A New Transformation of Silanols. Palladium-Catalyzed Cross-Coupling with Organic Halides in the Presence of Silver(I) Oxide

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Supporting Information

General. All of the reactions were carried out under an argon atmosphere. Hexane was distilled from sodium/benzophenone and dimethylformamide (DMF) from calcium hydride. Tetrahydrofuran was distilled from sodium/benzophenone prior to use. Hexamethylcyclotrisiloxane (D_3) was kindly donated by Shin-Etsu Chemical Co. Ltd and used as such. Ag_2O was purchased from Wako Pure Chemical Inc. and used without further purification.

Preparation of arylsilanols. To a solution of aryl bromide (12 mmol) in Et_2O was slowly added BuLi (7.6 mL, 12 mmol, 1.59 M in hexane) at -78 °C. The mixture was stirred at -78 °C for 1 h. To the reaction mixture was added D_3 (0.89 g, 4.0 mmol), and the resulting mixture was stirred at room temperature for 13 h. The resulting solution was quenched with H_2O (10 mL) and the organic layer was separated. The aqueous layer was extracted with diethyl ether (15 mL × 3). The combined extracts were washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by bulb-to-bulb distillation under reduced pressure to give the corresponding arylsilanols.

Hydroxy(dimethyl)(4-methoxyphenyl)silane. 63% (colorless oil) Bp 130 °C / 0.5 mmHg. ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6 H), 1.84 (br, 1 H), 3.82 (s, 3 H), 6.93 (dt, J = 2.1, 8.7 Hz, 2 H), 7.53 (dt, J = 2.1, 8.7 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ 0.0, 55.0, 113.5, 130.2, 134.6, 160.6. IR (neat) 3300, 2957, 2838, 1595, 1505, 1464, 1399, 1281, 1183, 1032, 866 cm^{-1}. Anal. Calcd for $C_9H_{14}OSi$: C, 59.30; H, 7.74. Found: C, 59.16; H, 7.69.

Hydroxy(dimethyl)(4-trifluoromethylphenyl)-silane. 83% (colorless oil) Bp 115 °C / 0.7 mmHg. ^{1}H NMR ($CDCl_3$) δ 0.43 (s, 6 H), 1.94 (br, 1 H), 7.62 (d, J = 8.3 Hz, 2 H), 7.71 (d, J = 8.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ -0.1, 124.13 (q, J, = 272.3 Hz), 124.37 (q, J = 4.0 Hz), 131.47 (q, J = 32.2 Hz), 133.32, 143.82. IR (neat) 3300, 2963, 1393, 1327, 1258, 1167, 1130, 1061, 1020, 959, 870 cm^{-1}. Anal. Calcd for $C_9H_{11}F_3OSi$: C, 49.08; H, 5.03. Found: C, 49.13; H, 5.26.

Hydroxy(dimethyl)(2-methylphenyl)silane. 81% (colorless oil) Bp 105 °C / 0.4 mmHg. ^{1}H NMR ($CDCl_3$) δ 0.46 (s, 6 H), 2.52 (s, 3 H), 7.17-7.31 (m, 4 H), 7.55 (d, J = 7.5 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 0.9, 22.7, 124.8, 129.7, 129.7, 134.1, 137.3, 143.1. IR (neat) 3300, 3006, 1592, 1408, 1379, 1285, 1202, 1059, 864 cm^{-1}. MS (EI): 166 (20), 151 (100), 133 (16), 123 (14), 91 (21), 75 (11). HRMS (EI, *m/e*) calcd for $C_9H_{14}OSi$ (M^+) 166.0813, found 166.0813.

(*E*)-Hydroxy(dimethyl)silyl-1-octene. A solution of 1-chloro(dimethyl)silyl-1-octene[1] (3.0 g, 14.7 mmol) in diethyl ether (10 mL) was slowly added to a solution of NaOH (0.68 g, 17 mmol) in diethyl ether/H_2O (20 mL/10 mL) at 0 ˚C over 1 h. After stirring at 0 ˚C for 10 min, the mixture was extracted with diethyl ether (15 mL x 3). Organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was subjected to bulb-to-bulb distillation (170 ˚C, 1.0 mmHg) to give 2.10 g of the product (78%). This compound contains a small amount of regio or stereoisomer (not identified). ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 6 H), 0.89 (t, *J* = 6.6 Hz, 3 H), 1.27-1.43 (m, 8 H), 1.55 (br, 1 H), 2.08-2.17 (m, 2H), 5.64 (dt, *J* = 1.8, 18.6 Hz), 6.19 (dt, *J* = 6.3, 18.6 Hz). ^{13}C NMR ($CDCl_3$) δ 0.1, 14.2, 22.7, 28.6, 29.0, 31.8, 36.7, 128.3, 149.5. IR (neat) 3278, 2959, 2928, 1619, 1379, 1252, 1067, 990, 866 cm^{-1}. MS (EI): 186 (2), 171 (23), 149 (12), 116 (12), 75 (100). HRMS (EI, *m*/*e*) calcd for $C_{10}H_{22}OSi$ (M^+) 186.1440, found 186.1440.

General procedure for the coupling reaction of a silanol with an aryl halide. To a solution of $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) and Ag_2O (46.3 mg, 0.2 mmol) in THF (2 mL) were added sequentially aryl halide (0.2 mmol) and silanol (0.24 mmol) at room temperature. The mixture was stirred at 60 °C for 36 h. The reaction mixture was diluted with Et_2O (10 mL), and then was passed briefly through an alumina pad. Further, the pad was washed with Et_2O (10 mL X 2). The elute was washed with 1 M aqueous HCl (5 mL), saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL). The combined organics were dried over anhydrous $MgSO_4$, filtered and then concentrated with a rotary evaporator. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexanes or toluene/hexanes as eluents) to afford the corresponding product.

4’-Methoxybiphenyl-4-yl trifluoromethane-sulfonate. ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 6 H), 6.99 (d, *J* = 9.0 Hz, 2 H), 7.31 (d, *J* = 8.7 Hz, 2 H), 7.49 (d, *J* = 8.7 Hz), 7.60 (d, *J* = 9.0 Hz). ^{13}C NMR ($CDCl_3$) d 55.4, 114.4, 118.8 (q, *J* = 320.9 Hz), 121.5, 128.2, 128.3, 131.7, 141.3, 148.5, 159.7. IR (KBr) 1609, 1495, 1427, 1297, 1215, 1142, 1035, 893 cm^{-1}. Anal. Calcd for $C_{14}H_{11}F_3O_4$: C, 50.60; H, 3.34. Found: C, 50.48; H, 3.28.

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