DIORGANOSILACYCLOPENT-3-ENE DERIVATIVES FROM DIORGANODICHLOROSILANES AND BUTADIENEMAGNESIUM: EVIDENCE FOR CROTYL-GRIGNARD INTERMEDIATES

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Summary

Reactions of substituted dichlorosilanes, $R^1R^2SiCl_2$ ($R^1 = CH_3$, $R^2 = Ph$, vinyl), with butadienemagnesium yield methoxybutenylsilane derivatives and silacyclopent-3-enes after treatment with methanol at $-70°C$. For R = vinyl, a substituted cyclodeca-3,8-diene is formed in addition to the 1,4-disilylated butenylic species. The nature of the range of products suggests that silyl-substituted crotyl-Grignard compounds are the major intermediates.

Introduction

Recently we reported that substituted silacyclopent-3-ene derivatives could be formed in good yield by treating diorganodichlorosilanes with butadienemagnesium (**1**) (eq. 1) [1].

We suggested, by analogy to the reaction of dichlorophosphines with butadiene-magnesium [2], that vinylsilirane species might be involved as intermediates. Vinyl-siliranes are believed to be involved in the reaction of photochemically generated silylene with butadienes [3] but have never been isolated, and would presumably rearrange rapidly to give substituted silacyclopent-3-enes or, on methanolysis, methoxybutenylsilicon derivatives.

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 phenylmethyldichlorosilane in toluene at −78°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 methoxybutenylsilane derivatives 3 to 5 (X = OCH$_3$) in 12% yield. If the reaction is quenched after 60 h at −70°C, only isomer 3 is isolated.

X = OCH$_3$	3	4 5 : Z-isomer
X = Cl	6	7 8 : Z-isomer
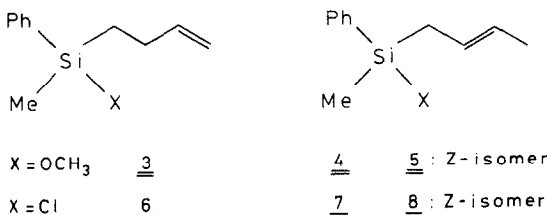
If in the absence of amine only enough methanol is added to destroy the unchanged phenylmethyldichlorosilane, then the chloro-substituted analogues of 3 to 5 (X = Cl, 6 to 8) can be identified (GC/MS) in the mixture.

When vinylmethyldichlorosilane 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%).
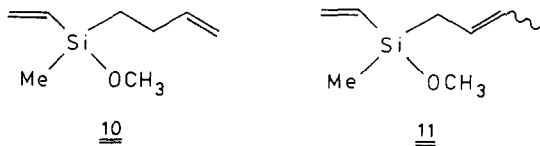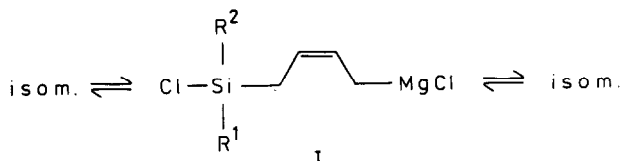

In addition, (R^*,R^*)- and (R^*,S^*)-3,8-dimethoxy-3,8-dimethyl-3,8-disiladeca-1,5,9-trienes (12a and 12b) and the dimeric species 1,6-divinyl-1,6-dimethyl-1,6-disilacyclodeca-3,8-diene (13), in three isomeric forms, are generated in 8% yield. (The 1,1,6,6-tetramethyl compound analogous to 13 is known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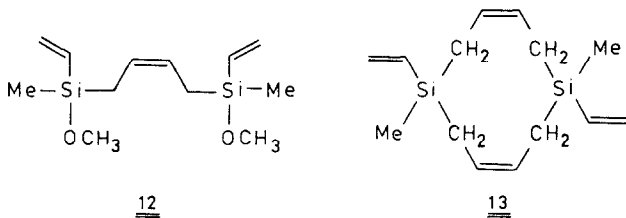
basis of ^{1}H NMR and IR measurements; the remaining isomer probably has a *cis/trans*-arrangement of the double bonds.

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 $ZrCl_2(\eta^5\text{-}C_5H_5)$ with butadienemagnesium [6].

$$\text{isom.} \rightleftharpoons \underset{\overset{|}{R^1}}{\overset{\overset{R^2}{|}}{Cl-Si}}\diagdown\diagup\diagdown\diagup\diagdown MgCl \rightleftharpoons \text{isom.}$$

I

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 $MgCl_2$ 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 (R = Ph) which was shown to be $3/4/5 = 5/2/1$, whereas only **3** is formed after reaction at $-70°C$ (60 h).

If R = vinyl, the intermediate appears to be more reactive towards both dimeriza-

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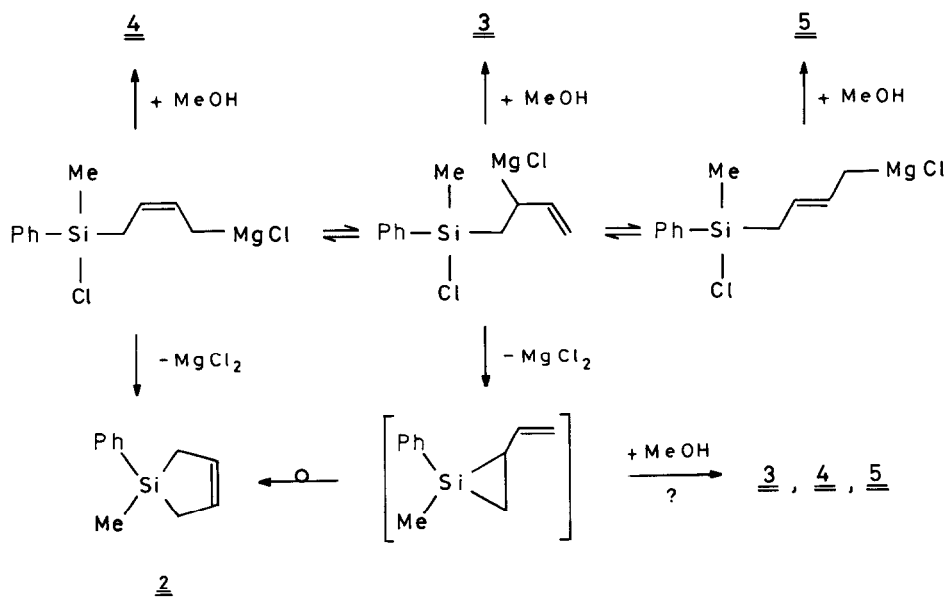
tion and reaction with the starting dichlorosilane, since a 1/1 ratio of the two isomers of **12** is formed along with **13** on methanolysis. In the absence of methanol both **13** and the precursor to **12**, the 3,8-dichlorosilane **14**, are observed (GC/MS).

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}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. Butadiene-magnesium (**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 $-70°$C. The mixture was kept at $-70°$C for 24 hour then treated with Et$_3$N/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°C/ 60–320°C/330°C, 8°C/min, He 1.5 bar) gave pure **3** (^{1}H NMR: 0.35, s (CH$_3$, 3H); 2, m (CH$_2$, 4H); 3.42, s (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}H NMR: 0.34, s (CH$_3$); 1.48, 2d (C–CH$_3$); 1.74, m (CH$_2$); 3.43, s (O–CH$_3$); 5.36, m (HC=CH), 7.3, 7.5, m (phenyl). MS (*m/e*): 206, 151 (100%), 121 (40%), 59 (compare ref. 3).

Reaction of 1 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 1 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 Et$_3$N (2.2 ml). A 8.5 g fraction found to contain 54% of toluene, 3.5% of **9**, and 6.3% of 3-butenylvinyl-methylmethoxysilane (**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°C/60–240°C/250°C, 0.8 bar H$_2$).

10: ^{1}H NMR: 0.14, s (CH$_3$, 3H); 0.72, m (SiCH$_2$, 2H); 2.0, m (CH$_2$, 2H); 3.28, s (OCH$_3$, 3H), 5.0–6.0, m (2 vinyl, 6H). MS (*m/e*): 156 (1%), 141, 128 (20%), 101 (100%), 75 (30%). C$_8$H$_{16}$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}H NMR: 0.17, s (CH$_3$, 3H); 1.55, d (CH$_3$, 3H); 1.63, d (SiCH$_2$, 2H); 3.31, s (OCH$_3$, 3H); 5.5, m (HC=CH, 2H); 6.0, m (vinyl, 3H). MS (*m/e*): 156 (5%), 141, 101 (100%), 75 (20%).

12: ^{1}H NMR: 0.19, s (CH_3, 6H); 1.65, m ($SiCH_2$, 4H); 3.32, s (OCH_3, 6H); 5.47, m (HC=CH, 2H); 6.0, m (2 vinyl, 6H). MS (m/e): 256, 241, 215, 161, 101 (100%), 75 (25%), 45. IR: 1625 cm^{-1}, shoulder at 1638 cm^{-1}, predominantly (Z). The GC clearly shows two peaks, retention time 33.8 and 34.5 min, presumably ($R^\star, R^\star$) and ($S^\star, R^\star$) isomers.

13: ^{1}H NMR: 3 isomers, 53/29/18 ratio; major isomer Z, Z, C_s symmetry: 0.08, s (CH_3, 6H); 1.58, m ($SiCH_2$, 8H); 5.39, qu (HC=CH, 4H); 5.70, 5.96, 6.15 (vinyl, 6H). Second isomer, Z, Z, C_2 symmetry: 0.07, s (CH_3, 6H); 1.6, m ($SiCH_2$, 8H); 5.27, qu (HC=CH, 4H); 5.70, 5.96, 6.15 (vinyl, 6H). Third isomer, presumably Z, E; similar ^{1}H NMR spectrum. MS (m/e): 248 (20%), 124 (15%), 109, 96 (100%), 71 (40%), 55. IR: 3005, 1640 cm^{-1}, Z-isomer; 1660 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; 100–300°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.

References

1 W.J. Richter, Synthesis, (1982) 1102.
2 W.J. Richter, Chem. Ber., 116 (1983) 3293.
3 M. Ishikawa, K. Nakagawa, R. Enokida and M. Kumada, J. Organomet. Chem., 201 (1980) 151.
4 R.A. Benkeser, Synthesis, (1971) 347.
5 D.R. Weyenberg, L.H. Toporcer, and L.E. Nelson, J. Org. Chem., 33 (1968) 1975.
6 U. Dorf, K. Engel and G. Erker, Organometallics, 2 (1983) 462.