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An Extremely Mild Desulfurization of Thiiranes; An Efficient Transformation from Geraniol to (+)- and (–)-Linalool

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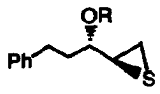
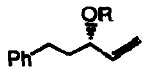
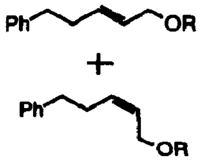
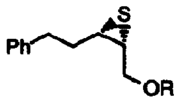
Abstracts: Thiirane was transformed to alkene very efficiently at -78°C by triethylborane initiated radical reaction with tributyltin hydride. Enantiomerically pure (+)- and (-)-linalools were derived from geraniol in four steps including the alkene formation reaction.

Transformations of three membered heterocycles to alkenes have been well documented in the literature.1) Particularly in the cases of oxiranes, the deoxygenation processes were reported to be retention of configuration,2) inversion of configuration3) or non-stereo selective4) depending on the reducing reagents. Preparations of alkene from thiirane by desulfurization have also been studied.5) The reaction usually required high temperature treating with phosphine,6) phosphite,7) iodomethane,8) and also tributyltin hydride.9) However not much studies concerning the stereochemistry has been done, particularly there is no report for a case of thiirane bearing hydroxy asymmetric center in the molecule. Herein we describe very mild and stereoselective desulfurization of optically active thiiranes promoted by tributyltin hydride and a catalytic amount of triethylborane,10) and its potential utilities in efficient transformation from geraniol to (+)- and (-)-linalools.

When optically active thiirane **1a** was treated with tributyltin hydride in the presence of cat. triethylborane in toluene at -78°C, 5-phenyl-3-[(*tert*-butyldimethylsilyl)oxy]-pentene (**2a**) was obtained in 84% yield.11) Benzoyl derivative **1b** also gave the corresponding allyl benzoate, **2b** in 85% yield. AIBN initiated reaction of **1a** and **1b** with tributyltin hydride required at refluxing temperature in benzene to give **2a** and **2b** in similar yields, respectively. The reaction of **1c** under the triethylborane catalyzed reaction conditions at -78°C, also proceeded very cleanly to provide the alkene **2c** in 90% yield. In all the reactions, the asymmetric center retained under the conditions. Next, stereochemistries of the reaction in cis and trans thiiranes, **3a~c** and **5a~c** were examined. Treatment of **3a** with tributyltin hydride and cat. triethylborane gave a 1 : 6.6 mixture of Z and E alkenes of **4a**, which were identified by the authentic materials prepared independently. On the other hand, the corresponding cis isomer **5a** also gave **4a** in a similar ratio. In all the cases, E alkene was formed predominantly. The results were listed in Table.

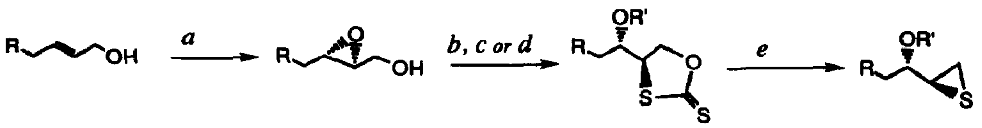
This paper is dedicated to Dr. Yasumitsu Tamura (Emeritus Professor of Osaka University) on the occasion of his 70th birthday.

Table Triethylborane Initiated Alkene Formation from Thiirane by Bu^n_3SnH

Substrate[a]		R	Product (Z : E)[b]	Yield (%)	
	1a	Bu^tMe_2Si	2a	84	
	1b	PhCO	2b	85	
	1c	H	2c	90	
	3a	Bu^tMe_2Si	4a (1 : 6.6)	84	
	3b	PhCO	4b (1 : 3.3)	98	
	3c	H	4c (1 : 6.5)	89	
	5a	Bu^tMe_2Si	4a (1 : 6.1)	98	
	5b	PhCO	4b (1 : 3.1)	85	
	5c	H	4c (1 : 6.1)	89	

a) Ref. 15, *b*) Geometric ratios were determined by ^1H NMR.

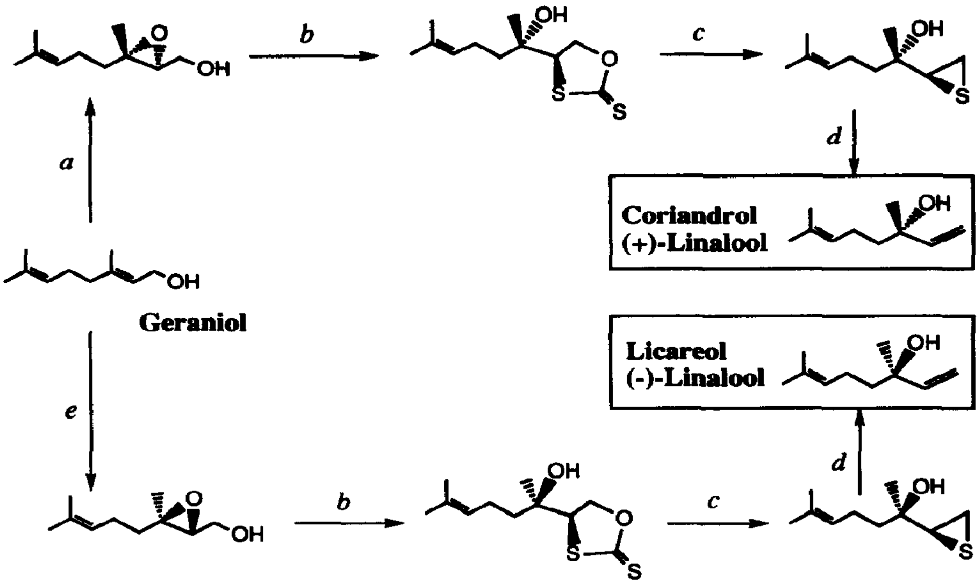
Shevlin reported that the reaction of trans thiirane with phenyl radical proceeded via a β-phenylthio radical intermediate to give Z and E alkenes in 18 : 82 ratio.[12] While, cis thiirane gave them in 74 : 26 ratio. The results indicated that about 80% of substrate retained the stereochemistry. However in our case, the reaction was not stereospecific but took place stereoselectively to lead Z and E alkenes in 1 : 3~7 ratio depending on the protecting group of the alcohols. These results indicated that an intermediary β-tributylstannylthio radical might be stable enough to be a conformational equilibrium by the C-C bond free rotation even at -78°C, and eventually to eliminate tributylstannylthio radical leading a stable E-isomer predominantly. These differences might be due to the rate in the elimination step of β-phenylthio radical and β-tributylstannylthio radical.[13]



R': TBDMS or PhCO

Scheme 1 *Reagents and Conditions; a)* Ti(OPr^i)$_4$, Bu^tOOH, (+)-Diethyl tartrate, in CH_2Cl_2; *b)* NaH, CS_2 in THF; *c)* TBDMSOTf, 2,6-lutidine in CH_2Cl_2; *d)* PhCOCl, DMAP in pyridine; *e)* K_2CO_3 in MeOH.

We have reported preparation of cyclic xanthate from allylic alcohol,[14] and the thiirane formation from the cyclic xanthate by methanolysis under basic conditions.[15] The typical preparation of asymmetric alkoxy thiirane was represented in Scheme 1. A combination of the reaction sequence and the alkene formation may serve 1,3-hydroxy group transposition under a stereocontrolled manner. In order to examine the applicability, stereospecific syntheses of (+)- and (-)-linalool were demonstrated in Scheme 2.[16] Linalool is known to be an important component in many essential oils. The (S)-(+)-isomer is called coriandrol, on the other hand, (-)-linalool is called licareol and has R-chiral center. These enantiomeric isomers exhibit quite a different flavors. The Sharpless asymmetric epoxidation of geraniol by using (+)-diethyl tartrate as a chiral inducer afforded optically pure epoxy alcohol in more than 95% enantiomeric excess. Stereospecific ring opening of the epoxide by NaH and carbon disulfide gave cyclic xanthate in 69% yield. Treatment of the xanthate with potassium carbonate in methanol gave thiirane in 90% yield. Finally, the thiirane was subjected to the above desulfurization conditions at 0°C[17] for 5 min to lead (+)-linalool in 84% yield, possessing $[\alpha]_D^{24}$ + 17° (*c* 1.0, ethanol).[17] Exactly by the same procedure described for (+)-linalool synthesis except using (-)-diethyl tartrate in the asymmetric epoxidation step, (-)-linalool was obtained in 47% yield from geraniol and the product showed the same specific rotation but an opposite sign.[18]



Scheme 2 *Reagents and Conditions; a)* Ti(OPr^i)$_4$, Bu^{t}OOH, (+)-Diethyl tartrate, -20°C in CH_2Cl_2 ; *b)* NaH, CS_2, -78~0°C in THF; *c)* K_2CO_3, rt, in MeOH; *d)* Bu$^n_3$SnH, cat. Et_3B, 0°C, in toluene ; *e)* Ti(OPr^i)$_4$, Bu^{t}OOH, (-)-Diethyl tartrate, -20°C in CH_2Cl_2.

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11, Typical reaction procedure; A mixture of thiirane (1 mmole) and tributyltin hydride (1.1 mmole) in dryl toluene (5 ml) was degassed and cooled to -78°C. A hexane solution of triethylborane (0.1 ml in 1M solution) was dropped to the mixture and stirred for 5 min at -78°C. The standard work up by ether and sodium bicarbonate and purification by silica gel column chromatography gave the desired alkene.

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13, Krief reported the reaction of a simple trans thiirane with tributylstannyl radical at 110°C for 1 hr to give Z-alkene preferenrially in 22 : 78 ratio, see ref. 9.

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16, The chemical transformation of geraniol to linalool via 1,3-hydroxy transposition was reported by Germain and Lygo et al. E. Balmer, A. Germain, W. P. Jackson and B. Lygo, *J. Chem. Soc., Perkin Trans. 1*, 1993, 399.

17, Due to a poor solubility of this substrate in toluene below -5°C, the reaction was carried out on a ice bath.

18, The reported degrees in "The Dictionary of Organic Compounds"; Coriandrol, $[\alpha]_D^{24}$ + 16.9° (*c* 1.0, ethanol); Licareol, $[\alpha]_D^{24}$ - 17° (*c* 1.0, ethanol).

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