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Regio- and stereospecific cleavage of stannylepoxides with lithium phenylsulfide

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Abstract—Unsubstituted and α or β C-substituted epoxystannanes react with lithium phenylsulfide to give regio- and stereodefined α-phenylthio-β-hydroxystannanes resulting from α-opening with inversion of configuration. On the other hand, α- or β-*trans*-silyl epoxystannanes afford stereospecific α- or β-silylated vinylsulfides formed by nucleophilic attack at the carbon which bears the tin group and subsequent *syn*-elimination of $HOSnBu_3$. Both types of products are interesting synthons in organic chemistry. © 2001 Elsevier Science Ltd. All rights reserved.

Although the behavior of silylepoxides toward nucleophilic reagents has been widely studied,[1] there are few references concerning the reactivity of stannylepoxides. We have only found reported their conversion in ketones[2] by cleavage with formic acid followed by treatment with lithium hydroxide in aqueous THF, their transformation in olefins[3] by a reductive alkylation with alkyl lithium reagents, ring-opening with metal hydrides[4] and organocuprates[5] and transmetalation with an organolithium.[6]

In previous papers, we have described the regio- and stereospecific cleavage of epoxysilanes with lithium diphenylphosphide[7] and lithium phenylsulfide.[8] In the latter case we obtained vinyl sulfides resulting from α-opening or silyl enol ethers, α-silylaldehydes and α-hydroxy-β-phenylthiosilanes, all resulting from β-opening.

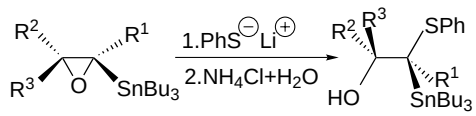
We have now extended our research to the study of the reactivity of stannylepoxides toward nucleophile reagents and in this communication we report the results obtained in the treatment of stannylepoxides with lithium phenyl sulfide.

The starting compounds are α and β C- and Si-substituted epoxystannanes prepared by reaction with MCPBA of the corresponding vinylstannanes, obtained by tributylstannyl cupration from alkynes[9] or allenes.[10]

The behavior of epoxystannanes toward lithium phenylsulfide is different from that shown for epoxysilanes.[8] Unsubstituted or differently C-substituted stannylepoxides **1a–d** react at 0°C with lithium phenylsulfide in THF[11] to give in excellent yields regio- and stereodefined α-phenylthio-β-hydroxystannanes **2a–d** formed by hydrolysis of the lithium β-oxido stannanes resulting from α-opening with inversion of configuration (Scheme 1).

All new compounds showed satisfactory spectroscopic and analytical data.[12]

These α-phenylthio-β-hydroxystannanes are very versatile synthons. They experience acid-catalyzed *anti* elimination of $HOSnBu_3$ affording alkenylsulfides, which are stereoisomers of those we had previously obtained by reaction of trimethylsilyl- or dimethylphenylsilylepoxides with the same reagent.[8] Conversely, they undergo thermal *syn*-elimination by heating at reflux of xylene. Although both eliminations are stereospecific, when the β-substituent is a phenyl group the initial *Z*-alkenylsulfide was isomerized to the more stable *E* isomer (Scheme 2).



1a;R^1=R^2=R^3=H — **2a** (90%)
1b;R^1=R^2=H,R^3=Me — **2b** (85%)
1c;R^1=R^3=H,R^2=Ph — **2c** (83%)
1d;R^1=Me,R^2=R^3=H — **2d** (86%)

Scheme 1.

Keywords: epoxystannanes; thiostannanes; vinylsulfides; vinylsilanes.
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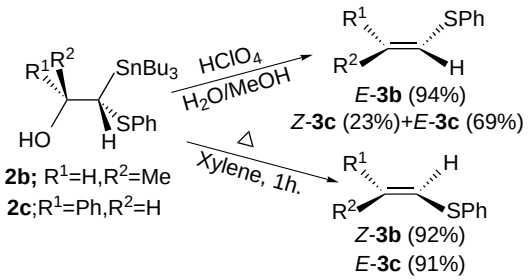


Scheme 2.

Moreover, the presence of a tributylstannyl group *gem* to the phenylthio makes the compounds **2** synthetic equivalents of stereodefined α-phenylthio-stabilized carbanions capable of being trapped by electrophiles to provide a route to interesting synthons. In fact, **2b** was stereoselectively transmetalated by treatment with BuLi and the intermediate **4b** was quenched with ethyl chloroformate to give the β-hydroxyester derivative **5b** as the sole diastereomer[13] (verified by ^{1}H NMR and TLC of the reaction mixture) (Scheme 3).

We have also studied the behavior of silylated epoxystannanes with the aim of knowing which of the two metalated groups controlled the regiochemistry of the ring opening as this will determine the nature of the reaction products.

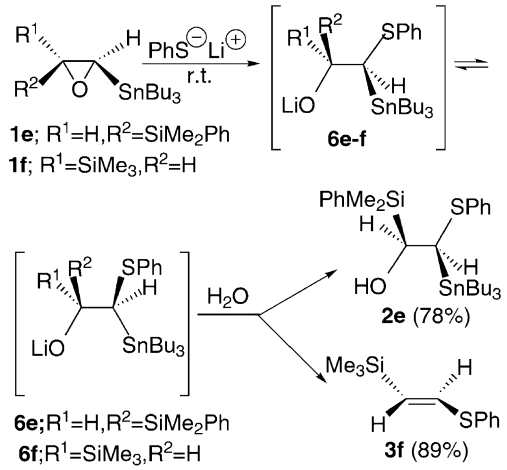
The β-silylated epoxystannanes **1e** and **1f** were exclusively attacked by phenylsulfide at the carbon α to the tin group giving an intermediate lithium α-phenylthio-β-silyl-β-oxido stannanes **6e** or **6f**, which was hydrolyzed to the corresponding β-hydroxystannane **2e** or underwent spontaneous *syn*-elimination of $HOSnBu_3$ affording the β-silyl vinylsulfide **3f** (Scheme 4).

The different behavior of *cis* and *trans* β-silyl epoxystannanes **1e** and **1f** may depend on the stability of the conformation necessary for the *syn*-elimination of $HOSnBu_3$. Probably, the intermediate **6e** does not undergo elimination due to the fact that in this conformation two bulky groups (dimethylphenylsilyl and phenylthio) should be eclipsed (Scheme 4).

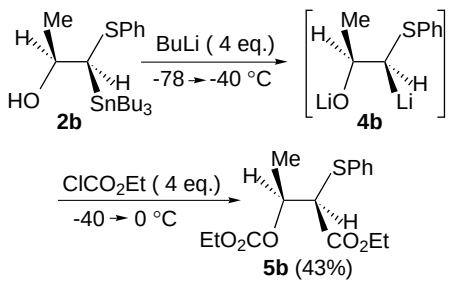
On the other hand, the α-silylepoxystannane **1g** is opened by nucleophilic α-attack to give the intermediate **6g**. According to the results previously described by us[8] in the opening of epoxysilanes with lithium phenylsulfide and those obtained now in the reactions of epoxystannanes with the same reagent, the intermediate **6g** should undergo Peterson-elimination to give the corresponding α-stannylated vinylsulfide. Surprisingly,[14] the product isolated was in all conditions (0°C, rt, neutral, acid or basic hydrolysis) exclusively the α-silylated vinylsulfide **3g** resulting from elimination of $HOSnBu_3$ (Scheme 5).

The α-silyl epoxystannane **1h** bearing a hindered *tert*-butyldiphenylsilyl group was recovered untransformed even after prolonged heating with lithium phenylsulfide in THF at reflux (12 h). It was necessary to add aluminum chloride in order for the reaction to take place. After 21 h at rt, the corresponding α-*tert*-butyldiphenylsilyl vinylsulfide **3h** resulting from α-opening was obtained in low yield (8%). However, when the reaction was heated at reflux of THF for 3 h, 2,3-*bis*-*tert*-butyldiphenylsilylbuta-1,3-diene **7h** was isolated in good yield. The compound **7h** is probably obtained by thermal dimerization from the initially formed vinylsulfide **3h** (Scheme 6).

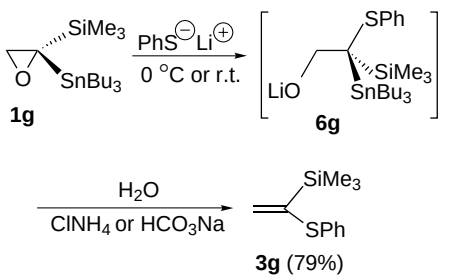
This strong tendency for nucleophilic attack at the carbon α to the tin group contrasts with the acid-catalyzed β-opening observed by us[8] in the reactions of *tert*-butyldiphenylsilylepoxides with the same reagent. Moreover, the reactivity of the tin and silicon dimeta-



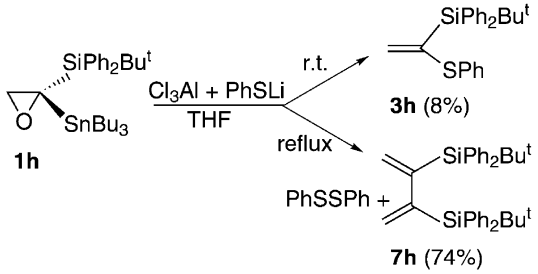
Scheme 4.



Scheme 3.



Scheme 5.



Scheme 6.

lated epoxides is dominated by the stannyl group. The nucleophilic attack always takes place in the carbon bearing the stannyl group and the evolution of the resulting intermediate is also controlled and directed by this group. In contrast to what was observed in the reactions of epoxysilanes with lithium phenylsulfide,[8] the lithium β-oxido stannanes **6f** and **6g** intermediates containing also an α-alkoxy and β-alkoxysilane moiety respectively, do not undergo Brook rearrangement or Peterson-elimination. They afford the corresponding 1- or 2-silylated vinylsulfide **3f** and **3g** resulting from *syn*-elimination of $HOSnBu_3$.

In conclusion, the opening of epoxystannanes with lithium phenylsulfide is an easy method for preparing new diastereomerically pure alcohols **2** bearing synthetically versatile functionality in fixed regiospecific relationships. Furthermore, these *erythro* or *threo* β-hydroxy stannanes undergo stereospecific s*yn* or *anti*-elimination of $HOSnBu_3$. This has allowed us to prepare *Z* or *E* vinyl sulfides.[15] Especially interesting are the 1- and 2-silylated vinylsulfides **3f–h** which among other applications,[16–18] have been used for synthesizing thiophenyl-functionalized cyclopentenones via Nazarov cyclizations.[19] Finally, the 2,3 disilylated diene **7h** is a potentially attractive reaction partner in [4+2] cycloadditions since the adducts are expected to be prone to various functionalizations of the disilylated vinylic unit.

Acknowledgements

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11. General procedure. To a stirred THF solution of lithium phenylsulfide [prepared from benzenethiol (0.1 mL, 1 mmol) and butyllithium (0.625 mL, 1.6 M solution in hexane, 1 mmol) in THF (5 mL) at −78°C under N_2 for 10 min] was added dropwise a solution of epoxystannane (1 mmol) in THF (5 mL). The resulting mixture was allowed to warm up to 0°C for **1a–d** and **1g** or to room temperature for **1e** and **1f** and stirred at these temperatures until TLC indicated complete reaction. Ammonium chloride solution was added and the mixture was extracted with ether, washed with sodium hydroxide solution, dried ($MgSO_4$) and chromatographed.
12. Selected spectroscopy data: **2b**; ^{1}H NMR ($CDCl_3$) δ 7.40 (dd, $J=7.2$ and 1.4 Hz, 2H), 7.27 (t, $J=7.2$ Hz, 2H), 7.15 (dd, $J=7.2$ and 1.4 Hz, 1H), 4.10 (ddq, $J=5.8$, 5.1 and 6.2 Hz, 1H), 3.08 (d $J=5.8$ Hz, $J_{Sn-H}=53$ Hz, 1H), 2.33 (d, $J=5.1$ Hz, 1H), 1.54 (m, 6H), 1.35 (m, 6H), 1.23 (d, $J=6.2$ Hz, 3H), 1.03 (m, 6H), and 0.91 (t, $J=7.3$ Hz, 9H); ^{13}C NMR ($CDCl_3$) δ 139.29, 128.79, 128.49, 125.75, 70.32, 39.04, 29.06, 27.39, 23.03, 13.67, and 10.50; MS (EI) *m*/*z* 401 (M^+−Bu, 6%), 265 (22), 150 (34), 135 (17), 109 (13), 71 (52), and 41 (100). Anal. calcd for $C_{21}H_{38}OSSn$: C, 55.15; H, 8.38. Found: C, 55.32; H, 8.46. *Z*-**3b**; ^{1}H NMR ($CDCl_3$) δ 7.37–7.16 (m, 5H), 6.22 (dq, $J=9.2$ and 1.6 Hz, 1H), 5.89 (dq, $J=9.2$ and 6.7 Hz, 1H), 1.85 (dd, $J=6.7$ and 1.6 Hz, 3H). *E*-**3b**; ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 5H), 6.14 (dq, $J=14.8$ and 1.3 Hz, 1H), 6.00 (dq, $J=14.8$ and 6.5 Hz, 1H), and 1.84 (dd, $J=6.5$ and 1.3 Hz, 3H). **5b**; IR (CCl_4) 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.47–7.19 (m, 5H), 5.10 (dq, $J=9.1$ and 6.3 Hz, 1H), 4.15 (q, $J=7.1$ Hz, 2H), 4.14 (q, $J=7.0$ Hz, 2H), 3.75 (d, $J=9.1$ Hz, 1H), 1.52 (d, $J=6.3$ Hz, 3H), 1.27 (t, $J=7.1$ Hz, 3H), and 1.19 (t, $J=7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$) 169.58, 153.93, 133.27, 132.42, 129.10, 128.40, 73.70, 64.04, 61.35, 55.63, 17.58, 14.14, and 13.92. Anal. calcd for $C_{15}H_{20}O_5S$: C, 57.67; H, 6.45. Found: C, 57.79; H, 6.38. **2e**; ^{1}H NMR ($CDCl_3$) δ 7.53–7.14 (m, 10H), 3.88 (dd, $J=7.9$ and 4.1 Hz, 1H), 3.38 (d, $J=4.1$ Hz, $J_{Sn-H}=50$ Hz, 1H), 2.04 (d, $J=7.9$ Hz, 1H), 1.44 (m, 6H), 1.29 (m, 12H), 0.87 (t, $J=7.1$ Hz, 9H), 0.37 (s, 3H), and 0.28 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 138.74, 137.52, 134.12, 129.04, 128.69, 127.81, 127.44, 127.12, 69.15, 37.40, 29.03, 27.39, 13.67, 10.68, −3.50, and −4.06. Anal.

calcd for $C_{28}H_{46}OSSiSn$: C, 58.28; H, 8.03. Found: C, 58.10; H, 8.12. **7h**; ^{1}H NMR ($CDCl_3$) δ 7.71 (m, 8H), 7.41 (m, 12H), 6.04 (d, $J=3.0$ Hz, 2H), 5.91 (d, $J=3.0$ Hz, 2H), and 0.99 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 148.82, 144.51, 134.76, 131.52, 129.55, 127.62, 26.75, and 19.12. Anal. calcd for $C_{36}H_{42}Si_2$: C, 81.45; H, 7.97. Found: C, 81.63; H, 7.89.

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