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PHOTOCHEMISTRY OF 1-PHENYL-4-(PENTAMETHYLDISILANYL)BUTA-1,3-DIYNE: $[PdCl_2(PPh_3)_2]$-CATALYZED REACTION

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Abstract — $PdCl_2(PPh_3)_2$-catalyzed photolysis of 1-phenyl-4-(pentamethyldisilanyl)buta-1,3-diyne (**1**) in dry benzene gives 1,4-disilacyclohexa-2,5-diene type dimerization products(**3-6**) via silacyclopropene. The silacyclopropene is formed from the singlet excited state of 1 and this silacyclopropene reacts with $(PPh_3)_2Pd^0$ to form palladasilacyclobutene. In this reaction, the silylene-palladium complex is generated and reacts with **1** to give another silacyclopropene. $PdCl_2(PPh_3)_2$-catalyzed photolysis of **1** with other alkynes supports the involvement of this silylene complex.

INTRODUCTION

Considerable attention has been devoted to investigations of transition-metal-catalyzed reaction of silacyclopropenes and it has been known that the nickel (0) - and palladium (0) - catalyzed reactions of silacyclopropenes produce reactive intermediates such as metalasilacyclobutenes arising from insertion of metals into Si-C bond in a silacyclopropene ring.[1-6] In the absence of acetylenes or even in the presence of an unreactive acetylene such as diphenylacetylene, palladium-catalyzed photolysis of (phenylethynyl) pentamethyldisilane gives 1,4-disilacyclohexa-2,5-diene type dimerization, while with acetylene dicarboxylic ester the acetylene is incorporated in the product.[4] We have recently reported the photophysical and photochemical properties of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne.[7,8] The photochemical generation of silacyclopropene from $PdCl_2(PPh_3)_2$ catalyzed photoreaction of 1-phenyl-4-(pentamethyldisilanyl)buta-1,3-diyne is investigated in this report.

MATERIALS AND METHODS

Instruments. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer with chemical shifts being referenced against the signal of the solvent $CDCl_3$. Mass spectra were determined at 70 eV with a Hewlett-Packard 5985A GC/MS by the electron impact (EI) method. FT-IR spectra were recorded on a Bomem MB-100 spectrometer in KBr pellets. High-performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatograph (Mildford, MA) equipped with a Model 6000A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm, and Model U6K universal injector. Lichrosorb Si-60 column was used for preparative analyses.

Materials. Benzene was freshly distilled from sodium prior to use. Bis(triphenylphosphine)palladium dichloride and phenylacetylene were purchased from Aldrich and used without further purification. 1-Phenyl-4-(pentamethyldisilanyl) buta-1,3-diyne (**1**),[7] 1-phenyl penta-1,3-diyne,[9] and 1-phenyl-4-(trimethylsilyl)buta-1, 3 -diyne (**2**)[9] were prepared by reported methods.

Photolysis of 1-phenyl-4-(pentamethyldisilanyl)buta-1, 3-diyne in the presence of $PdCl_2(PPh_3)_2$. Deaerated solution of 1-phenyl-4-(pentamethyldisilanyl)buta-1,3-diyne (**1**, 50 m*M*) and $PdCl_2(PPh_3)_2$ (4 m*M*) in dry benzene was irradiated at 300 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamp at 35 °C. After irradiation for 12 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts (**2-6**) were isolated in 14%, 17%, 12%, 3%, 5% yield, respectively, by silica gel column chromatography using n-hexane/diethyl ether (80/1, v/v) as an eluent and followed by normal phase HPLC using the following conditions: eluents; (**3**): n-hexane, (**4-6**): n-hexane/diethyl ether (600/1, v/v). 1,4-disilacyclohexa-2,5-diene **3**: mp 175-176 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.42 (m, 4 H), 7.34 (m, 6 H), 0.41 (s, 12 H), 0.34 (s, 18 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 169.8, 154.9, 131.0, 128.4, 128.2, 124.1, 101.8, 92.6, 0.9, -0.4; IR (KBr) 2940.6, 1594.2, 1490.1, 1246.2, 838.9 cm^{-1}; MS, m/e 512 (M^+). 1,4-disilacyclohexa-2,5-diene **4**: mp107-108 °C; ^1H NMR($CDCl_3$, 200 MHz) δ 7.40-7.09 (m, 10 H), 0.43 (s, 6 H), 0.34 (s, 9 H), 0.26 (s, 6 H), 0.15 (s, 6 H), -0.01 (s, 9 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.8, 164.6, 152.8, 143.9, 138.2, 131.0, 128.4, 128.2, 127.8, 127.2, 126.2, 123.9,

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107.2, 103.1, 102.2, 92.3, 0.9, -0.7, -2.0, -2.7, -3.2; IR (KBr) 2955.7, 2114.4, 1490.8, 1247.0, 837.4 cm^{-1}; MS, m/e 570 (M^+). 1,4-disilacyclohexa-2,5-diene **5**: mp 120-121 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.37-7.14 (m, 10 H), 0.38 (s, 6 H), 0.33 (s, 9 H), 0.26 (s, 6 H), -0.01(s, 9 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.7, 165.2, 152.8, 143.8, 137.9, 131.0, 128.4, 128.3, 127.8, 127.2, 126.3, 123.9, 105.3, 104.0, 102.2, 92.3, 0.9, -0.2, -0.7, -1.9; IR (KBr) 2956.7, 2115.2, 1491.5, 1246.7, 840.2 cm^{-1}; MS, m/e 512 (M^+). 1,4-disilacyclohexa-2,5-diene **6**: mp 60-61 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.40-7.01 (m, 10 H), 0.42 (s, 6 H), 0.31 (s, 9 H), 0.16 (s, 6 H), -0.01 (s, 6 H), -0.04 (s, 9 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.9, 168.0, 152.4, 144.4, 135.4, 131.2, 128.4, 128.3, 127.8, 127.2, 126.0, 124.0, 106.7, 102.7, 102.6, 92.3, 1.1, -0.5, -2.5, -2.7, -3.2; IR (KBr) 2940.2, 2113.8, 1742.7, 1491.9, 1246.3, 836.4 cm^{-1}; MS, m/e 570 (M^+).

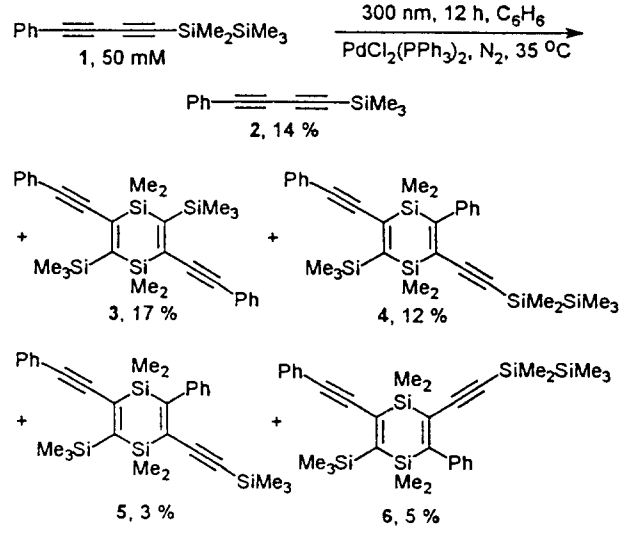
Photolysis of 1-phenyl-4-(pentamethyldisilanyl)buta-1,3-diyne in the presence of $PdCl_2(PPh_3)_2$ with other alkynes. Photolysis of deaerated solution of 1-phenyl-4-(pentamethyldisilanyl)buta-1,3-diyne (**1**, 50 m*M*), alkynes (1-phenylpenta-1,3-diyne, 1-phenyl-4-(trimethylsilyl)buta-1,3-diyne, phenylacetylene, 50 m*M*) and $PdCl_2(PPh_3)_2$ (4 m*M*) in dry benzene gives adducts (**3-8**) in 23%, 10%, 17%, 10%, 5% and 33% yield, respectively. 1,4-disilacyclohexa-2,5-diene **7**: mp 122-123 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.35-7.07 (m, 10 H), 0.43 (s, 6 H), 0.31 (s, 9 H), 0.17 (s, 6 H), -0.03 (s, 9 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.9, 168.7, 152.4, 144.3, 135.1, 131.1, 128.4, 128.3, 127.7, 127.2, 126.0, 124.0, 104.9, 103.5, 102.7, 101.5, 1.1, -0.2, -0.5, -2.8; IR (KBr) 2956.9, 2119.5, 1490.7, 1246.7, 840.3 cm^{-1}; MS, m/e 512 (M^+).

Desilylation of 1,4-disilacyclohexa-2,5-dienes (3-6) in basic condition. The solution of 1,4-disilacyclohexa-2,5-dienes (0.05 mmol) and NaOH (0.1 mmol) in MeOH (10 mL) was stirred for 4 h at 60℃. The mixture was extracted with diethyl ether and dried over $MgSO_4$. Desilylation products were separated in 60-70% yield by column chromatography using n-hexane/diethyl ether (70/1, v/v) as an eluent. Desilylation was confirmed by the appearance of proton signal of terminal acetylene with disappearance of silyl group in ^1H NMR.

RESULTS AND DISCUSSION

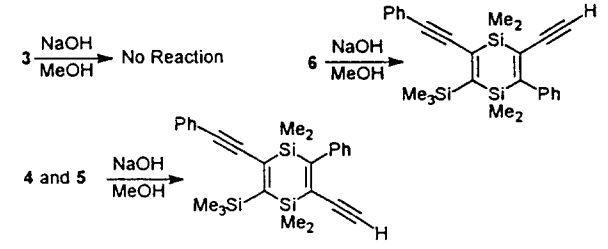
$PdCl_2(PPh_3)_2$-catalyzed photolysis of 1-phenyl-4 (pentamethyldisilanyl)buta-1,3-diyne (**1**) in dry benzene gives 1,4-disilacyclohexa-2,5-diene type dimerization products (**3-6**) and 1-pheny l-4 -(trimethylsilyl) buta-1,3-diyne (**2**) (Scheme 1).

Products are purified by HPLC and the structure of these products is determined by various physical methods such as ^1H and ^{13}C NMR spectroscopy. The 1,4-disilacyclohexa-2,5-diene unit of these products is confirmed by comparison with reported results.[5] The reaction site on diyne unit and regiochemistry of these products are determined by the addition rule of ^{13}C chemical shift.[10-12] The mass spectra of **3** and **5** show the molecular ion peaks (M^+) at 512 indicating



Scheme 1

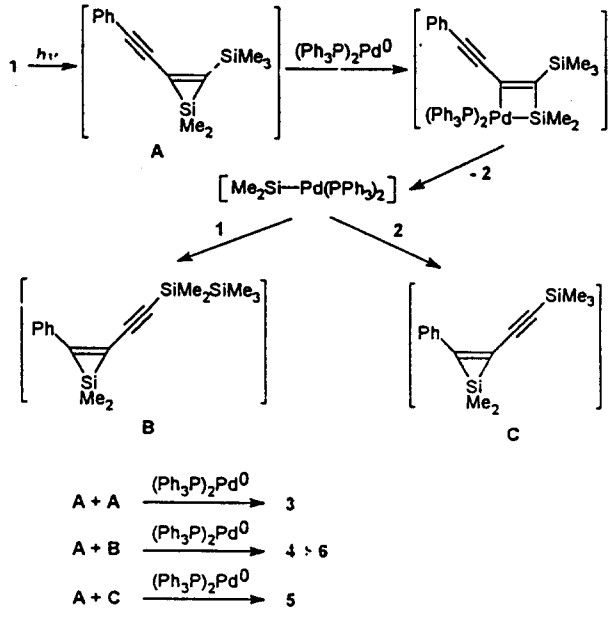
that these products are dimerization products. For **4** and **6**, the molecular ion peaks (M^+) indicate that these adducts have an additional silylene group ($SiMe_2$). In a basic condition, the 1,4-disilacyclohexa-2,5-diene structure of adducts is stable and desilylation reaction proceeds to give terminal alkynes (Scheme 2). Desilylation was confirmed by the appearance of the proton signal of terminal acetylene at 3.13 - 3.16 ppm with disappearance of silyl group in ^1H NMR.



Scheme 2

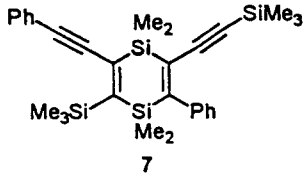
Seyferth *et al.* have suggested that the silylene formed from silacyclopropene reacts with an alkyne to give another silacyclopropene in the presence of $PdCl_2(PPh_3)_2$ and $(PPh_3)_2Pd^0$ is the active catalyst.[13] We propose the following plausible reaction mechanism (Scheme 3), *i.e.*, the silacyclopropene **A** is formed from the singlet excited state of **1**[7] and this silacyclopropene **A** reacts with $(PPh_3)_2Pd^0$ to form palladasilacyclobutene. The silylene complex formed from palladasilacyclobutene reacts with **1** and **2** to give silacyclopropene **B** and **C**. In this reaction, the

reactive site is the C1-C2 triple bond of **1** and we could not detect any adduct formed via the silacyclopropene arising from the addition of silylene complex to the C3-C4-triple bond of **1**. From these silacyclopropenes **A**, **B** and **C**, dimerization products (**3-6**) are obtained.



Scheme 3

The photolysis with other alkynes is investigated to elucidate the involvement of silylene in this reaction. $PdCl_2(PPh_3)_2$-catalyzed photolysis of **1** with 1-phenyl-4-(trimethylsilyl)buta-1,3-diyne (**2**) yields **5** in high yield (17%) and additional adduct **7** with 5% yield via silacyclopropene **C**, suggesting the reaction of silylene complex with **2**.[13]



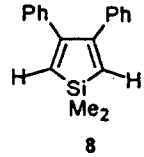


Figure 1

Photolysis of **1** with phenylacetylene in the presence of $PdCl_2(PPh_3)_2$ gives adduct **8** having silacyclopentadiene moiety in 36% yield with **2**. Silacyclopentadienes are known to be formed from the thermal or catalyzed reactions of silacyclopropenes with terminal alkynes and spectral data of **8** are consistent with reported results.[14-15] These results support the involvement of silylene complex in this photolysis.

CONCLUSION

$PdCl_2(PPh_3)_2$-catalyzed photolysis of 1-phenyl-4-(pentamethyldisilanyl)buta-1,3-diyne (**1**) gives 1,4-disilacyclohexa-2,5-dienes via silacyclopropene. The silacyclopropene is formed from the singlet excited state of **1**. In this reaction, the silylene-palladium complex is generated and reacts with **1** to give another silacyclopropene. The results of $PdCl_2(PPh_3)_2$-catalyzed photolysis of **1** with other alkynes support the involvement of this silylene complex.

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