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An efficient catalyst-free synthesis of thiiranes from oxiranes using polyethylene glycol as the reaction medium☆

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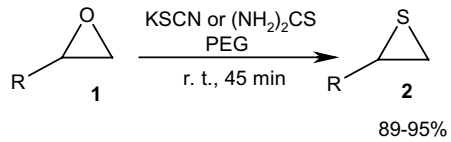
Abstract—A catalyst-free, high-yielding conversion of oxiranes into thiiranes has efficiently been carried out by treatment with KSCN or thiourea at room temperature using polyethylene glycol (PEG-400) as the reaction medium.

Thiiranes are frequently used in pharmaceutical, pesticide and polymer industries.[1] Various methods have been developed for the preparation of these compounds[2] with the most general being the conversion of oxiranes into thiiranes. For this purpose, several sulfur-introducing agents including inorganic thiocyanates,[3a–e] 3-methylbenzothiozole-2-thione,[3f] dimethylthioformamide,[3g] thiourea[3h,i] and phosphine sulfide[3j] have been utilized. Along with each sulfurated reagent, a protic acid such as TFA[3f,g,j] or a Lewis acid such as $RuCl_3$,[3b] $BiCl_3$,[3c] $TiO(CF_3COO)_2$,[3d] $TiCl_3(CF_3SO_3)$[3d] or $InBr_3$[3e] is employed. Recently, an ionic liquid has also been applied to the conversion of oxiranes into thiiranes.[4]

In continuation of our work[5] on the development of useful synthetic methodologies, we have recently observed that oxiranes can conveniently be converted into thiiranes by treatment with KSCN or $(NH_2)_2CS$ in polyethylene glycol (PEG-400) at room temperature (Scheme 1).



Scheme 1.

A series of thiiranes were prepared from several oxiranes (Table 1) by following the above method. No additional catalyst was required and the conversion was complete within 45 min. Different types of oxiranes such as styrene oxides and aliphatic and bicyclic oxiranes underwent the conversion smoothly. A chiral oxirane (Table 1, entry 1) was also converted into the corresponding thiirane with inversion of configuration. The products were formed in excellent yields and no side products were detected. In the absence of PEG, the conversion of oxiranes under neat reaction conditions was very slow and the yields were also very low (12–16% in 24 h). In the present study, both KSCN and $(NH_2)_2CS$ showed a similar activity as the reaction times were the same (45 min) and the yields were very similar. The structures of the products were established from their spectral (^1H NMR and MS) data.

Polyethylene glycol (PEG-400)[6] has been applied here as an efficient reaction medium for the preparation of thiiranes. It is a biologically acceptable inexpensive polymer and is eco-friendly. Its applications as a reaction medium in organic syntheses have not yet been fully explored. In the present conversion, the role of PEG is possibly to activate the oxiranes through hydrogen bonding. The PEG was recovered from the reaction mixture and recycled without loss of activity.

In conclusion, we have developed a simple and efficient protocol for the synthesis of thiiranes from oxiranes by treatment with KSCN or $(NH_2)_2CS$ using PEG at room temperature. The mildness and eco-friendly nature of the synthesis, catalyst-free conversion, short reaction

Keywords: Oxirane; Thiirane; KSCN; Thiourea; PEG-400.

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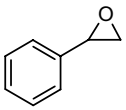
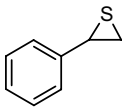
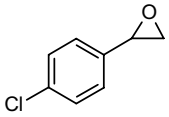
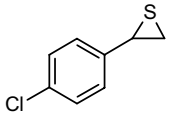
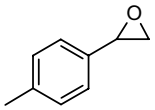
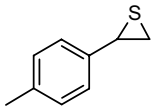
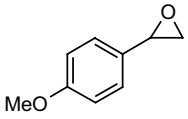
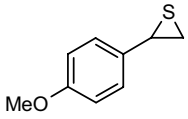
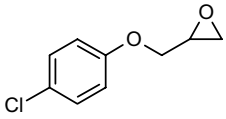
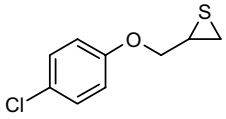
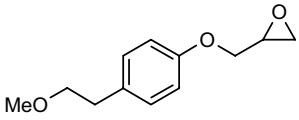
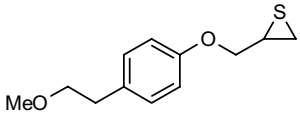
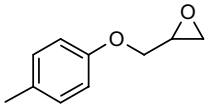
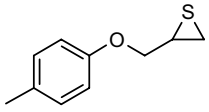
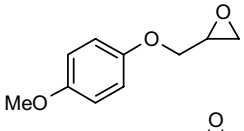
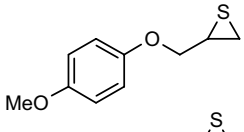
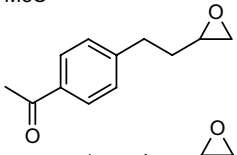
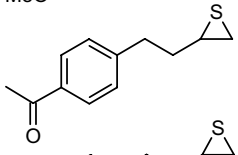
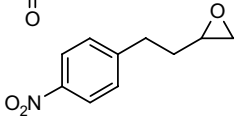
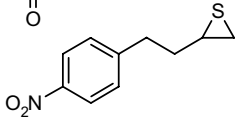
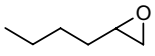
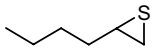
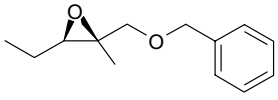
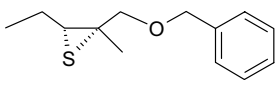
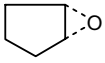
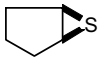
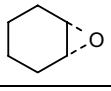
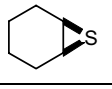
Table 1. Preparation of thiiranes from oxiranes using KSCN and PEG[a]

Entry	Oxirane **1**	Thiirane **2**	Isolated yield (%)
a			95
b			90
c			92
d			95
e			91
f			89
g			92
h			94
i			90
j			89
k			92
l			91
m			94
n			93

[a] The structures of the thiiranes were determined from their spectral (^{1}H NMR and MS) data.

time and excellent yields are notable advantages of the protocol.

General experimental procedure: To a stirred suspension of an oxirane (1 mmol) in PEG-400 (2 g), KSCN or $(NH_2)_2CS$ (1.2 mmol) was added and the mixture was stirred at room temperature for 45 min (TLC showed the completion of the reaction). The mixture was poured onto water (10 mL) and extracted with EtOAc (3×10 mL). The combined extract was concentrated

and the crude product was subjected to column chromatography (silica gel, hexane–EtOAc, 9:1) to afford pure thiirane.

Acknowledgements

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