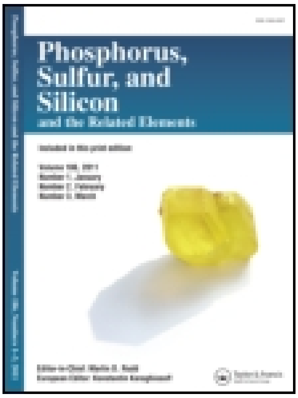

Phosphorus, Sulfur, and Silicon and the Related Elements

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A Practical and Eco-Friendly Method for Conversion of Epoxides to Thiiranes with Immobilized Thiourea on $CaCO_3$

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A PRACTICAL AND ECO-FRIENDLY METHOD FOR CONVERSION OF EPOXIDES TO THIIRANES WITH IMMOBILIZED THIOUREA ON $CaCO_3$

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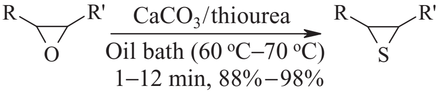
GRAPHICAL ABSTRACT



Abstract *Solvent-free conversion of various epoxides to the corresponding thiiranes was carried out efficiently with immobilized thiourea on* $CaCO_3$*. The reactions were completed within 1–12 min under oil bath (60 °C–70 °C) conditions to afford thiiranes in 88%–98% yields.*

[Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *for the following free supplemental resource: Figures S1–S3.]*

Keywords Epoxide; $CaCO_3$; thiirane; thiourea; solvent free

INTRODUCTION

Synthetic chemists continue to explore new methods to carry out chemical transformations. One of these new methods is to run reactions on the surface of solids. Surfaces have properties that are not duplicated in the solution or gas phase; hence entirely new chemistry may occur.[1] Even in the absence of new chemistry, a surface reaction may be more desirable than a solution counterpart, because the reaction can be more convenient to run or a higher yield of the product is attained. For these reasons, surface synthetic organic chemistry is a rapidly growing field of study. In organic syntheses, increasing attention is being focused on green chemistry,[2] using environmentally benign reagents and conditions, particularly solvent-free procedures,[3] which often lead to clean, eco-friendly, and highly efficient procedures involving simplified workups. The absence of solvent reduces the risk of hazardous explosion when the reaction takes place in a closed vessel. Moreover, aprotic

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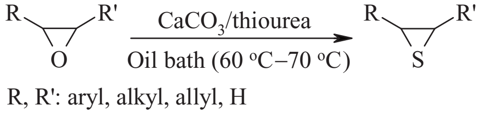
dipolar solvents with high boiling points are expensive and are difficult to remove from reaction mixtures.

Thiiranes are the simplest sulfur heterocycles and occur in nature. They have been used advantageously in the pharmaceutical, polymer, pesticide, and herbicide industries.[4] The general procedure for the synthesis of thiiranes is the conversion of epoxides by an oxygen–sulfur exchange reaction. Sulfur transferring agents such as thiourea,[5] inorganic thiocyanates,[6] silica-supported KSCN[7] or $(NH_2)_2CS$,[8] polymer-supported thiocyanates,[9] and Dowex-50WX8-supported thiourea[10] have been used for this purpose. Conversion of epoxides to thiiranes with thiourea or NH_4SCN in the presence of Lewis acids or other promoters such as $RuCl_3$,[11] $BiCl_3$,[12] TiO_2,[13] $TiCl_3(OTf)$,[14] $Mg(HSO_4)_2$,[15] $LiBF_4$,[16] $LiClO_4$,[17] I_2,[18] montmorillonite K10,[19] $(NH_4)_8[CeW_{10}O_{36}]\cdot 20H_2O$,[20] CAN,[21] $Sn(TTP)(OTf)_2$,[22] $[bmim]PF_6$,[23] poly(4-vinylpyridine)-supported $Ce(OTf)_4$,[24] polystyrene-supported $AlCl_3$,[25] etidronic acid,[26] NH_4Cl,[27] HBF_4/SiO_2,[28] and silica chloride[29] have been also reported. Although, a vast variety of reagents or methods have been reported for the preparation of thiiranes from epoxides; however, most of these protocols suffer from some disadvantages.

As a part of our research program to the synthesis of thiiranes, herein, we wish to report a green and practical method for solvent-free conversion of epoxides to the corresponding thiiranes by $CaCO_3$-supported thiourea under oil bath conditions (60 °C–70 °C) (Scheme 1).



Scheme 1

RESULTS AND DISCUSSION

A literature review shows that solvent-free conversion of epoxides to the corresponding thiiranes has been rarely studied and this goal was achieved with thiourea at 120 °C[5] and thiourea/SiO_2 system.[8] Nevertheless, these methods suffered from high reaction temperature and moderate yields. In this context, we have reported Dowex-50WX8-supported thiourea as an efficient polymeric supporting system for solvent-free conversion of epoxides to thiiranes.[10] Lack of information related to the application of alkali and alkali metal carbonates and sulfates in the preparation of thiiranes from epoxides encouraged us to investigate the capability of some costless and eco-friendly reagents such as Na_2CO_3, K_2CO_3, Cs_2CO_3, $MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$, $NaHCO_3$, $KHCO_3$, $NaHSO_4$, $KHSO_4$, and Na_2SO_4 for the titled transformation. Reaction of styrene oxide with the immobilized thiourea on the carbonates and sulfates was carried out under solvent and solvent-free conditions (Table 1). The results showed that among the reagents only $CaCO_3$ presented the perfect capability in the conversion of styrene oxide to styrene episulfide. In addition, the rate enhancement and efficiency under solvent-free conditions was higher than the solution phase.

In order to clarify the effect of Ca^{2+} or CO_3^{2-} ions in the observed promotion, we also examined the oxygen–sulfur exchange reaction of styrene oxide with the immobilized

Table 1 Optimization experiments for conversion of styrene oxide to styrene episulfide with thiourea under different conditions[a]

Reaction component	Molar ratio	Solvent	Condition[b]	Time (min)	Conversion (%)
Epoxide/thiourea/$NaHCO_3$	1:2:2	CH_3CN	Reflux	60	20
Epoxide/thiourea/$NaHCO_3$	1:2:2	Solvent free	r.t.	50	30
Epoxide/thiourea/$NaHSO_4$	1:2:2	Solvent free	r.t.	50	0
Epoxide/thiourea/Na_2SO_4	1:2:2	Solvent free	r.t.	50	50
Epoxide/thiourea/Na_2CO_3	1:2:2	Solvent free	r.t.	30	0
Epoxide/thiourea/$KHCO_3$	1:2:2	Solvent free	r.t.	50	25
Epoxide/thiourea/$KHSO_4$	1:2:2	Solvent free	r.t.	60	5
Epoxide/thiourea/K_2CO_3	1:2:2	Solvent free	r.t.	30	0
Epoxide/thiourea/$BaCO_3$	1:2:2	Solvent free	Oil bath	30	40
Epoxide/thiourea/$BaCO_3$	1:2:2	CH_3CN	Reflux	120	70
Epoxide/thiourea/$CaCO_3$	1:2:2	CH_3CN	Reflux	90	95
Epoxide/thiourea/$CaCO_3$	1:2:2	THF	Reflux	120	96
Epoxide/thiourea/$CaCO_3$	1:2:2	EtOH	Reflux	35	100
Epoxide/thiourea/$CaCO_3$	1:2:2	Solvent free	r.t.	4	100
Epoxide/thiourea/$CaCO_3$	1:2:2	Solvent free	Oil bath	1	100
Epoxide/thiourea/$CaCO_3$	1:2:3	Solvent free	Oil bath	1	100
Epoxide/thiourea/$CaCO_3$	1:2:5	solvent free	Oil bath	0.5	100
Epoxide/thiourea/CaO	1:2:3	CH_3CN	Reflux	90	30
Epoxide/thiourea/CaO	1:2:3	Solvent free	r.t.	30	20
Epoxide/thiourea/$CaCl_2$	1:2:2	CH_3CN	Reflux	60	5
Epoxide/thiourea/$CaCl_2$	1:2:2	Solvent free	r.t.	60	10
Epoxide/thiourea/$MgSO_4$	1:2:2	Solvent free	r.t.	60	40
Epoxide/thiourea/$MgSO_4$	1:2:2	CH_3CN	Reflux	60	40
Epoxide/thiourea/$MgCO_3$	1:2:2	Solvent free	Oil bath	60	55
Epoxide/thiourea/Cs_2CO_3	1:2:2	Solvent free	r.t.	60	20
Epoxide/thiourea/$SrCO_3$	1:2:2	Solvent free	r.t.	60	15

[a]All reactions were carried out with 1 mmol of epoxide. [b]Temperature of oil bath was 60 °C–70 °C.

thiourea on CaO and $CaCl_2$ (Table 1). The experiments showed that calcium oxide and chloride did not show any efficiency in solution or even under solvent-free conditions. On the basis of these observations, we therefore concluded that the integrated form of Ca^{2+} and $CO_3{}^{2-}$ ions as $CaCO_3$ synergistically promoted the conversion of styrene oxide to styrene episulfide. Moreover, the immobilization of thiourea (2 mmol) on $CaCO_3$ (2 mmol) was the requirement for the complete reaction of styrene oxide (1 mmol) within 1–4 min. In addition, performing the reaction in an oil bath (60 °C–70 °C) exhibited the more rate enhancement than room temperature conditions. The capability of thiourea/$CaCO_3$ system was further investigated by the reaction of activated, deactivated, and cyclic epoxides under the optimized conditions. Table 2 shows the general trend and versatility of this synthetic method. Generally, activated epoxides showed higher-rate enhancement than deactivated ones; however, all reactions were carried out successfully in an oil bath (60 °C–70 °C) at solvent-free conditions, and subsequently the corresponding thiiranes were obtained in high to excellent yields within 1–12 min.

The benefits of the immobilized thiourea on $CaCO_3$ was highlighted by comparison of our results with those of reported for thiourea/120 °C,[5] silica-gel-supported thiourea,[8] Dowex-50WX8-supported thiourea,[10] and thiourea/NH_4Cl[27] protocols (Table 3). A case study shows that in viewpoints of availability and costless of the reagents, mild reaction

Table 2 Solvent-free conversion of epoxides to thiiranes with CaCO immobilized thiourea[a]

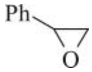
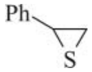
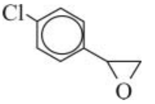
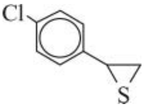
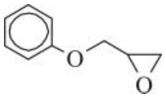
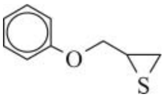
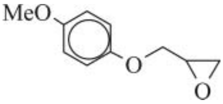
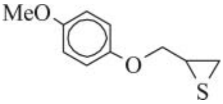
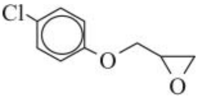
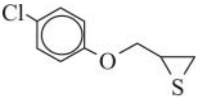
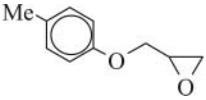
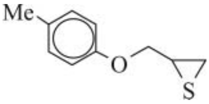
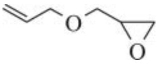
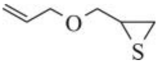
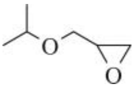
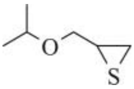
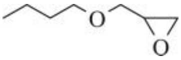
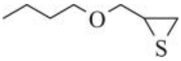
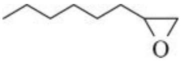
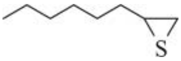
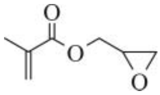
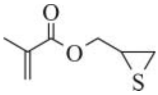
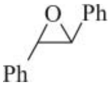
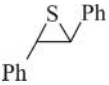
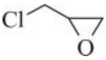
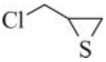
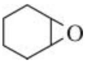
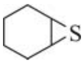
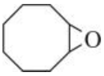
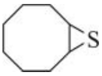
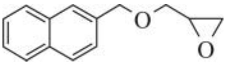
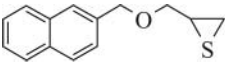
Epoxide	Thiirane	Molar ratio epoxide/thiourea/ CaCO$_3$	Time (min)	Yield (%)[b]	Reference
		1:2:2	1	96	27
		1:2:2	2	98	26
		1:2:2	10	95	27
		1:2:2	12	96	23
		1:2:2	8	95	23
		1:2:2	12	97	23
		1:2:2	1	98	27
		1:2:2	5	97	27
		1:2:2	4	92	23
		1:2:2	3	94	23
		1:2:2	7	97	27
		1:2:2	3	98	27
		1:2:2	6	88	23
		1:2:2	3	90	27
		1:2:2	8	91	27
		1:2:2	10	98	28

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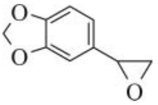
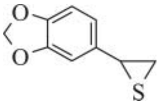
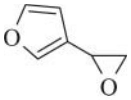
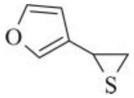
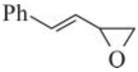
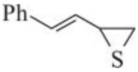
Table 2 Solvent-free conversion of epoxides to thiiranes with CaCO immobilized thiourea[a] *(Continued)*

Epoxide	Thiirane	Molar ratio epoxide/thiourea/ $CaCO_3$	Time (min)	Yield (%)[b]	Reference
		1:2:2	2	97	28
		1:2:2	2	90	28
		1:2:2	3	95	28

[a]All reactions were carried out in oil bath (60 °C–70 °C) at solvent-free conditions. [b]Isolated yields.

conditions, and the yield of thiiranes, the present method shows the more or comparable efficiency than the other methods.

In conclusion, we have shown that various epoxides are easily and efficiently converted to the corresponding thiiranes with thiourea immobilized on $CaCO_3$ in oil bath and under solvent-free conditions. The cheapness and easy preparation of thiourea/$CaCO_3$ system, mild reaction conditions, high yield of thiiranes, simple workup procedure as well as the benefits of solvent-free conditions make this method a useful addition to the present methodologies.

EXPERIMENTAL

General

All reagents and substrates were purchased from commercial sources with the best quality and were used without further purification. IR and $^1H/^{13}C$ NMR spectra were recorded on Thermo Nicolet Nexus 670 FT-IR and 300 MHz Bruker Avance spectrometers, respectively. The products were characterized by their spectra data and comparison with the reported data in literature. TLC was applied for the purity determination of substrates, products, and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

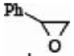
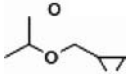
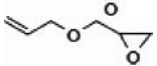
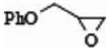
Preparation of Immobilized Thiourea on $CaCO_3$

A mixture of thiourea (0.152 g, 2 mmol) and $CaCO_3$ (0.2 g, 2 mmol) were placed in a mortar and then were thoroughly mixed for 2 min at room temperature to give $CaCO_3$ immobilized thiourea (0.35 g, 76% w/w). FT-IR (ν_{max}/cm^{-1}, KBr): 3808, 3388, 3285, 3180, 2692, 2519, 2365, 1787, 1613, 1508, 1085, 858, 729, 633, 497. FT-IR spectrum of thiourea, $CaCO_3$, and $CaCO_3$/thiourea system are provided as supplementary data.

General Procedure for Solvent-Free Conversion of Epoxides to Thiiranes with Thiourea Immobilized on $CaCO_3$

In an experimental tube equipped with a magnetic stirrer, the epoxide (1 mmol) and $CaCO_3$ immobilized thiourea (0.35 g, 76% w/w) were well mixed. The reaction mixture was

Table 3 Comparison of solvent-free conversion of epoxides to thiiranes with thiourea by different protocols

	Thiourea/$CaCO_3$[a]				Thiourea/Dowex-50WX[10]				Thiourea/NH_4C1[27]				Thiourea/SiO_2[8]				Thiourea/120 °C[5]		
Epoxide	Thiourea (mmol)	$CaCO_3$ (mmol)	Time (min)	Yield (%)	Thiourea (mmol)	Dowex (g)	Time (min)	Yield (%)	Thiourea (mmol)	NH_4C1 (g)	Time (min)	Yield (%)	Thiourea (mmol)	Silica (g)	Time (min)	Yield (%)	Thiourea (mmol)	Time (min)	Yield (%)
	2	2	1	96	2	0.5	60	93	2	0.5	30	95	2	2.8	80	95	2	15	65
	2	2	5	97	2	0.5	20	95	2	0.5	30	96	2	2.8	45	93	2	60	80
	2	2	1	98	2	0.5	30	96	2	0.5	15	93	2	2.8	40	92	2	60	77
	2	2	10	95	2	0.5	20	91	2	0.5	75	94	2	2.8	120	95	2	15	84

[a] The present method.

stirred and heated in an oil bath (60 °C–70 °C) for the appropriate time mentioned in Table 2. The progress of the reaction was monitored by TLC. After completion of the reaction, simply washing of the reaction mixture with an organic solvent and then evaporation of the filtrate under reduced pressure afforded the pure thiirane in 88%–98% yield.

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