Palladium-Catalyzed Reductive Homocoupling Reaction of 3-Silylpropargyl Carbonates. New Entry into Allene-Yne Compounds

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In the presence of palladium(0) catalyst, propargylic electrophiles undergo carbon–carbon bond formation with organometallic compounds predominantly at the allenyl position.[1,2] This is because the propargylic electrophiles employed in these reactions tend to form an allenylpalladium intermediate by oxidative addition. In contrast, there is no report on catalytic reactions of propargyl electrophiles proceeding via a propargyl palladium intermediate exclusively. Only propargyl electrophiles with a bulky group, e.g. trimethylsilyl or *tert*-butyl group, on the 3-position and two hydrogens on the propargyl position generate propargylpalladium complexes exclusively.[3] We wish to report here the palladium-catalyzed reductive homocoupling reaction of 3-silylpropargyl carbonates to give the propargyl framework.

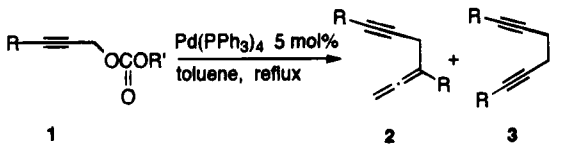
In the presence of palladium(0) catalyst, the reaction of 3-(trimethylsilyl)propargyl ethyl carbonate (**1a**) in toluene at reflux temperature gave a mixture of allene-yne product **2a** and diyne product **3a**. Typical results with analogous substrates are listed in Table 1. The isopropyl carbonate **1c** also gave the same products in comparable yields, while the methyl and phenyl carbonates (**1b**, **1d**) gave the much lower yields. The carbonates with a more bulky silyl group (**1e**, **1f**, **1g**) afforded homocoupling products in higher yield and selectivity. A cross-coupling reaction employing both **1a** and **1b** was also attempted, but no selectivity was observed.[4] The poor yield with the *tert*-butyl analog **1h** suggests that substitution of the silyl group at the 3-position is necessary to obtain homocoupling products.

Both **2** and **3** are two electron reduction products compared with the starting material. A plausible mechanism is shown in Scheme 1. Oxidative addition of **1** to the palladium(0) species gives a propargyl intermediate A. Carbopalladation of **1** with A may give intermediate B, and the subsequent β-elimination leads to formation of allene-yne product **2** and palladium dicarbonate C. The presence of the silyl group at the carbon–carbon triple bond might facilitate the carbopalladation of **1**. Decarboxylation from the intermediate A, followed by β-elimination of Pd–OEt bond gives propargylpalladium hydride, and subsequent reductive elimination leads to the formation of the byproduct, 1-silylpropyne.[5]

An alternative pathway is also shown in Scheme 2. Intermediate A undergoes disproportionation to give C, D, and E. The intermediates D and E might isomerize to each other. Fast reductive elimination from D (sp^2-sp^3) and a slow one from E (sp^3-sp^3) lead to formation of the major product **2** and the minor one **3**, respectively.[6] The diallenylpalladium intermediate F might not be generated, because of large steric repulsion.

In the both pathways, the intermediate C is generated. The intermediate C expels carbon dioxide to give diethoxypalladium in which the subsequent β-elimination occurs to give CH_3CHO and hydrido(ethoxy)palladium. The latter may undergo reductive elimination to lead to the formation of CH_3CH_2OH and regeneration of palladium(0) species (Scheme 3).[7] Actually, acetaldehyde and ethanol were observed in the catalytic reaction of

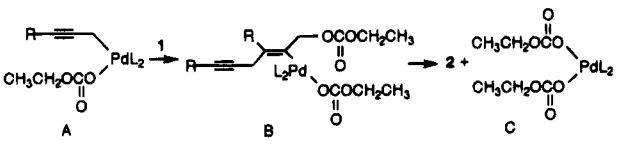
Table 1.



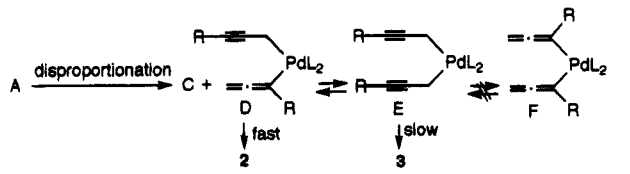
carbonates	R	R′	time, h	yield, %[a]	2/3
1a	$SiMe_3$	Et	1	48[b] (27)	**2a/3a** = 79/21
1b	$SiMe_3$	Me	2	6[b]	**2a/3a** = 80/20
1c	$SiMe_3$	^{i}Pr	1.5	32[b]	**2a/3a** = 81/19
1d	$SiMe_3$	Ph	0.5	4[c]	**2a/3a** = 75/25
1e	$SiMe_2Bu^t$	Et	1	75[b] (52)	**2e/3e** = 91/9
1f	Si^iBu_3	Et	5	73 (71)[d]	**2f/3f** = 93/7
1g	Si^iPr_3	Et	24	85 (70)[e,f]	**2g/3g** = 95/5
1h	Bu^t	Et	3	7[g]	**2h/3h** = 71/29

[a] GC yield. Isolated yields are in parentheses. [b] Large amounts of 1-silylpropyne and allene were observed on GCMS. [c] A 49% of Me_3SiOPh was observed. [d] Considerable amounts of 1-silylpropyne were isolated (17%). [e] Considerable amounts of 1-silylpropyne were isolated (15%). [f] A 10 mol% of $Pd(PPh_3)_4$ was used. [g] Large amounts of 1-*tert*-butylpropyne and allene were observed on GCMS.

Scheme 1



Scheme 2



(1) (a) Luong, T. J.; Listrumelle, G. *Tetrahedron Lett.* **1980**, *21*, 5019. (b) Ruitenberg, H. Kleijn, H, Elsevier, C. J.; Vermeer, P. *Tetrahedron Lett.* **1981**, *22*, 1451. (c) Elsevier, C. J.; Stehouwer, P. M.; Westmijze, H.; Vermeer, P. *J. Org. Chem.* **1983**, *48*, 1103. (d) Keinan, E.; Bosch, E. *J. Org. Chem.* **1986**, *51*, 4006 and references cited therein.

(2) Use of 1,3-dicarbonyl compounds as carbon nucleophiles leads to formation of dihydrofuran compounds or 2,3-dialkylated propene derivatives. Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225.

(3) Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics* **1986**, *5*, 716.

(4) The reaction of **1a** with **1e** gave a mixture of **2a**, **3a**, **2e**, **3e** and two cross-coupling products (**2a** + **3a**/**2e** + **3e**/crosscoupling products = 1/1/1).

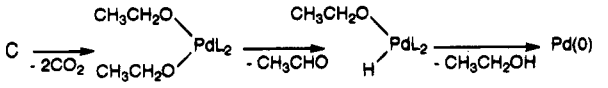
(5) See for a related reaction. Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1984**, *25*, 2791.

(6) A sp^2 carbon (allenyl carbon) is preferred to a sp^3 carbon (propargyl carbon) in the reductive elimination step. Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989**, *8*, 180. Brown, J. M.; Cooley, N. A. *Organometallics* **1990**, *9*, 353. Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431. Komiya, S.; Ozaki, S.; Shibue, A.; *J. Chem. Soc., Chem. Commun.* **1986**, 1555.

(7) Dimethoxy nickel(II) complexes also undergo self-reduction to nickel(0) concomitant with generation of HCHO and CH_3OH. Sacco, A.; Mastrorilli, P. *J. Chem. Soc. Dalton Trans.* **1994**, 2761.

0022-3263/95/1960-4650$09.00/0

Scheme 3



1e in toluene-d_8.[8] Thus, in this reaction, carbonate moieties act as a reductant for a palladium(II) species.

In summary, we achieved an unusual reductive homocoupling reaction of 3-silylpropargyl carbonates, through a propargylpalladium intermediate.

Experimental Section

General Procedures. ^{1}H NMR (270 MHz) and ^{13}C NMR (68 MHz) spectra were recorded in $CDCl_3$ with a reference to residual $CHCl_3$ (δ 7.26). GLC analyses (25 m × 0.2 mm CBP1-M25-0.25 capillary column) were performed with a flame ionization detector and He carrier gas. The compound **3a** is known,[9] and **3e−g** could be observed in very small amount by only GLC after purification. The structure of **3a** and **3e−g** was determined by ^{1}H NMR resonance of propargyl proton in reaction mixture.

Typical Procedure for Preparation of 3-(Triisopropylsilyl)propargyl Ethyl Carbonate (1g). To a solution of 7.3 g (52 mmol) of tetrahydro-2-(2-propynyloxy)-2*H*-pyran in 200 mL of dry THF was added 32.5 mL of n-BuLi (1.6 M/hexane) at −78 °C, and the mixture was stirred for 20 min, warmed to −20 °C, and cooled to −78 °C again. A solution of 10.0 g (51.9 mmol) of triisopropylsilyl chloride in 150 mL of dry THF was added dropwise to the mixture. The reaction mixture was stirred for 20 min at −78 °C and then for 5 h at 0 °C, washed with saturated NH_4Cl aqueous solution, and extracted with ether. The organic layer was dried over $MgSO_4$ and concentrated. The concentrate was distilled (130−133 °C/1 mmHg) to give 12.2 g (79%) of tetrahydro-2-[[3-(triisopropylsilyl)-2-propynyl]oxy]-2*H*-pyran. A solution of 11.3 g (38 mmol) of tetrahydro-2-[[3-(triisopropylsilyl)-2-propynyl]oxy]-2*H*-pyran in 190 mL of EtOH was heated at 80 °C for 9 h, and the reaction was followed by GLC. The reaction mixture was concentrated, and the concentrate was filtered through a short column (silica gel, 200 mesh) with EtOAc. Then the filtrate was evaporated, and the residue was distilled (94−96 °C/1 mmHg) to give 6.4 g (80%) of 3-(triisopropylsilyl)-2-propyn-1-ol.[10] To a solution of 6.4 g (30 mmol) of 3-(triisopropylsilyl)-2-propyn-1-ol and 2.5 mL of dry pyridine in 150 mL of dry ether was added dropwise 3 mL of ethyl chloroformate at 0 °C, and the reaction was followed by GLC. After alcohol was consumed, the mixture was washed with water and brine. The organic layer was dried over $MgSO_4$ and evaporated. The residue was distilled (85−87 °C/1 mmHg) to give 6.7 g (77%) of **1g**.

3-(Trimethylsilyl)propargyl ethyl carbonate (1a): bp 89−94 °C/8 mmHg; IR (direct) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9H), 1.31 (t, J = 7.1 Hz, 3H), 4.22 (q, J = 7.1 Hz, 2H), 4.72 (s, 2H); ^{13}C NMR ($CDCl_3$) δ −0.39, 14.2, 55.9, 64.5, 92.8, 98.2, 154.5. Anal. Calcd for $C_9H_{16}O_3Si$: C, 53.97; H, 8.05. Found: C, 53.93; H, 8.15.

3-(Trimethylsilyl)propargyl methyl carbonate (1b): bp 86−87 °C/8 mmHg; IR (direct) 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9H), 3.81 (s, 3H), 4.73 (s, 2H); ^{13}C NMR ($CDCl_3$) δ −0.41, 55.08, 56.09, 92.95, 98.12, 155.12. Anal. Calcd for $C_8H_{14}O_3Si$: C, 51.58; H, 7.58. Found: C, 51.59; H, 7.74.

3-(Trimethylsilyl)propargyl isopropyl carbonate (1c): bp 84−86 °C/2.5 mmHg; IR (direct) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9H), 1.31 (d, J = 6.4 Hz, 6H) 4.72 (s, 2H), 4.90 (hep, J = 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.35, 21.73, 55.76, 72.61, 92.78, 98.34, 153.98. Anal. Calcd for $C_{10}H_{18}O_3Si$: C, 56.04; H, 8.46. Found: C, 55.86; H, 8.55.

3-(Trimethylsilyl)propargyl phenyl carbonate (1d): bp 100−105 °C/1 mmHg; IR (direct) 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H), 4.84 (s, 2H), 7.18 (m, 2H), 7.25 (m, 1H), 7.38 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.40, 56.74, 93.62, 97.62, 120.91, 126.16, 129.48, 151.02, 153.07. Anal. Calcd for $C_{13}H_{16}O_3Si$: C, 62.87; H, 6.49. Found: C, 63.16 H, 6.64.

3-(*tert*-Butyldimethylsilyl)propargyl ethyl carbonate (1e): bp 97−102 °C/2 mmHg; IR (direct) 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 6H), 0.93 (s, 9H), 1.31 (t, J = 7.1 Hz, 3H), 4.22 (q, J = 7.1 Hz, 2H), 4.73 (s, 2H); ^{13}C NMR ($CDCl_3$) δ −4.91, 14.22, 16.39, 25.94, 55.91, 64.42, 91.17, 98.89, 154.47. Anal. Calcd for $C_{12}H_{22}O_3Si$: C, 59.46; H, 9.15. Found: C, 59.29; H, 9.32.

Tetrahydro-2-[[3-(triisobutylsilyl)-2-propynyl]oxy]-2*H*-pyran: bp 122−134 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.63 (d, J = 6.8 Hz, 6H), 0.97 (d, J = 6.4 Hz, 18 H), 1.45−1.78 (m, 6H), 1.86 (m, 3H), 3.52 (m, 1H), 3.85 (m, 1H), 4.24 (d, J = 16.1 Hz, 1H), 4.31 (d, J = 16.1 Hz, 1H), 4.87 (t, J = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.19, 24.89, 24.96, 25.39, 26.23, 30.29, 54.59, 62.64, 90.18, 96.30, 103.16. Anal. Calcd for $C_{20}H_{38}O_2Si$: C, 70.94; H, 11.31. Found: C, 70.88; H, 11.44.

3-(Triisobutylsilyl)propargyl ethyl carbonate (1f): bp 122−130 °C/1 mmHg; IR (direct) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.64 (d, J = 6.8 Hz, 6H), 0.97 (d, J = 6.8 Hz, 18H), 1.32 (t, J = 7.1 Hz, 3H), 1.85 (m, 3H), 4.22 (q, J = 7.1 Hz, 2H), 4.72 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.22, 24.70, 24.93, 26.20, 56.00, 64.36, 92.32, 99.89, 154.51. Anal. Calcd for $C_{18}H_{34}O_3Si$: C, 66.21; H, 10.49. Found: C, 66.38 H, 10.59.

Tetrahydro-2-[[3-(triisopropylsilyl)-2-propynyl]oxy]-2*H*-pyran: bp 130−133 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ 1.06 (m, 21H), 1.45−1.90 (m, 6H), 3.52 (m, 1H), 3.84 (m, 1H), 4.27 (d, J = 16.2 Hz, 1H), 4.34 (d, J = 16.1 Hz, 1H), 4.91 (t, J = 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.13, 18.54, 19.21, 25.39, 30.32, 54.66, 62.15, 87.04, 96.28, 103.36. Anal. Calcd for $C_{17}H_{32}O_2Si$: C, 68.86; H, 10.88. Found: C, 68.71; H, 11.06.

3-(Triisopropylsilyl)propargyl ethyl carbonate (1g): bp 85−87 °C/1 mmHg; IR (direct) 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07 (brs, 21H), 1.32 (t, J = 7.3 Hz, 3H), 4.23 (q, J = 7.3 Hz, 2H), 4.76 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 11.04, 14.22, 18.47, 56.00, 64.36, 89.21, 100.17, 154.50. Anal. Calcd for $C_{15}H_{28}O_3Si$: C, 63.33; H, 9.92. Found: C, 63.58 H, 10.12.

3-*tert*-Butylpropargyl ethyl carbonate (1h): bp 104−106 °C/20 mmHg; IR (direct) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9H), 1.32 (t, J = 7.2 Hz, 3H), 4.22 (q, J = 7.2 Hz, 2H), 4.72 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.22, 27.41, 30.66, 56.06, 64.24, 71.89, 96.35, 154.60. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.47; H, 8.88.

Typical Procedure for Homocoupling Reaction of 1g. To a solution of 114 mg (0.1 mmol) of $Pd(PPh_3)_4$ in 5 mL of dry toluene was added 569 mg (2 mmol) of **1g** under an atmosphere of argon, and the mixture was stirred at reflux temperature. The reaction was followed by GLC. The reaction mixture was separated by column (silica gel, 100−200 mesh, hexane) to give a mixture of **2g** and **3g** (70%, **2g**/**3g** = 95/5) and 1-(triisopropylsilyl)propyne (15%).

3,6-Bis(trimethylsilyl)-1,2-hexadien-5-yne (2a). A 601 mg (3 mmol) of **1a** was used: yield 27% (90 mg, R_f = 0.55); ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H), 0.16 (s, 9H), 2.98 (t, J = 3.1 Hz, 2H), 4.46 (t, J = 3.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −0.15, 0.07, 21.37, 70.04, 86.23, 91.08, 104.70, 209.33. Anal. Calcd for $C_{12}H_{22}Si_2$: C, 64.78; H, 9.97. Found: C, 64.93; H, 10.25.

3,6-Bis(*tert*-butyldimethylsilyl)-1,2-hexadien-5-yne (2e): yield 52% (160 mg, R_f = 0.70); ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 12H), 0.92 (s, 9H), 0.94 (s, 9H), 2.96 (t, J = 3.2 Hz, 2H), 4.49 (t, J = 3.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −6.06, −4.38, 16.46, 18.17, 21.97, 26.11, 26.65, 70.75, 84.36, 89.13, 105.08, 210.87. Anal. Calcd for $C_{18}H_{34}Si_2$: C, 70.51; H, 11.18. Found: C, 69.02; H, 11.10.

3,6-Bis(triisobutylsilyl)-1,2-hexadien-5-yne (2f): yield 71% (337 mg, R_f = 0.79); ^{1}H NMR ($CDCl_3$) δ 0.61 (d, J = 6.9 Hz, 6H), 0.68 (d, J = 6.9 Hz, 6H), 0.95 (d, J = 6.6 Hz, 18H), 0.97 (d, J = 6.6 Hz, 18H), 1.81 (m, 3H), 1.88 (m, 3H), 2.94 (t, J = 3.1 Hz, 2H), 4.44 (t, J = 3.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.41, 23.41, 24.78, 24.99, 25.29, 26.35, 26.36, 70.68, 84.81, 90.02, 105.93, 210.48. Anal. Calcd for $C_{18}H_{34}Si_2$: C, 75.87; H, 12.31. Found: C, 73.70; H, 12.13.

3,6-Bis(triisopropylsilyl)-1,2-hexadien-5-yne (2g): yield 70% (275 mg, R_f = 0.63); ^{1}H NMR ($CDCl_3$) δ 1.1 (m, 42H), 2.97 (t, J = 3.2 Hz, 2H), 4.49 (t, J = 3.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.29, 11.37, 18.54, 18.61, 21.68, 70.85, 81.65, 87.07, 106.01,

(8) In a sealed NMR tube, the reaction resulted in low yield and low selectivity.

(9) Auderset, P. C.; Dreiding, A. S.; Gesing, E. R. F. *Synth. Commun.* **1983**, *13*, 881.

(10) Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 4407.

211.50. Anal. Calcd for $C_{24}H_{46}Si_2$: C, 73.76; H, 11.86. Found: C, 73.49; H, 11.76.

1-(Triisobutylsilyl)propyne: bp 100 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.60 (d, J = 6.8 Hz, 6H), 0.98 (d, J = 6.8 Hz, 18H), 1.85 (m, 3H), 1.88 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 4.91, 25.00, 25.2, 26.2, 82.8, 104.2. Anal. Calcd for $C_{15}H_{30}Si$: C, 75.54; H, 12.68. Found: C, 75.74; H, 12.85.

1-(Triisopropylsilyl)propyne: bp 70 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ 1.06 (m, 21H), 1.92 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 4.76, 11.34, 18.60, 79.42, 104.27. Anal. Calcd for $C_{12}H_{24}Si$: C, 73.38; H, 12.32. Found: C, 73.16; H, 12.48.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **2e** and **2f** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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