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The Synthesis of α-Stannyl-Silanes and Their Use in the Formation of Alkenes

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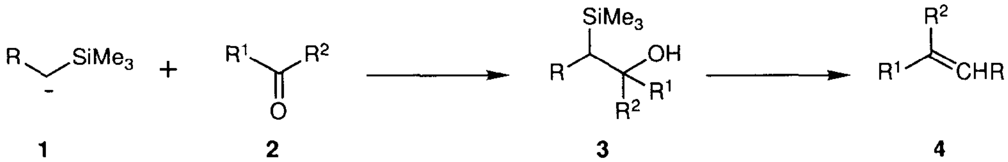
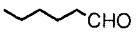
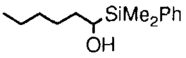
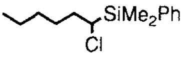
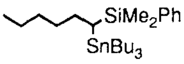
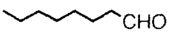
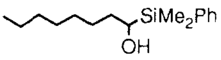
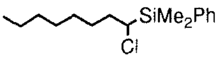
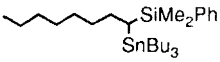
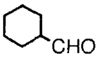
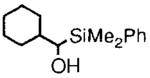
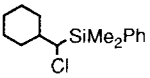
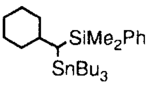
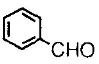
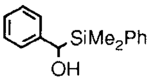
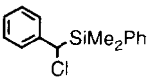
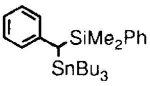
Abstract: α-Stannyl-silanes were prepared from aldehydes via α-hydroxy- and α-chloro-silanes. Stannyl-silane **5d** was transmetallated using *n*-butyllithium and the resultant α-lithio-silane condensed with aldehydes to yield alkenes.

The addition of an α-trimethylsilyl carbanion **1** to an aldehyde or ketone **2** followed by the *syn* or *anti* elimination of the β-hydroxy-silane **3** represents a powerful method for the synthesis of alkenes **4** (Peterson olefination).[1,2] However difficulties associated with the generation of reagents **1** have seriously limited the use of the procedure. Recently we described that (1-iodoalkyl)trimethylsilanes were convenient precursors to **1** via lithium-halogen exchange.[3] Herein we report on an alternative general approach to carbanions **1** via the metal-lithium exchange reaction of α-stannyl-silanes. Such transmetallation reactions have precedent but only for certain α-seleno-silanes[2f] and α-stannyl-silanes bearing electron withdrawing groups.[4a] The parent (trimethylsilylmethyl)lithium has also been prepared in a similar manner.[4b,c] However, these reactions are limited due to the dearth of methods for the preparation of simple branched α-stannyl-silanes.



Four aldehydes **5a**-**8a** were reacted with (phenyldimethylsilyl)lithium[5] to cleanly provide the corresponding α-hydroxy-silanes **5b**-**8b**. These reactions proceeded smoothly and without any significant complications from competitive Brook rearrangement chemistry.[6,7] Subsequent reaction of these alcohols with triphenylphosphine and carbon tetrachloride provided the α-chloro-silanes **5c**-**8c**.[7] Much to our delight, tributylstannyllithium[8] reacted smoothly with the chlorides **5c**-**8c** to produce the target α-stannyl-silanes **5d**-**8d**.[7] In this process there were no complications either from elimination reactions or from Wurtz coupling chemistry. All these results are summarized in **Table 1**. Finally transmetallation of the stannane **5d** using *n*-butyllithium was carried out in THF solution to produce 1-(phenyldimethylsilyl)hexyllithium, the reagent needed for the Peterson olefination reactions. The addition of aldehydes and subsequent acid or base catalyzed elimination of phenyldimethylsilanol gave the corresponding disubstituted alkenes.[7] In all cases these were formed as mixtures of geometric isomers in ratios that probably reflected the ratios of the diastereoisomeric β-hydroxy-silane intermediates. In one case, using benzaldehyde, the acid mediated elimination gave mostly the *trans* isomer presumably as a result of isomerization after the elimination process. The alkenes synthesized are listed in **Table 2**. Representative experimental procedures for the preparation of α-stannyl-silanes and the use of these species for Peterson olefination are provided below.

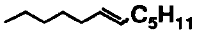
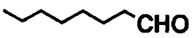
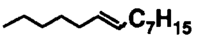
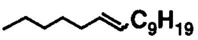
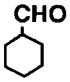
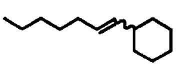
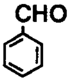
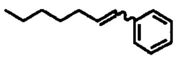
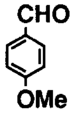
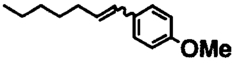
TABLE 1

ALDEHYDE	α– HYDROXY SILANE	α– CHLORO SILANE	α– STANNYL SILANE
 **5a**	 **5b** (73%)*	 **5c** (85%)	 **5d** (81%)
 **6a**	 **6b** (76%)	 **6c** (87%)	 **6d** (83%)
 **7a**	 **7b** (92%)	 **7c** (82%)	 **7d** (69%)
 **8a**	 **8b** (67%)	 **8c** (65%)	 **8d** (57%)

*Isolated yields in parenthesis

A solution of (phenyldimethylsilyl)lithium[5] (1.1 eq) in THF (150 mL) at 0 °C was added dropwise to a solution of hexanal **5a** (13 mL, 1.0 eq) in THF (300 mL) at -78 °C. After warming up to 0 °C, the reaction mixture was poured into aq NH_4Cl (300 mL) and extracted with ether. The extract was dried ($MgSO_4$), evaporated, and the residue chromatographed on silica (eluant hexanes:ether 9:1) to give **5b** as a colorless oil (18.8 g, 73%). Alcohol **5b** (18.8 g), THF (300 mL), CCl_4 (50 mL), and Ph_3P (27.0 g, 1.3 eq) were heated to reflux for 6 h. After cooling, the solvent was removed and the residue extracted with hexanes. Evaporation and chromatography of the residue on silica (eluant hexanes) gave chloride **5c** (17.2 g, 85%) as a colorless oil. To a solution of chloride **5c** (4.0 g, 1.0 eq) in THF (40 mL) was added a solution of tributylstannyllithium[8] (2.0 eq) in THF (20 mL) at 0 °C. After 15 min the reaction mixture was poured into ether, washed with water, dried ($MgSO_4$) and evaporated. Chromatography of the residue (eluant hexanes) gave **5d** (6.5 g, 81%) as a colorless oil.

TABLE 2

ALDEHYDE	ALKENE	ELIMINATION	CIS:TRANS(YIELD)
		TFA KH	61:39* (51) 33:67 (49)
		TFA KH	58:42 (43) 40:60 (62)
		TFA KH	59:41 (36) 41:59 (49)
		TFA KH	54:46 (38) 32:68 (64)
		TFA KH	5:95 (40) 58:30(68)
		TFA KH	29:71 (58) 63:35 (63)

*All ratios were determined by GC/MS

In a typical Peterson olefination reaction, *n*-butyllithium (1.6 M in hexanes) (1.2 eq) was added to a solution of **5d** (555 mg, 1.0 eq) in THF (5 mL) at 0 °C. After 30 min at 0 °C the reaction mixture was warmed to room temperature for 15 min before being added via cannula to a solution of hexanal (170 µL, 1.3 eq) in THF (5 mL) at -78 °C. After 1 h, the reaction mixture was poured into ether, washed with water, dried ($MgSO_4$) and evaporated. Chromatography on silica gave (eluant hexanes) tetrabutyltin and (eluant ether) the crude β-hydroxy-silane. The silane was dissolved in THF (5 mL) and added to either a slurry of potassium hydride (0.5 g) or a solution of trifluoroacetic acid (1.0 mL) in THF (5 mL), at room temperature. After 12 h, the reaction mixture was poured into ether and quenched with either isopropanol (KH reaction) or aqueous sodium bicarbonate (trifluoroacetic acid reaction). The organic layer was dried ($MgSO_4$), evaporated, and the residue was chromatographed on silica (eluant hexanes) to provide 6-dodecene. All the alkenes in **Table 2** were prepared using these procedures. However in the case of the aromatic aldehydes, the solution containing the β-silyl-alkoxide was added directly to the potassium hydride or trifluoroacetic acid solution without work up.

It is clear from these results that α-branched stannyl-silanes can be readily synthesized and used as key intermediates for the synthesis of alkenes from aldehydes. The methodology should find considerable use in future syntheses.

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7) All new compounds were fully characterized by spectral data and microanalysis or high resolution mass spectra. The structures of the *E* and *Z* alkenes were determined either by comparisons of spectral data (IR, ^{1}H NMR, ^{13}C NMR) or by comparisons with published data, see: a) Hamatani, T.; Matsubara, S.; Matsuda, H.; Schlosser, M. *Tetrahedron* **1988**, *44*, 2875. b) Hoshi, M.; Masuda, Y.; Arase, A. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3985. c) Wenkert, E.; Michelotti, E.L.; Swindell, C.S.; Tingoli, M. *J. Org. Chem.* **1984**, *49*, 4894. d) Blue, C.D.; Nelson, D.J. *J. Org. Chem.* **1983**, *48*, 4538.

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