Heteroatom Chemistry
Volume 6, Number 1, 1995

Palladium-Catalyzed Hydrosilylation of Silyl-Substituted Butadienes

Wu-Wang Weng, Ruey-Min Chen, and Tien-Yau Luh*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

Received 2 August 1994; revised 29 September 1994

ABSTRACT

Palladium-catalyzed hydrosilylation of silyl-substituted butadienes **1** *and* **2** *with* $MeSiCl_2H$ *has been investigated. Both steric effects and the presence of an aryl substituent affect the regiochemistry of the hydrosilylation reaction. Hydrosilylation of siloxane-tethered bis-dienes* **9** *exhibits high regio- and diastereoselectivity.*

INTRODUCTION

Transition metal-catalyzed hydrosilylation of alkenes and alkynes is highly versatile in organic synthesis. Conjugated dienes can give 1,2- and 1,4-addition products, and the product distribution depends on the kinds of dienes and silanes and the nature of the catalyst [1]. Palladium catalysts are most commonly used for this purpose and 1,4-addition leading to allylsilanes having the Z-configuration are normally obtained [2]. When substituted dienes are used, the addition reaction is in general less selective, a mixture of isomers being obtained. The trimethylsilyl group is a bulky one and an addition reaction would be expected to occur away from this group. Indeed, hydrosilylation of vinylsilanes gives predominantly, if not exclusively, 1,2-bissilylethanes [3]. Furthermore, we recently found that cyclopropanation with dibromocarbene occurs regioselectively at the double bond remote from the silyl substituent [4]. In continuation of our interest in the synthesis [5] and applications of silyl-substituted dienes [6], we report herewith our preliminary findings on the palladium-catalyzed hydrosilylation of silyl-substituted butadienes.

RESULTS AND DISCUSSION

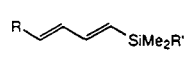
The silyl-substituted dienes **1a–c** and **2** were prepared according to our published procedure [5]. Treatment of **1a** with 2 equivalents of $MeSiCl_2H$ in the presence of 1 mol% $PdCl_2(PPh_3)_2$ in a sealed tube at 80°C for 16 hours followed by workup with methanol under basic conditions gave **3a** as the sole product in 70% yield. Similar to literature examples [2], the addition reaction occurred in a 1,4-addition manner and the resulting double bond was in the Z-configuration. Interestingly, the internal silyl-substituted diene **2** also gave a similar hydrosilylation pattern, leading to **4** in 70% yield (Equation 3). The corresponding *t*-butyl analog **5** was employed for comparison, allylsilane **6** being isolated as the sole product under similar conditions. Because of the steric effect, the newly formed Si–C bond in all these cases took place at the less sterically hindered C-4. Alternatively, the aryl substituent at C-4 may exert a substituent effect leading to the regioselective formation of the Si–C bond. We have tested this viewpoint by studying the reactions of silyl-substituted dienes without the presence of an aryl substituent. Thus, treatment of **1b** with $MeSiCl_2H$ under the same conditions afforded a 6.6:1 mixture of 1,4-adducts **3b** and **7b**. In a similar manner, the reaction of **1c** gave a 2:1

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

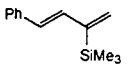
*To whom correspondence should be addressed.

1042-7163/95/$5.00 + .25

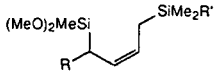
mixture of **3c** and **7c**. These results indicated that both the steric effect and the presence of an aryl substituent determine the regioselectivity of the hydrosilylation of conjugated dienes.



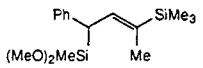
1a R = Ph, R' = Me
1b R = Me, R' = Ph
1c R = i-Pr, R' = Me



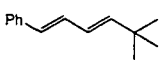
2



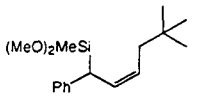
3a R = Ph, R' = Me
3b R = Me, R' = Ph
3c R = i-Pr, R' = Me



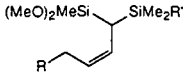
4



5



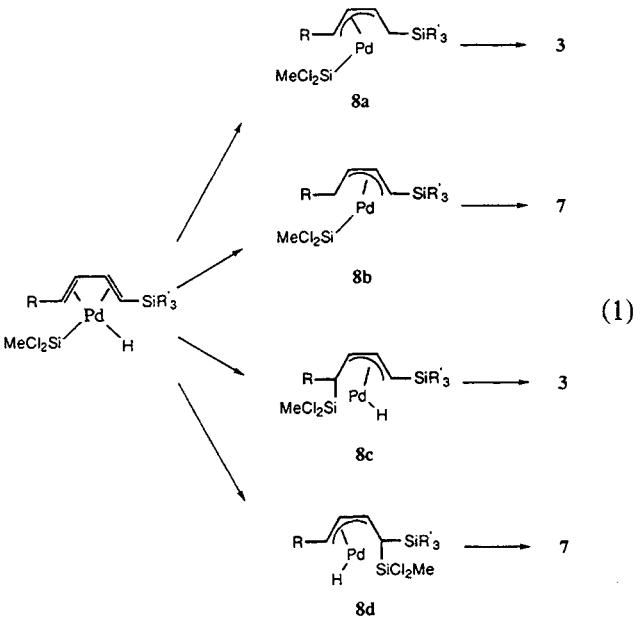
6



7b R = Me, R' = Ph
7c R = i-Pr, R' = Me

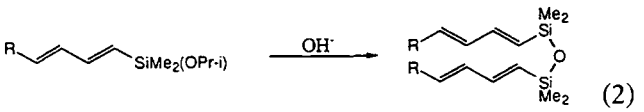
The mechanism of the hydrosilylation reaction of dienes has been suggested (Equation 1) [2]. Oxidative addition across the Si–H bond, followed by an insertion step, will generate a π-allylpalladium intermediate **8a** or **8b**. The orientation of this insertion step apparently depends on the steric factor and on the relative stability of the π-allyl complex. In the presence of the phenyl substituent, the insertion process is regioselective, giving the more stable π-allyl intermediate. When the phenyl substituent is replaced by an alkyl group, the reaction becomes less selective and, hence, a mixture of **3** and **7** is isolated. Nevertheless, the production of the less hindered π-allyl complex appeared to be the predominant pathway in this overall catalytic process. However, we could not rule out at this stage the alternative possibility, which may involve the migratory insertion of the silyl group giving a π-allylpalladium intermediate **8c** or **8d**, followed by reductive elimination leading to the formation of **3** or **7**. The steric preponderance may determine the regioselectivity of the overall reaction.

We have recently found that, in the presence of base, silyl-substituted dienes **8** undergo dimerization reactions to give the siloxane-tethered bis-dienes **9** (Equation 2) [6b]. It is known that tethered bis-dienes readily undergo intramolecular cyclization reactions by use of transition metal catalysts [7]. Apparently, there would be some kind of interaction between this bis-diene moiety and the metal catalyst. We felt that such interaction may cause the stereoelectronic effect of the transition metal-catalyzed addition reactions, and, therefore, the stereochemistry of the product in each case may be controlled.



8a
8b
8c
8d

(1)

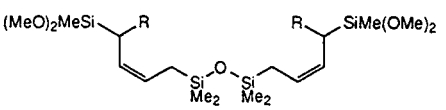


8

9a R = Ph
9b R = Me

(2)

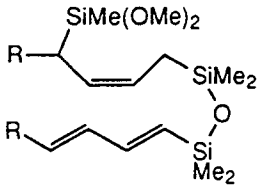
Treatment of **9a** with $MeSiCl_2H$ in the presence of $PdCl_2(PPh_3)_2$ under similar conditions afforded **10a** in 40% yield. A similar result was observed for the reaction of **9b** under the same conditions affording **10b** in 59% yield. Two interesting features are worthy of comment. First, no other regioisomers were detected besides **10**. Second, both ^1H and ^{13}C NMR spectra suggested that **10a** or **10b** was a single diastereomer, either a meso form or a *dl* mixture, which could not be differentiated at this stage.



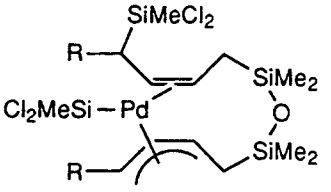
10a R = Ph
10b R = Me

These observed regio- and stereoselectivities are somewhat striking. As in the simple diene case, hydrosilylation of one of the diene moieties in **9** would occur regioselectively to give **11**. Further reaction of the remaining diene group may furnish the corresponding π-allylpalladium intermediate **12**. Coordination of the double bond of the allylsilane moiety to palladium, as shown in **12**, may take place stereoselectively so that a further reductive elim-

ination process would give **10** as a single diastereomer. Also, the regioselectivity of this addition reaction may be rationalized within this framework.



11



12

In summary, we have demonstrated a convenient synthesis of bis-1,4-silyl-2-butenes by regioselective hydrosilylation of silyl-substituted butadienes. The application of the hydrosilylation reactions and an investigation of further synthetic uses of the bis-silylated products are in progress.

EXPERIMENTAL

^{1}H NMR spectra were obtained on a Bruker AC300 (300 MHz) NMR spectrometer. Chemical shifts are reported in the δ scale using tetramethylsilane as the internal standard, and $CDCl_3$ was used as the solvent. ^{13}C NMR spectra were recorded on a Bruker AC300 spectrometer operating at 75 MHz using $CDCl_3$ (δ 77.0) as the internal standard. Infrared spectra were measured on a Bio-Rad FTS-40 infrared spectrophotometer. Mass spectral (MS) data were obtained on a Finigan TSQ-16C mass spectrometer or a JEOL JMS-HX110 mass spectrometer. Preparative HPLC was operated on a Waters 590 instrument using a silica gel column.

General Procedure

Into a 25 mL pressure tube was added a mixture of silyl-substituted diene (2.0 mmol), dichloromethylsilane (460 mg, 4.0 mmol), and $PdCl_2(PPh_3)_2$ (15 mg, 0.021 mmol). The tube was stirred at 80°C for 16 hours. After the contents had been allowed to cool to room temperature, ether (100 mL) was introduced and the mixture was transferred to a round-bottomed flask to which methanol (1.0 mL) and triethylamine (2.0 mL) were added. The mixture was heated under reflux for 1 hour. After being cooled to room temperature, the solution was filtered through florisil and washed with ether. The solvent was evaporated in vacuo, and the residue was subjected to chromatographic separation on silica gel using hexane/ethyl acetate (100/4) as eluent.

Hydrosilylation of **1a**

According to the general procedure, a mixture of **1a** (404 mg, 2.0 mmol), dichloromethylsilane (460 mg, 4.0 mmol), and $PdCl_2(PPh_3)_2$ (15 mg, 1.1 mmol) was transformed into **3a** (496 mg, 68%); IR (neat) ν 3024, 2966, 2838, 1723, 1493, 1452, 1392, 1251, 1091, 839, 773, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.06 (s, 9H), 0.06 (s, 3H), 1.40 (dd, J = 7.1, 13.8 Hz, 1H), 1.64 (dd, J = 9.4, 13.8 Hz, 1H), 3.31 (d, J = 11.0 Hz, 1H), 3.42 (s, 3H), 3.43 (s, 3H), 5.48 (m, 1H), 5.71 (t, J = 11.0 Hz, 1H), 7.03–7.13 (m, 1H), 7.15–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −7.1, −1.8, 18.4, 36.0, 50.7, 50.8, 124.7, 125.2, 125.3, 127.9, 128.2, 141.8; MS (rel intensity) 308 (M^+, 80), 293 (37), 277 (23), 204 (39), 188 (47), 105 (100); HRMS calcd for $C_{16}H_{28}O_2Si_2$: 308.1628; found: 308.1619.

Hydrosilylation of **2**

According to the general procedure, a mixture of **2** (202 mg, 1.0 mmol), dichloromethylsilane (230 mg, 2.0 mmol), and $PdCl_2(PPh_3)_2$ (8 mg, 1.1 mmol) was transformed into **4** (216 mg, 70%); IR (neat) ν 2954, 2906, 2838, 1599, 1492, 1248, 1188, 1093, 835, 772, 750, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 3H), 0.05 (s, 9H), 1.74 (s, 3H), 3.40 (s, 3H), 3.41 (s, 3H), 3.56 (d, J = 10.8 Hz, 1H), 6.11 (d, J = 10.8 Hz, 1H), 7.05–7.15 (m, 1H), 7.20–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −6.8, −2.1, 14.7, 38.5, 50.7, 50.7, 50.9, 124.9, 127.9, 128.4, 135.0, 136.7, 141.4; MS (rel intensity) 308 (M^+, 51), 293 (59), 277 (75), 204 (92), 172 (100), 105 (75); HRMS calcd for $C_{16}H_{28}O_2Si_2$: 308.1628; found: 308.1612.

Hydrosilylation of **5**

According to the general procedure, a mixture of **5** (93 mg, 0.5 mmol), dichloromethylsilane (115 mg, 1.0 mmol), and $PdCl_2(PPh_3)_2$ (4 mg, 1.1 mmol) was transformed into **6** (181 mg, 62%); IR (neat) ν 2956, 1599, 1493, 1258, 1189, 1091, 833, 771, 700; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 3H), 0.87 (s, 9H), 1.90 (dd, J = 6.1, 14.3 Hz, 1H), 2.11 (dd, J = 9.0, 14.3 Hz, 1H), 3.39 (d, J = 11.0 Hz, 1H), 3.43 (s, 3H), 3.53 (s, 3H), 5.20 (m, 1H), 5.87 (t, J = 1.0 Hz, 1H), 7.05–7.15 (m, 1H), 7.20–7.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −6.9, 29.3, 31.0, 36.5, 41.1, 50.7, 50.8, 124.8, 126.3, 127.9, 128.3, 128.9, 141.6; MS (rel intensity) 292 (M^+, 40), 277 (8), 261 (38), 186 (25), 105 (100); HRMS calcd for $C_{17}H_{28}O_2Si$: 292.1859; found: 292.1858.

Hydrosilylation of **1b**

According to the general procedure, a mixture of **1b** (202 mg, 1.0 mmol), dichloromethylsilane (230 mg, 2.0 mmol), and $PdCl_2(PPh_3)_2$ (8 mg, 1.1 mmol) was transformed into **3b** and **7b** (188 mg, 61%, **1b**/**7b** = 6.6:1) The mixture was separated by preparative HPLC. **1b**: IR (neat) ν 2956, 1480, 1257, 1089, 1026, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 3H), 0.29 (s, 6H), 0.95 (d, J = 10.6 Hz, 3H), 1.56 (dd, J = 7.8, 14.0 Hz, 1H), 1.84 (dd, J = 10.1, 14.0 Hz, 1H), 1.84–2.00 (m, 1H), 3.49 (s, 3H), 3.50 (s, 3H),

5.14 (t, J = 10.6 Hz, 1H), 5.32 (ddd, J = 7.8, 10.1, 10.6 Hz, 1H), 7.30–7.40 (m, 1H), 7.48–7.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −7.6, −3.4, −3.3, 14.6, 17.4, 20.5, 50.5, 50.6, 122.8, 127.7, 128.9, 129.7, 133.6, 140.0; MS m/z (rel intensity) 308 (M^+, 100), 294 (18), 239 (45), 142 (48), 105 (36); HRMS calcd for $C_{16}H_{28}O_2Si_2$: 308.1628; found: 308.1632. **7b**: IR (neat) ν 2961, 1427, 1255, 1089, 1026, 988 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.09 (s, 3H), 0.32 (s, 3H), 0.33 (s, 3H), 0.82 (t, J = 7.5 Hz, 3H), 1.80–1.95 (m, 3H), 3.38 (s, 3H), 3.39 (s, 3H), 5.18–5.31 (m, 1H), 7.25–7.32 (m, 3H), 7.45–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.3, −2.9, −2.6, 13.9, 19.6, 20.3, 50.2, 50.3, 62.1, 123.7, 127.4, 128.7, 130.0, 134.0, 139.1; MS m/z (rel intensity) 308 (M^+, 73), 293 (15), 188 (16), 142 (100), 135 (25); HRMS calcd for $C_{16}H_{28}O_2Si_2$: 308.1628; found: 308.1621.

Hydrosilylation of **1c**

According to the general procedure, a mixture of **1c** (336 mg, 2.0 mmol), dichloromethylsilane (460 mg, 4.0 mmol), and $PdCl_2(PPh_3)_2$ (15 mg, 1.1 mmol) was transformed into **3c** and **7c** (247 mg, 45%, **3c**/**7c** = 2:1) The mixture was separated by preparative HPLC. **3c**: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 9H), 0.09 (s, 3H), 0.91 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H), 1.80–1.95 (m, 2H), 3.48 (s, 3H), 3.50 (s, 3H), 5.21 (t, J = 11.0 Hz, 1H), 5.43 (ddd, J = 6.5, 9.9, 11.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −6.0, −1.6, 18.2, 21.4, 23.2, 28.6, 34.2, 50.5, 125.2, 125.5; MS m/z (rel intensity) 274 (8), 259 (4), 170 (9), 142 (17), 126 (22), 105 (100); HRMS calcd for $C_{13}H_{30}O_2Si_2$: 274.1784; found: 274.1771. **7c**: ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9H), 0.01 (s, 3H), 0.87 (d, J = 6.6 Hz, 6H), 1.45–1.65 (m, 2H), 1.78–1.90 (m, 2H), 3.46 (s, 3H), 3.48 (s, 3H), 5.25–5.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.1, −1.0, 15.6, 19.9, 22.5, 22.6, 28.6, 36.3, 50.2, 50.4, 125.4, 126.6; MS m/z (rel intensity) 274 (M^+, 41), 259 (35), 231 (28), 170 (100), 142 (65), 127 (99), 105 (87); HRMS calcd for $C_{13}H_{30}O_2Si_2$: 274.1784; found: 274.1781.

Hydrosilylation of **9a**

According to the general procedure, a mixture of **9a** (195 mg, 0.5 mmol), dichloromethylsilane (173 mg, 1.5 mmol), and $PdCl_2(PPh_3)_2$ (4 mg, 1.1 mmol) was transformed into **10a** (120 mg, 40%); IR (neat) ν 3023, 2957, 1598, 1492, 1451, 1392, 1256, 1093, 838, 801, 766, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ −0.04 (s, 12H), 0.06 (s, 6H), 1.43 (dd, J = 7.1, 14.0 Hz, 2H), 1.67 (dd, J = 9.9, 14.0 Hz, 2H), 3.29 (d, J = 10.9 Hz, 2H), 3.41 (s, 6H), 3.42 (s, 6H), 5.46 (m, 2H), 5.73.(t, J = 10.9 Hz, 2H), 7.00–7.15 (m, 2H), 7.15–7.30 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.04, 0.20, 20.1, 36.0, 50.7, 50.8, 124.7, 124.8, 125.9, 127.9, 128.3, 141.7; MS m/z (rel intensity) 602 (1), 571 (1), 482 (3), 465 (12), 369 (100), 247 (49), 195 (80), 179 (76), 105 (83); HRMS calcd for $C_{30}H_{50}O_5Si_4$: 602.2736; found: 602.2743.

Hydrosilylation of **9b**

According to the general procedure, a mixture of **9b** (269 mg, 1.0 mmol), dichloromethylsilane (460 mg, 4.0 mmol), and $PdCl_2(PPh_3)_2$ (15 mg, 2.1 mmol) was transformed into **10b** (281 mg, 59%); ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 12H), 0.02 (s, 6H), 1.04 (d, J = 7.2 Hz, 6H), 1.36 (dd, J = 6.6, 13.8 Hz, 2H), 1.60 (dd, J = 12.9, 13.8 Hz, 2H), 1.89–2.00 (m, 2H), 3.50 (s, 6H), 3.51 (s, 6H), 5.14 (t, J = 10.6 Hz, 2H), 5.26–5.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −7.6, −0.06, 14.6, 20.1, 20.4, 50.5, 50.6, 122.6, 122.5.

ACKNOWLEDGMENT

We are grateful to the National Science Council of the Republic of China for support.

REFERENCES

[1] For recent reviews, see T. Hiyama, T. Kusumoto: in B. M. Trost, I. Fleming (eds): *Comprehensive Organic Synthesis*, Pergamon, Elmsford, NY, vol. 8, p. 763 (1991); (b) I. Ojima, T. Kogure, *Rev. Silicon, Germanium, Tin Lead Compd.*, 5, 1981, 7; (c) I. Ojima: in S. Patai, Z. Rappoport (eds): *The Chemistry of Organic Silicon Compounds*, Wiley, New York, ch. 25 (1989).

[2] (a) I. Ojima, M. Kumagai, *J. Organomet. Chem., 157*, 1978, 359; (b) J. Tsuji, M. Hara, K. Ohno, *Tetrahedron 30*, 1974, 2143; (c) I. Ojima, M. Kumagai, Y. Miyazawa, *Tetrahedron Lett.*, 1977, 1385; (d) T. Hayashi, S. Hengrasmee, Y. Matsumoto, *Chem. Lett.*, 1990, 1377; (e) T. Hayashi, K. Kabeta, T. Yamamoto, K. Tamao, M. Kumada, *Tetrahedron Lett., 24*, 1983, 5661; (f) T. Hayashi, K. Kabeta, *Tetrahedron Lett., 26*, 1985, 3023; (g) T. Hayashi, Y. Matsumoto, I. Morikawa, Y. Ito, *Tetrahedron Asymmetry, 1*, 1990, 151.

[3] (a) B. Marciniec, J. Guli'nski, W. Urbaniak, *Synth. React. Inorg. Metal-Org. Chem., 12*, 1982, 139; (b) B. Marciniec, E. Mac'kowska, J. Guli'nski, W. Urbaniak, *Z. Anorg. Allg. Chem., 529*, 1985, 222.

[4] W.-W. Weng, T.-Y. Luh, *J. Chem. Soc., Perkin Trans*, 1, 1993, 2687.

[5] (a) Z.-J. Ni, P.-F. Yang, D. K. P. Ng, Y.-L. Tzeng, T.-Y. Luh, *J. Am. Chem. Soc., 112*, 1990, 9356; (b) K.-T. Wong, T.-Y. Luh, *J. Chem. Soc., Chem. Commun.*, 1992, 564; (c) N.-J. Ni, T.-Y. Luh, *Org. Syn., 70*, 1992, 240; (d) for a review, see T.-Y. Luh, K.-T. Wong, *Synthesis*, 1993, 349.

[6] (a) W.-W. Weng, T.-Y. Luh, *J. Org. Chem., 58*, 1993, 5574; (b) R.-M. Chen, W.-W. Weng, T.-Y. Luh, unpublished results.

[7] For example, J. M. Takacs, J. Zhu, S. Chandramouli, *J. Am. Chem. Soc., 114*, 1992, 773.