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DESTANNYLATIVE PUMMERER-TYPE REARRANGEMENT OF 1-(PHENYLSULFINYL)-1-(TRIBUTYLSTANNYL)CYCLOPROPANE

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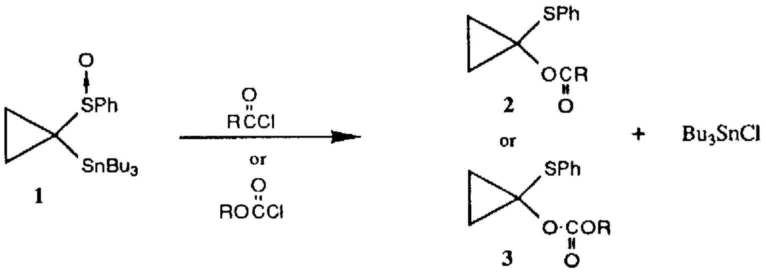
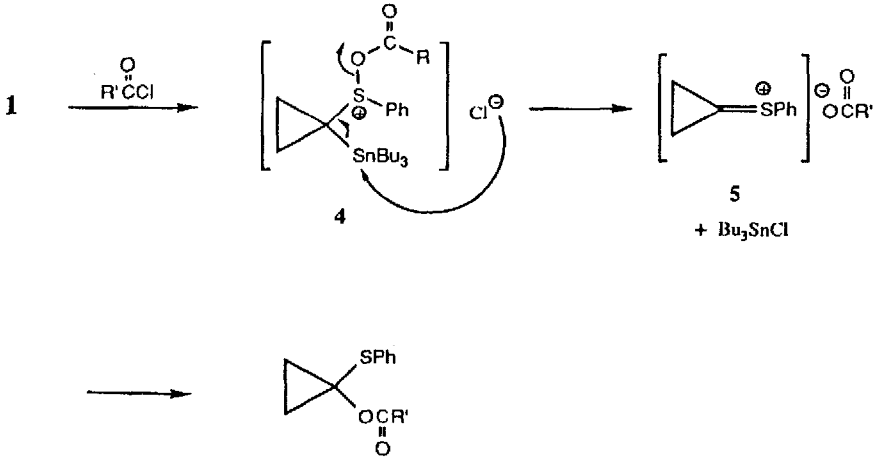
SUMMARY: 1-(Phenylsulfinyl)-1-(tributylstannyl)cyclopropane on treatment with acyl chlorides or alkyl chloroformate in refluxing dichloromethane afforded 1-acyloxy-1-phenylsulfenyl- and 1-alkoxycarbonyloxy-1-phenylsulfenylcyclopropanes, respectively. The reaction involves the Pummerer-type rearrangement with loss of tributylstannyl group.

α-Silyl substituted sulfoxides have long been known to undergo the sila-Pummerer rearrangement at ambient temperature. The rearrangement has been extensively examined and is very useful for converting sulfoxides to carbonyl compounds.[1] On the other hand, much less is known about the chemistry of α-stannyl substituted sulfoxides.[2] In connection with a programme to explore the chemical reactivity of some organic compounds containing sulfur and tin elements as useful reagents, we had an occasion to investigate the reaction of 1-(phenylsulfinyl)-1-(tributylstannyl)cyclopropane (1).[3] We found that the reaction of the α-stannyl sulfoxide 1 (1 equiv.) with acyl chloride (1.2 equiv.) or alkyl chloroformate (1.2 equiv.) in dichloromethane under reflux for 5 hr gave 1-acyloxy- or 1-alkoxycarbonyloxy-1-(phenylsulfenyl)cyclopropane 2 or 3 in good yield.[4] The results are summarized in Table I.



A mechanism for the formation of compound 2 or 3 involves the acylation of the α-stannyl sulfoxide 1 to give α-stannyl acylsulfoxonium salt 3 followed by the attack of chloride ion on the tributylstannyl group, affording the thionium salt 5 and tributylstannyl chloride. The recombination of the thionium ion with the carboxylate anion furnishes the α-acyloxy phenylthiocyclopropane 2 or 3 (see Scheme I).[5]

Scheme I



2, R' = alkyl

3, R' = alkoxy

TABLE I Destannylative Pummerer-type rearrangement of the α-stannyl sulfoxide 1 leading to compound 2 or 3.

Electrophile	Product 2 or 3 (% yield)[7]		
CH_3COCl	**2a**,	$R=CH_3$	(84%)
CH_3CH_2COCl	**2b**,	$R=CH_3CH_2$	(70%)
$(CH_3)_2CHCOCl$	**2c**,	$R=(CH_3)_2CH$	(73%)
$(CH_3)_3CCOCl$	**2d**,	$R=(CH_3)_3C$	(94%)
PhCOCl	**2e**,	R=Ph	(90%)
CH_3OCOCl	**3a**,	$R=CH_3$	(78%)
CH_3CH_2OCOCl	**3b**,	$R=CH_3CH_2$	(62%)
$CH_3CH_2CH_2CH_2OCOCl$	**3c**,	$R=CH_3CH_2CH_2CH_2$	(87%)

It should be noted that the α-stannyl sulfoxide **1** does not undergo the Pummerer-type rearrangement the same way as the α-silyl sulfoxide analogues[1,6] under thermal conditions. Thus, refluxing of the solution of the α-stannyl sulfoxide **1** in dichloromethane or toluene for 7 hr led to the recovery of the starting material in quantitative yield. Similar result was observed when the α-stannyl sulfoxide 1 was allowed to react with acetic anhydride (1.2 equiv.) in dichloromethane or toluene under reflux for 6 hr.

The above results demonstrated the first destannylative Pummerer-type rearrangement of α-stannyl sulfoxides such as **1**, leading to α-acyloxy- and α-alkoxycarbonyloxy-derivatives **2** and **3** which are masked cyclopropanones.[8] The rearrangement provides a convenient entry to this class of potentially valuable synthetic intermediates. Further study of this reaction with other α-stannyl sulfoxides as well as their synthetic applications are currently under investigation.

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4. The crude product obtained from the reaction was treated with excess KF in water/ ether to remove Bu_3SnCl, followed by preparative thin-layer chromatography (silica gel): Leibner, J.E.; Jacobus, J. J.Org.Chem., 1979, 44, 449.

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6. The sila-Pummerer rearrangement of 1-trimethylsilyl-1-phenylsulfinylcyclopropane has been reported: Cohen, Th.; Bhupathy, M. Tetrahedron Lett., 1987, 28, 4793.

7. All products gave satisfactory spectral data (IR, ^{1}H-NMR and MS). **2a**: IR 1750 cm^{-1}; NMR(CCl_4) δ1.3(br.s,4H), 2.0(s,3H), 7.3(m,5H); MS 208(M^+). **2b**: m.p.65-67°; IR 1750 cm^{-1}; NMR($CDCl_3$) δ1.1(t,J=7Hz,3H), 1.3(br.s, 4H), 2.25(q,J=7Hz,2H), 7.3(m, 5H). MS 222(M^+). **2c**: IR 1760 cm^{-1}; NMR(CCl_4) δ1.1(d,J=7Hz,6H), 1.25(s, 4H), 2.4(sept.J=7Hz, 1H), 7.25(m, 5H); MS 236(M^+). **2d**: IR 1750 cm^{-1}; NMR(CCl_4) δ1.15(s, 9H), 1.25(s, 4H), 7.3(m, 5H); MS 250(M^+). **2e**: IR 1730 cm^{-1}; NMR(CCl_4) δ1.4(br.s, 4H), 7.35 and 7.95 (m, 10H); MS 270(M^+). **3a**: IR 1760 cm^{-1}; NMR(CCl_4) δ1.3(m, 4H), 3.7(s, 3H), 7.3(m, 5H); MS 224(M^+). **3b**: IR 1760 cm^{-1}; NMR(CCl_4) δ1.3(m, 7H), 4.2(q,J=7Hz,2H), 7.3 (m, 5H); MS 238(M^+). **3c**: IR 1760 cm^{-1}; NMR(CCl_4) δ0.7-1.8(m, 11H), 4.1(t,J=7Hz,2H), δ7.25(m, 5H); MS 268(M^+).

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