Serendipitous Synthesis of Oligo(6-vinylsilyl-5-silacyclohepta-1,3-diene)s

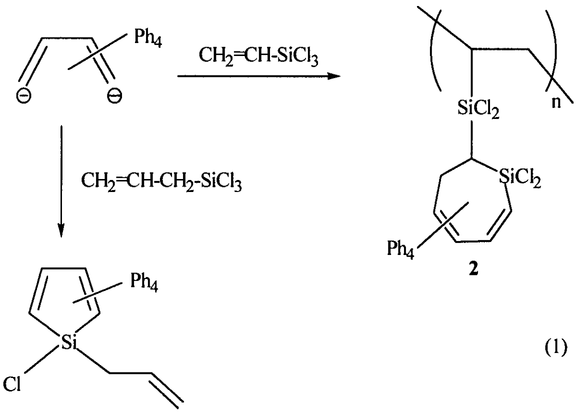
Hee-Gweon Woo,* Bo-Hye Kim, and Honglae Sohn*[†]
Department of Chemistry and Institute of Basic Science, Chonnam National University, Kwangju 500-757, Korea
[†]*Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA 92093, U. S. A.*

(Received February 16, 2000; CL-000164)

The reaction of 1,4-dilithiotetraphenylbutadiene with excess vinyltrichlorosilane produces both the 1,2,3,4-tetraphenyl-6-dichlorovinylsilyl-5-dichlorosilacyclohepta-1,3-diene (**1**) and its oligomer (**2**). The precipitation of **2** in methanol yields its dimethoxy derivative (**3**). The dimethyl (**4**) and diphenyl (**5**) derivatives of **2** are obtained in good yields by reacting 1,4-dilithiotetraphenylbutadiene with excess chlorodimethylvinylsilane and chlorodiphenylvinylsilane, respectively, without forming their respective monomer. In contrast, the reaction of l,4-dilithio-tetraphenylbutadiene with excess allyltrichlorosilane grves 1-allyl-l-chloro-2,3,4,5-tetraphenylsilole only.

Inorganic polymers such as polysilanes[2,3] and polysiloles[4-9] are of great interest because of their extraordinary physicochemical properties.[1] Polymerization of vinyl monomers with useful substituents may produce interesting functional polymers.[10,11] In order to develop a new type of optoelectronic vinyl polymers containing siloles as pendant groups, we decided to prepare 1-vinylsiloles. The radical polymerization of vinylsilanes is known to be difficult.[12] Since silicon stabilizes adjacent α-carbanions by σ^*-π hyperconjugation,[13] l-vinylsiloles are possible candidates for living anionic polymerization. In general, siloles can be prepared by the reaction of 1,4-dilithiobutadiene derivatives with suitable dihalosilanes.[14 15] George *et al*. reported the preparation of 1-methyl-1-vinyl-2,3,4,5-tetraphenylsilole by the stoichiometric reaction of 1,4-dilithiotetraphenylbutadiene with methylvinyldichlorosilane in THF.[16] During the course of our synthesis of 1-vinylsiloles under the similar reaction condition as used by West *et al.*,[15] we found the formation of unexpected 6-vinylsilyl-5-silacyclohepta-1,3-dienes and their oligomers.

In a typical experiment, a 500 mL Schlenk flask was charged with diphenylacetylene (17.8 g, 100 mmol), lithium metal (1.39 g, 200 mmol equiv; cut into *ca.* 5 mm pieces), and diethyl ether (130 mL) under an argon atmosphere. The mixture was allowed to stir at room temperature for 3 h, yielding a brown solution along with a yellow precipitate. The solution was then frozen with liquid nitrogen bath. To the frozen solution was added vinyltrichlorosilane (16.5 mL, 130 mmol) by a syringe in one portion, and the cooling bath was removed 5 min later. The resulting solution was allowed to warm up slowly to ambient temperature and to stir for 2 days to give a yellow solution. After removal of leftover lithium metal pieces, the volatiles were removed under vacuum. The residue was extracted with diethyl ether. The combined extracts were concentrated at reduced pressure and cooled to -20 °C to yield 1,2,3,4-tetraphenyl-6-dichlorovinylsilyl-5-dichlorosilacyclohepta-1,3-diene (**1**, 11.5 g, 38%) as yellowish green crystals. The volatiles were removed *in vacuo* from the remaining mother liquor to give the oligomer (**2**) of **1** (18.8 g, 62%) as a yellow powder.[17] The dimethoxy derivative (**3**) of **2** was obtained in 89% isolated yield by precipitating the solution of **2** in THF (10 mL) into anhydrous methanol (200 mL), filtering, and drying *in vacuo*.[17] In the similar manner, the dimethyl derivative (**4**) and diphenyl derivative (**5**) of **2** were prepared in 60% and 75% isolated yields, respectively, by the reaction of 1,4-dilithiotetraphenylbutadiene with chlorodimethylvinylsilane in diethyl ether at ambient temperature for 2 days and with chlorodiphenylvinylsilane in THF-refluxing temperature for 7 days, respectively, without appreciable formation of their respective vinyl monomers.[18] A11 the oligomers have the vinyl end group judged by ^{1}H NMR spectroscopy.[17,18] No further polymerization of the oligomers could be due to the steric bulkiness of 5-silacyclohepta-1,3-dienyl pendant group. No convincing evidence for the formation of the 1-vinylsiloles was found from the above reactions under the reaction conditions. Interestingly, the reaction of 1,4-dilithiotetraphenylbutadiene with excess vinylmethyldichlorosilane in diethyl ether at ambient temperature for 2 days produced a mixture of l-methyl-1-vinyl-2,3,4,5-tetraphenylsilole, l,2,3,4-tetraphenyl-6-chloromethylvinylsilyl-5-chloromethylsilacyclohepta-1,3-diene, and oligomer.[19] The possible mechanism for the formation of the oligomers may be envisioned as follows. The concomitant nucleophilic attack of tetraphenylbutadiene dianion only on the silicon site of a chlorovinylsilane molecule will give the expected silole. Instead, the serial nucleophilic attack of tetraphenylbutadiene dianion first on the silicon site and second on the vinyl site of a chlorovinylsilane molecule will produce 5-silacyclohepta-1,3-dienyl anion. The nucleophilic attack of resulting anion on the silicon site of another chlorovinylsilane molecule will produce the 6-vinylsilyl-5-silacyclohepta-1,3-diene. Another mechanism for the formation of 5-silacyclohepta-1,3-dienyl anion *via* Si=C intermediate may be considered based on the results of Jones and Auner.[20,21] The Si=C intermediate can be formed by the loss of LiCl from the intermediate, obtained by the nucleophilic attack of tetraphenylbutadiene dianion first on the vinyl site of a chlorovinylsilane molecule. However, the alternative mechanism is less likely to operate in the present reactions because we could not trap the Si=C intermediate with butadiene in the trapping experiment.[19] 6-Vinylsilyl-5-silacyclohepta-1,3-diene might then undergo oligomerization *via* a radical-anionic process. Lithium metal may here act as an initiator like aromaic radical anion such as sodium naphthalene.[22] Conventional initiator organic radicals such as AIBN (2,2'-azobisisobutyronitrile) and benzoyl peroxide were ineffective to the oligomerization of **1** (1 mol% initiator, 125 °C, 1 day). In contrast, the reaction of 1,4-dilithiotetraphenylbutadiene with allyltrichlorosilane in diethyl ether at ambient temperature for 1 day produced l-chloro-1-allyl-2,3,4,5-tetraphenylsilole without appreciable oligomer formation (eq 1).[19]



(1)

This research was supported by the Non-directed Research Fund, Korea Research Foundation (1998-001-D00436). The authors greatly acknowledge the kind advice and useful discussions provided by Professor Robert West at University of Wisconsin-Madison.

References and Notes

1 J. E. Marks, H. R. Allcock, and R. West, "Inorganic polymers", Prentice Hall, New Jersey (1992).

2 R. D. Miller and J. Michl, *Chem, Rev.*, **89**, 1359 (1989) and references cited theirin.

3 R. West, *J. Organomet. Chem.*, **300**, 327 (1986).

4 K. Tamao and S. Yamaguchi, *Pure Appl. Chem.*, **68**, 139 (1996).

5 S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans.*, **1998**, 3693.

6 S. Yamaguchi and K. Tamao, *Bull. Chem. Soc. Jpn.*, **69**, 2327 (1996).

7 S. Yamaguchi, R.-Z. Jin, and K. Tamao, *J. Am. Chem. Soc.*, **121**, 2937 (1999).

8 H. Sohn, R. R. Huddleston, D. R. Powell, and R. West, *J. Am. Chem. Soc.*, **121**, 2935 (1999).

9 T. Sanji, T. Sakai, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **120**, 4552 (1998).

10 K. Kimura, M. Sumida, and M. Yokoyama, *J. Chem. Soc., Chem. Commun.*, **1997**, 1417.

11 I. Imae, K. Nawa, Y. Ohsedo, N. Noma, and Y. Shirota, *Macromolecules*, **30**, 380 (1997).

12 D. Seyferth, M. Tasi, and H.-G. Woo, *Chem. Mater.*, **7**, 236 (1995).

13 We are grateful to a reviewer for providing us with this reference: A. R. Bassindale, S. J. Glynn, and P. G. Taylor, In "The Chemistry of Organic Silicon Compounds" ed by Z. Rappoport and Y. Apeloig, John Wiley & Sons, New York, Volume 2, Chapter 7 (1999).

14 W. R. Weyenberg, L. H. Toporcer, and A. E. Bey, *J. Org. Chem.*, **30**, 4096 (1965).

15 U. Bankwitz, H. Sohn, D. R. Powell, and R. West, *J. Organomet. Chem.*, **499**, C7 (1995).

16 R. Balasubramanian and M. V. George, *Tetrahedron*, **29**, 2395 (1973).

17 **1**: mp 178–180 °C. MS(EI), *m/z* (relative intensity): 608 (100) [M^+], 481 (5) [M^+ - Si(CH=CH_2)Cl_2]. High-resolution mass: Found: 608.0313. Calcd for $C_{32}H_{26}Si_2Cl_4$: 608.0303. IR (pellet, KBr, cm^{-1}): 3057 w, 3053 m, 3010 m, 2950 m, 1598 m, 1491 m, 1440 m, 1250 m, 1100 w, 840 s, 702 s. ^{1}H NMR (δ , $CDCl_3$, 300 MHz): 6.70–7.55 (m, 20 H, Ph), 6.05–6.35 (m, 3 H, vinyl), 3.77 (dd, J = 14.0, 12.5 Hz, 1 H, $CH_{2,\ \mathrm{diastereotopic}}$), 3.28 (dd, J = 15.0, 3.7 Hz, 1 H, $CH_{2',\ \mathrm{diastereotopic}}$), 2.17 (dd, J = 14.0, 3.7 Hz, 1 H, SiCHSi). **2**: IR (pellet, KBr, cm^{-1}): 3056 w, 3051 m, 3010 m, 2951 m, 1598 m, 1491 m, 1441 m, 1253 m, 1102 w, 841 s, 705 s. ^{1}H NMR (δ , $CDCl_3$, 300 MHz): 6.40–7.65 (m, 20 H, Ph), 6.00–6.35 (m, vinyl end group), 3.3–3.8 (m, 2H, CH_2), 2.2–2.4 (m, 1 H, SiCHSi), 1.2–1.4 (m, backbone CH_2), 0.85–0.95 (m, backbone CHSi). M_n = 850 (cryoscopy in benzene). **3**: IR (pellet, KBr, cm^{-1}): 3055 w, 3052 m, 3022 m, 2938 m, 2940 m, 2838 w, 1598 m, 1491 m, 1440 m, 1260 m, 1086 s, l030 s, 804 s, 750 s, 697 s. ^{1}H NMR (δ , $CDCl_3$, 300 MHz): 6.38–7.50 (m, 20 H, Ph), 6.00–6.31 (m, vinyl end group), 3.49 (s, OCH_3), 3.3–3.8 (m, 2 H, CH_2), 2.2–2.4 (m, 1 H, SiCHSi), 1.2–1.4 (m, backbone CH_2), 0.80–0.90 (m, backbone CHSi). GPC: M_w = 4050, M_n = 1910.

18 **4**: IR (pellet, KBr, cm^{-1}): 3055 w, 3052 m, 3022 m, 2950 m, 2940 m, 2838 w, 1598 m, 1491 m, 1440 m, 1250 m, 1030 s, 840 s, 825 s, 800 s, 702 s. ^{1}H NMR (δ , $CDCl_3$, 300 MHz): 6.50–7.50 (m, 20 H, Ph), 3.2–3.5 (m, 2H, CH_2), 2.2–2.4 (m, 1 H, SiCHSi), l.2–1.4 (m, backbone CH_2), 0.80–0.90 (m, backbone CHSi), -0.5–0.5 (m, 12 H, $SiCH_3$). GPC: M_w = 4450, M_n = 2340. **5**: IR (pellet, KBr, cm^{-1}): 3054 m, 3016 m, 2932 w, 2921 w, 1598 m, 1491 m, 1430 m, 1424 m, 1260 m, 1112 m, 1085 s, 1031 s, 696 s. ^{1}H NMR (δ , $CDCl_3$, 300 MHz): 6.45–7.55 (m, 20 H, Ph), 6.00–6.33 (m, vinyl end group), 3.3–3.8 (m, 2 H, CH_2), 2.2–2.4 (m, 1 H, SiCHSi), 1.2–1.4 (m, backbone CH_2), 0.80–0.90 (m, backbone CHSi). GPC: M_w = 3650, M_n = 2100.

19 H.-G. Woo, B.-H. Kim, and H. Sohn, unpublished results.

20 We thank a reviewer for suggesting this alternative mechanism: P. R. Jones and T. F. O. Lim, *J. Am. Chem. Soc.*, **99**, 2013 (1977).

21 N. Auner, *J. Prakt. Chem.*, **337**, 79 (1995).

22 G. Odian, "Principles of Polymerization", 3rd ed, John Wiley & Sons, New York, p 400-403 (1991).