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An Easy Stereoselective Approach to Polyunsaturated Silylated Sulfides

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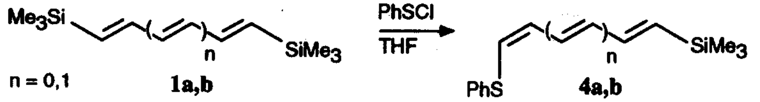
Abstract: Stereodefined monosilylated dienyl and trienylsulfides have been easily prepared by means of chemoselective substitution reactions on unsaturated disilyl derivatives.

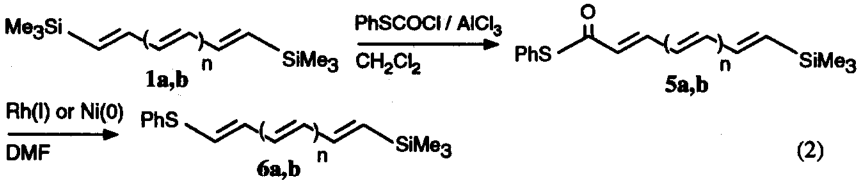
We have recently pursued a program of research that utilizes simple and readily available organosilicon derivatives[1]. In the frame of such a program herein we report a very convenient route to monosilylated sulfides with a conjugate diene and triene structure, a class of compounds having silicon and sulfur functionalities which are both useful[2,3]. The procedure is based upon chemoselective substitution reactions on unsaturated disilyl derivatives **1**.

Accordingly, we started our investigation performing the reactions of compounds **1** with the readily accessible phenylsulfenyl chloride and we found that the reaction of 1,4-disilylated diene **1a** (n=0) or 1,6-disilylated triene **1b** (n=1) with PhSCl in THF at room temperature (eq. 1) led to the monosubstitution product **4a** with inversion of configuration (*Z,E*/*E,E* = 95/5, by capillary GLC analysis) (70% yield) or **4b** (*Z,E,E*/*E,E,E* = 90/10) (51% yield)[4], in accordance with the electrophilic substitution of the silyl group with bromine in simple alkenylsilanes[5].



(1)

Moreover, to obtain the stereoisomers of *E* configuration, we adopted a variation of the strategy (eq. 2).



(2)

In particular, we performed the substitution reaction of compounds **1** with the commercially available S-phenyl carbonochloridothioate in the presence of $AlCl_3$, obtaining the corresponding monosilylated thioesters **5a** (85% yield) or **5b** (77% yield) with high retention of configuration (stereoisomeric purities ≥ 98%). A straightforward decarbonylation reaction[6,7], performed with $RhCl(PPh_3)_3$[6] on compound **5a** or with $Ni(PPh_3)_4$[7] on compound **5b**, led to the corresponding sulfide **6a** (*E,E*/*Z,E* = 96/4) (72% yield) or **6b** (*E,E,E*/*Z,E,E* = 85/15) (65% yield). The stereochemical course of this reaction is in agreement with the fact that the Rh(I)- and Ni(0)-promoted decarbonylation of α,β-unsaturated thioesters proceeds with retention of configuration[6,7]. It is worth noting that the Ni(0)-decarbonylation of **5a** leads to lower yields of product **6a**, whereas a low value of stereoselectivity is observed in the Rh(I)-decarbonylation reaction of **5b**.

Representative procedures for the synthesis of **4a** and **6a**. A THF solution (10 mL) of PhSCl (3.0 mmol) was added at room temperature under nitrogen to a solution of **1a** (2.5 mmol) in THF (5 mL). After 2 h, the mixture was quenched with saturated aqueous NH_4Cl and the usual workup followed by flash chromatography over silica gel (petroleum ether as eluant) gave the product **4a**[8] in 70% yield.

A CH_2Cl_2 solution (10 mL) of PhSCOCl (5 mmol) was added, under nitrogen, to a cold (0°C) stirred suspension of anhydrous $AlCl_3$ (5 mmol) in CH_2Cl_2 (5 mL). After 10 min at 0°C, the clear solution was transferred *via* syringe, under nitrogen, to the addition funnel of a three-necked flask containing a CH_2Cl_2 solution (10 mL) of **1a** (5 mmol). After complete addition at 0°C and stirring for 1 h, the mixture was quenched with saturated aqueous NH_4Cl and the residue purified by distillation to give 1.11 g (85% yield) of **5a** (b.p. 128-130°C, 1 mbar)[8]. Decarbonylation of **5a**: $RhCl(PPh_3)_3$ (1.67 mmol) and **5a** (1.67 mmol) were dissolved in DMF (20 mL) under nitrogen and the system was maintained at 80°C for 1 h. After cooling to room temperature, water was added, and the mixture was extracted with ether. The solvent was evaporated, the residue taken up in a minimum of petroleum ether and passed through a short Florisil column, in order to remove the complex. The product **6a**[8] was isolated in 72% yield after flash chromatography.

In conclusion the process described here, because of its procedural simplicity, appears to be a useful route to conjugated monosilylated sulfides, which in principle could be easily converted into a variety of dienyl or trienylsilanes, by means of cross-coupling reactions performed in the presence of transition metal catalysts[2] and with the phenylthio group acting as a leaving group. Moreover, the synthesis of compounds **5** is also important in its own right since it should provide a convenient preparation of unsaturated thioesters.

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4. The reaction of **1a** with PhSCl in benzene or in CH_2Cl_2 led to a low amount of the monosubstitution product, together with a low amount of the 1,4-disilylated unsaturated sulfide, derived from the addition of phenylsulphenyl cloride and subsequent elimination of HCl instead of Me_3SiCl.
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8. **4a**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ:0.24 (s, 9H), 6.09 (d, *J*=18.2 Hz, 1H), 6.32 (d, *J*=9.3 Hz, 1H), 6.4 (dd, *J*=9.3, 9.3 Hz, 1H), 7.07 (dd, *J*=18.2, 9.3 Hz, 1H), 7.29-7.48 (m, $5H_{arom}$) ppm. ^{13}C-NMR ($CDCl_3$, 50.3 MHz) δ:-1.27, 125.24, 126.71, 129.13, 129.22, 129.27, 132.20, 136.61, 138.74 ppm. MS:m/e 234 (M^+, 11), 219 (4), 157 (26), 109 (14), 73 (100). **5a:**^{1}H-NMR ($CDCl_3$) δ:0.09 (s, 9H), 6.23 (d, *J*=15.2 Hz, 1H), 6.5 (d, *J*=18.1 Hz, 1H), 6.65 (dd, *J*=18.1, 9.2 Hz, 1H), 7.23 (dd, *J*=15.2, 9.2 Hz, 1H), 7.35-7.60 (m, $5H_{arom}$) ppm. ^{13}C-NMR ($CDCl_3$) δ: -1.64, 127.36, 129.16, 129.23, 129.38, 134.59, 140.91, 143.12, 147.71, 188.28 ppm. MS:m/e 262 (M^+, 2), 247 (2), 182 (13), 153 (100), 125 (33), 109 (44), 95 (27), 73 (83). **6a**: ^{1}H-NMR ($CDCl_3$) δ:0.08 (s, 9H), 5.78 (d, *J*=17.7 Hz, 1H), 6.46 (d, *J*=14.7 Hz, 1H), 6.52-6.70 (m, 2H), 7.20-7.45 (m, $5H_{arom}$) ppm. ^{13}C-NMR ($CDCl_3$) δ:-1.33, 127.07, 127.67, 129.12, 129.21, 130.18, 133.10, 134.03, 142.20 ppm. MS:m/e 234 (M^+, 9), 219 (5), 157 (23), 109 (16), 73 (100).

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