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A SIMPLE SYNTHESIS OF 1-TRIMETHYLSILYL-2,3-DIENES

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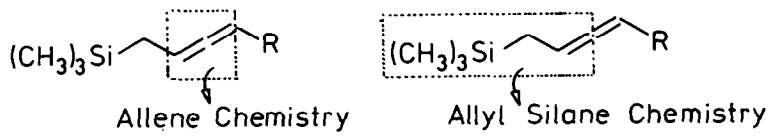
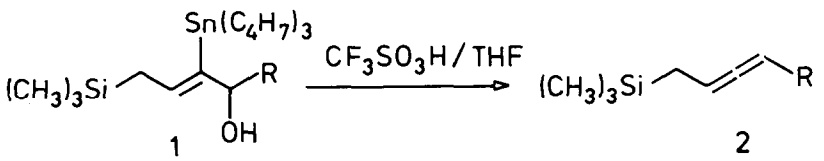
Summary. 1-Trimethylsilyl-2,3-dienes have been prepared through a conjugative acidic elimination of a tributylstannyl and a hydroxy group from β-hydroxy-vinylstannanes.

Allenes have always played an important role in the synthesis of terpenoids and differently substituted dienic and polyenic systems[1].
Although 1-trimethylsilyl-1,2-dienes (trimethylsilyl allenes) have been widely synthesised using different methods[2], 1-trimethylsilyl-2,3-dienes (α-allenylsilanes) have not attracted much attention as revealed by the few reports dealing with their chemistry[3].
Nevertheless 1-trimethylsilyl-2,3-dienes have a peculiar structure with the possibility of a double functionalisation. They can be regarded as dienes in which the normal functionalisation can be achieved on the allenic part[4] without affecting the C-Si bond, or as allylsilane analogues particularly useful for the synthesis of 1,3 dienes.



Here we report a new high yield synthesis of 1-trimethylsilyl-2,3-dienes, based on a conjugative α,β elimination of a -$SnBu_3$ and a -OH in acidic media from vinylstannanes 1.



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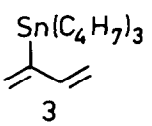

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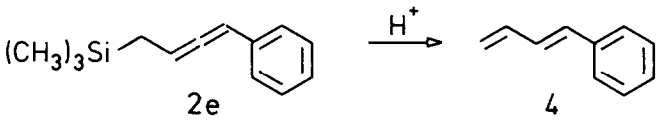
Product		Yield
R=H	**2a**	40 %
$R=C_3H_7$	**2b**	72 %
$R=CH(CH_3)_2$	**2c**	74 %
$R=C_6H_{13}$	**2d**	69 %
$R=C_6H_5$	**2e**	92 %

In fact, on treating a solution of **1d** (2.2 g, 4.3 mmol) in dry THF (7 mL) at 0°C with CF_3SO_3H (0.6 g, 4.3 mmol), after 1 min. tlc analysis showed the disappearence of the starting material. After hydrolysis with a saturated ammonium chloride solution followed by extraction in diethyl ether, compound (**2d**) was isolated by column chromatography on silica gel (eluant hexane), 600 mg, (68% yield)[5]. Stannyl derivatives **1** can be easily prepared by hydrostannylation of the corresponding propargylalcohols[6].

When the reaction was performed on **1a**, there was also about 40 % formation of the diene **3** was observed.

Allenes **2b-f** easily undergo protodesilylation to give the corresponding dienes as shown in the following example:



2e 4

Further applications of this procedure are currently underway in our laboratory.

References and notes.

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2) R.L.Danheiser, D.J.Carini, A.Basak, J.Am.Chem.Soc., **103**, 1604 (1981) ; R.L.Danheiser, D.J.Carini, D.M.Fink, A.Basak, Tetrahedron **39**, 935 (1983) and references therein; T.Tabuchi, J,Inanaga, M.Yamaguchi, Tetrahedron Lett, **27**, 5237 (1986).

3) To our knowledge the only report dealing with the preparation of 1-trimethylsilyl,2,3-dienes is : M.Montury, B.Psaume, J.Gore',Tetrahedron. Lett., **21**, 163 (1980).

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5) **2a** NMR (CCl_4) δ : 0.19 (s, 9H, Me_3Si), 1.06 (m, 2H, CH_2), 5.3-5.5 (m, 3H, alleny part), Mass spectrum m/e : 126 (M^+). **2b** NMR (CCl_4) δ : 0.00 (9H, s, Me_3Si), 0.7-1.1 (5H, m, CH_3,CH_2), 1.2-1.6 (2H, m, CH_2), 1.9-2.0 (2H, m, CH_2) 4.6-4.9 (1H, m, CH=), 5.3-5.5 (1H, m, CH=). Mass spectrum m/e: 153 (M^+-15).**2c** NMR (CCl_4) δ : 0.51 (9H, s, Me_3Si), 0.8-1.1 (8H, m, $2CH_3$, CH_2), 2.2(1H, m, CH), 4.9-5.1 (1H, m, CH=), 5.5-5.8 (1H, m, CH=).Mass spectrum: m/e 168 (M^+).**2d** NMR (CCL_4) δ : 0.22 (9H, s, Me_3Si), 0.9-1.2 (5H, m, CH_3, CH_2), 1.3-1.5 (10H, m, $5CH_2$), 2.0-2.4 (1H, m, CH), 5.0-5.3 (2H, m, 2CH=).Mass spectrum m/e: 167 (M^+-C_3H_7). **2e** NMR (CCl_4) δ : 0.00 (9H, s, Me_3Si), 1.2-1.5 (2H, m, CH_2), 5.3-5.5 (1H, m, CH=), 5.9-6.1 (1H, m, CH=), 6.9-7.2 (5H, m, Arom.).Mass spectrum m/e : 190 (M^+).

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