Tetrahedron Letters,Vol.28,No.16,pp 1807-1810,1987
Printed in Great Britain

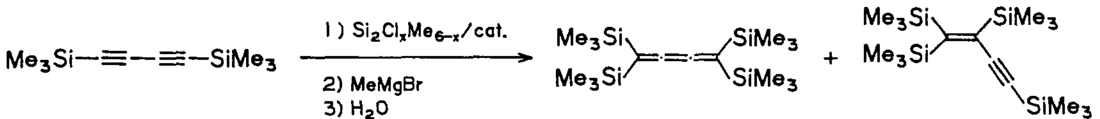
0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

PALLADIUM CATALYZED DOUBLE SILYLATION OF BIS(TRIMETHYLSILYL)BUTADIYNE BY MEANS OF DISILANES

Tetsuo Kusumoto and Tamejiro Hiyama*
Sagami Chemical Research Center
4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229, Japan

Summary: Reaction of bis(trimethylsilyl)butadiyne with $Si_2Cl_xMe_{6-x}$ in the presence of a palladium catalyst gives, after methylation, 1,1,4,4-tetrakis(trimethylsilyl)butatriene and/or 1,1,2,4-tetrakis-(trimethylsilyl)-1-buten-3-yne selectively.

It is expected that butadiyne, produced as a by-product in the transformation of natural gas to acetylene, is useful compound as a highly unsaturated C_4 synthetic unit.[1)] Its application to organic synthesis, however, has been limited mainly due to the intrinsic explosive nature. The disilyl derivative, bis(trimethylsilyl)butadiyne (**1**), is a stable crystalline compound, and thus we have studied introduction of functional groups into the triple bonds of **1** by carbometallation,[2)] hydrosilylation[3)] and also by the reaction with trimethylsilyl cyanide.[4)] We report herein that **1** reacts with methylated chlorodisilanes in the presence of a palladium catalyst to afford 1,1,4,4-tetrakis(trimethylsilyl)butatriene (**2**)[5)] and/or 1,1,2,4-tetrakis-(trimethylsilyl)-1-buten-3-yne (**3**) depending on the structure of the catalyst and disilanes.



1 2 3

In a typical procedure, a mixture of **1** (0.2 mmol), disilane fraction (bp 145-155 °C, 1:1 mixture of $MeCl_2Si\text{-}SiClMe_2$ and $MeCl_2Si\text{-}SiCl_2Me$) (0.2 g) and $PdCl_2(PEt_3)_2$ (0.006 mmol) was heated at 100 °C for 13 h under an argon atmosphere in a sealed vial. Excess methylmagnesium bromide in ether was added to the reaction mixture at -20 °C. Workup and purification by preparative TLC on silica gel gave **2** (26 mg, 42% yield) and **3**[6)] (11 mg, 18% yield). When a series of $PdCl_2(PR_3)_2$ was employed, both reactivity and selectivity changed according to the structure of the phosphine ligand as shown in Table 1. In general, **2** was produced as the major product. Use of $PdCl_2(PEt_3)_2$ and $PdCl_2[P(CH_2Ph)_3]_2$ much improved the combined yields of **2** and **3** (runs 5 and

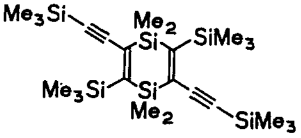
Table 1 Reaction of **1** with disilanes using a palladium catalyst.

Run[a]	Disilane[b]	Catalyst (mol %)	Conditions	Yield (%)[c]	
				2	**3**
1	Disilane Fraction[d]	$PdCl_2(PPh_3)_2$ (5.2)	120 °C, 10 h	19	8
2		$PdCl_2(PMePh_2)_2$ (5.1)	120 °C, 9 h	36	23
3		$PdCl_2(PMe_2Ph)_2$ (2.9)	120 °C, 7.5 h	20	24
4		$PdCl_2(PMe_3)_2$ (2.9)	120 °C, 9 h	7	6
5		$PdCl_2(PEt_3)_2$ (3.2)	100 °C, 10 h	42	18
6[e]		" (1.7)	110 °C, 9 h	54	20
7		$PdCl_2[P(CH_2Ph)_3]_2$ (1.8)	110 °C, 5 h	29	29
8		$PdCl_2(PBu_3)_2$ (2.9)	110 °C, 8 h	10	8
9		$Pd(PPh_3)_4$ (4.1)	140 °C, 13 h	24	5
10	$MeCl_2Si\text{-}SiCl_2Me$	$PdCl_2(PEt_3)_2$ (2.9)	100 °C, 5 h; 110 °C, 2 h	49	22
11		$PdCl_2[P(CH_2Ph)_3]_2$ (3.1)	120 °C, 1 h	45	36
12		$Pd(PPh_3)_4$ (3.2)	120 °C, 6 h	35	13
13	$MeCl_2Si\text{-}SiClMe_2$	$PdCl_2(PEt_3)_2$ (3.8)	120 °C, 3 h	48	14
14		$PdCl_2[P(CH_2Ph)_3]_2$ (2.1)	120 °C, 5 h	12	11
15		$Pd(PPh_3)_4$ (3.3)	120 °C, 6 h	23	8
16	$Me_2ClSi\text{-}SiClMe_2$	$PdCl_2(PEt_3)_2$ (1.6)	120 °C, 4 h	5	72
17		$PdCl_2[P(CH_2Ph)_3]_2$ (2.1)	120 °C, 10 h	trace	52
18[f]		" (1.6)	120 °C, 11 h	4	74
19		$PdCl_2(PMe_3)_2$ (4.3)	120 °C, 16 h	3	36
20		$Pd(PPh_3)_4$ (3.8)	140 °C, 29 h 160 °C, 22 h	6	7
21	$Me_2ClSi\text{-}SiMe_3$	$PdCl_2(PEt_3)_2$ (4.4)	120 °C, 8 h	trace	26
22		$PdCl_2[P(CH_2Ph)_3]_2$ (2.1)	120 °C, 8 h	13	40
23	$Me_3Si\text{-}SiMe_3$	$PdCl_2(PEt_3)_2$ (5.1)	140 °C, 16 h	--	14[g]
24		$PdCl_2[P(CH_2Ph)_3]_2$ (2.5)	140 °C, 17 h; 160 °C, 5 h	--	7[g]
25		$PdCl_2(PMe_3)_2$ (4.1)	140 °C, 20 h	--	3[g]

a) About 0.2 mmol of **1** was used. b) Disilanes of 3-6 mol equivalents were used. c) Isolated yields by preparative TLC. d) A 1:1 mixture of $MeCl_2Si\text{-}SiCl_2Me$ and $MeCl_2Si\text{-}SiClMe_2$. e) Reaction of **1** (0.8 g, 4.2 mmol) with 1.6 g of disilane fraction. f) Reaction of **1** (1.5 g, 7.7 mmol) with 3 g of $Me_2ClSi\text{-}SiClMe_2$. g) Most of the starting material **1** was recovered.

7).[7] In these reactions, small amounts of **4**, **5**[8] and $(SiMe_2)_n$ all derived from silylenes always formed as the by-products.

We next compared the reactivity of various disilanes. Both $MeCl_2Si\text{-}SiCl_2Me$ and $MeCl_2Si\text{-}SiClMe_2$ gave **2** and **3** in similar yields to disilane fraction in the presence of $PdCl_2(PEt_3)_2$ or $Pd(PPh_3)_4$ (runs 5, 9, 10, 12, 13, and 15). With $PdCl_2[P(CH_2Ph)_3]_2$ catalyst, $MeCl_2Si\text{-}SiCl_2Me$ gave **2** and **3** in



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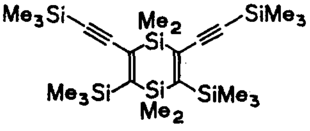

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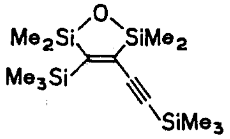

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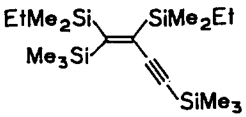

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higher yields, but $MeCl_2Si-SiClMe_2$ did less efficiently. (runs 7, 11, and 14). The enyne 3 was mainly obtained with $MeCl_2Si-SiCl_2Me$ in the presence of $PdCl_2(PEt_3)_2$ or $PdCl_2[P(CH_2Ph)_3]_2$ (runs 16 and 17). Hexamethyldisilane gave only a small amount of **3** (runs 23, 24, and 25). Hexachlorodisilane underwent polysilane formation solely. These results show that highly chlorinated disilanes prefer 1,4-disilylation to give **2**, whereas less chlorinated disilanes afford **3** by 1,2-addition in some cases as the sole product.[9]

Isolation of the primary silylation product before methylation allowed us to establish the stereochemical course of the disilylation. The crude primary product from **1** and $Me_2ClSi-SiClMe_2$ was subjected to GLC separation. Hereby only **3'** was isolated which was proved to be an E/Z mixture. Other disilanes in Table 2 gave the similar stereochemical outcome. Three possible mechanisms for the formation of the E/Z isomers emerges: (1) random stereochemical course, (2) cis-double silylation followed by (E)-(Z) isomerization under the reaction conditions as observed by Nagai et al.,[7] or (3) cis-double silylation and thermal isomerization upon GLC separation. Thus, we repeated the reaction of run 1 of Table 2, and hydrolyzed the crude product to obtain a cyclic siloxane **6**[11] (55% yield). Treatment of the primary disilylated product with excess ethylmagnesium bromide afforded **7** in 64 % overall yield as a single product, which was isolated by preparative TLC. Upon GLC analysis,

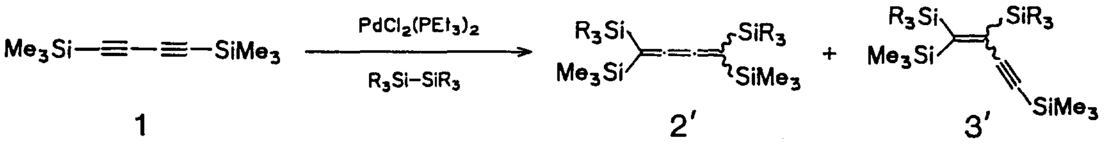

Table 2 Stereochemical aspect of the double silylation

Run	$R_3Si-SiR_3$	Conditions	Yield (%)[a)] 2'	3'
1	$Me_2ClSi-SiClMe_2$	120 °C, 8 h	--	61[b)]
2	$Me_2FSi-SiFMe_2$	120 °C, 9 h	--	86[c)]
3	$Me_2(i\text{-}PrO)Si-Si(OPr\text{-}i)Me_2$	120 °C, 9 h	--	55[b)]
4	$Me_2PhSi-SiPhMe_2$	120 °C, 6 h	13[b)]	26[b)]

a) Isolated yields by GLC (Diasolid, 3 m, 200 °C). b) A 1:1 mixture of the (E) and (Z) isomers. c) The E/Z ratio could not be estimated.

7 isomerized to a 1:1 mixture of (E) and (Z) isomers. By reviewing these experimental results, we can conclude that the disilylation under the reaction conditions took place in a cis-manner, and the primary products are stereochemically stable under the reaction conditions (120 °C). The (E)-(Z) isomerizatoin does not take place till heating at 200 °C. The facile geometrical isomerizaton is characteristic of highly silylated ethenes.[12)]

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6) MS m/z (rel. intensity) 340 (M^+, 53), 237 (80), 179 ($C_4Si_2Me_5$, 76), 155 (55), 73 (100); ^{1}H NMR ($CDCl_3$, $CHCl_3$ standard) δ 0.18 (s, 1 H), 0.22 (s, 1 H), 0.28 (s, 1 H), 0.29 (s, 1 H); ^{13}C NMR ($CDCl_3$, $CDCl_3$ standard) δ -0.21 (qm), 1.82 (qm), 2.20 (qm), 3.16 (qm), 107.1 (m), 110.4 (s), 156.3 (m), 176.7 (m); IR (neat) 2971, 2920, 2110 (C≡C), 1250 ($SiMe_3$), 910, 840, 760, 695, 640, 540 cm^{-1}. Anal. Calcd for $C_{16}H_{36}Si_4$: C, 56.39; H, 10.65. Found: C, 56.26; H, 10.50.
7) The palladium(II) complex having dppp, $P(c\text{-}C_6H_{11})_3$, $P(CH_2CH_2CN)_3$, $PHPh_2$, $P(OMe)_3$, or PhCN ligand was totally inactive.
8) **4**: ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 3 H), 0.25 (s, 3 H), 0.29 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ -0.60 (qq), -0.23 (qm), 0.81 (qm), 107.6 (m), 108.0 (s), 155.5 (m), 171.1 (m); **5**: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 1 H), 0.19 (s, 3 H), 0.24 (s, 1 H), 0.26 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ -2.77 (qq), -0.23 (qm), 1.01 (qm), 1.30 (qq), 107.5 (s), 107.9 (m), 151.7 (m), 174.7 (m).
9) Formation of **3** may be ascribed to silylmetallation of C≡C by $\equiv$Si-Pd-Si$\equiv$ (i) followed by reductive elimination. When a more chlorinated disilane was employed, the Si ligand in (i) becomes less nucleophilic or the electron density at Pd is reduced, and thus the reductive elimination to give rise to **2** may follow a 1,3-rearrangement of palladium so as to release the steric interactions.
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11) ^{1}H NMR spectra of **6**: δ 0.18 (s, 3 H), 0.20 (s, 3 H), 0.22 (s, 2 H), 0.25 (s, 2 H); **7**: δ 0.17 (s, 9 H), 0.18 (s, 6 H), 0.23 (s, 6 H), 0.26 (s, 9H), 0.68 (q, J=7.9 Hz, 2 H), 0.76 (q, J=7.9 Hz, 2 H), 0.92 (t, J=7.9 Hz, 3 H), 0.96 (t, J=7.9 Hz, 3H).
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(Received in Japan 29 January 1987)