

THE PALLADIUM COMPLEX-CATALYZED REACTIONS OF HEXAORGANODISILANES WITH DIENES¹⁾

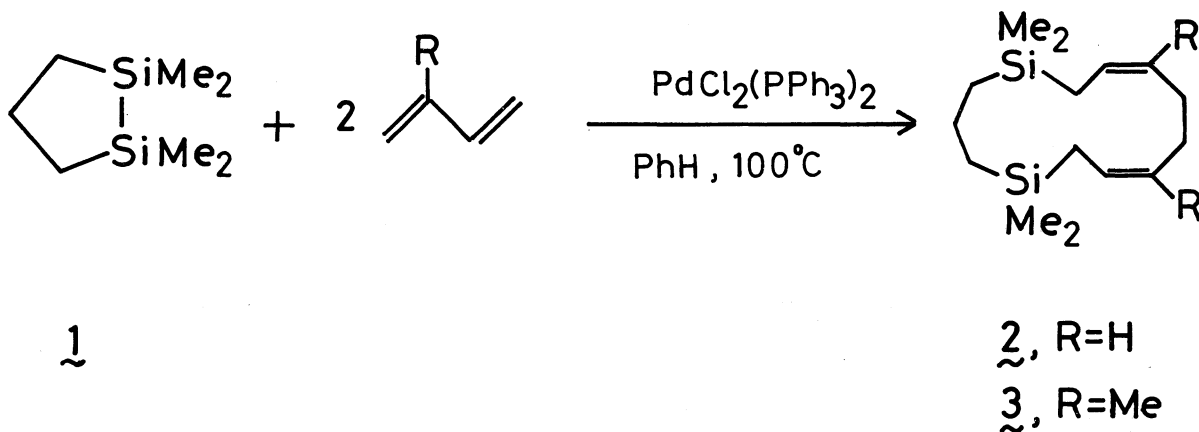
Hideki SAKURAI, Yoshiyasu KAMIYAMA, and Yasuhiro NAKADAIRA

Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980

Organodisilanes undergo a novel 1:2 cycloaddition reaction with butadiene or isoprene in the presence of a palladium complex. For example, the reaction of 1,1,2,2-tetramethyl-1,2-disilacyclopentane with isoprene gave 1,1,5,5,8,11-hexamethyl-1,5-disilacyclotrideca-7,11-diene in 76% yield.

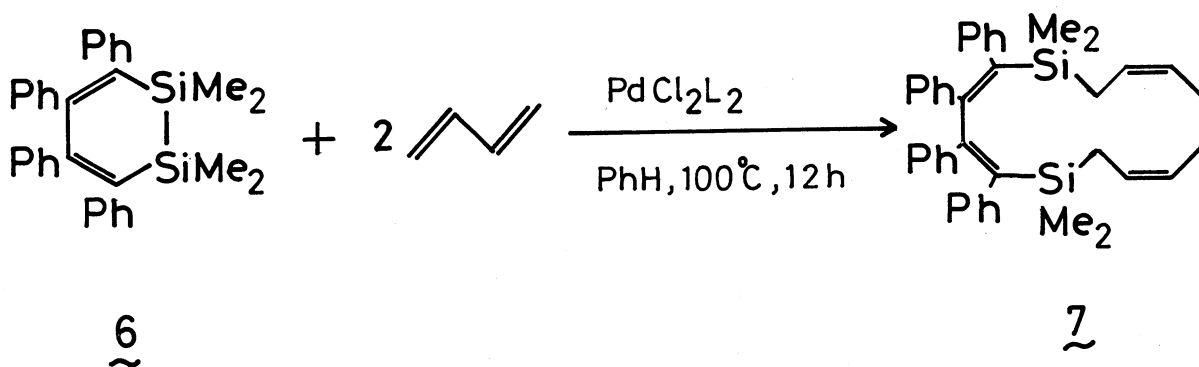
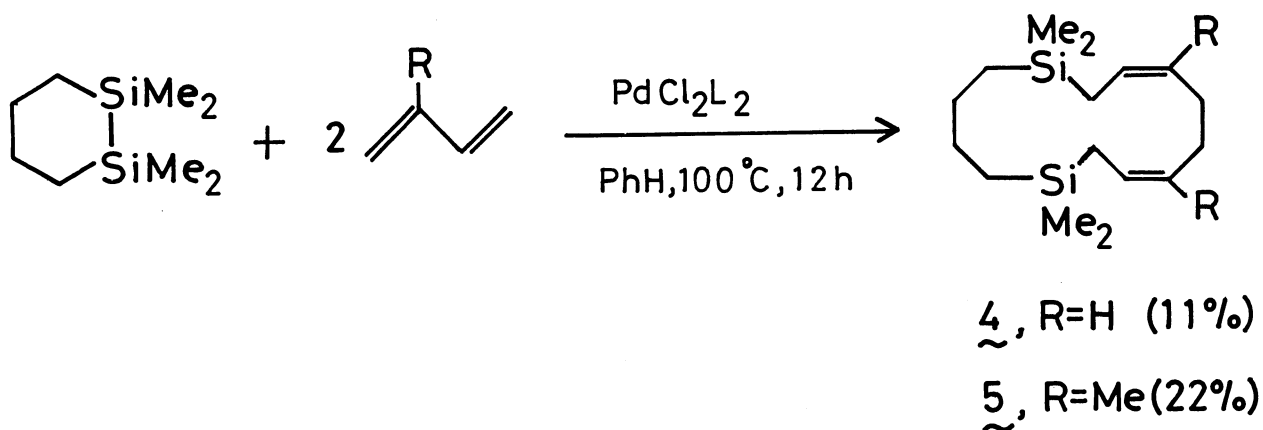
In a previous paper, we reported novel $[\sigma+\pi]$ type reaction of hexaorganodisilanes with acetylenes catalyzed by palladium complexes.²⁾ We report here an entirely new catalyzed addition of organodisilanes to dienes leading to various interesting compounds.

When a solution of 1,1,2,2-tetramethyl-1,2-disilacyclopentane (1, 1.02mmol),^{3,4)} excess 1,3-butadiene (2 ml), and bis(triphenylphosphine)palladium dichloride (0.01 mmol) in benzene (10 ml) was heated at 100°C for 13h under an argon atmosphere in a small high-pressure vessel, a clear yellow solution was obtained. After evaporation of volatile materials, the residue was subjected to silica gel tlc, and 1,1,5,5-tetramethyl-1,5-disilacyclotrideca-7,11-diene (2) was obtained as an oil in 83% yield.^{5,6)} A similar reaction of 1 with isoprene gave 1,1,5,5,8,11-hexamethyl-1,5-disilacyclotrideca-7,11-diene (3) in 76% yield.⁷⁾

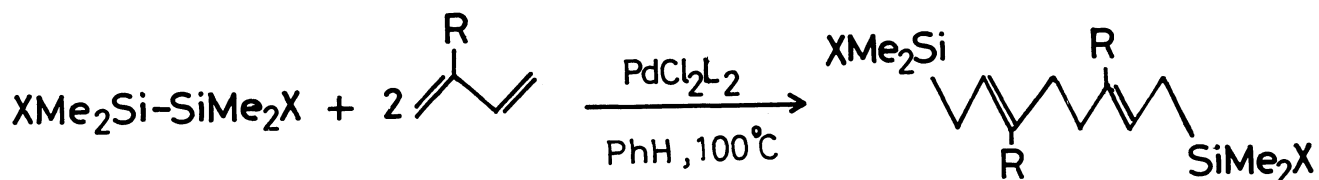


The nmr data and especially a large (12.5%) nuclear Overhauser effect (NOE) between methyl and hydrogen groups attached to the double bond indicate the assigned structure for 3 unequivocally. Interestingly, only the head-to-head dimeric structure for the isoprene part was obtained with cis stereochemistry.

Six-membered carbodisilanes undergo similar reactions with butadiene and isoprene to give 4 and 5, respectively.^{8,9)} 1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-disila-3,5-cyclohexadiene (6)¹⁰⁾ also gave 7 by the reaction with butadiene in 86% yield.¹¹⁾



Unstrained organodisilanes such as hexamethyldisilane and 1,2-dichlorotetramethyldisilane similarly undergo the reaction but slowly. In these cases it is noteworthy that isoprene gave similar head-to-head dimeric products but with trans olefinic junctions.¹²⁻¹⁴⁾



8, X=Me

9, X=Cl

10, X=Me; R=H (14 %)

11, X=Me; R=Me (7 %)

12, X=Cl; R=Me (5 %)

Various Pd(II) complexes such as $\text{PdCl}_2(\text{PPh}_3)_2$, $\text{PdCl}_2(\text{PET}_3)_2$, and $\text{PdCl}_2(\text{PhCN})_2$ are effective in the reaction, but Pd(O) complexes such as $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}(\text{PPh}_3)_2(\text{olefin})$ and Pd-charcoal are less effective. In general, $\text{PdCl}_2(\text{PPh}_3)_2$ and $\text{PdCl}_2(\text{PhCN})_2$ are the most effective catalyst, although the activity of the catalysts seems to depend on a subtle shifting of both the donor property of disilanes⁴⁾ and the structure of dienes.

One-step formation of large rings and the head-to-head dimeric structure of the isoprene part in the products are quite unique in the reaction. Such products may be useful as intermediates in synthesis because of the known reactivity of allylsilane linkages.

Acknowledgment

We thank Toshiba Silicones Co., Ltd., for gifts of chlorosilanes.

References and Notes

- 1) Chemistry of Organosilicon compounds 82.
- 2) H.Sakurai, Y.Kamiyama, and Y.Nakadaira, J.Amer.Chem.Soc., 97, 931 (1975).
- 3) M.Kumada, K.Tamao, T.Takubo, and M.Ishikawa, J.Organometal.Chem., 9, 43 (1967).
- 4) For the donor properties and reactivities of this compound, see H.Sakurai and Y.Kamiyama, J.Amer.Chem.Soc., 96, 6192 (1974).
- 5) All new compounds gave correct elemental analyses. Yield described in this paper are those after isolation with tlc on silica gel and are not necessarily optimized.
- 6) Compound 2: an oil; n_D^{23} 1.4920; M^+ 266(26.6), m/e 97(100); ir(cm^{-1}) (neat) 2930, 1250, 835; λ_{max} (n-hexane) 212.0(10,300); NMR δ (CCl_4) 0.08(12H, s, Si-CH₃), 0.67(4H, t, J=7.5Hz, Si-CH₂-CH₂-), 1.47(2H, m, Si-CH₂-CH₂), 1.50(4H, d, J=7Hz, Si-CH₂-CH=), 2.18(4H, t, J=3Hz, =CH-CH₂-), 5.39(4H, m, =CH-).
- 7) Compound 3: an oil; n_D^{23} 1.5000; M^+ 294(14), m/e 111(100); ir(cm^{-1}) (neat) 2930, 1250, 830; λ_{max} (n-hexane) 213.0(10,000); NMR δ (CCl_4) 0.09(12H, s, Si-CH₃), 0.62(4H, t, J=8Hz, Si-CH₂-), 1.40(2H, m, SiCH₂-CH₂-), 1.45(4H, d, J=8Hz, Si-CH₂-CH=), 1.60(6H, s, =CH-CH₃), 2.26(4H, s, =CH-CH₂-CH₂-), 5.20(2H, t, J=8Hz, =CH-); NOE 12.5% between peaks at δ 1.60 and 5.20.
- 8) Compound 4: an oil; n_D^{20} 1.4930; M^+ 280(2.7) m/e 112(100); ir(cm^{-1}) (neat) 2930, 1250, 835; λ_{max} (n-hexane) 213.0(8,900); NMR δ (CCl_4) 0.07(12H, s, Si-CH₃), 0.60(4H, m, Si-CH₂-CH₂-), 1.50(4H, m, Si-CH₂-CH₂-), 1.50(4H, d, J=7Hz, Si-CH₂-CH=), 2.16(4H, broad s, =CH-CH₂-CH₂-), 5.50(4H, broad s, =CH-).
- 9) Compound 5: an oil; n_D^{20} 1.4960; M^+ 308(9.5), m/e 125(100); ir(cm^{-1}) (neat) 2900, 1250, 825; λ_{max} (n-hexane) 213.5(8,500); NMR δ (CCl_4) -0.05(12H, s, Si-CH₃), 0.47(4H, t, J=8Hz, Si-CH₂-CH₂) 1.30(8H, m, SiCH₂-CH₂-, Si-CH₂-CH=), 1.50(6H, s, =CH-CH₃), 2.14(4H, broad s, =CH-CH₂-CH₂), 5.60(2H, t, J=8Hz, =CH-).
- 10) Y.Nakadaira and H.Sakurai, J.Organometal.Chem., 47, 61 (1973).
- 11) Compound 7: mp 171.0-171.5°C; M^+ 580(9.4) m/e 413(100); ir(cm^{-1}) (KBr) 1250, 960, 835, 690; λ_{max} (n-hexane) <210.0, 238.0(26,000); NMR δ (CCl_4) -0.47(6H, s, Si-CH₃), 0.50(6H, s, Si-CH₃), 1.40(4H, m, Si-CH₂-CH=), 2.20(4H, m, -CH₂-CH₂-CH=), 5.40(4H, m, =CH-), 7.20(20H, m, Ph).
- 12) Compound 10: an oil; n_D^{23} 1.4564; M^+ 254(1.6) m/e 73(100); ir(cm^{-1}) (neat) 2930, 1250, 850; λ_{max} (n-hexane) 211.7(9,500); NMR δ (CCl_4) 0.10(18H, s, Si-CH₃), 1.46(4H, d, J=7Hz, Si-CH₂-CH=), 2.10(4H, t, J=3Hz, CH₂-CH₂-CH=), 5.33(4H, m, =CH-).
- 13) Compound 11: an oil; n_D^{23} 1.4630; M^+ 282(3.2), m/e 73(100); ir(cm^{-1}) (neat) 2950, 1250, 850; λ_{max} (n-hexane) 212.0(12,000); NMR δ (CCl_4) 0.05(18H, s, Si-CH₃), 1.46(4H, d, J=8Hz, Si-CH₂-CH=), 1.65(6H, s, =CH-CH₃), 2.16(4H, s, -CH₂-CH₂-CH=), 5.22(2H, t, J=8Hz, -CH=); NOE 12.0% between peaks at δ 2.16 and 5.22.
- 14) Compound 12 was isolated and characterized as 11 after methylation with methylmagnesium bromide.

(Received June 17, 1975)