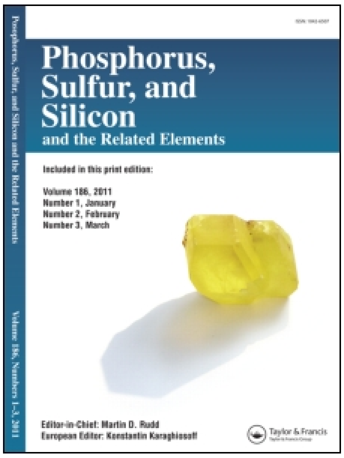

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Solvent-Free Conversion of Epoxides to Thiiranes by Thiourea/NH_4Cl System

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Solvent-Free Conversion of Epoxides to Thiiranes by Thiourea/NH_4Cl System

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Epoxides were readily converted to the corresponding thiiranes by thiourea/NH_4Cl system under solvent-free conditions. The reactions were completed within 15–75 min at 60–70°C. The thiiranes were obtained in 65–96% yields.

Keywords Ammonium chloride; epoxide; solvent-free; thiirane; thiourea

INTRODUCTION

Thiiranes are the simplest sulfur heterocycles and occur in nature. They are of interest from both theoretical and synthetic point of view and are used in polymer, pharmaceutical, pesticide and herbicide industries.[1] Thiiranes are prepared by various methods.[2] However, the most straight forward synthesis is the conversion of epoxides to thiiranes by an oxygen-sulfur exchange reaction. This transformation has been achieved by several sulfur transfer agents such as thiourea,[3] inorganic thiocyanates,[4] phosphine sulfides,[5] dimethylthioformamide/CF_3CO_2H,[6] S/NH_4OAc/$(EtO)_2POH$,[7] P_4S_{10}/NH_4OAc/Al_2O_3[8] and 3-methylbenzothiazole-2-thione.[9] Moreover, some of these sulfurating agents in combination with different reagents/catalysts such as ceric ammonium nitrate,[10] $RuCl_3$,[11] $BiCl_3$,[12a] $Bi(TFA)_3$, $Bi(OTf)_3$,[12b] $TiO(O_2CCF_3)_2$, $TiCl_3(O_3SCF_3)$,[13] $InBr_3$,[14] β-cyclodextrin,[15] $Sn(TTP)(OTf)_2$,[16] 2,4,6-trichloro-1,3,5-triazine,[17] $Mg(HSO_4)_2$,[18] TiO_2,[19] SiO_2 supported KSCN,[20] polymer supported thiocyanates,[21] poly(4-vinylpyridine) supported $Ce(OTf)_4$,[22] polystyrene supported $AlCl_3$,[23] poly(vinylamine) or poly(allylamine),[24] and (bmim)PF_6/H_2O[25] have been used for the

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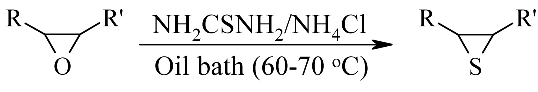
conversion of epoxides to thiiranes. However, most of these methods suffer from long reaction times, use of organic solvents, acidic, moisture sensitive or expensive reagents/catalysts, tedious work-up procedures, formation of polymeric by-products and low yields.

The toxic and volatile natures of many organic solvents, particularly of chlorinated hydrocarbons, which are widely used in organic synthesis, have posed serious threats to the environment. Consequently, methods that successfully minimize the use of solvents have attracted much attention. Working without solvents has the advantage of a simpler process and smaller plants, and eliminates the energy costs of removal, recycling and eventual disposal of waste solvents.[26]

As a part of our research program on the synthesis of thiiranes, we report here the efficient conversion of epoxides to thiiranes by the thiourea/NH_4Cl system at 60–70°C under solvent-free conditions (Scheme 1).

RESULTS AND DISCUSSION

A survey of the literature shows that the solvent-free conversion of epoxides to thiiranes with thiourea has been achieved by thiourea supported on silica gel[27a] and by thiourea at 120°C.[27b] Although these methods provide green protocols for the preparation of thiiranes from epoxides, they suffer from high reaction temperature (120°C) or moderate yields (65–88%), however. Because the solvent-free conversion of epoxides to thiiranes in the presence of ammonium salts has not been investigated yet, this idea encouraged us to study the influence of NH_4^+ ions on the transformation of epoxides to thiiranes. In a preliminary experiment the reaction of phenyl glycidyl ether as a model compound with 2 molar equivalents of thiourea (as sulfur transfer agent) and $(NH_4)_2CO_3$ (0.5 g) was carried out at 60–70°C under solvent-free conditions. The epoxide was converted to the corresponding thiirane in 80% yield within 2.5 h. The influence of NH_4^+ ions in other ammonium salts was studied by performing the reaction in the presence of NH_4NO_3, NH_4OAc, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, NH_4I, and NH_4Cl. The summarized results in Table I showed that all the ammonium salts had a capability to promote the



R, R': Aryl, alkyl, allyl, H

SCHEME 1

TABLE I Optimization Experiments for the Conversion of Phenyl Glycidyl Ether to the Corresponding Thiirane under Different Conditions

Molar ratio	Ammonium salts (g)	Condition[a]	Time (h)	Conversion (%)
EPOXIDE/thiourea (1:2)	$(NH_4)_2CO_3$ (0.5)	Solvent-free/oil bath	2.5	80
EPOXIDE/thiourea (1:2)	NH_4NO_3 (0.5)	Solvent-free/oil bath	2	95
EPOXIDE/thiourea (1:2)	NH_4OAc (0.5)	Solvent-free/oil bath	3	85
EPOXIDE/thiourea (1:2)	$(NH_4)_2SO_4$ (1)	Solvent-free/oil bath	2.5	80
EPOXIDE/thiourea (1:2)	$(NH_4)_2HPO_4$ (1)	Solvent-free/oil bath	4	85
EPOXIDE/thiourea (1:2)	NH_4I (0.5)	Solvent-free/oil bath	1.3	95
EPOXIDE/thiourea (1:2)	NH_4C1 (0.5)	Solvent-free/oil bath	1.3	100
EPOXIDE/thiourea (1:2)	NH_4C1 (1)	Solvent-free/oil bath	2.5	90
EPOXIDE/NH_4SCN (l:2)	NH_4C1 (0.5)	Solvent-free/oil bath	1.3	70
EPOXIDE/thiourea (1:2)	NH_4C1 (0.5)	CH_3CN/reflux	3	20
EPOXIDE/thiourea (1:2)	NH_4C1 (0.5)	Solvent-free/microwave	5 min	5

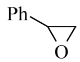
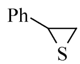
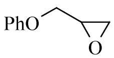
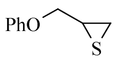
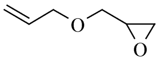
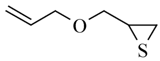
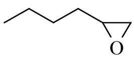
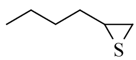
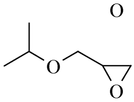
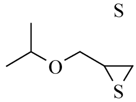
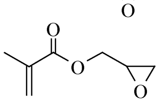
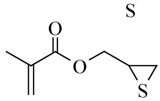
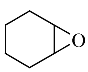
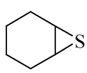
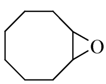
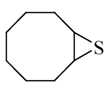
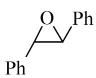
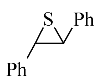
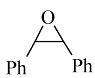
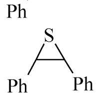
[a]Temperature of oil bath was 60–70°C.

conversion of phenyl glycidyl ether to the corresponding thiirane with a yield above 80%. Among them NH_4NO_3, NH_4I and NH_4Cl showed the best efficiency. The shorter reaction time and the complete conversion of phenyl glycidyl ether to the respective thiirane prompted us to select NH_4Cl as the best promoter for this transformation (Table I). Thiourea under the same reaction conditions showed the better efficiency than NH_4SCN as a sulfur transfer reagent (Table I).

Next, we investigated the influence of NH_4Cl under the optimized conditions on the conversion of mono or disubstituted epoxides to thiiranes bearing electron donating or electron withdrawing groups. Aryl, alkyl, allyl and sterically hindered epoxides reacted smoothly with thiourea to produce the corresponding thiiranes in good to excellent yields (65–96%). The reactions were completed within 30–55 min. Table II clearly indicates the scope and generality of this synthesis. In the case of cyclohexene epoxide, the reaction with thiourea gave the thiirane in a poor yield; however, NH_4SCN showed a better efficiency (Table II). In order to highlight the efficiency of our synthetic method, we compared some of our results with those of achieved by thiourea/silica gel[27a] and thiourea/120°C[27b] (Table III). The results show, that our protocol is more efficient than the reported methods. The exact mechanism of this synthesis is not known. A possible mechanism is presented in Scheme 2.

In conclusion, we have shown that structurally different epoxides are easily and efficiently converted to the corresponding thiiranes with the NH_2CSNH_2/NH_4Cl system under solvent-free conditions. The

TABLE II Conversion of Epoxides to Thiiranes in the Presence of NH_4Cl under Solvent-Free Conditions[a]

Epoxide	Thiirane	Time (min)	Yield (%)[b]	Mp or Bp (°C)/mm Hg Found	Mp or Bp (°C)/mm Hg Reported
		30	95	85–86/5	85–86/5[23]
		75	94	105–106/1	106/1[28]
		15	93	77–78/8	78–79/8[23]
		55	95	43–44/0.16	43/0.16[23]
		30	96	55/11	54/11[28]
		35	94	—	—
		40	65[c]	55/7	55–56/7[23]
		35	92	71–72/2	71/2[29]
		45	96	53–54	53–54[30]
		40	94	76–77	77–78[30]

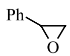
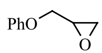
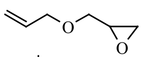
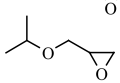
[a]All reactions were carried out with the molar ratio of epoxide:thiourea (1:2) in the presence of NH_4Cl (0.5 g) in an oil bath at 60–70°C. [b]Yields refer to isolated pure products. [c]In this reaction NH_4SCN was used as sulfur transfer reagent.

cheapness and availability of the reagents, the mild reaction conditions, the high yields of the thiiranes, the simple work-up procedure as well as the advantages of working under solvent-free conditions make this method a useful addition to the present methodologies.

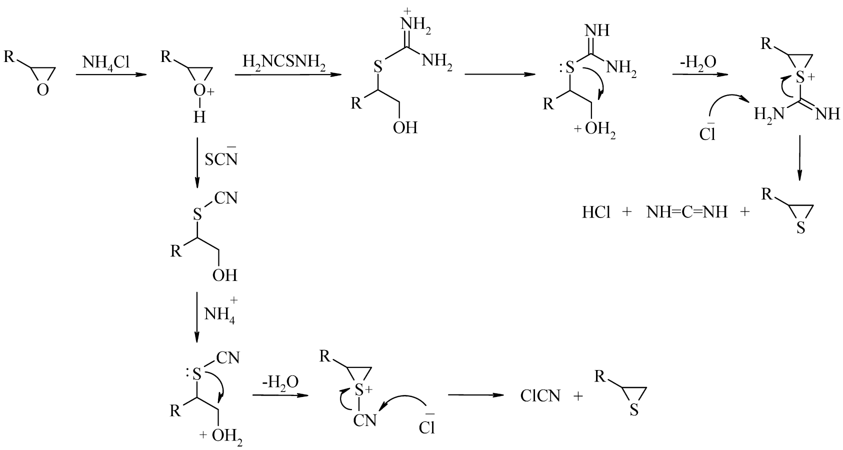
EXPERIMENTAL

All reagents and substrates were purchased from commercial sources with the best quality and were used without further purification. IR and ^1H NMR spectra were recorded on Thermo Nicolet Nexus

TABLE III Comparison of Solvent-Free Conversion of Epoxides to Thiiranes with Thiourea[a]

	Thiourea/NH_4Cl				Thiourea/Silica gel[27a]				Thiourea/120°C[27b]		
Epoxide	Thiourea (mmol)	NH_4Cl (g)	Time (min)	Yield (%)	Thiourea (mmol)	Silica (g)	Time (min)	Yield (%)	Thiourea (mmol)	Time (min)	Yield (%)
	2	0.5	30	95	2	2.8	5	86	2	15	65
	2	0.5	75	94	2	2.8	5	90	2	15	84
	2	0.5	15	93	2	2.8	3	88	2	60	77
	2	0.5	30	96	2	2.8	3	80	2	60	80

[a]All reactions were carried out with 1 mmol of epoxide under the defined conditions.



SCHEME 2

670 FT-IR spectrophotometer and a 300 MHz Bruker Avance spectrometer, respectively. The products were characterized by their ^{1}H NMR or IR spectra. All yields refer to isolated pure products. TLC over silica gel 60 F_{254} aluminum sheet was applied for the purity determination of the substrates, products, and for reaction monitoring.

General Procedure for Conversion of Epoxides to Thiiranes with the NH_2CSNH_2/NH_4Cl System under Solvent-Free Conditions

In an experimental tube, an epoxide (1 mmol), thiourea (0.152 g, 2 mmol) and NH_4Cl (0.5 g) was well mixed and then the tube was placed in an oil bath at 60–70°C for the appropriate time mentioned in Table II. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with CH_2Cl_2 (3 × 5 mL). Evaporation of the solvent from the combined extracts affords the pure thiirane in 65–96% yield.

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