

A REGIOSELECTIVE SYNTHESIS OF 2-TRIBUTYLSTANNYL-1,3-DIENES¹

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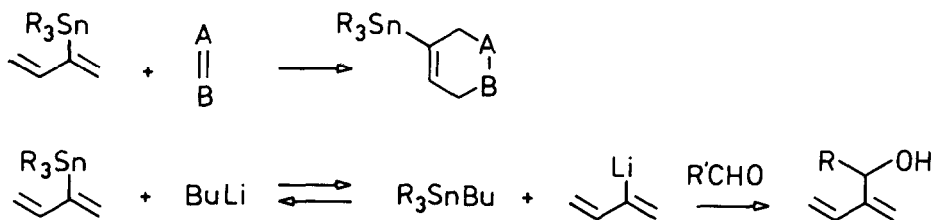
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Summary . Hydrostannylation of 1-trimethylsilyl-4-hydroxy-2-alkyne derivatives followed by acetylation of the OH group and fluoride ion-catalysed 1,4 elimination of the silyl and the acetate groups afforded 2-stannyl-1,3-dienes with high regio- and stereoselectivity.

Differently functionalized 1,3-dienes are attractive synthetic tools, particularly when the functional group does not affect their possibility to undergo [4+2] cycloadditions and when it can be usefully employed in further chemical elaborations of the adducts².

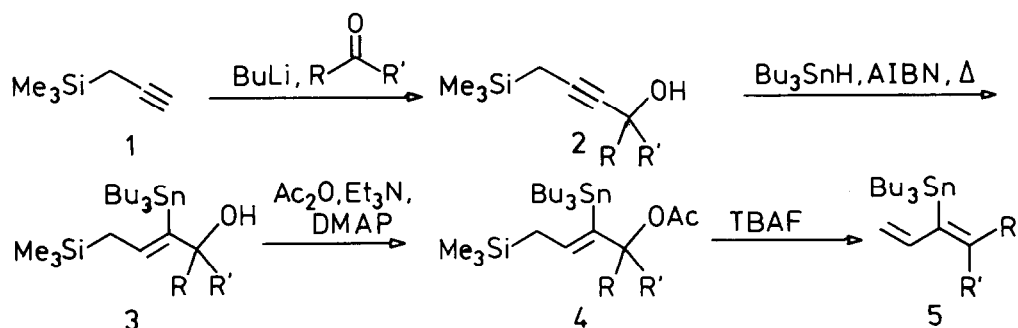
In this respect, 2-stannyldienes have been reported to be suitable reagents for Diels Alder³ reactions and for the stereocontrolled functionalisation of the C-Sn bond "via" tin-lithium exchange⁴.



Nevertheless the syntheses reported until now are limited to the parent compound 2-trialkylstannyl-1,3-butadiene^{5,6} and do not seem suitable for extension⁷.

We report herein a simple regioselective synthesis of differently substituted 2-tributylstannyl-1,3-dienes based on the TBAF catalysed 1,4 elimination of the trimethylsilyl and the acetate groups of the allylsilane **4** prepared as described in scheme 1.

Metallation of propargyltrimethylsilane **1** with BuLi in THF at -78° , followed by an equimolar amount of a carbonyl compound (see Table 1) in HMPT, gave the propargylalcohols **2** in yields varying from 62 to 89%.



The triple bond was then hydrostannylated with 1.2-1.5 eq. of tributylstannylhydride in presence of 0.1 eq. of AIBN at 120°C for 6-10 hs. NMR analysis of the mixture showed a quantitative reduction of the triple bond with formation of vinylstannanes **3** as a mixture of Z/E isomers with a high prevalence of the Z form (particularly in presence of hindered R groups) which was easily purified by column chromatography on silica gel (eluant: hexane-ethyl acetate 10/1 v/v). No traces of the regioisomer with the stannyl group on the carbon far from the hydroxyl group were detected by NMR analysis⁸.

Attribution of the structures was based on the presence of a triplet for the olefinic proton in the region 6.0-5.0 ppm and the stereochemistry was assigned looking at the $^1\text{H}-^{119}\text{Sn}$ coupling constants for that proton of 120-160 Hz., typical value for a trans H-Sn relationship.

Alcohols **3a-f** were acetylated in nearly quantitative yields with $\text{Et}_3\text{N}/\text{Ac}_2\text{O}$ in presence of catalytic amounts of DMAP in CH_2Cl_2 at room temperature, and further treatment of the crude **4a-f** with TBAF in THF at 0°C gave dienes **5a-f** in good yields after purification by column chromatography on silica gel (eluant: hexane)⁹.


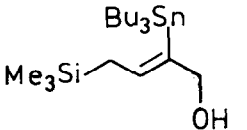
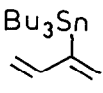

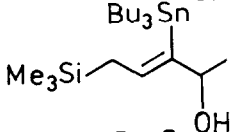
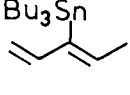
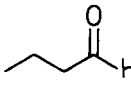
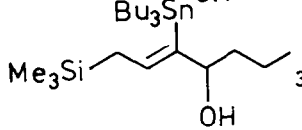
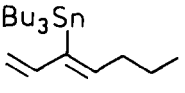
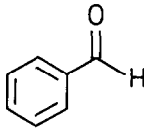
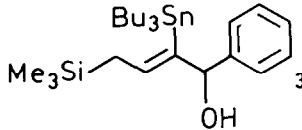
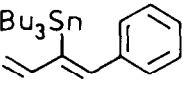
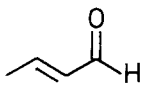
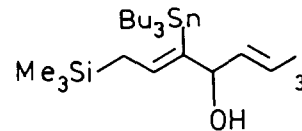
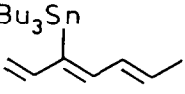
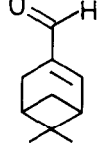
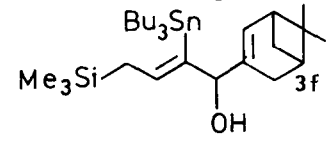
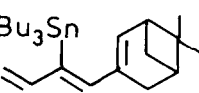
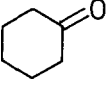
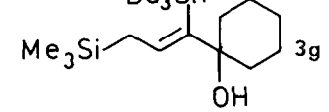
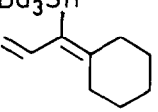

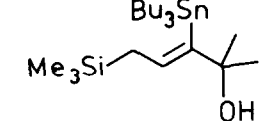
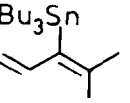
NMR analysis showed **5b-f** being in prevalence in the Z conformation up to 85-95%.

Tertiary alcohols **3g-h** did not undergo the acetylation neither under more strong conditions and the corresponding dienes **5g-h** were obtained treating directly the alcohol with KH in boiling diglyme for several hours¹⁰.

A more detailed description of the experimental section together with the work which is now in progress directed to the preparation of a wider range of polysubstituted 2-stannyl-1,3-dienes (and polyenes) will be soon reported in a forthcoming full paper.

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Table 1. Synthesis of 2-tributylstannyl-1,3-dienes **5**

Carbonyl Compound	Alcohol 3	Yield ^a	Dienes 5	Z/E ratio ^b	Yield ^c
		3a 62%		5a --	54%
		3b 72%		5b 8:1	65%
		3c 60%		5c 8:1	50%
		3d 66%		5d 11:1	56%
		3e 65%		5e 8:1	53%
		3f 75%		5f 11:1	41%
		3g 70%		5g --	41%
		3h 59%		5h --	44%

a) Yields of isolated and fully characterized pure compounds.

b) Ratio determined by NMR (90 MHz).

c) Overall yield calculated on the starting propargyltrimethylsilane **1**.

References and notes.

- 1) Presented in part at the V^o International Conference on the Organometallic and Coordination Chemistry of Ge, Sn, Pb . Padua (I) Sep. 7-12 , 1986.
- 2) For the more recent literature on functionalized dienes : S, Nunomoto, Y. Yamashita, J.Org.Chem. **44** 4788 (1979). P.A. Brown, P.R. Jenkins, Tetrahedron Lett. **23** 3733 (1982). B. Trost, P.G.J. McDougal, J. Am. Chem. Soc. **106** 383 (1984). K.K. Wang, S.S. Nikati, M.M. Marcano, Tetrahedron Lett. **27** 1123 (1986). A. Hosomi, Y. Sakata, H. Sakurai, Tetrahedron Lett. **26** 5175 (1985). M.D. Fryzuk, G.S. Dates, C. Stone, Tetrahedron Lett. **27** 1537 (1986).
- 3) M. Taddei, A. Mann, Tetrahedron Lett. **27** 2913 (1986).
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- 5) C.A. Aufdermarch Jr. J.Org.Chem. **29** 1994 (1964).
- 6) I. Fleming, M. Taddei, Synthesis 1942 (1985).
- 7) When the work was in progress a communication reported the synthesis of some stannyl alkenes and dienes using the coupling between enol triflates and hexamethyldistannane in presence of Pd complexes. W.D. Wulff, G.A. Peterson, W.A. Bouta, K.S. Chan, K.L. Faron, S.R. Gilberston, R.W. Koesler, D.C. Young, C.K. Murray, J.Org.Chem. **51** 279 (1986).
- 8) At the moment we have no explanations for this regioselectivity in the hydrostannylation of a not symmetrical triple bond, but further work is still in progress to clarify this aspect. For some literature on the regiochemistry of hydrostannylation see : G. Bohr, S. Pawlenka, Houben-Weyl Methoden der Organischen Chemie, Metallorganische Verbindungen, Ge, Sn . B13, T6, (1978), 239-244. See also : H.E. Ensley, R.R. Buescher, K. Lee, J.Org.Chem. **47** 404 (1981). G.A. Tolstikov, M.S. Miftakhov, N.A. Danilova, Ya.L. Vel'der, Synthesis 496 (1986).
- 9) **5a** NMR (CCl₄) δ : 0.9-1.7 (27H, m, Bu₃Sn), 5.1-6.0 (4H, m, 2 CH=), 6.7 (1H, m, CH=). **5b** NMR (CCl₄) δ : 0.8-1.6 (27H, m, Bu₃Sn) 1.7 (3H, d, J=6Hz, CH₃), 4.7 (1H, m, CH=), 4.8 (1H, m, CH=), 6.5 (2H, m, 2CH=). **5c** NMR (CCl₄) δ : 0.7-2.0 (32H, m, Bu₃Sn, CH₂, CH₃), 2.1 (2H, m, CH₂), 4.9 (1H, m, CH=), 5.0 (1H, m, CH=), 6.6 (2H, m, 2CH=). **5d** NMR (CCl₄) δ : 0.7-2.0 (27H, m, Bu₃Sn), 5.1 (1H, m, CH=), 5.2 (1H, m, CH=), 6.6 (2H, m, 2CH=), 7.2 (5H, m, Arom.). **5e** NMR (CCl₄) δ : 0.9-1.8 (27H, m, Bu₃Sn), 1.9 (3H, d, J=7Hz, CH₃), 5.0 (2H, m, CH₂=), 6.2-6.7 (4H, m, 4CH=). **5f** NMR (CCl₄) δ : 0.4-1.7 (38H, m, Bu₃Sn and myrtenyl alkylic part), 2.1 (3H, m, allylic CH₂ and CH), 4.5 (2H, m, CH₂=), 5.0 (1H, m, CH=), 6.1 (1H, m, CH=).
- 10) **5g** NMR (CCl₄) δ : 0.6-2.1 (37H, m, Bu₃Sn and cyclohexyl group), 5.8 (1H, m, CH=), 6.3 (2H, m, 2CH=): **5h** NMR (CCl₄) δ : 0.2-2.0 (33H, m, Bu₃Sn, 2CH₃), 5.7 (1H, m, CH=), 6.3 (2H, m, 2CH=).

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