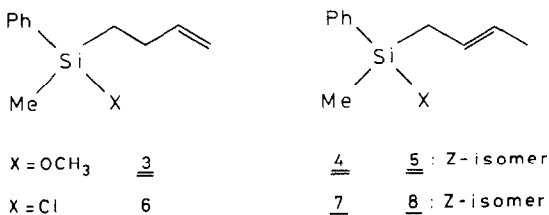




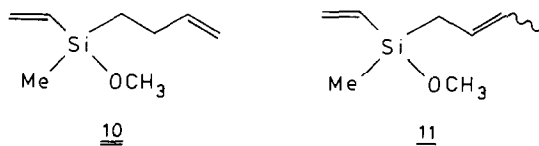
## Results

We now describe some further reactions between diorganodichlorosilanes and butadienemagnesium which suggest that a silicon-substituted crotyl-Grignard compound is the key intermediate. Reaction of butadienemagnesium with phenylmethyl-dichlorosilane in toluene at  $-78^{\circ}\text{C}$  followed, after 24 h, by treatment with excess methanol and triethylamine gave phenylmethylsilacyclopent-3-ene (**2**) (50% yield, based on reacted starting material) as the major product, along with the methoxy-butenylsilane derivatives **3** to **5** ( $\text{X} = \text{OCH}_3$ ) in 12% yield. If the reaction is quenched after 60 h at  $-70^{\circ}\text{C}$ , only isomer **3** is isolated.

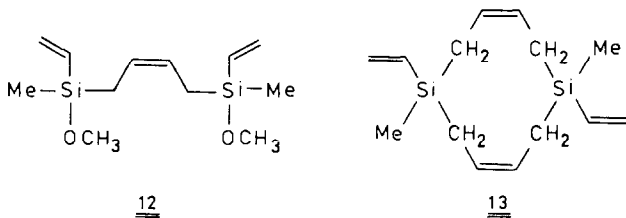


If in the absence of amine only enough methanol is added to destroy the unchanged phenylmethyl-dichlorosilane, then the chloro-substituted analogues of **3** to **5** ( $\text{X} = \text{Cl}$ , **6** to **8**) can be identified (GC/MS) in the mixture.

When vinylmethyl-dichlorosilane and butadienemagnesium are brought into reaction and the mixture is subsequently treated with methanol in the presence of triethylamine only minor amounts of 3-butenylmethylvinylmethoxysilane (**10**) and its isomer **11** analogous to **4** or **5** are formed, but vinylmethylsilacyclopent-3-ene (**9**) is a major product (20%).



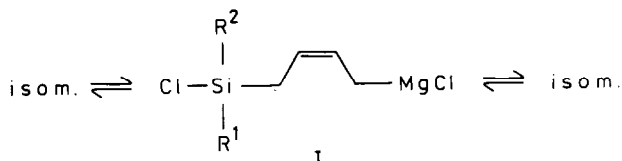
In addition, ( $R^*, R^*$ )- and ( $R^*, S^*$ )-3,8-dimethoxy-3,8-dimethyl-3,8-disiladeca-1,5,9-trienes (**12a** and **12b**) and the dimeric species 1,6-divinyl-1,6-dimethyl-1,6-disilacyclodeca-3,8-diene (**13**), in three isomeric forms, are generated in 8% yield. (The 1,1,6,6-tetramethyl compound analogous to **13** is known [5].) The *cis/cis*-arrangement of double bonds in two of these products has been assigned on the



basis of  $^1\text{H}$  NMR and IR measurements; the remaining isomer probably has a *cis/trans*-arrangement of the double bonds.

### Discussion

On the basis of these results we suggest that in reactions involving butadiene-magnesium a substituted crotyl-Grignard compound **I** is formed initially. A structurally related intermediate has recently been suggested for the reaction of  $\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)$  with butadienemagnesium [6].

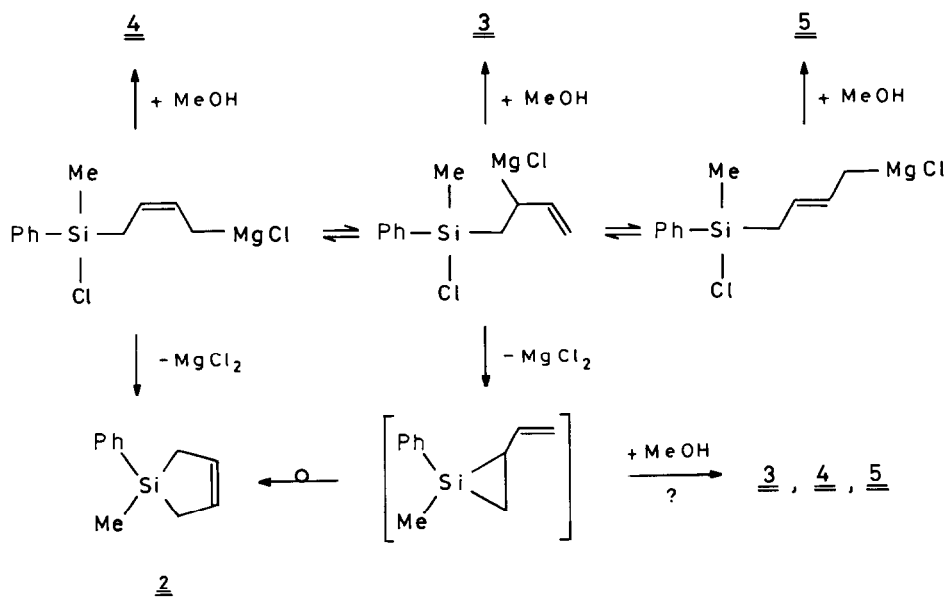


**I** is the product of an initial electrophilic attack of silicon on a terminal carbon atom of the butadiene dianion equivalent, which then may further react to give either **3** to **5** (on methanolysis) or the silacyclopent-3-ene (**2**). This latter product may be formed directly by elimination of  $\text{MgCl}_2$  from **Ia**, or alternatively **Ib** may cyclize to a vinylsilarane, which would be expected to rearrange to **2** [3].

Methanolysis of crotyl-Grignard gives 1-butene as the major product rather than 2-butene [4], and this parallels the isomer distribution in methanolysis of **I** ( $\text{R} = \text{Ph}$ ) which was shown to be  $3/4/5 = 5/2/1$ , whereas only **3** is formed after reaction at  $-70^\circ\text{C}$  (60 h).

If  $\text{R} = \text{vinyl}$ , the intermediate appears to be more reactive towards both dimeriza-

SCHEME 1



tion and reaction with the starting dichlorosilane, since a 1/1 ratio of the two isomers of **12** is formed along with **13** on methanolysis. In the absence of methanol both **13** and the precursor to **12**, the 3,8-dichlorosilane **14**, are observed (GC/MS).

These results suggest that the silyl-substituted Grignard I is the major intermediate involved in the reaction of butadienemagnesium and dichlorosilanes.

## Experimental

Infrared spectra were recorded on a Nicolet 7000 spectrometer. The  $^1\text{H}$  NMR spectra were obtained with a Bruker WP-80 or a Varian WH-270. GC analyses were made with Siemens I or Varian 3700 instruments. Mass spectra were recorded on a Varian MAT CH-5. All reactions were carried out in an atmosphere of argon.

*Reaction of butadienemagnesium with phenylmethyldichlorosilane.* Butadienemagnesium (**1**) (7.2 g, 32.4 mmol) was added in portions to a stirred solution of phenylmethyldichlorosilane (6 g, 31.4 mmol) in 150 ml of dry toluene at  $-70^\circ\text{C}$ . The mixture was kept at  $-70^\circ\text{C}$  for 24 hour then treated with  $\text{Et}_3\text{N}/\text{MeOH}$  (4.5 ml/2.5 ml). After filtration and removal of the solvent the residual mixture was distilled. A 2.5 g fraction contained 20% of phenylmethyldimethoxysilane, 59% of **2**, 1.3% of *Z*-**4**, 0.5% of *E*-2-butenylphenylmethylmethoxysilane (**5**), and 2.6% of 3-butenylphenylmethylmethoxysilane (**3**). Preparative GC (22 m PS; FID;  $220^\circ\text{C}/60\text{--}320^\circ\text{C}/330^\circ\text{C}$ ,  $8^\circ\text{C}/\text{min}$ , He 1.5 bar) gave pure **3** ( $^1\text{H}$  NMR: 0.35, s ( $\text{CH}_3$ , 3H); 2, m ( $\text{CH}_2$ , 4H); 3.42, s ( $\text{OCH}_3$ , 3H); 4.8 and 5.90, m (vinyl, 3H); 7.3, 7.5, m (phenyl, 5H). MS ( $m/e$ ): 206 (3%), 181, 178 (20%), 151 (100%), 121 (40%), 59, and **4** and **5** (not fully separated) ( $^1\text{H}$  NMR: 0.34, s ( $\text{CH}_3$ ); 1.48, 2d ( $\text{C}-\text{CH}_3$ ); 1.74, m ( $\text{CH}_2$ ); 3.43, s ( $\text{O}-\text{CH}_3$ ); 5.36, m ( $\text{HC}=\text{CH}$ ), 7.3, 7.5, m (phenyl). MS ( $m/e$ ): 206, 151 (100%), 121 (40%), 59 (compare ref. 3).

*Reaction of I with phenylmethyldichlorosilane followed by treatment with MeOH.* The procedure was as described above, but only one equivalent of MeOH was added after 24 h. A fraction of 2.5 g was isolated, and this consisted of 19% of unreacted phenylmethyldichlorosilane, 51% of phenylmethyldimethoxysilane, 7% of **2**, and 4.0%, 7.1% of *Z*-**6**, *E*-2-butenylphenylmethylchlorosilane and 3.1% of **8**, and 3-butenylphenylmethylchlorosilane (**7**) (Retention times 17.0, 17.5 and 17.9). MS ( $m/e$ ) for **6** and **8**: 212, 210, 157 (40%), 155 (100%), 91, 63. For **7**: 212, 210, 182, 171, 169, 157 (40%), 155 (100%), 117, 91, 63.

*Reaction of I with vinylmethyldichlorosilane.* This mixture formed from 11.5 g (82 mmol) of vinylmethyldichlorosilane in 500 ml of dry toluene and 20 g of **1** was kept for 20 h and then treated with 3.3 ml of MeOH (82 mmol) and  $\text{Et}_3\text{N}$  (2.2 ml). A 8.5 g fraction found to contain 54% of toluene, 3.5% of **9**, and 6.3% of 3-butenylvinylmethylmethoxysilane (**10**), 4.6% of 2-butenylvinylmethylmethoxysilane (**11**), 5.6% of 3,8-dimethoxy-3,8-dimethyl-3,8-disiladeca-1,5,9-triene (**12**), and 3.3% of 1,6-divinyl-1,6-dimethyl-1,6-disilacyclodeca-3,8-diene (**13**) and was separated by preparative GC. For GC 55 m PS-240, FID,  $200^\circ\text{C}/60\text{--}240^\circ\text{C}/250^\circ\text{C}$ , 0.8 bar  $\text{H}_2$ ).

**10**:  $^1\text{H}$  NMR: 0.14, s ( $\text{CH}_3$ , 3H); 0.72, m ( $\text{SiCH}_2$ , 2H); 2.0, m ( $\text{CH}_2$ , 2H); 3.28, s ( $\text{OCH}_3$ , 3H), 5.0–6.0, m (2 vinyl, 6H). MS ( $m/e$ ): 156 (1%), 141, 128 (20%), 101 (100%), 75 (30%).  $\text{C}_8\text{H}_{16}\text{OSi}$  (156.21) Found: C, 61.9; H, 9.9; Si, 17.8 Calcd.: C, 61.5; H, 10.3, Si, 17.9.

**11**:  $^1\text{H}$  NMR: 0.17, s ( $\text{CH}_3$ , 3H); 1.55, d ( $\text{CH}_3$ , 3H); 1.63, d ( $\text{SiCH}_2$ , 2H); 3.31, s ( $\text{OCH}_3$ , 3H); 5.5, m ( $\text{HC}=\text{CH}$ , 2H); 6.0, m (vinyl, 3H). MS ( $m/e$ ): 156 (5%), 141, 101 (100%), 75 (20%).

**12:**  $^1\text{H NMR}$ : 0.19, s ( $\text{CH}_3$ , 6H); 1.65, m ( $\text{SiCH}_2$ , 4H); 3.32, s ( $\text{OCH}_3$ , 6H); 5.47, m ( $\text{HC}=\text{CH}$ , 2H); 6.0, m (2 vinyl, 6H). MS ( $m/e$ ): 256, 241, 215, 161, 101 (100%), 75 (25%), 45. IR:  $1625\text{ cm}^{-1}$ , shoulder at  $1638\text{ cm}^{-1}$ , predominantly (*Z*). The GC clearly shows two peaks, retention time 33.8 and 34.5 min, presumably ( $R^*$ ,  $R^*$ ) and ( $S^*$ ,  $R^*$ ) isomers.

**13:**  $^1\text{H NMR}$ : 3 isomers, 53/29/18 ratio; major isomer *Z,Z*,  $C_s$  symmetry: 0.08, s ( $\text{CH}_3$ , 6H); 1.58, m ( $\text{SiCH}_2$ , 8H); 5.39, qu ( $\text{HC}=\text{CH}$ , 4H); 5.70, 5.96, 6.15 (vinyl, 6H). Second isomer, *Z,Z*,  $C_2$  symmetry: 0.07, s ( $\text{CH}_3$ , 6H); 1.6, m ( $\text{SiCH}_2$ , 8H); 5.27, qu ( $\text{HC}=\text{CH}$ , 4H); 5.70, 5.96, 6.15 (vinyl, 6H). Third isomer, presumably *Z,E*; similar  $^1\text{H NMR}$  spectrum. MS ( $m/e$ ): 248 (20%), 124 (15%), 109, 96 (100%), 71 (40%), 55. IR:  $3005, 1640\text{ cm}^{-1}$ , *Z*-isomer;  $1660\text{ cm}^{-1}$ , weak, *E*-isomer.

*Reaction of 1 with vinylmethyldichlorosilane, followed by treatment with MeOH.* After a procedure analogous to that above analysis by GC/MS (20 m OV 1;  $100\text{--}300^\circ\text{C}$ , He 0.55 bar showed to produce 3,8-dimethyl-3,8-dichloro-3,8-disiladeca-1,9-diene (**14**); MS ( $m/e$ ): 266, 264, 223, 124, 107, 105 (100%), 96 (90%), 79 (60%), 63.

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