Tetrahedron Vol. 49, No. 30, pp. 6651-6660, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Destannylative Pummerer-type Rearrangement of 1-(Tributylstannyl)-1-(Phenylsulfinyl)- Cyclopropane and -Ethene.

Manat Pohmakotr*, Srisamorn Sithikanchanakul and Sujitra Khosavanna[1]

Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Rd.,
Bangkok 10400, Thailand.

(*Received in UK* 14 *April* 1993)

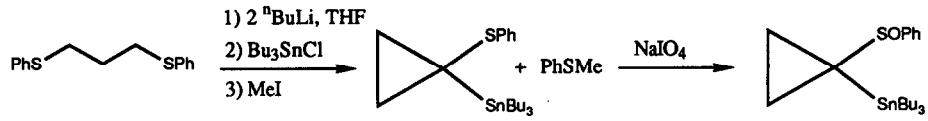
Abstract: 1-(Tributylstannyl)-1-(phenylsulfinyl)-cyclopropane and -ethene were found to react with acyl chlorides to provide the corresponding 1-acyloxy-1-(phenylthio)-cyclopropanes and -ethenes. The reaction involves the Pummerer-type rearrangement with loss of the tributylstannyl group.

Sulfoxides bearing α-hydrogens undergo the Pummerer rearrangement leading to α-functionalised sulfides. This rearrangement has been widely used in organic synthesis.[2] The extension has been made to the α-silylsubstituted sulfoxides, which can be rearranged under thermal conditions without added reagent to give α-siloxy sulfides.[3,4] This is called the sila-Pummerer rearrangement. The similar reaction can occur as well with α-silyl vinyl sulfoxides to give *O,S*-keteneacetals.[5] On the other hand, much less is known about the chemistry of α-stannyl substituted sulfoxides. It was of interest whether α-stannyl sulfoxides could undergo the similar rearrangement as that of the α-silyl substituted analogues. In connection with our preliminary studies concerning the destannylative Pummerer-type rearrangement of 1-(tributylstannyl)-1-(phenylsulfinyl)cyclopropane,[6] we wish to disclose here the details of these results as well as the rearrangement of 1-(tributylstannyl)-1-(phenylsulfinyl)ethene.

RESULTS AND DISCUSSION

1. The Destannylative Pummerer-type Rearrangement of 1-(Tributylstannyl)-1-(phenylsulfinyl)cyclopropane (1).

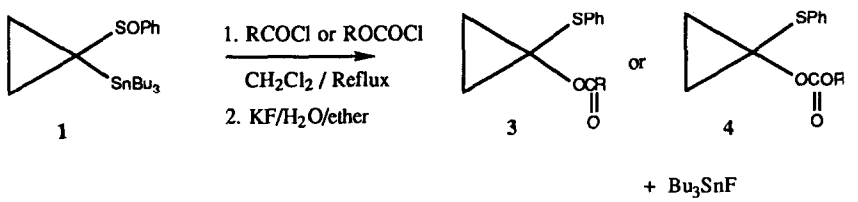
The starting α-stannyl cyclopropyl sulfoxide **1** was prepared by reacting α-lithio (phenylsulfinyl)cyclopropane with Bu_3SnCl as described recently by us.[7] Alternatively, it could also be obtained in 47% overall yield starting from bis(phenylthio)propane as shown in **Scheme 1**. Treatment of 1,3-bis(phenylthio)propane with 2 equivalents of butyllithium in tetrahydrofuran[8] followed by the addition of Bu_3SnCl afforded α-stannyl cyclopropyl sulfide **2** (88%), which was further oxidised by using sodium metaperiodate in aqueous methanol to provide **1** in 53% yield.



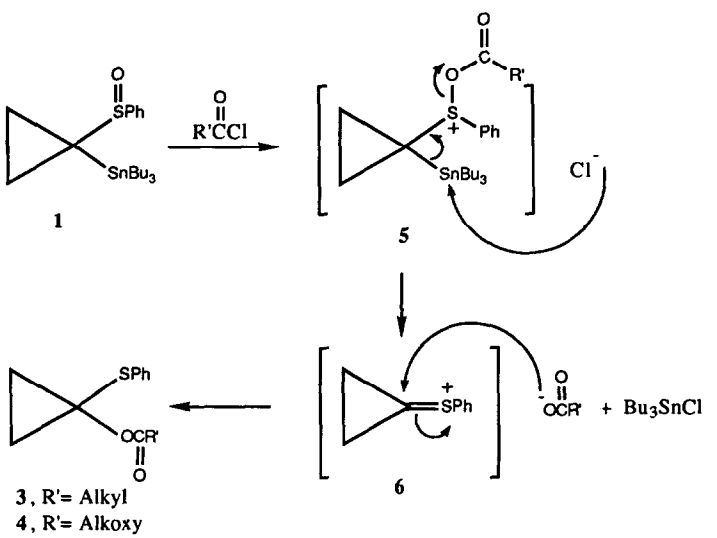
2 **1**

Scheme 1

At the beginning of our investigation, we set out to examine the stability of the α-stannyl sulfoxide **1** under thermal conditions. Thus, refluxing of **1** in dry dichloromethane (CH_2Cl_2) or dry toluene for 7 h led to the recovery of **1** in quantitative yield.[9] Similar results were observed when the α-stannyl sulfoxide **1** was allowed to react with acetic anhydride in CH_2Cl_2 or toluene under reflux for 6-7 h. Treatment of the α-stannyl sulfoxide **1** with the more reactive acetyl chloride (1.2 equiv.) in refluxing CH_2Cl_2 for 5 h gave 1-acetoxy-1-(phenylthio)cyclopropane (**3a**)[10] in 84% yield after removal of the produced Bu_3SnCl by treating with aqueous KF in ether and chromatography (**Table 1**, entry 1). The same reactions proceeded well with other acyl chlorides as indicated in **Table 1** leading to the expected products of type **3** in good yields (**Table 1**, entries 2-5). We next examined the reaction of the α-stannyl sulfoxide **1** with methyl chloroformate under the similar conditions, expecting that 1-(methoxycarbonyloxy)-1-(phenylthio)cyclopropane (**4a**) or 1-methoxy-1-(phenylthio)cyclopropane would result. Thus, treatment of the α-stannyl sulfoxide **1** with methyl chloroformate in CH_2Cl_2 at reflux for 5 h afforded the 1-(methoxycarbonyloxy) derivative **4a** in 78% isolated yield. Ethyl- and butyl chloroformate also reacted with the α-stannyl sulfoxide **1** to give the expected products **4b** and **4c** in quite good yields (**Scheme 2, Table 1**, entries 7 and 8). The mechanism for the formation of the *O,S*-acetal derivative **3** or **4** from the α-stannyl sulfoxide **1** may be rationalized as follows. The acylation of the α-stannyl sulfoxide **1** gives the α-stannyl acyloxy sulfonium salt **5**, which is followed by the attack of the chloride ion on the tributylstannyl group affording the thionium salt **6** and tributylstannyl chloride. The recombination of the thionium ion intermediate **6** with the carboxylate anion furnished the 1-acyloxy-1-(phenylthio)cyclopropane **3** or 1-(alkoxycarbonyloxy)-1-(phenylthio)cyclopropane **4** (**Scheme 3**).



Scheme 2



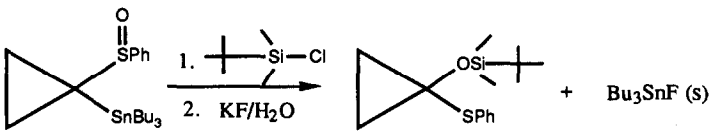
Scheme 3

Table 1. The Destannylative Pummerer-type Rearrangement of the α-Stannyl Sulfoxide **1**.

Entry	Acyl Chloride	Product 3 or 4	Yield (%)[a]
1	CH_3COCl	**3a**, R = CH_3-	84
2	CH_3CH_2COCl	**3b**, R = CH_3CH_2-	70
3	$(CH_3)_2CHCOCl$	**3c**, R = $(CH_3)_2CH$-	73
4	$(CH_3)_3CCOCl$	**3d**, R = $(CH_3)_3C$-	94
5	PhCOCl	**3e**, R = Ph-	90
6	CH_3OCOCl	**4a**, R = CH_3-	78
7	CH_3CH_2OCOCl	**4b**, R = CH_3CH_2-	62
8	$CH_3(CH_2)_3OCOCl$	**4c**, R = $CH_3(CH_2)_3$-	87

[a] = Isolated yields.

Since the rearrangement provided a convenient entry to the potentially valuable synthetic intermediates **3** and **4**, we extended briefly our investigation to the reaction of the α-stannyl sulfoxide **1** with *tert*-butyldimethylchlorosilane. As expected, the α-silyloxycyclopropane **7**[9] was obtained in 75% yield after chromatography.

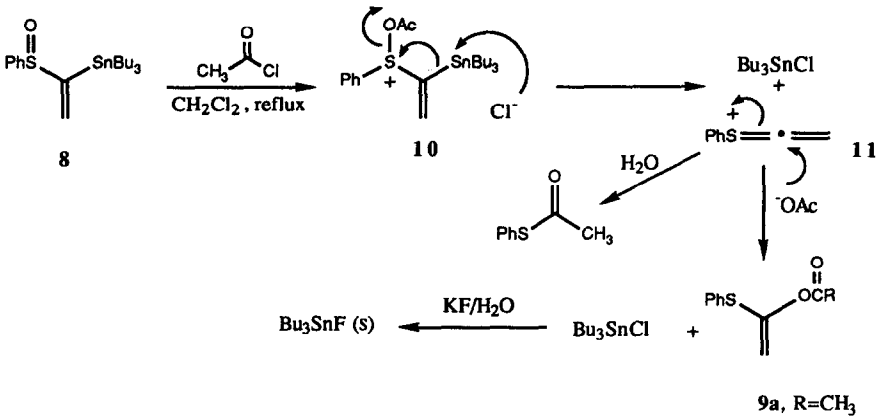


1 **7** (75%)

2. The Destannylative Pummerer-type Rearrangement of 1-(Tributylstannyl)-1-(phenylsulfinyl)ethene (8).

Continuing investigation on the destannylative Pummerer-type rearrangement (the stanna- Pummerer rearrangement) of the α-stannyl sulfoxide **1** prompted us to extend our study to the α-stannyl vinyl sulfoxide **8**, hoping that the rearrangement can proceed to *O,S*-acetals **9** after reacting with acyl chlorides. The α-stannyl sulfoxide **8** was readily prepared from phenyl vinyl sulfide using the method recently described.[11] Initially, the reaction of the α-stannyl sulfoxide **8** with acetyl chloride was explored. It was found that treatment of **8** (1 equiv) with acetyl chloride (1.2 equiv) in dry CH_2Cl_2 under reflux for 3 h afforded the required α-acetoxy phenyl vinyl sulfide **9a** (δ 2.0 ppm due to CH_3COO-) along with small amount of *S*-phenyl ethanethioate (δ 2.35 ppm due to CH_3COSPh) as revealed by the ^{1}H-NMR spectrum of the crude product obtained. It should be noted that the reaction proceeded cleanly as monitored by thin-layer chromatography (silica gel). However, a low yield of the crude product was always achieved. This is presumably due to the lability of the expected product **9a**. Attempts to isolate the product **9a** from the by-product *S*-phenyl ethanethioate by preparative thin-layer or flash column chromatography (silica gel) were unsuccessful.

The formation of the α-acetoxy phenyl vinyl sulfide **9a** resulted, as expected, from the destannylative Pummerer-type rearrangement of the α-stannyl sulfoxide **8** initiated by acetyl chloride. The reaction proceeds *via* the acetylation of the sulfoxide function leading to a sulfonium salt **10** and then to a thionium ion intermediate **11**. Subsequent addition of the acetoxy anion yields the *O,S*-acetal **9a** (**Scheme 4**). The presence of *S*-phenyl ethanethioate may arise from the addition of water (moisture) to the thionium ion **11** during the reaction period or workup. The reaction of the α-stannyl sulfoxide **8** with a variety of acyl chlorides in refluxing CH_2Cl_2 (3 h) afforded **9b-f** in moderate yields (51-58%) after preparative thin-layer chromatography. The results are summarized in **Table 2**. In all cases, the by-product, *S*-phenyl ethanethioate, was also present, but it could be separated from the expected *O,S*-acetals **9b-f**. Finally, the reaction of the α-stannyl sulfoxide **8** with ethyl chloroformate under the standard conditions was tried. It was observed that the reaction gave a complex mixture of unidentified products.



Scheme 4

Table 2. The Destannylative Pummerer-type Rearrangement of **8**.

Entry	Acyl Chloride	Product 9	Yield (%)[a]
1	CH_3COCl	**9a**, R = CH_3-	49[b]
2	PhCOCl	**9b**, R = Ph-	53
3	$CH_3CH_2CH_2COCl$	**9c**, R = $CH_3CH_2CH_2$-	58
4	$(CH_3)_2CHCOCl$	**9d**, R = $(CH_3)_2CH$-	51
5	$CH_3(CH_2)_3COCl$	**9e**, R = $CH_3(CH_2)_3$-	55
6	$(CH_3)_3CCOCl$	**9f**, R = $(CH_3)_3C$-	57

[a] = Isolated yields.
[b] = Contaminated with *ca.* 15% of *S*-phenyl ethanethioate.

After we had completed our study concerning the destannylative Pummerer-type rearrangement at the sp^2-carbon employing the α-stannyl sulfoxide **8**, a report describing similar findings appeared in the literature.[12]

CONCLUSION

It is clear from the above results that the destannylative Pummerer-type rearrangement (" the stanna - Pummerer rearrangement ")[13] of the α-stannyl sulfoxides can occur both at sp^2- and sp^3- hybridized carbons such as **1** and **8**. The rearrangement provides a convenient entry to 1-acyloxy-1-(phenylthio)-cyclopropanes (**3** and **4**)[14] and -ethenes (**9**), which are classes of potentially valuable synthetic intermediates.

EXPERIMENTAL SECTION

The IR spectra were determined on a Jasco A-302 Spectrophotometer. The ^{1}H-NMR spectra were recorded at 60 MHz with a Varian EM-360L Spectrometer. Mass spectra were obtained on a INCOS 50 Mass spectrophotometer at 70 eV. Melting points were measured by a Buechi 50 Melting Point Apparatus and are uncorrected.

Preparation of 1-(Tributylstannyl)-1-(phenylsulfinyl)cyclopropane (1).

To a cooled (-78 °C) solution of 1,3-bis(phenylthio)propane (5.2 g, 20 mmol) in THF (50 ml) was slowly added BuLi (1.78 M in hexane, 25 ml, 44.5 mmol). The resulting mixture was stirred at -78 °C for 1 h and 0 °C for 3 h. After cooling again to -78 °C, tributyltin chloride (6.0 ml, 22.2 mmol) was added dropwise. The resulting mixture was slowly warmed up to room temperature by stirring overnight (15 h). It was cooled to 0 °C and iodomethane (1.5 ml, 24.1 mmol) was added dropwise following by stirring at the same temperature for 1 h. The reaction mixture was diluted with water (100 ml) and ethyl acetate (150 ml). The aqueous layer was extracted with ethyl acetate (3x70 ml). The organic layers were combined and washed with water, brine and dried over anhydrous $MgSO_4$ The crude product (12.3 g) was purified by flash column chromatography (silica gel, hexane) to give a colorless liquid of 1- (tributylstannyl)-1-(phenylthio)cyclopropane (7.7 g, 88%). IR (neat): ν_{max} 3075, 2975, 1590, 1480, 1460, 1440, 1430, 1380, 1340, 1295, 1180, 1150, 1090, 1070, 1025, 960, 890, 740, 695, 660 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 0.4-1.7 (m, 31H, *-SnBu$_3$* and *methylene protons*), 6.8-7.4 (m, 5H, *-SPh*). It was used for further oxidation as follows: A solution of 1-(tributylstannyl)-1-(phenylthio)cyclopropane (3.5 g, 8 mmol) in methanol (10 ml) was slowly added to a suspension of powdered $NaIO_4$ (2.1 g, 10 mmol) in water (5 ml) at 0 °C. After stirring for 16 h, the precipitates were filtered and washed several times with methanol. The residue obtained after evaporation off methanol was diluted with 50 ml of water and 50 ml of ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3x75 ml). The combined organic layers were washed several times with water, brine and dried over anhydrous $MgSO_4$. Filtration followed by evaporation gave a pale yellow liquid of the crude product (3.2 g), which was purified by flash column chromatography (silica gel, 5-15% ethyl acetate in hexane) to furnish a pale yellow liquid of **1** (1.9 g, 53%, b.p. 138 °C/0.07 mmHg). IR (neat): ν_{max} 3050, 2950, 2925, 2850, 1640, 1585, 1480, 1470, 1460, 1445, 1430, 1380, 1360, 1340, 1310, 1295, 1280, 1250, 1210, 1200, 1180, 1150, 1130, 1120, 1090, 1070, 1050, 1025, 1000, 960, 940, 900, 880, 850, 790, 750, 730, 700, 670, 600, 550 cm^{-1}; ^{1}H-NMR (CCl_4) : δ 0.3-1.8 (m, 31H, *-SnBu$_3$* and *methylene protons*), 7.23-7.76 (m, 5H, *SOPh*); MS: m/e(%) relative intensity 455(M^+, 2), 399(43), 397(31), 149(5), 125(28), 109(7), 97(13), 77(19), 57(100).

Preparation of 1-(Acyloxy)- and 1-(Alkoxycarbonyloxy)-1-(phenylthio)cyclopropanes 3 and 4.

General Procedure : Acyl chloride or alkyl chloroformate (2.5 mmol) was added to a solution of **1** in dry CH_2Cl_2 (15 ml) under argon. The resulting mixture was refluxed for 5 h, then cooled and quenched with a saturated aqueous KF solution (20 ml). The resulting mixture was stirred vigorously at room temperature overnight and the precipitates of Bu_3SnF were filtered and washed several times with CH_2Cl_2 (in order to remove Bu_3SnCl, it could be alternatively done by treating the crude product obtained with a saturated aqueous KF solution and ether at room temperature).[15] The organic layer was separated and the aqueous layer was

extracted with CH_2Cl_2 (2x50 ml).The combined organic layer was washed with a saturated $NaHCO_3$ solution, water, brine and dried over anhydrous $MgSO_4$. Filtration followed by evaporation afforded a crude product which was purified by preparative thin-layer chromatography (silica gel, 2-3% ethyl acetate in hexane) to give **3** or **4**.

1-Acetoxy-1-(phenylthio)cyclopropane (3a):[10] 84% ; liquid; IR (neat): ν_{max} 3050, 3000,1750, 1580, 1440, 1370, 1230, 1150, 1090, 1020, 990, 880, 830, 740, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.26 (br. s, 3H, *cyclopropyl protons*), 2.0 (s, 3H, CH_3CO), 7.1-7.6 (m, 5H, *SPh*); MS: m/e(%) relative intensity: 208(M^+, 12), 166(8), 153(26), 133(14), 110(58), 105(18), 99(65), 91(8), 77(7), 65(15), 56(12), 43(100).

1-(Phenylthio)-1-(propanoyloxy)cyclopropane (3b): 70% ; m.p. 65-67 °C (ether-hexane); IR (nujol): ν_{max} 1750, 1580, 1420, 1260, 1190, 1140, 1080, 1030, 840, 740, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.1 (t, J = 7 Hz, CH_3CH_2CO), 1.25 (br. s, 4H, *cyclopropyl protons*), 2.25 (q, J = 7 Hz, 2H, CH_3CH_2CO), 7.1-7.55 (m, 5H, *SPh*); MS: m/e(%) relative intensity: 222(M^+, 4), 167(13), 149(4), 133(4), 113(55), 110(18), 109(19), 105(8), 65(10), 57(100). Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35. Found: C, 64.46; H, 6.26.

1-(Isobutyryloxy)-1-(phenylthio)cyclopropane (3c): 73%; colorless liquid; IR (neat): ν_{max} 3050, 3000, 1750, 1585, 1470, 1440, 1405, 1380, 1340, 1230, 1120, 1040, 1020, 980, 830, 730, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.1 [d, J = 7 Hz, $CH(CH_3)_2$], 1.26 (s, 4H, *cyclopropyl protons*), 2.4 [sept., J = 7 Hz, 1H, $CH(CH_3)_2$], 7.0-7.5 (m, 5H, *SPh*); MS: m/e(%) relative intensity: 236(M^+, 4), 193(4), 181(6), 149(4), 128(5), 127(7), 110(21), 109(15), 105(8), 99(6), 71(73), 65(8), 43(100). Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.10; H, 6.78. Found: C, 66.29; H, 6.92.

1-(Pivaloyloxy)-1-(phenylthio)cyclopropane (3d): 94%; colorless liquid; IR (neat): ν_{max} 2960, 1750, 1580, 1480, 1440, 1360, 1280, 1260, 1120, 1030, 990, 840, 740, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.16 [s, 9H, $C(CH_3)_3$], 1.25 (s, 4H, *cyclopropyl protons*), 7.05-7.5 (m, 5H, *SPh*); MS: m/e(%) relative intensity: 250(M^+, 3), 193(5), 166(4), 141(39), 133(12), 110(18), 109(12), 105(14), 85(17), 71(10), 57(100), 43(14). Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.20; H, 7.20. Found: C, 67.41; H, 7.59.

1-(Benzoyloxy)-1-(phenylthio)cyclopropane (3e): 90%; colorless liquid; IR (neat): ν_{max} 1730, 1580, 1480, 1450, 1440, 1320, 1280, 1250, 1160, 1090, 1070, 1030, 840, 740, 710, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.4 (br. s, 4H, *cyclopropyl protons*), 7.0-7.7 and 7.75-8.2 (m, 10H, Ar*H*); MS: m/e(%) relative intensity: 270(M^+, 0.5), 215(2), 161(23), 109(6), 105(100), 77(27), 65(3), 51(6). Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.11; H, 5.18. Found: C, 70.91; H, 5.24.

1-(Methoxycarbonyloxy)-1-(phenylthio)cyclopropane (4a): 78%; colorless liquid; IR (neat): ν_{max} 3050, 3000, 2950, 1755, 1580, 1480, 1440, 1280, 1250, 1160, 1090, 1030, 1000, 940, 910, 840, 790, 740, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.1-1.5 (m, 4H, *cyclopropyl protons*), 3.75 (s, 3H, OCH_3), 7.0-7.55 (m, 5H, *SPh*); MS: m/e(%) relative intensity: 224(M^+, 37), 169(6), 149(30), 148(77), 137(13), 124(31), 115(29), 109(100), 105(47), 91(87), 77(20), 65(36), 59(43), 41(20). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.88; H, 5.60.

1-(Ethoxycarbonyloxy)-1-(phenylthio)cyclopropane (4b): 62%; colorless liquid; IR (neat): ν_{max} 3000, 1760, 1580, 1480, 1440, 1370, 1270, 1250, 1160, 1090, 1010, 920, 830, 790, 740, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.1-1.5 (m, 7H, *cyclopropyl protons* and $-OCH_2CH_3$), 4.2 (q, J = 7 Hz, 2H, OCH_2CH_3), 7.05-7.55 (m, 5H, *SPh*); MS: m/e(%) relative intensity: 238(M^+, 28), 166(20), 149(23), 138(18), 133(62),

123(29), 110(100), 109(69), 105(89), 91(31), 77(15), 65(24), 57(29), 51(11), 45(12). Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.50; H, 6.72. Found: C, 60.69; H, 6.17.

1-(Butoxycarbonyloxy)-1-(phenylthio)cyclopropane (4c): 78%; colorless liquid; IR (neat): ν_{max} 3060, 2960, 1760, 1585, 1480, 1440, 1420, 1390, 1260, 1230, 1150, 1080, 1020, 990, 920, 830, 780, 730, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.6-1.8 (m, 11H, *cyclopropyl and propyl protons*), 4.05 (br. t, J = 6 Hz, 2H, OCH_2CH_2), 7.0-7.5 (m, 5H, *SPh*); MS: m/e(%) relative intensity: 268(M^+, 1), 266(20), 166(32), 149(20), 134(13), 133(82), 111(12), 110(90), 109(34), 105(74), 91(23), 65(15), 57(100), 41(48). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 62.69; H, 6.72. Found: C, 62.81; H, 6.89.

1-(*tert*-Butyldimethylsiloxy)-1-(phenylthio)cyclopropane (7). A solution of *tert*-butyldimethylchlorosilane (3.0 g, 20.1 mmol) and compound **1** (6.7 g, 15 mmol) in dry CH_2Cl_2 was refluxed for 12 h. After usual workup, the crude product was purified by flash column chromatography (silica gel, hexane) to give a colorless liquid of **7** (3.1 g, 75%). IR (neat): ν_{max} 3050, 2950, 2850, 1580, 1480, 1440, 1420, 1360, 1260, 1180, 1090, 1040, 1010, 950, 860, 840, 780, 740, 700 cm^{-1}; ^{1}H-NMR (CCl_4): δ 0.15 [s, 6H, *-Si(CH$_3$)$_2$*], 0.85 (s, 9H, *tert-butyl*), 1.15 (m, 4H, *cyclopropyl protons*), 7.0-7.6 (m, 5H, *SPh*); MS: m/e(%) relative intensity: 282(M^+, 0.4), 280(5), 224(19), 223(100), 167(34), 115(11), 105(15), 91(30), 75(65), 73(85), 59(10), 45(8). Anal. Calcd for $C_{15}H_{24}OSSi$: C, 64.23; H,8.62. Found: C, 63.88; H, 8.71.

1-(Tributylstannyl)-1-(phenylsulfinyl)ethene (8) was prepared according to the reported procedure:[11] A colorless liquid; IR (neat): ν_{max} 1585, 1470, 1450, 1420, 1380, 1340, 1300, 1180, 1150, 1080, 1040, 940, 880, 750, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 0.6-1.8 (m, 2H, *-SnBu3*), 5.9 and 6.6 (each s, 2H, *olefinic protons*), 7.3-7.7 (m, 5H, Ar*H*); MS: m/e(%) relative intensity: 441(M^+, 1), 385(100), 271(12), 245(23), 229(13), 197(5), 177(27), 137(43), 121(32), 91(16), 77(26), 57(30). Anal. Calcd for $C_{20}H_{34}OSSn$: C, 54.44; H, 7.77. Found: C, 54.02; H, 8.16.

Preparation of 1-Acyloxy-1-(phenylsulfinyl)ethene (9).

General Procedure: Acyl chloride (2.5 mmol) was added to a solution of compound **8** (1.0 g, 2.3 mmol) in dry CH_2Cl_2 (15 ml) under argon. The resulting solution was refluxed for 3 h, and after cooling, quenched with a saturated aqueous KF solution (15 ml) and stirred vigorously at room temperature overnight (16 h). The precipitates of Bu_3SnF were filtered and washed several times with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2x50 ml). The organic layer were combined and washed with a saturated aqueous $NaHCO_3$ solution, water, brine and dried over anhydrous $MgSO_4$. Filtration followed by evaporation gave a crude liquid product, which was purified by preparative thin-layer chromatography (silica gel, 1% ethyl acetate in hexane) to afford **9**.

1-Acetoxy-1-(phenylthio)ethene (9a):[12] 49% (contaminated with *ca.* 15% of *S*-phenyl ethanethioate); colorless liquid; IR (neat): ν_{max} 1770 cm^{-1}; ^{1}H-NMR (CCl_4): δ 2.0 (s, 3H, *CH$_3$*COO-), 5.15 (m, 2H, *olefinic protons*), 7.4 (m, 5H, Ar*H*).

1-(Benzoyloxy)-1-(phenylthio)ethene (9b):[12] 53%; colorless liquid; IR (neat): ν_{max} 3050, 1740, 1620, 1600, 1590, 1480, 1455, 1440, 1320, 1260, 1135, 1080, 1060, 1025, 1000, 920, 800, 750, 710, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 5.4 (s, 2H, *olefinic protons*), 7.0-8.3 (m, 10H, Ar*H*); MS: m/e(%) relative intensity

256(M^+, 3), 214(7), 106(8), 105(100), 77(51), 65(7), 51(17). Anal. Calcd for $C_{15}H_{10}O_2S$: C, 61.83; H, 5.19. Found: C, 70.29; H, 4.60.

1-(Butanoyloxy)-1-(phenylthio)ethene (9c): 58% ; colorless liquid; IR (neat): ν_{max} 3075, 3050, 2975, 2925, 2875, 1760, 1620, 1590, 1480, 1460, 1440, 1420, 1360, 1310, 1250, 1120, 1030, 1000, 960, 890, 810, 750, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 0.85 (t, J = 7 Hz, 3H, -$CH_2CH_2CH_3$), 1.5 (sext., 2H, $CH_2CH_2CH_3$), 2.16 (t, J = 7 Hz, 2H, -$OCOCH_2CH_2CH_3$), 5.05-5.25 (m, 2H, *olefinic protons*), 7.0-7.65 (m, 5H, Ar*H*); MS: m/e(%) relative intensity 223(M^++1, 10), 181(15), 180(69), 153(19), 152(80), 151(14), 150(19), 135(29), 111(14), 110(78), 109(42), 92(35), 91(36), 85(10), 72(100), 65(9), 57(6). Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35. Found: C, 64.43; H, 6.13.

1-(2-Methylpropanoyloxy)-1-(phenylthio)ethene (9d): 51% ; colorless liquid; IR (neat): ν_{max} 3075, 3050, 2975, 2950, 2875, 1760, 1620, 1585, 1480, 1470, 1445, 1390, 1370, 1350, 1235, 1120, 1080, 1040, 1025, 950, 890, 750, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.1 [d, J = 7 Hz, 6H, -$CH(CH_3)_2$], 2.4 [m, 1H, $OCOCH(CH_3)_2$], 5.1-5.33 (m, 2H, *olefinic protons*), 7.1-7.6 (m, 5H, Ar*H*); MS: m/e(%) relative intensity 222(M^+, 8), 180(16), 152(21), 111(15), 110(100), 109(33), 71(55), 69(23), 65(23), 57(18), 55(20), 51(15). Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35. Found: C, 64.58; H, 6.25.

1-(Pentanoyloxy)-1-(phenylthio)ethene (9e): 55% ; colorless liquid; IR (neat); ν_{max} 3075, 2975, 2950, 2875, 1760, 1620, 1580, 1480, 1440, 1380, 1360, 1230, 1120, 1080, 1050, 1025, 940, 990, 870, 840, 750, 700 cm^{-1}; ^{1}H-NMR (CCl_4):δ 0.6-1.8 (m, 7H, -$OCOCH_2CH_2CH_2CH_3$), 2.16 (t, J = 7 Hz, 2H, -$OCOCH_2CH_2$-), 5.0-5.2 (m, 2H, *olefinic protons*), 7.05-7.5 (m, 5H, Ar*H*); MS: m/e(%) relative intensity 237(M^++1, 2), 236(M^+, 9), 194(11), 152(31), 135(9), 110(51), 109(26), 91(10), 85(100), 65(14), 57(73), 51(7). Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: C, 65.87; H, 6.82.

1-(2,2-Dimethylpropanoyloxy)-1-(phenylthio)ethene (9f): 57% ; colorless liquid; IR (neat): ν_{max} 3075, 3050, 2975, 2950, 2875, 1760, 1620, 1585, 1480, 1460, 1445, 1400, 1370, 1365, 1150, 1110, 1030, 930, 880, 750, 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.05 [s, 9H, -$C(CH_3)_3$], 5.1 and 5.23 (each d, J = 1.5 Hz, 2H, *olefinic protons*), 7.15-7.6 (m, 5H, Ar*H*); MS: m/e(%) relative intensity 236(M^+, 6), 152(20), 110(33), 109(12), 92(9), 91(9), 85(22), 65(9), 57(100). Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: C, 65.88; H, 6.78.

ACKNOWLEDGEMENT

We would like to thank Mrs. Pucharin Poochaiwatananon, Miss Amporn Srisuttipruet and Miss Kingkaew Serikul for carrying out the IR-, ^{1}H-NMR- and MS- spectra as well as the microanalyses.

REFERENCES AND NOTES

1. Taken in part from the ***M.Sc Thesis of SK.***
2. De Lucchi, O.; Miotti, U.; Modena, G. *Organic Reactions*, John Wiley & Sons Inc.,**1991**, *vol. 40*, p. 157.
3. Bloch, E.; Aslam, M. *Tetrahedron*, **1988**, *44*, 284 and references cited therein.
4. Ager, D.J. *Chem. Soc. Rev.* **1982**, 493 and references cited therein.

5. Hart, D.J.; Tsai, Y. M. *Tetrahedron Lett.* **1983**, *41*, 4387.
6. Pohmakotr, M.; Sithikanchanakul, S. *Tetrahedron Lett.* **1989**, *30*, 6773.
7. Pohmakotr, M.; Sithikanchanakul, S. *Synth. Commun.* **1989**, *19*, 3011.
8. Tanaka, K.; Uneme, H.; Matsui, S.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2965.
9. 1-(Trimethylsilyl)-1-(phenylsulfinyl)cyclopropanes were reported to undergo the *sila*-Pummerer rearrangement in refluxing benzene to afford the corresponding 1-(trimethylsilyloxy)-1-(phenylthio)cyclopropane derivatives : Bhupathy, M.; Cohen, T. *Tetrahedron Lett.* **1987**, *28*, 4793.
10. Masuda, T.; Numata, T.; Furukawa, N.; Oae, S. *Chem. Lett.* **1977**, 745.
11. Harirchian, B.; Magnus, P. *J. C. S. Chem. Commun.* **1977**, 522. We used LDA / THF in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) at -78 °C for 30 min for the lithiation of phenyl vinyl sulfide.
12. Beddoes, R.L.; MacLeod, D.; Moorcroft, D.; Quayle, P.; Zhao, Y. *Tetrahedron Lett.* **1992**, *33*, 417.
13. Desilylative Pummerer-like rearrangement of α-silyl sulfoxides: Ishibashi, H.; Nakatani, H.; Maruyama, K.; Minami, K.; Ikeda, M. *J. C. S. Chem. Commun.* **1987**, 1443.
14. Compounds **3** and **4** can be considered as masked cyclopropanones : Salaun, *J. Chem. Rev.* **1983**, *83*, 619 and references cited therein.
15. Leibner, J.E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449.