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ADDITION OF CHLORODISILANES TO 1,3-BUTADIENES IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0). A FACILE ROUTE TO (*Z*)-1,4-BIS(CHLOROSILYL)BUT-2-ENES

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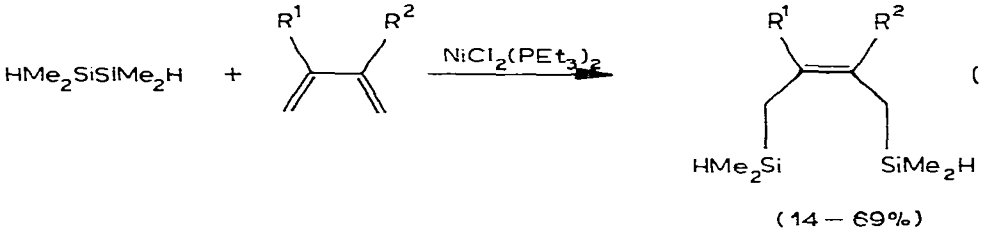
Summary

In the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0), chlorodisilanes of type $Me_nSi_2Cl_{6-n}$ (n = 0, 2, 3 and 4) add to 1,3-butadienes to give (*Z*)-1,4-bis(chlorosilyl)but-2-enes.

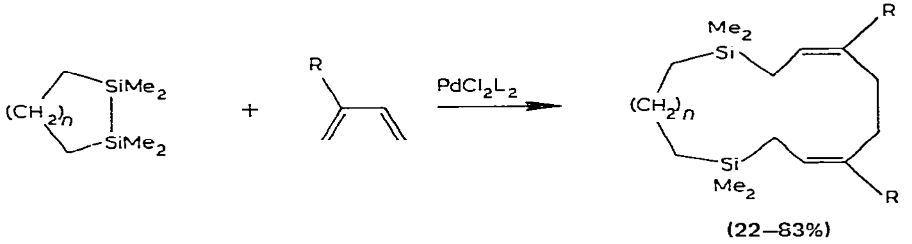
Introduction

The double silylation of 1,3-dienes was first reported by Kumada and coworkers who found that 1,2-dihydro-1,1,2,2-tetramethyldisilane adds to 1,3-butadienes in the presence of $NiCl_2(PEt_3)_2$ to give 1,4-bis(dimethylsilyl)but-2-enes [1].



(1)

They suggested that the reaction involves initial oxidative addition of the dihydrodisilane to the nickel catalyst through the rupture of the Si—H bond [1]. In this case, the prerequisite of the double silylation is the presence of hydrogen atoms on the disilane unit. Sakurai and coworkers subsequently reported that a novel 1 : 2 cycloaddition reaction occurs between strained disilacycloalkanes and dienes in the presence of palladium catalysts [2]. They noted that unstrained disilanes such as hexamethyldisilane and 1,2-dichloro-1,1,2,2-tetramethyldisilane similarly undergo the reaction, but only slowly, to give the 1,8-



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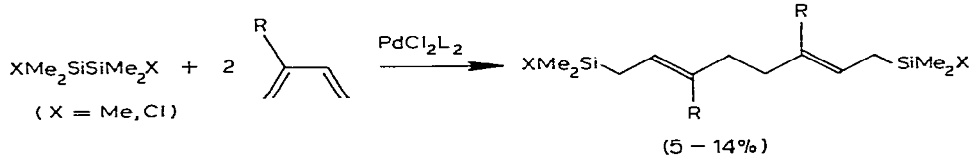
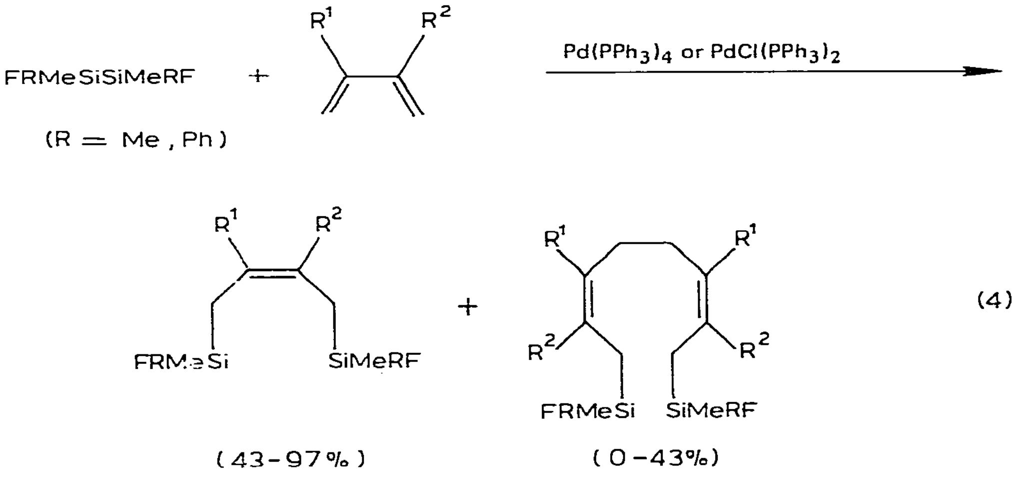


(3)

bis(silyl)octa-2,6-dienes in 5—14% yields. No details were provided concerning the formation of 1 : 1 adducts, i.e., 1,4-bis(silyl)but-2-enes [2]. More recently, Kumada and coworkers reported that highly reactive 1,2-difluorodisilanes add to dienes to give both 1 : 1 and 1 : 2 adducts [3] (eq. 4). They pointed out that there is some similarity in reactivity toward palladium complexes between strained electron-rich Si—Si compounds and those which are strain-free but electron-deficient [3].



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Since these reactions constitute a silicon—carbon bond forming process of a new type and should be of synthetic value, we have undertaken an investigation of reactions of chlorodisilanes with dienes in the presence of tetrakis(triphenylphosphine)palladium(0). At the beginning of this work, it was expected from thermochemical considerations that the reaction should be exothermic (ΔH = ca. —40 kcal/mol) [4]. It should also be noted that the hydrodisilane [5], the disilacycloalkanes [6] and the fluorodisilanes [7] used by previous workers are usually prepared from the corresponding chlorodisilanes which are more readily accessible [8]. The present paper describes the first example of the addition of chlorodisilanes to 1,3-butadienes to give 1 : 1 adducts exclusively [9].

Results and discussion

We found that, in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0), chlorodisilanes such as hexachlorodisilane, 1,1,2,2-tetrachloro-1,2-dimethyldisilane, 1,1,2-trichloro-1,2,2-trimethyldisilane and 1,2-dichloro-1,1,2,2-tetramethyldisilane reacted with 1,3-butadienes to give 1 : 1 adducts.

$$\mathrm{Cl_{3-\mathit{m}}Me_{\mathit{m}}SiSiMe_{\mathit{n}}Cl_{3-\mathit{n}} + CH_2{=}CR^1CR^2{=}CH_2 \xrightarrow{Pd^{(0)}} Cl_{3-\mathit{m}}Me_{\mathit{m}}SiCH_2CR^1{=}CR^2CH_2SiMe_{\mathit{n}}Cl_{3-\mathit{n}}} \qquad (5)$$

The addition reactions were carried out at temperatures of 60—130°C under nitrogen either in a sealed stainless steel reaction vessel or in an open system at reflux, using a 1 : 2 mixtures of the chlorodisilane and the diene. The results are listed in Table 1. Structural assignments for the 1 : 1 adducts were made, after isolation by distillation, based on their IR and NMR parameters and elemental analyses, as shown in Table 2.

Inspection of Table 1 discloses that hexachlorodisilane, the tetrachlorodimethyldisilane or the trichlorotrimethyldisilane add smoothly to 1,3-butadiene, isoprene or 2,3-dimethyl-1,3-butadiene to give the corresponding 1,4-bis(chlorosilyl)but-2-enes in fair to good yields. The formation of the 1 : 2 adducts was negligible. The reactions of dichlorotetramethyldisilane were slower than those of disilanes possessing three or more chlorine atoms, and a higher temperature or a longer reaction time was required to achieve reasonable conversion. Thus,

TABLE 1

REACTIONS OF CHLORODISILANES WITH 1,3-BUTADIENES IN THE PRESENCE OF TETRAKIS-(TRIPHENYLPHOSPHINE)PALLADIUM(0) [a]

Disilane	Diene	Conditions	1,4-Bis(chlorosilyl)but-2-enes obtained	Yield [b] (%)
$Cl_3SiSiCl_3$	$CH_2{=}CHCH{=}CH_2$	60°C, 10 h	(*Z*)-$Cl_3SiCH_2CH{=}CHCH_2SiCl_3$ (I)	54
$Cl_2MeSiSiMeCl_2$	$CH_2{=}CHCH{=}CH_2$	100°C, 4 h	(*Z*)-$Cl_2MeSiCH_2CH{=}CHCH_2SiMeCl_2$ (II)	82 (75)
	$CH_2{=}CMeCH{=}CH_2$ [c]	reflux, 5 h	(*Z*)-$Cl_2MeSiCH_2CMe{=}CHCH_2SiMeCl_2$ (III)	79 (68)
	$CH_2{=}CMeCMe{=}CH_2$	reflux, 5 h	(*Z*)-$Cl_2MeSiCH_2CMe{=}CMeCH_2SiMeCl_2$ (IV)	70 (50)
$Cl_2MeSiSiMe_2Cl$	$CH_2{=}CHCH{=}CH_2$	100°C, 5 h	(*Z*)-$Cl_2MeSiCH_2CH{=}CHCH_2SiMe_2Cl$ (V)	48
$ClMe_2SiSiMe_2Cl$	$CH_2{=}CHCH{=}CH_2$ [d]	130°C, 18 h	(*Z*)-$ClMe_2SiCH_2CH{=}CHCH_2SiMe_2Cl$ (VI)	44 (38)
	$CH_2{=}CMeCH{=}CH_2$ [c,e]	reflux, 70 h	(*Z*)-$ClMe_2SiCH_2CMe{=}CHCH_2SiMe_2Cl$ (VII)	53 (47)

[a] Reactions were carried out under nitrogen employing a 1 : 2 : 0.01 mixture of a disilane, a diene and the palladium(0) complex unless otherwise stated. [b] Determined by GLC (based on the disilane charged); isolated yields given in parentheses. [c] Toluene was used as a solvent. [d] Conversion of the disilane charged was 80%. [e] Conversion of the disilane charged was 90%.

TABLE 2

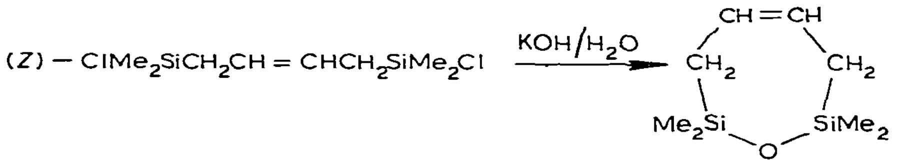
CHARACTERIZATION OF 1,4-BIS(CHLOROSILYL)BUT-2-ENES OBTAINED

Compound	Bp (°C/mmHg)	IR, principal absorptions [a] (cm^{-1})	NMR [b] (δ, ppm)	Anal. found (calcd.) (%) hydrolyzable Cl
I [c]	74/4	3010m, 1640w, 760s, 680s	2.40 (m, 4H, $-CH_2-$) 5.67 (m, 4H, $-CH{=}CH-$)	
II	95/5	3015m, 1645w, 1260s, 788s, 690m	0.80 (s, 6H, SiMe) 2.03 (d, 4H, $-CH_2-$, J = 6 Hz) 5.57 (m, 2H, $-CH{=}CH-$)	49.74 (49.56)
III	110/6	3010m, 1645w, 1260s, 760s, 680m	0.70 (s, 6H, SiMe) 1.75 (m, 7H, $=CMe-$ and $-CH_2-$) 5.11 (t, 1H, $=CH-$, J = 6 Hz)	47.57 (47.88)
IV	103/5	3010m, 1650w, 1257s, 810s, 780s, 680m	0.80 (s, 6H, SiMe) 1.80 (s, 6H, $=CMe-$) 2.15 (s, 4H, $-CH_2-$)	45.58 (45.71)
V	116/13	3010m, 1645w, 1255s, 830s, 800s, 690m	0.44 (s, 6H, $-$SiMe) 0.80 (s, 3H, $-$SiMe) 1.79 (d, 2H, $-CH_2-$, J = 6 Hz) 2.09 (d, 2H, $-CH_2-$, J = 6 Hz) 5.2—5.8 (m, 2H, $-CH{=}CH-$)	40.60 (40.62)
VI	86/8	3001m, 1642w, 1252s, 765m, 698m	0.42 (s, 12H, SiMe) 1.73 (d, 4H, J = 6 Hz) 5.42 (t, 2H, J = 6 Hz)	28.78 (29.38)
VII	81/5	3010m, 1645w, 1260s, 830s, 760m, 690m	0.40 (s, 12H, SiMe) 1.80 (m, 7H, $=CMe$ and $-CH_2-$) 5.10 (t, 1H, $=CH-$, J = 6 Hz)	27.12 (27.77)

[a] All spectra were taken with neat samples. [b] All spectra were taken in CCl_4 using Me_4Si as internal standard. [c] Ref. 21.

the addition of the disilane to 1,3-butadiene at 130°C for 13 h or to isoprene at reflux for 70 h afforded the 1 : 1 adduct in 44 and 53% yield, respectively.

It was also found that the mode of the addition is stereospecific to give (*Z*)-butenes. The assignment of the (*Z*)-configuration of the 1 : 1 adducts was made based on the their IR spectra which are devoid of the absorption band due to (*E*)-isomers around 950 cm^{-1}. In order to confirm such a structural assignment, the addition products were subjected to hydrolysis [3,10]. For instance, the treatment of 1,4-bis(chlorodimethylsilyl)but-2-ene with aqueous KOH solution gave 2,2,7,7-tetramethyl-2,7-disila-1-oxacyclohept-4-ene in excellent yield, and this fact clearly supports the (*Z*)-configuration.



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The highly stereoselective (*Z*)-stereochemistry has also been encountered in the addition of fluorinated disilanes to 1,3-butadienes catalyzed by $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ [3].

Competition experiments to determine relative reactivities of the chlorodisilanes or dienes toward the double silylation were carried out in order to obtain information about the controlling factors in this particular system. In order to do so, two different chlorodisilanes were allowed to react with a deficiency of 1,3-butadiene, or two different dienes were allowed to react with a deficiency of 1,1,2,2-tetrachloro-1,2-dimethyldisilane. Thus, the reactivities of each set of reactants were found to fall in the following order: $Cl_2MeSiSiMeCl_2$ (22) > $Cl_2MeSiSiMe_2Cl$ (14) > $ClMe_2SiSiMe_2Cl$ (1) and $CH_2{=}CHCH{=}CH_2$ (3.8) > $CH_2{=}CMeCH{=}CH_2$ (1.5) > $CH_2{=}CMeCMe{=}CH_2$ (1.0). Apparently, introduction of a chlorine atom on silicon substantially increases the reactivity of disilanes, while successive methyl substitution on 1,3-butadiene decreases the rate of the addition. The accelerating effect of chlorine atoms may be attributable to their strong electron-withdrawing character which decreases the electron density of the Si—Si bond and results in increased π-accepter strength of silicon [11]. The retarding effect of methyl groups in the dienes may be simply explained in terms of steric considerations.

An attempt was made to extend the present addition to other 1,3-dienes, but results were not encouraging. For instance, heating a 1 : 2 mixture of 1,1,2,2-tetrachloro-1,2-dimethyldisilane and 1,3-pentadiene at 130°C for 15 h in the presence of the palladium(0) complex resulted in recovery of the reactants, and the 1 : 1 adduct was not produced to any significant extent. Also, the chlorodisilane did not react with 1,3-cyclooctadiene under comparable conditions.

In spite of such limitations, the present double silylation may provide a convenient route to (*Z*)-1,4-bis(chlorosilyl)but-2-enes which would be difficult to prepare by other methods. The product chlorosilanes can be readily converted to many other derivatives such as alkyl-, alkoxy- and hydro-silanes etc. In fact, we prepared (*Z*)-1,4-bis(trimethylsilyl)but-2-ene and (*Z*)-1,4-bis(trimethylsilyl)-2-methylbut-2-ene in good yields by the reactions of II and III with methylmagnesium bromide.

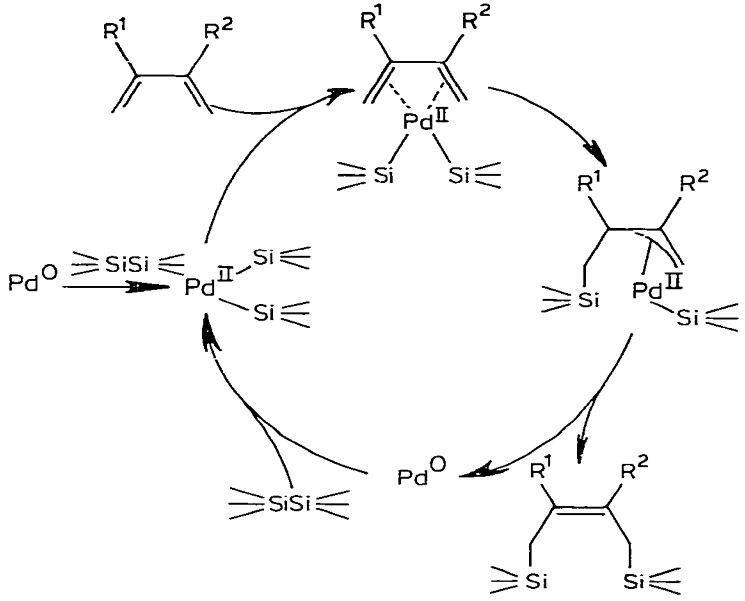
$$\underset{\text{(II)}}{(Z)\text{-}Cl_2MeSiCH_2CH{=}CHCH_2SiMeCl_2} \xrightarrow{MeMgBr} (Z)\text{-}Me_3SiCH_2CH{=}CHCH_2SiMe_3 \qquad (7)$$

$$\underset{\text{(III)}}{(Z)\text{-}Cl_2MeSiCH_2CMe{=}CHCH_2SiMeCl_2} \xrightarrow{MeMgBr} (Z)\text{-}Me_3SiCH_2CMe{=}CHCH_2SiMe_3 \qquad (8)$$

Each compound obtained possesses an allyltrimethylsilane structure and may find applications in organic synthesis [12].

Catalyst efficiency was tested briefly for other common Group VIII metal-phosphine complexes using the reaction of 1,1,2,2-tetrachloro-1,2-dimethyldisilane with isoprene as a standard. Dichlorobis(triphenylphosphine)palladium(II) was found to be another effective catalyst for the addition reaction. For example, the reaction in the presence of 1 mol% of the complex gave a 54% yield of 1,4-bis(dichloromethylsilyl)-2-methylbut-2-ene after refluxing a 1 : 2 mixture of the disilane and the diene for 8 h. However, the complexes $Pt(PPh_3)_4$, $NiCl_2(PPh_3)_2$, $RhCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ failed to effect the expected reaction to any appreciable extent under comparable conditions. Further, triphenylphosphine was tested as a potential catalyst, and the reaction in the presence of 4 mol% of the phosphine did not give any 1,4-bis(silyl)butenes after refluxing for 8 h.

We do not as yet have any direct mechanistic information on the present double silylation. However, by the analogy of the mechanism proposed for the palladium-catalyzed double silylation of acetylenes [13], we suggest the following scheme as a working hypothesis.



Experimental

IR spectra were taken on a Hitachi EPI-3G spectrophotometer. NMR spectra were taken on a Varian EM-360 spectrometer. GLC analyses were carried out with an Ohkura 802T instrument, using Teflon columns (100—150 × 0.4 cm) packed with Silicone KF-96, SE-30 and DCQF-1 on Celite 545 (60/80).

1,1,2,2-Tetrachloro-1,2-dimethyldisilane [8h], 1,1,2-trichloro-1,2,2-trimethyldisilane [8i] and 1,2-dichloro-1,1,2,2-tetramethyldisilane [8i] were prepared according to published methods. Hexachlorodisilane, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and 1,3-cyclooctadiene were commercially available and purified by distillation prior to use. 1,3-Butadiene was purchased as a special grade and used without further purification. The complexes $Pd(PPh_3)_4$ [14], $PdCl_2(PPh_3)_2$ [15], $Pt(PPh_3)_4$ [16], $RhCl(PPh_3)_3$ [17], $NiCl_2(PPh_3)_2$ [18] and $RuCl_2(PPh_3)_3$ [19] were prepared according to literature directions.

Procedure for the addition reactions

The reactions were conducted under nitrogen either in a sealed stainless steel reaction vessel or in a reflux system. Typical examples are described below.

(a) Reaction of 1,1,2,2-tetrachloro-1,2-dimethyldisilane with 1,3-butadiene in the presence of the palladium(0) complex. The disilane (9.12 g, 40 mmol), the diene (4.3 g, 80 mmol) and the palladium(0) complex (0.46 g, 0.4 mmol)

were sealed in a 200 ml stainless steel reaction vessel, and heated at 100°C for 4 h. GLC analysis of the resulting mixture disclosed that the disilane had been completely consumed and that (*Z*)-1,4-bis(dichloromethylsilyl)but-2-ene II had been produced in 82% yield. The mixture then was diluted with pentane (50 ml) and the precipitated catalyst was removed by filtration. Evaporation of the solvent and subsequent distillation under reduced pressure gave 7.4 g (75% yield) of the product. The identity of this compound was established by its IR and NMR spectra and elemental analysis.

(b) Reaction of 1,1,2,2-tetrachloro-1,2-dimethyldisilane with isoprene in the presence of the palladium(0) complex. A solution of the disilane (11.4 g, 50 mmol), the diene (6.8 g, 100 mmol), the complex (0.58 g, 0.5 mmol) and toluene (20 ml) was refluxed for 5 h with stirring. Work-up gave 10.1 g (68% yield) of (*Z*)-1,4-bis(dichloromethylsilyl)-2-methylbut-2-ene III. The identity of the product was established by its IR and NMR spectra and elemental analysis.

(c) Reaction of 1,1,2,2-tetrachloro-1,2-dimethyldisilane with isoprene in the presence of $PdCl_2(PPh_3)_2$, $Pt(PPh_3)_4$, $RhCl(PPh_3)_3$, $NiCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$ *or* PPh_3. A solution of the disilane (2.29 g, 10 mmol), the diene (1.4 g, 20 mmol), the palladium(II) complex (0.068 g, 0.1 mmol) and toluene (3 ml) was refluxed for 8 h with stirring. GLC analysis of the resulting solution disclosed the production of III in 54% yield.

A similar reaction in the presence of the Pt^0, Rh^I, Ni^{II} and Ru^{II} complexes (1 mol% based on the disilane charged) or PPh_3 (4 mol%) was found by GLC analysis to give no traces of III after refluxing for 8 h.

Hydrolysis of VI

To an ethereal solution of VI (0.55 g, 2.3 mmol) was added a 0.1 *N* aqueous solution of potassium hydroxide (100 ml) at 0°C with stirring. After additional stirring at room temperature for 1 h, the organic layer was separated, washed with water, dried over anhydrous magnesium sulfate and evaporated to give 0.35 g (83% yield) of 2,2,7,7-tetramethyl-2,7-disila-1-oxacyclohept-4-ene: n_D^{25} 1.4437 [lit. [10] n_D^{25} 1.4438].

Competition reactions of chlorodisilanes with 1,3-butadiene in the presence of the palladium(0) complex

A mixture of 3.7 g (20 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane, 4.6 g (20 mmol) of 1,1,2,2-tetrachloro-1,2-dimethyldisilane, 0.50 g (10 mmol) of the diene, 0.11 g (0.1 mmol) of the complex and toluene (2 ml) was heated at 100°C for 2 h in a sealed stainless steel reaction vessel. Quantitative analysis by GLC showed that 0.18 mmol of VI and 3.50 mmol of II had been produced. The relative rate was calculated using the following equation [20].

$$\frac{k(Me_2Si_2Cl_4)}{k(Me_4Si_2Cl_2)} = \frac{[Me_4Si_2Cl_2]_i}{[Me_2Si_2Cl_4]_i} \times \frac{[II]_f}{[VI]_f}$$

where $k(Me_2Si_2Cl_4)/k(Me_4Si_2Cl_2)$ is the ratio of the rate constants for $Me_2Si_2Cl_4$ and $Me_4Si_2Cl_2$, $[Me_2Si_2Cl_4]_i$ and $[Me_4Si_2Cl_2]_i$ are the initial concentrations of the disilanes, and $[II]_f$ and $[VI]_f$ are the molar amounts of 1,4-bis(silyl)but-2-enes produced.

A similar competition reaction between $Cl_2MeSiSiMe_2Cl$ and $ClMe_2SiSiMe_2Cl$ was conducted at 100° C for 2 h, and the result was evaluated in similar fashion.

Competition reactions of dienes with 1,1,2,2-tetrachlorodisilane in the presence of the palladium(0) complex

A mixture of 0.68 g (10 mmol) of isoprene, 0.82 g (10 mmol) of 2,3-dimethyl-1,3-butadiene, 1.1 g (5 mmol) of 1,1,2,2-tetrachloro-1,2-dimethyldisilane, 0.056 g (0.05 mmol) of the palladium(0) complex and toluene (2 ml) was heated at 80° C for 2 h in a sealed stainless steel reaction vessel. GLC analysis showed the formation of 1.9 mmol of III and 1.3 mmol of IV. The relative rate was calculated using the following equation [20].

$$\frac{k(CH_2{=}CMeCH{=}CH_2)}{k(CH_2{=}CMeCMe{=}CH_2)} = \frac{[CH_2{=}CMeCMe{=}CH_2]_i}{[CH_2{=}CMeCH{=}CH_2]_i} \times \frac{[III]_f}{[IV]_f}$$

A similar competitive reaction between $CH_2{=}CHCH{=}CH_2$ and $CH_2{=}CMeCMe{=}CH_2$ was conducted at 80° C for 1.5 h, and the result was evaluated in similar fashion.

Reaction of II or III with methylmagnesium bromide

To an ethereal solution of methylmagnesium bromide (ca. 100 mmol) was added an ethereal solution of II (5.64 g, 20 mmol) at room temperature. After additional stirring for 15 h, the resulting mixture was hydrolyzed and worked up in the usual manner. Removal of the solvent and distillation gave 2.43 g (61% yield) of (*Z*)-1,4-bis(trimethylsilyl)but-2-ene: b.p. 60—62° C/8 mmHg; n_D^{25} 1.4404 [lit. [10] b.p. 102° C/48 mmHg; n_D^{25} 1.4406]. The IR and NMR spectra of this product were in good agreement with the reported values [10].

Essentially the same procedure as above employing 5.92 g (20 mmol) of III afforded (*Z*)-1,4-bis(trimethylsilyl)-2-methylbut-2-ene (2.46 g, 57% yield): b.p. 50—53° C/3 mmHg; n_D^{25} 1.4457 [lit. [10] b.p. 104—106° C/40 mmHg; n_D^{25} 1.4458]. The IR and NMR spectra of the product were in good agreement with the reported values [10].

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