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GROUP VIII METAL PHOSPHINE COMPLEXES-CATALYZED ADDITION OF DISILANES TO ALLENIC COMPOUNDS *

FORMATION OF NEW ORGANOSILICON COMPOUNDS CONTAINING BOTH VINYLSILANE AND ALLYLSILANE UNITS

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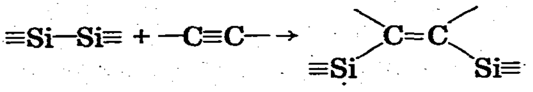
Summary

Addition of chloromethyl- and methoxymethyldisilanes, $X_{3-m}Me_mSiSiMe_n$-X_{3-n} (X = Cl and OMe; m, n = 0—2), as well as hexamethyldisilane, to allene and 1,2-butadiene in the presence of $Pd(PPh_3)_4$ catalyst gave regioselectively new functionalized organosilicon compounds, 2,3-bis(organosilyl)prop-1-enes and 2,3-bis(organosilyl)but-1-enes, respectively. Other Group VIII metal-phosphine complexes also affected the reaction, but results were found to be less satisfactory. Also, the reaction of an unsymmetrical disilane with an allenic compound gave only a single product; e.g., the addition of chloropentamethyldisilane to 1,2-butadiene in the presence of $Pd(PPh_3)_4$ gave $CH_2{=}C(SiMe_3)CH(SiMe_2Cl)Me$ in 93% yield.

Introduction

Recently Kumada et al. and Sakurai et al. reported that in the presence of palladium complexes hydrodisilanes, fluorodisilanes or strained 1,2-disilacycloalkanes add to various acetylenes and conjugated dienes to give double silylation products [1,2]. In previous papers, we pointed out that the additions of a disilane to an acetylene, and a conjugated diene leading to disilylolefins, are quite exothermic (ca. 40 kcal/mol) on the basis of thermochemical considerations (eqs. 1 and 2) [3,4]. Thus, we concluded that double silylations of acety-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[*] For the previous paper in this series see ref. 24.

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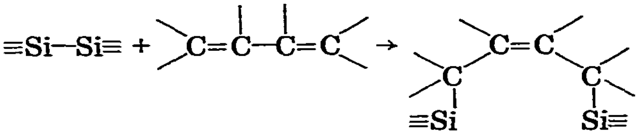
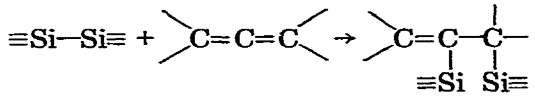


(2)

lenic compounds and conjugated dienes should occur not only with unusual disilanes, such as those cited above, but also with other common disilanes under the appropriate reaction conditions. This was shown to be the case as evidenced by the double silylation of acetylenes, such as $PhC\equiv CH$, $BuC\equiv CH$, $Me_3SiC\equiv CH$ and $HC\equiv CH$, with methoxymethyl- and chloromethyldisilanes, as well as with hexamethyldisilane [3—6]. Also conjugated dienes, such as $CH_2{=}CH{-}CH{=}CH_2$, $CH_2{=}CMe{-}CH{=}CH_2$ and $CH_2{=}CMe{-}CMe{=}CH_2$ could be made to react with chloromethyl- [4] and methoxymethyldisilanes [7]. These findings encouraged us to extend the double silylation to other unsaturated compounds, and we have undertaken an investigation of the addition of common disilanes, such as chloro- and methoxydisilanes as well as hexamethyldisilane, to allenic compounds in the presence of various Group VIII-metal triphenylphosphine complexes, as shown in eq. 3. The heat of reaction for the addition of a disilane to



(3)

an allene is estimated to be in a range of —40 to —50 kcal/mol [8] and this means that the double silylation of allenes should also occur with ease.

The present paper deals with the first example of the addition of disilanes to allenic compounds, such as allene and 1,2-butadiene, to give 1 : 1 adducts regioselectively. The present double silylation should be of great interest from a synthetic point of view, since the reaction produces a new type of functionalized organosilicon compound containing both vinylsilane and allylsilane units.

Results and discussion

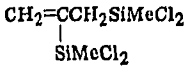
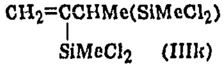
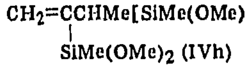
In order to find effective catalysts for the reaction shown by eq. 4, the catalytic activities of phosphine complexes of six metals, Ni^{II}, Rh^{I}, Pd^{0}, Pd^{II}, Pt^{0} and Pt^{II}, were examined, employing the reactions of dimethyltetrachlorodisilane with allene and 1,2-butadiene as standards. The results for the double silylation catalyzed by these complexes are summarized in Table 1.

It can be seen from Table 1 that Pd and Pt complexes were catalytically active in both systems to give the double silylation product in varying yields (17—85%) and that Rh^{I} and Ni^{II} complexes were virtually ineffective. From these results, $Pd(PPh_3)_4$ was selected as the best catalyst among those examined for the double silylation.

The double silylation of allene and 1,2-butadiene in the presence of the Pd^0 complex catalyst using various chloromethyl- and methoxymethyldisilanes of type $X_{3-m}Me_mSiSiMe_nX_{3-n}$ (X = Cl and OMe; m, n = 0—3) was next investigated. The reactions of these disilanes proceeded smoothly to give the corresponding 1 : 1 adducts in reasonable to good yields (24—88%). The results are listed in Tables 2 and 3. No other products, such as 1,2-regioisomers and 1 : 2

TABLE 1

DOUBLE SILYLATION OF ALLENES WITH DISILANES IN THE PRESENCE OF VARIOUS PHOSPHINE COMPLEXES AS CATALYST [a]

Run	Allene	Disilane	Catalyst	Adduct	Yield (%) [b]	Conversion of disilane (%) [c]
1	$CH_2{=}C{=}CH_2$ [d]	$Cl_2MeSiSiMeCl_2$	$Pd(PPh_3)_4$	 $CH_2{=}\underset{\underset{SiMeCl_2}{\vert}}{C}CH_2SiMeCl_2$ (IIIe)	85	100
2	"	"	$PdCl_2(PPh_2)_2$	"	66	"
3	"	"	$PtCl_2(PPh_3)_2$	"	37	"
4	"	"	$Pt(PPh_3)_4$	"	17	"
5	"	"	$RhCl(PPh_3)_3$	"	0	"
6 [e]	$CH_2{=}C{=}CHMe$ [f]	"	$Pd(PPh_3)_4$	 $CH_2{=}\underset{\underset{SiMeCl_2}{\vert}}{C}CHMe(SiMeCl_2)$ (IIIk)	83	"
7 [e]	"	"	$PdCl_2(PPh_3)_2$	"	60	"
8 [e]	"	"	$Pt(PPh_3)_4$	"	57	"
9 [e]	"	"	$PtCl_2(PPh_3)_2$	"	40	"
10 [e]	"	"	$RhCl(PPh_3)_3$	"	trace	50
11 [e]	"	"	$NiCl_2(PPh_3)_2$	"	0	3
12	"	$(MeO)_2MeSiSiMe(OMe)_2$	$Pd(PPh_3)_4$	 $CH_2{=}\underset{\underset{SiMe(OMe)_2}{\vert}}{C}CHMe[SiMe(OMe)_2]$ (IVh)	88	100
13	"	"	$PdCl_2(PPh_3)_2$	"	61	98

[a] Mol ratio, allene/disilane/cat. = 5/5/0.05 (mmol); 120°C, 15 h. [b] GLC yield based on the disilane used. [c] By GLC. [d] Mol ratio, allene/disilane/cat. = 20/10/0.1 (mmol). [e] 100°C, 3 h. [f] A 50 : 50 mixture of 1,2-butadiene and but-2-ene, which is commercially available.

TABLE 2

ADDITION OF CHLORODISILANES TO ALLENE AND 1,2-BUTADIENE IN THE PRESENCE OF $Pd(PPh_3)_4$ CATALYST [a]

Run	Disilane	Allene	Temp. (°C)	Time (h)	Adduct	Yield (%) [b]	Conversion of disilane (%) [c]
1 [d]	$Me_3SiSiMe_3$	$CH_2{=}C{=}CH_2$	120	20	IIIa	29	30
2	$Me_3SiSiMe_2Cl$	"	"	15	IIIb	86(75)	100
3	$ClMe_2SiSiMe_2Cl$	"	"	"	IIIc	93(68)	"
4	$Cl_2MeSiSiMe_2Cl$	"	"	"	IIId	77(53)	"
5	$Cl_2MeSiSiMeCl_2$	"	"	"	IIIe	85(67)	"
6 [e]	$Cl_3SiSiCl_3$	"	175	24	IIIf	33	51
7	$Me_3SiSiMe_3$	$CH_2{=}C{=}CHMe$ [f]	120	15	IIIg	83(73)	100
8	$Me_3SiSiMe_2Cl$	"	150	18	IIIh	93(70)	"
9	$ClMe_2SiSiMe_2Cl$	"	130	15	IIIi	84(75)	98
10	$Cl_2MeSiSiMe_2Cl$	"	100	"	IIIj	81(59)	100
11 [g]	$Cl_2MeSiSiMeCl_2$	"	"	5	IIIk	(84)	"
12	$Cl_3SiSiCl_3$	"	120	"	IIIl	84(48)	98

[a] Allene/disilane/cat. = 20/10/0.1 (mmol). [b] GLC yield based on the disilane used; isolated yield is given in parentheses. [c] By GLC. [d] Benzene (1.2 ml) was used as solvent. [e] Mesitylene (1.2 ml) was used as solvent. [f] A 50 : 50 mixture of 1,2-butadiene and but-2-ene which is commercially available; allene/disilane/cat. = 10/10/0.1 (mmol). [g] Allene/disilane/cat. = 100/100/1 (mmol).

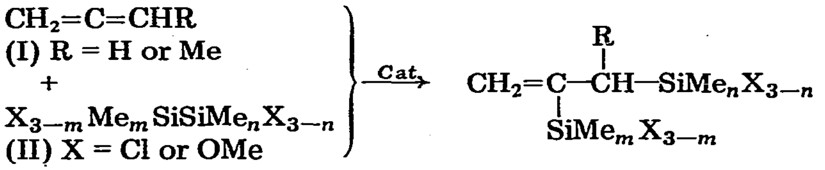
adducts, were detected to any appreciable extent. A solvent like benzene or mesitylene was required in the reaction of hexamethyl- and hexachlorodisilane with allene, however, and the yields were somewhat lower than in other comparable cases (29—33% by GLC).

TABLE 3

ADDITION OF METHOXYDISILANES TO ALLENE AND 1,2-BUTADIENE IN THE PRESENCE OF $Pd(PPh_3)_4$ CATALYST [a]

Run	Disilane	Allene	Temp. (°C)	Time (h)	Adduct	Yield (%) [b]	Conversion of disilane (%) [c]
1 [d]	$Me_3SiSiMe_3$	$CH_2{=}C{=}CH_2$	120	20	IIIa	29	30
2	$(MeO)Me_2SiSiMe_3$	"	"	"	IVa	96(81)	100
3	$(MeO)Me_2SiSiMe_2(OMe)$	"	100	16	IVb	48(32)	84
4	"	"	120	20	"	50(32)	93
5	$(MeO)_2MeSiSiMe_2(OMe)$	"	"	"	IVc	64(55)	100
6	$(MeO)_2MeSiSiMe(OMe)_2$	"	"	6	IVd	49(24)	82
7	"	"	"	20	"	50(40)	99
8	$Me_3SiSiMe_3$	$CH_2{=}C{=}CHMe$ [e]	"	15	IIIg	83(73)	100
9	$(MeO)Me_2SiSiMe_3$	"	"	"	IVe	100(87)	"
10	$(MeO)Me_2SiSiMe_2(OMe)$	"	"	"	IVf	97(88)	"
11	"	"	"	5	"	91(80)	93
12	$(MeO)_2MeSiSiMe_2(OMe)$	"	"	15	IVg	57	100
13	$(MeO)_2MeSiSiMe(OMe)_2$	"	"	"	IVh	88(86)	"
14	"	"	100	16	"	92(80)	"
15	$(MeO)_3SiSi(OMe)_3$	"	120	15	IVi	83(73)	"

[a] Allene/disilane/cat. = 20/10/0.1 (mmol). [b] GLC yield based on the disilane used; isolated yield is given in parenthesis. [c] By GLC. [d] Benzene (1.2 ml) was used as solvent. [e] A 50 : 50 mixture of 1,2-butadiene and but-2-ene which is commercially available; allene/disilane/cat. = 10/10/0.1 (mmol).



$$\left.\begin{array}{l} CH_2{=}C{=}CHR \\ \text{(I) } R = H \text{ or } Me \\ \quad + \\ X_{3-m}Me_mSiSiMe_nX_{3-n} \\ \text{(II) } X = Cl \text{ or } OMe \end{array}\right\} \xrightarrow{Cat} CH_2{=}\underset{\substack{|\\ SiMe_mX_{3-m}}}{C}{-}\overset{\substack{R\\ |}}{C}H{-}SiMe_nX_{3-n} \qquad (4)$$

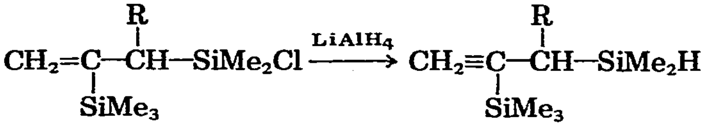
R = H; X = Cl	R = Me; X = Cl
IIIa, $m = n = 3$	IIIg, $m = n = 3$
IIIb, $m = 3; n = 2$	IIIh, $m = 3; n = 2$
IIIc, $m = n = 2$	IIIi, $m = n = 2$
IIId, $m = 2; n = 1$	IIIj, $m = 2; n = 1$
IIIe, $m = n = 1$	IIIk, $m = n = 1$
IIIf, $m = n = 0$	IIIl, $m = n = 0$

R = H; X = OMe	R = Me; X = OMe
IVa, $m = 3; n = 2$	IVe, $m = 3; n = 2$
IVb, $m = n = 2$	IVf, $m = n = 2$
IVc, $m = 2; n = 1$	IVg, $m = 2; n = 1$
IVd, $m = n = 1$	IVh, $m = n = 1$
	IVi, $m = n = 0$

It should be emphasized at this point that the reaction of 1,2-butadiene gave 2,3-adducts only; no 1,2-products were observed. Furthermore, the orientation of the double silylation with unsymmetrical disilanes gave in each case only one disilylbut-1-ene regioisomer.

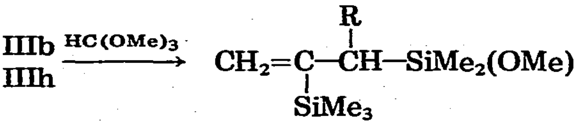
The assignment of the structures of the double silylation products was made based on ^{1}H NMR and IR spectroscopic studies and comparison with those of their derivatives. The results of the elemental analysis and the spectral data of the products are summarized in Tables 4—7.

The products arising from the reactions between chlorodisilanes and allenes could be readily converted into the corresponding hydrosilylolefins and methoxysilylolefins by $LiAlH_4$-reduction and $HC(OMe)_3$-methoxylation, respectively (eqs. 5—7).



$$CH_2{=}\underset{\substack{|\\ SiMe_3}}{C}{-}\overset{\substack{R\\ |}}{C}H{-}SiMe_2Cl \xrightarrow{LiAlH_4} CH_2{\equiv}\underset{\substack{|\\ SiMe_3}}{C}{-}\overset{\substack{R\\ |}}{C}H{-}SiMe_2H \qquad (5)$$

IIIb, R = H; IIIh, R = Me → IVk, R = H; IVn; R = Me



$$\begin{array}{l} IIIb \\ IIIh \end{array} \xrightarrow{HC(OMe)_3} CH_2{=}\underset{\substack{|\\ SiMe_3}}{C}{-}\overset{\substack{R\\ |}}{C}H{-}SiMe_2(OMe) \qquad (6)$$

IVa, R = H;
IVe, R = Me

TABLE 4

ANALYTICAL AND PHYSICAL DATA OF THE ADDUCTS

Compound	Formula	Analysis (Found (calcd.) (%)) C	H	B.p. (°C/mmHg)	n_D^{25}
IIIa	$C_9H_{22}Si_2$	58.31(57.98)	11.88(11.89)	63/30	1.4384
IIIb	$C_8H_{19}ClSi_2$	46.71(46.45)	8.92(9.26)	95/28	1.4501
IIIc	$C_7H_{16}Cl_2Si_2$	37.43(37.46)	6.93(6.76)	103/42	1.4631
IIId	$C_6H_{13}Cl_3Si_2$	28.99(29.09)	5.06(5.29)	100/35	1.4700
IIIe	$C_5H_{10}Cl_4Si_2$	22.43(22.40)	3.63(3.76)	105/30	1.4780
IIIf	$C_3H_4Cl_6Si_2$	11.87(11.66)	1.67(1.30)	75/12	1.4868
IIIg	$C_{10}H_{24}Si_2$	60.32(59.91)	11.92(12.09)	82—84/30	1.4442
IIIh	$C_9H_{21}ClSi_2$	48.90(48.94)	9.70(9.58)	94/22	1.4545
IIIi	$C_8H_{18}Cl_2Si_2$	39.87(39.82)	7.51(7.52)	100—103/30	1.4660
IIIj	$C_7H_{15}Cl_3Si_2$	31.90(32.12)	5.53(5.78)	99/30	1.4755 [a]
IIIk	$C_6H_{12}Cl_4Si_2$	25.80(25.54)	4.03(4.29)	139—141/20	1.4801
IIIl	$C_4H_6Cl_6Si_2$	14.93(14.88)	2.08(1.87)	109/28	1.4881
IVa	$C_9H_{22}OSi_2$	53.85(53.40)	10.73(10.95)	—	1.4346
IVb	$C_9H_{22}O_2Si_2$	49.29(49.49)	10.13(10.15)	96/25	1.4329
IVc	$C_9H_{22}O_3Si_2$	45.75(46.11)	9.17(9.46)	70/5	1.4310
IVd	$C_9H_{22}O_4Si_2$	42.87(43.16)	8.56(8.86)	102/20)	1.4264
IVe	$C_{10}H_{24}OSi_2$	55.65(55.49)	11.04(11.17)	—	1.4408
IVf	$C_{10}H_{24}O_2Si_2$	51.74(51.67)	10.28(10.41)	103—104/30	1.4395
IVg	$C_{10}H_{24}O_3Si_2$	48.19(48.34)	9.45(9.74)	104—105/30	1.4383 [a]
IVh	$C_{10}H_{24}O_4Si_2$	45.38(45.42)	8.88(9.15)	105—107/27	1.4311 [a]
IVi	$C_{10}H_{24}O_6Si_2$	40.49(40.51)	7.79(8.16)	107/30	1.4236
IVk	$C_8H_{20}Si_2$	55.69(55.73)	11.72(11.69)	—	1.4037
IVn	$C_9H_{22}Si_2$	58.30(57.98)	11.62(11.89)	—	1.4442

[a] 20°C.

TABLE 5

NMR SPECTRA FOR THE ADDUCTS, $H_2C{=}C(SiMe_mX_{3-m}){-}CHR(SiMe_nX_{3-n})$

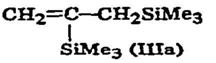
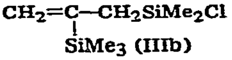
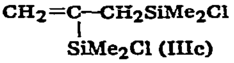
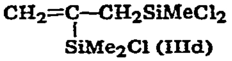
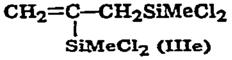
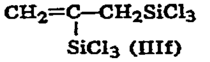
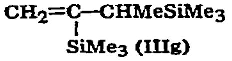
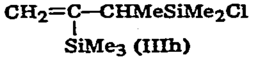
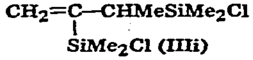
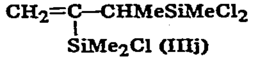
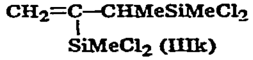
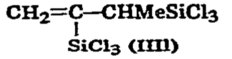
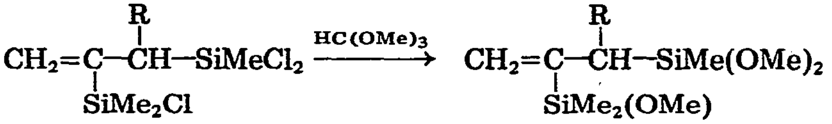
Compound	Chemical shifts (δ, ppm) (CCl$_4$, TMS)
 $CH_2{=}C(SiMe_3){-}CH_2SiMe_3$ (IIIa)	5.33 (m, 1 H), 5.15 (m, 1 H), 1.58 (s, 2 H), 0.06 (s, 9 H), 0.00 (s, 9 H).
 $CH_2{=}C(SiMe_3){-}CH_2SiMe_2Cl$ (IIIb)	5.51 (m, 1 H), 5.32 (d, 1 H), 1.92 (s, 2 H), 0.42 (s, 6 H), 0.12 (s, 9 H)
 $CH_2{=}C(SiMe_2Cl){-}CH_2SiMe_2Cl$ (IIIc)	5.68 (m, 1 H), 5.50 (d, 1 H), 2.00 (s, 2 H), 0.51 (s, 6 H), 0.45 (s, 6 H)
 $CH_2{=}C(SiMe_2Cl){-}CH_2SiMeCl_2$ (IIId)	5.85 (m, 1 H), 5.62 (s, 1 H), 2.26 (s, 2 H), 0.78 (s, 3 H), 0.51 (s, 6 H).
 $CH_2{=}C(SiMeCl_2){-}CH_2SiMeCl_2$ (IIIe)	6.03 (m, 1 H), 5.88 (s, 1 H), 2.34 (s, 2 H), 0.89 (s, 3 H), 0.83 (s, 3 H).
 $CH_2{=}C(SiCl_3){-}CH_2SiCl_3$ (IIIf)	6.23 (d, 2 H), 2.63 (s, 2 H).
 $CH_2{=}C(SiMe_3){-}CHMeSiMe_3$ (IIIg)	5.47 (d, 1 H), 5.32 (d, 1 H), 1.57 (q, 1 H), 1.10 (d, 3 H), 0.07 (s, 9 H), —0.01 (s, 9 H)
 $CH_2{=}C(SiMe_3){-}CHMeSiMe_2Cl$ (IIIh)	5.60 (d, 1 H), 5.42 (d, 1 H), 1.86 (q, 1 H), 1.18 (d, 3 H), 0.34 (d, 6 H), 0.08 (s, 9 H).
 $CH_2{=}C(SiMe_2Cl){-}CHMeSiMe_2Cl$ (IIIi)	5.71 (d, 1 H), 5.55 (d, 1 H), 1.94 (q, 1 H), 1.23 (d, 3 H), 0.48 (s, 6 H), 0.41 (s, 6 H).
 $CH_2{=}C(SiMe_2Cl){-}CHMeSiMeCl_2$ (IIIj)	5.98 (s, 1 H), 5.74 (s, 1 H), 2.28 (q, 1 H), 1.33 (d, 3H), 0.75 (s, 3 H), 0.52 (s, 3 H)
 $CH_2{=}C(SiMeCl_2){-}CHMeSiMeCl_2$ (IIIk)	6.05 (s, 1 H), 5.88 (s, 1 H), 2.32 (q, 1 H), 1.37 (d, 3 H), 0.89 (s, 6 H), 0.77 (s, 6 H)
 $CH_2{=}C(SiCl_3){-}CHMeSiCl_3$ (IIIl)	6.29 (d, 2 H), 2.63 (q, 1 H)

TABLE 6

NMR SPECTRA FOR THE ADDUCTS, $H_2C{=}C[SiMe_m(OMe)_{3-m}]{-}CHR[SiMe_n(OMe)_{3-n}]$

Compound	Chemical shifts (δ, ppm) (CCl_4, TMS)
$CH_2{=}\underset{\substack{\vert \\ SiMe_3}}{C}{-}CH_2SiMe_2(OMe)$ (IVa)	5.40 (m, 1 H), 5.18 (d, 1 H), 3.37 (s, 3 H), 1.63 (s, 2 H), 0.07 (s, 15 H)
$CH_2{=}\underset{\substack{\vert \\ SiMe_2(OMe)}}{C}{-}CH_2SiMe_2(OMe)$ (IVb)	5.42 (m, 1 H), 5.25 (d, 1 H), 3.37 (s, 6 H), 1.67 (s, 2 H), 0.15 (s, 6 H), 0.08 (s, 6 H)
$CH_2{=}\underset{\substack{\vert \\ SiMe_2(OMe)}}{C}{-}CH_2SiMe(OMe)_2$ (IVc)	5.53 (m, 1 H), 5.27 (d, 1 H), 3.47 (s, 6 H), 3.37 (s, 3 H), 1.63 (s, 2 H), 0.12 (s, 6 H), 0.02 (s, 3 H)
$CH_2{=}\underset{\substack{\vert \\ SiMe(OMe)_2}}{C}{-}CH_2SiMe(OMe)_2$ (IVd)	5.55 (m, 1 H), 5.35 (d, 1 H), 3.45 (s, 6 H), 1.63 (s, 2 H), 0.12 (s, 3 H), 0.05 (s, 3 H)
$CH_2{=}\underset{\substack{\vert \\ SiMe_3}}{C}{-}CHMeSiMe_2(OMe)$ (IVe)	5.49 (d, 1 H), 5.32 (d, 1 H), 3.36 (s, 3 H), 1.75 (q, 1 H), 1.08 (d, 3 H), 0.06 (s, 9 H), 0.00 (s, 6 H)
$CH_2{=}\underset{\substack{\vert \\ SiMe_2(OMe)}}{C}{-}CHMeSiMe_2(OMe)$ (IVf)	5.55 (d, 1 H), 5.38 (d, 1 H), 3.37 (s, 6 H), 1.81 (q, 1 H), 1.07 (d, 3 H), 0.09(s, 6 H), 0.02 (s, 6 H)
$CH_2{=}\underset{\substack{\vert \\ SiMe_2(OMe)}}{C}{-}CHMeSiMe(OMe)_2$ (IVg)	5.60 (d, 1 H), 5.40 (d, 1 H), 3.49 (s, 3 H), 3.35 (s, 3 H), 1.86 (q, 1 H), 1.11 (d, 3 H), 0.15 (s, 6 H), 0.00 (s, 3 H)
$CH_2{=}\underset{\substack{\vert \\ SiMe(OMe)_2}}{C}{-}CHMeSiMe(OMe)_2$ (IVh)	5.58 (d, 1 H), 5.43 (s, 1 H), 3.45 (s, 12 H), 1.88 (q, 1 H). 1.14 (d, 3 H), 0.10 (s, 3 H), 0.00 (s, 3 H)
$CH_2{=}\underset{\substack{\vert \\ Si(OMe)_3}}{C}{-}CHMeSi(OMe)_3$ (IVi)	5.73 (d, 1 H), 5.53 (d, 1 H), 3.52 (18 H), 1.87 (q, 1 H), 1.13 (d, 3 H)
$CH_2{=}\underset{\substack{\vert \\ SiMe_3}}{C}{-}CH_2SiMe_2H$ (IVk)	5.36 (m, 1 H), 5.16 (d, 1 H), 3.85 (m, 1 H), 1.64 (d, J = 3.6 Hz, 2 H), 0.07 (s, 9 H), 0.06 (d, J = 3.6 Hz, 6 H)
$CH_2{=}\underset{\substack{\vert \\ SiMe_3}}{C}{-}CHMeSiMe_2H$ (IVn)	5.43 (d, 1 H), 5.29 (d, 1 H), 3.78 (m, 1 H), 1.70 (m, 1 H), 1.09 (d, J = 7.0 Hz, 3 H), 0.07 (s, 9 H), 0.00 (d, J = 3.6 Hz, 6 H).



$$CH_2{=}\underset{\substack{\vert \\ SiMe_2Cl}}{C}{-}\overset{\substack{R \\ \vert}}{CH}{-}SiMeCl_2 \xrightarrow{HC(OMe)_3} CH_2{=}\underset{\substack{\vert \\ SiMe_2(OMe)}}{C}{-}\overset{\substack{R \\ \vert}}{CH}{-}SiMe(OMe)_2 \tag{7}$$

IIId, R = H IVc, R = H
IIIj, R = Me IVg, R = Me

The derivatives were quite helpful in determining the structures of the original products. Thus, the double silylation products from unsymmetrical disilanes were found by examination of their spectra to possess structures such that the silyl moiety, having more Cl or OMe substituent(s), occupies the 3-position and the other the 2-position. For example, in hydrosilane derivative IVk derived from IIIb, the signal which appeared at 1.64 (d, J = 3.6 Hz) (2 H) ($CH_2{-}Si$) is diagnostic and consistent with the assigned structure. Similarly, the structure of compound IVn obtained from the chlorosilylolefin IIIh was established unequivocally by examining signals at 3.78(m) (1 H) (SiH), 1.70(m) (1 H) (CH), 1.09 (d, J = 7.0 Hz) (3 H) (Me), 0.07(s) (9 H) (SiMe) and 0.00 (d, J = 3.6 Hz) (6 H) (SiMe) (Table 6). On the basis of the structures of compound IVk and IVn, the original products, IIIb and IIIh, can clearly be identified as compounds of the indicated structures.

TABLE 7

IR CHARACTERISTIC BANDS FOR THE ADDUCTS [a]

Compound	$\nu(H_2C{=})$ (m)	$\nu(C{=}C)$ (w)	$\delta(SiMe)$ (s)	$\nu(SiOC)$ (s)	$\delta(H_2C{=}C)$ (m or s)
IIIa	3050	1584	1248 1255(sh)	—	902
IIIb	3055	1590	1255	—	915
IIIc	3050	1590	1253	—	920
IIId	3050	1595	1260	—	932
IIIe	3050	1590	1260	—	940
IIIf	3070	1597	—	—	950
IIIg	3045	1590	1245 1258(sh)	—	888; 915
IIIh	3055	1593	1250 1260(sh)		888; 920
IIIi	3051	1592	1254	—	888; 930
IIIj	3055	1595	1258	—	888; 935
IIIk	3057	1595	1260	—	890; 944
IIIl	3075	1600	—	—	887; 955
IVa	3050	1589	1249 1258(sh)	1095	907; 955
IVb	3050	1590	1259	1060	910
IVc	3050	1590	1258	1090	920
IVd	3050	1596	1260	1090	928
IVe	3050	1589	1247 1255(sh)	1085	887; 912
IVf	3050	1590	1252	1095	890; 920
IVg	3050	1590	1256	1088	890; 910
IVh	3050	1590	1260	1090	893; 930
IVi	3050	1590	—	1095	900; 935
IVk [b]	3050	1589	1248	—	890; 905
IVn [b]	3050	1589	1248	—	910; 890

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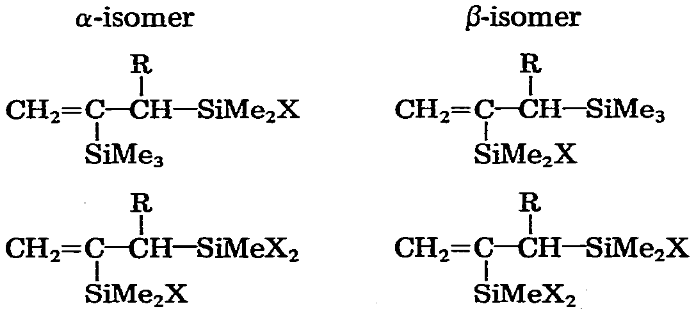
[a] Neat liquid film (sandwich method) cm^{-1}; Peak intensity, m: medium, w: weak, s: strong, sh: shoulder.

[b] $\nu(SiH)$: 2120 cm^{-1}.



α-isomer

$\mathrm{CH_2{=}\underset{\underset{\displaystyle SiMe_3}{|}}{C}{-}\overset{\overset{\displaystyle R}{|}}{C}H{-}SiMe_2X}$

$\mathrm{CH_2{=}\underset{\underset{\displaystyle SiMe_2X}{|}}{C}{-}\overset{\overset{\displaystyle R}{|}}{C}H{-}SiMeX_2}$

β-isomer

$\mathrm{CH_2{=}\underset{\underset{\displaystyle SiMe_2X}{|}}{C}{-}\overset{\overset{\displaystyle R}{|}}{C}H{-}SiMe_3}$

$\mathrm{CH_2{=}\underset{\underset{\displaystyle SiMeX_2}{|}}{C}{-}\overset{\overset{\displaystyle R}{|}}{C}H{-}SiMe_2X}$

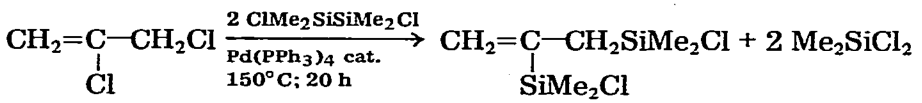
(X = H, Cl, OMe)

It follows that the double silylation of allenes proceeds with complete regiospecificity giving exclusively α-isomer in each reaction.

By analogy, it seemed highly likely that the products arising from the reactions of $Cl_2MeSiSiMe_2Cl$ with the allenes would possess structures in which the dichloromethylsilyl group would occupy the 3-position and the chlorodimethylsilyl group the 2-position.

In the case of the double silylation of methoxypentamethyldisilane, adducts IVa and IVe were found to be identical in every respect (spectral data and refractive indices) with the samples obtained by the methoxylation (eq. 6) of IIIb and IIIh, respectively. Structures of the double silylation products, IVc and IVg, were similarly determined by comparison with methoxylation products from IIId and IIIj. Thus, also in the case of the addition of unsymmetrical methoxydisilanes, only the α-isomer was formed.

The structure of the 1 : 1 adduct between allene and *sym*-dichlorotetramethyldisilane was further confirmed by an alternative synthesis in which the reaction of 2,3-dichloroprop-1-ene with *sym*-dichlorotetramethyldisilane in the presence of $Pd(PPh_3)_4$ furnished 2,3-bis(dimethylchlorosilyl)prop-1-ene (IIIc) in good yield [9]. NMR and IR spectra of the product thus formed were superimposable with those of the double silylation product of allene (eq. 8).

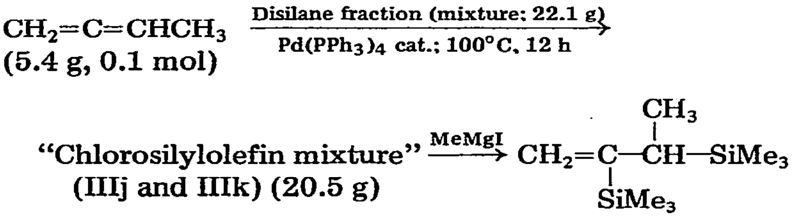


$$CH_2{=}C(Cl){-}CH_2Cl \xrightarrow[\text{Pd(PPh}_3)_4\text{ cat.; }150^\circ C;\ 20\ h]{2\ ClMe_2SiSiMe_2Cl} CH_2{=}C(SiMe_2Cl){-}CH_2SiMe_2Cl + 2\ Me_2SiCl_2 \qquad (8)$$

(IIIc)

All the NMR signals for the adducts of symmetrical disilanes were successfully assigned by the comparisons of their chemical shifts with those of trimethylvinylsilane [10] and -allylsilane [11] as well as those of the adducts of unsymmetrical disilane (see Tables 5 and 6).

Thus, it is obvious that the double silylation of allenic compounds can provide a convenient and simple route to new types of organosilicon compounds containing vinylsilane and allylsilane units that would be often quite difficult to prepare by other methods. The chlorosilane products can be readily converted into many other derivatives, as evidenced by methoxylation and reduction (see above). Further, in view of well-documented synthetic aspects of vinyl- and allylsilanes a large scale synthesis of 2,3-bis(trimethylsilyl)but-1-ene (IIIa) was accomplished. A disilane mixture (b.p. 145—155°C) obtained from the "Direct Process" was used to make 2,3-bis(chlorosilyl)but-1-enes. The latter was readily converted to IIIa by methylation in good yield (eq. 9).



$$\underset{(5.4\ g,\ 0.1\ mol)}{CH_2{=}C{=}CHCH_3} \xrightarrow[\text{Pd(PPh}_3)_4\text{ cat.; }100^\circ C,\ 12\ h]{\text{Disilane fraction (mixture; 22.1 g)}}$$

$$\underset{\text{(IIIj and IIIk) (20.5 g)}}{\text{"Chlorosilylolefin mixture"}} \xrightarrow{MeMgI} CH_2{=}C(SiMe_3){-}CH(CH_3){-}SiMe_3 \qquad (9)$$

(IIIa) (10.2 g, 51 mmol)

In order to obtain more information about the nature of the present double silylation, relative reactivities of disilanes or dienes were determined by means of a series of competition reactions, in which several disilanes were allowed to compete in pairs for a deficiency of 1,2-butadiene, and two allenes for a deficiency of *sym*-dimethyltetrachlorodisilane. Thus, the reactivities of each set of reactants were found to fall in the following order:

$CH_2{=}C{=}CHMe(40) > CH_2{=}C{=}CH_2\,(1)$

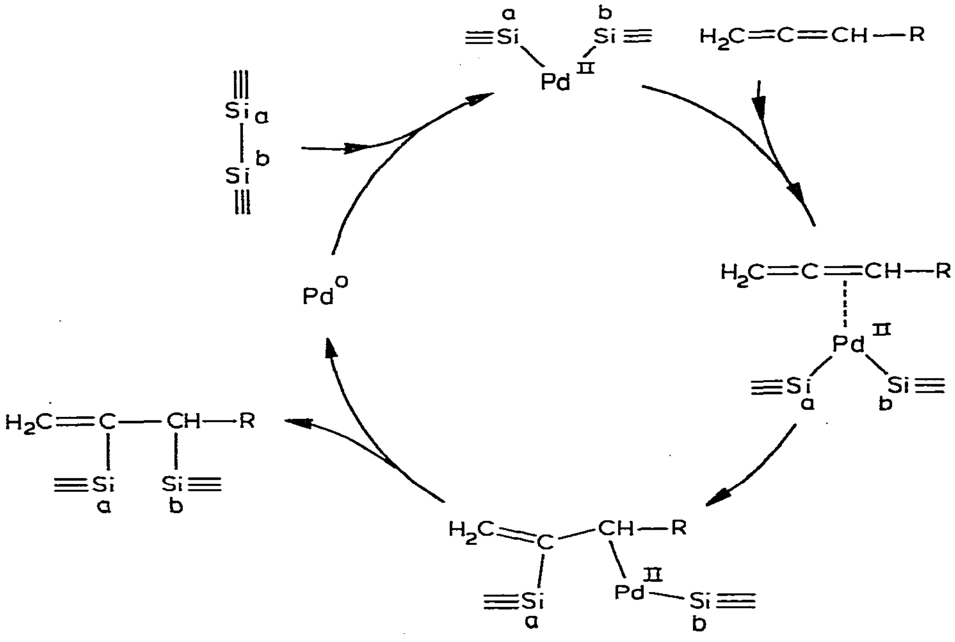
$Cl_4Me_2Si_2\,(7) > Cl_3Me_3Si_2\,(2) > Cl_2Me_4Si_2\,(1)$

$(MeO)_4Me_2Si_2\,(35) > (MeO)_2Me_4Si_2\,(9) > (MeO)Me_5Si_2\,(1)$

Evidently, 1,2-butadiene is much more reactive than allene, and successive introduction of a chlorine atom or a methoxy group in the two series of disilanes substantially increases their reactivities. The acceleration by chlorine atoms and methoxy groups may be due to their electron-withdrawing effects which decrease the electron density of the Si—Si bond and therefore increase the π-acceptor character of silicon [12]. On the other hand, the fact that the methyl substitution for allene greatly accelerates the reaction is in sharp contrast to the reactivity trend observed previously in conjugated dienes, such as $CH_2{=}CH{-}CH{=}CH_2$, $CH_2{=}CMe{-}CH{=}CH_2$ and $CH_2{=}CMe{-}CMe{=}CH_2$ [4] and this might reflect the differing natures of the two double silylation reactions.

At the present time, we do not have any conclusive information about the mechanism of the present double silylation. However, by analogy with the mechanism proposed previously in the double silylation of acetylenes [3,6], the reaction scheme might reasonably be depicted as follows:

SCHEME 1



Nevertheless, several important points of this reaction (e.g., exclusive 2,3-addition, exclusive formation of α-isomers) remain to be explained, and further work is obviously necessary.

Experimental

All boiling points are uncorrected. IR spectra were recorded using neat liquid films with a Hitachi EPI-G3 and a JASCO A-102 spectrometer, and NMR spectra were measured using a Varian EM-360A spectrometer in CCl_4 solution with TMS as internal standard. GLC analyses were performed using an Ohkura Model 802 instrument equipped with a 1 or 2 m × 4 mm Teflon column packed with silicones KF-96, SF-96 and DC-QF-1 (10—20%) on Celite 545-AW (60/80 mesh) (column temp. 100—180°C; He carrier). Unless otherwise specified, thermal conductivity correction using an external standard (n-alkanes or arenes selected from C_{10}—C_{15} hydrocarbons) has been made for the GLC product yields.

Materials

All the methoxymethyldisilanes used were prepared via methoxylation of the corresponding chlorodisilanes according to the method reported previously [13]. Monochloromethyldisilane was obtained by chlorination [14] of hexamethyldisilane which was prepared by the literature method [15]. Di-, tri- and tetrachloromethyldisilanes were prepared as reported previously [13,16]. Hexachlorodisilane was commercially available and used after distillation. Allene was commercially available in a cylinder. 1,2-Butadiene is commercially available in a cylinder as a ca. 50 : 50 mixture of 1,2-butadiene and but-2-ene. Metal-triphenylphosphine complexes were prepared by the literature methods as described previously [17—22].

Addition of chloro- and methoxy-methyldisilanes to allenic compounds in the presence of metal-triphenylphosphine complexes (eq. 4)

A. With allene. The method used for the addition reaction to give 2,3-bis(dichloromethylsilyl)prop-1-ene (IIIb) is representative. Under Ar, *sym*-dimethyltetrachlorodisilane (2.3 g, 10 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol; 1.0 mol% relative to the disilane used) and a small stirring bar were placed in a stainless-steel vessel which was immersed in a liq. N_2 bath and then evacuated. Allene (0.8 g: 0.5 ml, 20 mmol), condensed in a calibrated tube at —78°C (dry ice-acetone bath), was distilled into the vessel through the inlet valve and then the vessel was allowed to warm to room temperature. Subsequently, it was heated at 120°C (oil bath) for 15 h with stirring. After cooling, GLC analysis of the reaction mixture (2.5 g) showed that only one product was formed and no disilane remained (conversion: 100%). The product was isolated by preparative GLC and identified by the usual manner (elemental analysis, IR and NMR spectra) to be 2,3-bis(dichloromethylsilyl)prop-1-ene (IIIe) (85% based on the disilane used). Distillation afforded (IIIe), 1.6 g (67%), b.p. 105°C/30 mmHg; n_D^{25} 1.4780.

B. With 1,2-butadiene *. A typical method is given for the addition of *sym*-dimethoxytetramethyldisilane to yield the adduct IVf. In a similar manner to the above (A), to a mixture of *sym*-dimethoxytetramethyldisilane (1.8 g, 10

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* We employed a 50 : 50 mixture consisting of 1,2-butadiene and but-2-ene which is commercially available in a cylinder, rather than pure 1,2-butadiene, and found that in every case the reaction substantially resulted in exclusive formation of only one product which was derived from the allene.

mmol) and $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) in an evacuated stainless-steel vessel was introduced a ca. 50 : 50 mixture of 1,2-butadiene and but-2-ene (1.08 g, 1.6 ml which ca. 10 mmol of 1,2-butadiene contained; condensed in a calibrated tube at 0°C [ice-water bath] and then distilled into the vessel). The mixture was heated at 120°C (oil bath) for 15 h with stirring. After cooling, the resulting mixture (2.5 g) was subjected to GLC analysis. Only one product was formed which was isolated by preparative GLC and was found by means of elemental and spectral analyses to be 2,3-bis(dimethylmethoxysilyl)but-1-ene (IVf) (97% yield based on the disilane used). Upon distillation the resulting mixture gave (IVf), 2.1 g (88%), b.p. 103—104°C/30 mmHg; n_D^{25} 1.4395.

C. A preparative scale synthesis of 2,3-bis(trimethylsilyl)but-1-ene (IIIg) from a "disilane fraction" via methylation. Likewise, a double silylation reaction using a "disilane fraction" (b.p. 145—155°C; $Cl_4Me_2Si_2/Cl_3Me_3Si_2$ = 63/37; 22.1 g, 0.1 mol on the basis of Cl-content in the mixture), 1,2-butadiene (0.1 mol) and $Pd(PPh_3)_4$ (1 mmol) (100°C; 12 h) gave, after distillation, an adduct mixture of IIIj and IIIk, 20.5 g (74% based on the Cl content in the mixture used), b.p. 115—127°C/20 mmHg. A solution of this sample (20.5 g, 74 mmol) in ether (70 ml) was added to a MeMgI solution, prepared from MeI (50.1 g, 0.353 mol) and Mg (8.5 g, 0.35 g atom) in ether (120 ml), with stirring under N_2 over a period of 20 min. After 18 h-refluxing (Gilman test: negative), there was obtained a clear solution mixture consisting of two layers. The upper layer was separated and treated with a cold 10% hydrochloric acid (ca. 20 ml). The etheral solution, on work-up, afforded compound IIIa, 10.2 g, 69%), b.p. 84°C/30 mmHg (51% overall yield based on the "disilane fraction" used) (eq. 9).

Alternative synthesis of 2,3-bis(dimethylchlorosilyl)prop-1-ene (IIIc) by the reaction of 2,3-dichloroprop-1-ene with sym-dichlorotetramethyldisilane in the presence of $Pd(PPh_3)_4$ (eq. 8)

According to the literature method [9], a mixture of 2,3-dichloroprop-1-ene (0.55 g, 5 mmol), *sym*-dichlorotetramethyldisilane (3.75 g, 20 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol; 1 mol% relative to the dichloropropene used) in a stainless-steel vessel was heated under Ar at 150°C for 20 h with stirring. GLC analysis for the resulting mixture showed that a single product was formed. The product isolated by preparative GLC was identified as compound IIIc from the comparisons of IR and NMR spectra and refractive index with those of the sample obtained by the double silylation of allene (see above). The yield of IIIc by GLC was 100% (based on the dichloroprop-1-ene used). Distillation gave a crude sample of IIIc, 0.9 g (80%; purity: 80% by GLC), b.p. 70—71°C/40 mmHg.

Attempts to obtain 2,3-bis(trimethylsilyl)- (IIIa) and 2,3-bis(dichloromethylsilyl)-prop-1-ene (IIIe) by the reaction of 2,3-dichloroprop-1-ene with hexamethyldisilane and *sym*-dimethyltetrachlorodisilane, respectively, in the presence of $Pd(PPh_3)_4$ under various conditions employed (130°C, 20 h and 150°C, 24 h) were unsuccessful. Thus, in the attempts with hexamethyldisilane, the starting materials remained intact, and in the ones with *sym*-dimethyltetrachlorodisilane only trace amount of the desired product (by GLC) was formed, although the used disilane was completely consumed.

Conversion of double silylation products, chlorosilylolefins, into their hydrosilyl- and methoxysilyl-olefin derivatives (eqs. 5—7)

A. Reduction of IIIb and IIIh to IVk and IVn, respectively. The method used for the reduction to afford 2-trimethylsilyl-3-dimethylhydrosilylbut-1-ene (IVn) is representative. To a mixture of $LiAlH_4$ (0.44 g, 12 mmol) and ether (anhydrous) (10 ml) was added a solution of 2-trimethylsilyl-3-chlorodimethylsilylbut-1-ene (IIIh) (2.8 g, 12 mmol) in ether (anhydrous) (5 ml) and the mixture was refluxed for 5 h under N_2 and then hydrolyzed. The ethereal layer, after drying over $MgSO_4$, was concentrated to give crude product from which pure sample of the product was isolated by preparative GLC and identified as compound IVn.

B. Methoxylation of IIIb, IIId, IIIh and IIIj to IVa, IVc, IVj and IVg, respectively. A typical procedure is given for the methoxylation to afford 2-dimethylmethoxysilyl-3-dimethoxymethylsilylpropl-ene (IVc). A mixture of chlorosilylolefin IIId (1.1 g, 4.5 mmol) and methyl orthoformate (5.7 g, 50 mmol) was refluxed for 62 h under N_2 until the gas evolution of MeCl had ceased [*]. After removal of low boiling materials, the product thus formed was isolated by preparative GLC and identified by the usual means (elemental analysis and IR and NMR spectra) as compound IVc. Inspection of the spectral data and refractive index disclosed that this compound was identical with that obtained from the double silylation of allene with *unsym*-trimethoxytrimethyldisilane.

Competition reactions of disilanes and of allenes in the presence of $Pd(PPh_3)_4$ catalyst

A. For the reaction of disilanes with 1,2-butadiene. Typically, a mixture of *sym*-dichlorotetramethyldisilane (1.87 g, 10 mmol), *sym*-dimethyltetrachlorodisilane (2.28 g, 10 mmol), 1,2-butadiene (3 mmol) and the palladium(0) complex (35 mg, 0.03 mmol) was heated at 100°C for 2.5 h under Ar in a sealed stainless-steel vessel. Quantitative analysis by GLC showed that 2,3-bis(chlorosilyl)but-1-enes, IIIi (0.25 mmol) and IIIk (1.37 mmol), had been produced. The relative rate was calculated using the Doering equation [23]:

$$k_{rel} = \frac{k(Cl_4Me_2Si_2)}{k(Cl_2Me_4Si_2)} = \frac{[Cl_2Me_4Si_2]_i}{[Cl_4Me_2Si_2]_i} \times \frac{[IIIk]}{[IIIi]}$$

where $k(Cl_4Me_2Si_2)/k(Cl_2Me_4Si_2)_4$ is the ratio of the rate constants for $Cl_4Me_2Si_2$ and $Cl_2Me_4Si_2$, $[Cl_2Me_4Si_2]_i$ and $[Cl_4Me_2Si_2]_i$ are the initial concentrations of the disilanes, and [IIIk] and [IIIi] are the molar amounts of the products, IIIk and IIIi, formed, respectively.

Similarly, competition reactions of other several pairs of two disilanes selected from disilanes in the two series of chloro- and methoxy-disilanes were conducted at 100°C for 2.5 h, and the relative rates were evaluated in a similar manner.

B. For the reaction of allenes with disilane IIe. To a mixture of *sym*-dimethyltetrachlorodisilane (1.15 g, 5 mmol) and $Pd(PPh_3)_4$ catalyst (58 mg, 0.05 mmol) was introduced allene (0.8 g; 0.5 ml, 20 mmol) and 1,2-butadiene (20 mmol).

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[*] See ref. 12, p. 173, footnote.

The mixture was heated at 100°C for 2.5 h to give the adducts, 2,3-bis(chlorosilyl)-prop-1-ene (IIIe) and -but-1-ene (IIIk). The relative rate was calculated using the following equation [23]:

$$k_{\mathrm{rel}} = \frac{\mathrm{k(CH_2{=}C{=}CHMe)}}{\mathrm{k(CH_2{=}C{=}CH_2)}} = \frac{[\mathrm{CH_2{=}C{=}CH_2}]_i}{[\mathrm{CH_2{=}C{=}CHMe}]_i} \times \frac{[\mathrm{IIIk}]}{[\mathrm{IIIe}]}$$

where $k(\mathrm{CH_2{=}C{=}CHMe})/k(\mathrm{CH_2{=}C{=}CH_2})$ is the ratio of the rate constants for 1,2-butadiene and allene, $[\mathrm{CH_2{=}C{=}CH_2}]_i$ and $[\mathrm{CH_2{=}C{=}CHMe}]_i$ are the initial concentrations of the allenes, and [IIIk] and [IIIe] are the molar amounts of the products, IIIk and IIIe, formed, respectively.

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