Synthesis of *trans*-1,4-Bis[dimethylorganylsilyl]-2-butenes

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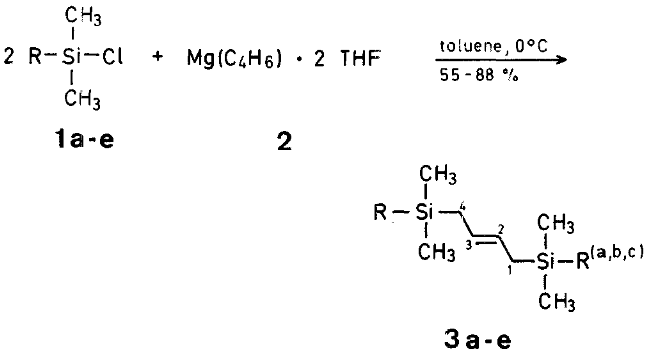
The reaction of chlorodimethylorganosilanes [$Cl—Si(CH_3)_2R$; R = CH_3, $—CH{=}CH_2$, $—CH_2Cl$, $—CH_2—CH{=}CH_2$, C_6H_5) with magnesium-butadiene at 0 °C in toluene gives *trans*-1,4-bis[dimethylorganylsilyl]-2-butenes in 55–88% yield. The amount of (*Z*)-isomer ranges from 0 to 17%, depending on the organic substituent; no 1,2-disylilated products were detected.

We have earlier shown[1] that substituted 1-silacyclopent-3-enes can be efficiently synthesized by reacting organo-substituted dichlorosilanes with magnesium-butadiene[2] and that organodichlorophosphines or diorganochlorophosphines react with magnesium-butadiene to give vinylphosphiranes or α-vinyl-*P,P'*-ethylene-bis(diorganophosphanes) respectively, as a result of a formal 1,2-addition to the butadiene[3]. Here we describe the reaction of organodimethylchlorosilanes **1a–e** with magnesium-butadiene (**2**) to give *trans*-1,4-bis[dimethylorganylsilyl]-2-butenes (**3**) in good yields. This reaction represents an easy entry to substituted allylsilanes, which are useful intermediates[4] in organic syntheses.



In the reaction of conjugated dienes with alkali metals, followed by treatment of the mixture with chlorotrimethylsilane, a remarkable effect of the nature of the alkali metal on the stereochemistry of the resultant disubstituted butenes has been observed[5]: whereas mainly *cis*-1,4-addition products are obtained using sodium in tetrahydrofuran, *trans*-1,4-addition products are obtained from the analogous reaction using lithium in tetrahydrofuran. It has further been reported[6] that the reaction of chlorotrimethylsilane with butadiene in the presence of magnesium and hexamethylphosphoric triamide also occurs with predominant 1,4-addition of the trimethylsilyl groups to give a mixture of both stereoisomers in addition to some (12%) 1,2-addition product.

Our procedure gives exclusively 1,4-adducts as demonstrated by G.L.C. and ^{1}H-N.M.R. analysis (Table). All compounds **3** show an intense Raman absorption band at $\nu = 1655\ cm^{-1}$, and an I.R. absorption band at $\nu = 960\ cm^{-1}$ which are indicative of a *trans*-substituted central double bond. The presence of (*E*)-isomers is also indicated by the ^{1}H-N.M.R. coupling constants, which were deduced from the spectra by simulation for all compounds except for **3c** with its allylic protons overlapping ($^3J_{2,3} = 15$ Hz)[7]. Incomplete separation of the signals of the minor (*Z*)-components did not allow assignment of their

Table 1. *trans*-1,4-Disilyl-2-butenes (3) prepared

3	R	Yield[a] [%]	b.p./torr [°C]	Molecular Formula[b]	M.S. (70 eV) m/e[c]
a	CH_3	65	102°/48	$C_{10}H_{24}Si_2$ (200.4)	200, 112, 97, **73**, 45
b	$-CH=CH_2$	65	125°/40	$C_{12}H_{24}Si_2$ (224.5)	224, 183, **85**, 59
c	$-CH_2-CH=CH_2$	55	130–133°/40	$C_{14}H_{28}Si_2$ (252.5)	252, 211, 183, **99**, 73, 59, 43
d	$-CH_2Cl$	75	85–88°/0.1	$C_{10}H_{22}Cl_2Si_2$ (269.4)	270, 268, 219, 107, 98, **79**
e[d]	C_6H_5	88	200°/1	$C_{20}H_{28}Si_2$ (324.6)	324, 197, 174, **135**

[a] Yield of isolated product, based on 2.
[b] The microanalyses were in good agreement with the calculated values: C ±0.15, H ±0.14, Si ±0.17. The analyses were performed by Analytisches Labor Dornis & Kolbe, D-4330 Mülheim/Ruhr.
[c] Base peaks are in bold-face.
[d] See Ref. 9 in which the stereochemistry of 3e is not assigned, however.

Table 2. Spectral Data of Compounds 3

3	I.R. (neat), Raman ν [cm⁻¹]	^{1}H-N.M.R. (C_6D_6/TMS_{int}), δ [ppm]						Stereochemistry
		1-H	2-H	CH_3	H[a]	H[b]	H[c]	
a	1655, 960	1.33	5.16	0.05	–	–	–	*trans*
b	1657, 1590, 960	1.42	5.25	0.02	5.65	5.91	6.17	*trans* (*cis* ≦ 10%)
c	1655, 1630, 1635 (w)	1.39	5.22	0.01	1.46	4.86	5.77	*trans* (*cis* ≦ 10%)
d	1655, 1635 (w), 960	1.41	5.16	0.02	2.52	–	–	*trans*
		1.44	5.23	0.04	n.d.			(*cis* ≦ 10%)
e	1655, 960	1.59	5.24	0.19	7.17	7.39		*trans*
		1.61	5.36	0.23	n.d.	n.d.		(*cis* ≦ 17%)

coupling constants. Although no further separation of products 3a–e could be achieved by G.L.C. (Varian 1400, 30 m PS, FID, 220°/60°–320°/300° C, 1.0 bar N_2), a second smaller downfield-shifted set of ^{1}H-N.M.R. signals ($Si-CH_3$, $CH_2-CH=$ groups) in 3b–e was present which is probably due to minor amounts (10–17%) of the (*Z*)-isomer. The presence of the (*Z*)-isomer of 3a could not be detected in the ^{1}H-N.M.R. spectrum.

The nature of the organic group at silicon has no influence on the reactions and vinyl- or allyldimethylchlorosilanes (**1b, c**) react as smoothly as phenyldimethylchlorosilane (**1e**) to give the corresponding 1,4-disilylated products. The chloromethylsilyl group of **1d** is inert towards magnesium-butadiene under the reaction conditions, i.e., no 1:1 adducts such as dimethylsilacyclohexene could be isolated. The functional groups at silicon in **3b, c, d** allow further derivatization of these disilylbutenes.

Chloro-(methoxy)-dimethylsilane[8] reacts with magnesium-butadiene in an anomalous manner to give a mixture of products which were not identified. The reaction of dichlorodimethylsilane with magnesium-butadiene to give *Si,Si*-dimethylsilacyclopentene has been described previously[1].

(*E*)-1,4-Bis[chloromethyldimethylsilyl]-2-butene [3d; (*E*)-1,8-Dichloro-2,2,7,7-tetramethyl-2,7-disilyl-4-octene]; Typical Procedure:
Magnesium-butadiene · 2 THF[2] [2, $Mg(C_4H_6) \cdot 2\ C_4H_8O$; 6.68 g, 30 mmol] is added portionwise to a well stirred, ice-cooled solution of chloro-(chloromethyl)-dimethylsilane (**1d**; 11.1 g, 65 mmol) in dry toluene (150 ml). Stirring is continued for 4 h and the mixture then filtered. The filtrate is evaporated and the residue fractionally distilled; yield of **3d**: 5.9 g (73%, based on **2**); b.p. 85°C/0.1 torr.

		C	H	Si
$C_{10}H_{22}Cl_2Si_2$	calc.	44.60	8.23	20.79
(269.4)	found	44.48	8.11	20.88

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1 Richter, W.J. *Synthesis* **1982**, 1102.
2 Fujita, K., Ohnuma, Y., Yasuda, H., Tani, H. *J. Organomet. Chem.* **1976**, *113*, 201.
3 Richter, W.J. *Chem. Ber.* **1983**, *116*, 3293; *Angew. Chem.* **1982**, *94*, 932; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 919.
4 Colvin, E. *Silicon in Organic Synthesis*, Butterworth, London, 1981.
5 Weyenberg, D.R., Toporcer, L.H., Nelson, L.E. *J. Org. Chem.* **1968**, *33*, 1975.
6 Dunogues, J., Arreguy, B., Biran, C., Calas, R., Pisciotti, F. *J. Organomet. Chem.* **1973**, *63*, 119.
7 Collection of N.M.R. data in Max Planck Institut für Kohlenforschung (see address of authors).
8 Van Wazer, J.R., Moedritzer, K. *J. Inorg. Nucl. Chem.* **1964**, *26*, 737.
9 Malinovskii, M.S., Krivosheeva, N.G., Dryuk, V.G., Gnovitskaya, O.D. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1976**, *19*, 581; *C.A.* **1976**, *85*, 124013.