, 2 mmol) and CAN (0.110g, 0.2 mmol) was taken in a Pyrex round-bottomed flask (25 ml) equipped with a reflux condenser (the reflux condenser was outside the microwave oven) containing 5 ml of dry CH₃CN. Epoxide (1 mmol) was added to the resulting mixture and then irradiated in a commercial microwave oven (200W) for 3–7 minutes. 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 CHCl₃ (2 × 10 ml). Evaporation of the solvent followed by chromatography on a short column of silica-gel (eluent: *n*-hexane) to give the pure products in 89–94% isolated yields.

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