Palladium-Catalyzed Synthesis of 1-Alkylphosphonium Salts from 1-Alkenes

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Supplementary Materials

¹H-NMR, ¹³C-NMR, and ³¹P-NMR spectra were obtained on a Varian Mercury (400 MHz). Chemical shift values are given in ppm relative to internal Me₄Si. IR spectra were recorded on a JASCO FT/IR-410. MS spectra were taken with a JEOL JMS-DX303 or a JEOL JMS-AX500 or 700. Elemental analyses were conducted with a Yanaco CHN corder MT-5. Melting Points were determined with a Yanaco micro melting point apparatus without correction.

Ethyltriphenylphosphonium Bis(trifluoromethanesulfonyl)imide (Table 2, entry 1). In a two-necked flask equipped with a reflux condenser were placed triphenylphosphine (5 mmol, 1.31 g), Pd₂dba₃•CHCl₃ (0.1 mol%, 5.2 mg), and bis(trifluoromethanesulfonyl)imide (5.5 mmol, 1.55 g) in chlorobenzene (6 mL) under an argon atmosphere. After substituting the argon balloon to ethylene, the solution was heated at 65 °C for 5 h, and then the solution was concentrated. The residue was washed with ether/hexane, and recrystallized from ethanol giving the title compound (2.79 g, 98%) as colorless solid. Mp 97.0–97.5 °C (EtOH). ¹H-NMR (400 MHz, CDCl₃) δ 1.37 (3H, dt, J = 19.6, 7.2 Hz), 3.21–3.28 (2H, m), 7.67 (6H, dd, J = 11.6, 7.2 Hz), 7.71 (6H, dt, J = 7.2, 3.6 Hz), 7.83 (3H, t, J = 7.2 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 6.4 (d, J = 4.5 Hz), 16.2 (d, J = 52.3 Hz), 117.5 (d, J = 85.7 Hz), 119.8 (q, J = 319.8 Hz), 130.5 (d, J = 12.1 Hz), 133.2 (d, J = 9.8 Hz), 135.2 (d, J = 3.0 Hz). ³¹P-NMR (162 MHz, CDCl₃) δ 24.9. IR (KBr) 3062, 2966, 2938, 1441, 1348, 1200, 1060, 735 cm⁻¹. MS (FAB) m/z 291 (M⁺-Tf₂N). Anal. Calcd. for C₂₂H₂₀F₆NO₄PS₂: C, 46.24% H, 3.53% N, 2.45% S, 11.22%. Found: C, 46.08% H, 3.55% N, 2.45% S, 11.27%.

1-Propyltriphenylphosphonium Bis(trifluoromethanesulfonyl)imide (Table 2, entry 2). Colorless solid. Mp 76.5–77.5 °C (EtOH). ¹H-NMR (400 MHz, CDCl₃) δ 1.17 (3H, t, J = 7.2 Hz), 1.69 (2H, septet, J = 7.2 Hz), 3.11–3.18 (2H, m), 7.67 (6H, dd, J = 13.2, 7.2 Hz), 7.71 (6H, dt, J = 7.2, 3.6 Hz), 7.82 (3H, dt, J = 7.2, 1.6 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 15.0 (d, J = 17.4 Hz), 16.4 (d, J = 4.5 Hz), 24.1 (d, J = 50.7 Hz), 117.8 (d, J = 86.4 Hz), 119.9 (q, J = 319.7 Hz), 130.6 (d, J = 12.9 Hz), 133.2 (d, J = 9.8 Hz), 135.3 (d, J = 3.0 Hz). ³¹P-NMR (162 MHz, CDCl₃) δ 22.7. IR (KBr) 3064, 2931, 1349, 1196, 1057, 739 cm⁻¹. MS (FAB) m/z 305 (M⁺-Tf₂N). Anal. Calcd. for C₂₃H₂₂F₆NO₄PS₂: C, 47.18% H, 3.79% N, 2.39% S, 10.95%. Found: C, 47.09% H, 3.67% N, 2.39% S, 11.06%.

1-Butyltriphenylphosphonium Bis(trifluoromethanesulfonyl)imide (Table 2, entry 3). 20 equivalents of 1-butene were reacted. Colorless solid. Mp 83.5–84.0 °C (EtOH). ¹H-NMR (400

MHz, CDCl₃) δ 0.93 (3H, t, J = 7.6 Hz), 1.57-1.63 (4H, m), 3.14-3.23 (2H, m), 7.66 (6H, dd, J = 12.4, 8.0 Hz), 7.72 (6H, dt, J = 8.0, 3.6 Hz), 7.83 (3H, dt, J = 8.0, 2.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 13.4, 22.2 (d, J = 51.5 Hz), 23.6 (d, J = 15.9 Hz), 24.4 (d, J = 4.6 Hz), 117.9 (d, J = 85.6 Hz), 119.9 (q, J = 319.0 Hz), 130.6 (d, J = 12.1 Hz), 133.3 (d, J = 9.9 Hz), 135.3 (d, J = 3.0 Hz). ³¹P-NMR (162 MHz, CDCl₃) δ 23.1. IR (KBr) 3064, 2969, 2937, 1441, 1354, 1201, 1049 cm⁻¹. MS (FAB) m/z 319 (M^+ -Tf₂N). Anal. Calcd. for C₂₄H₂₄F₆NO₄PS₂: C, 48.08% H, 4.03% N, 2.34% S, 10.70%. Found: C, 47.92% H, 3.78% N, 2.35% S, 10.73%.

1-Pentyltriphenylphosphonium Bis(trifluoromethanesulfonyl)imide (Table 2, entry 4). 20 equivalents of 1-pentene were reacted. Colorless solid. Mp 96.5–97.0 °C (EtOH : Et₂O = 2 : 1). ¹H-NMR (400 MHz, CDCl₃) δ 0.84 (3H, t, J = 7.2 Hz), 1.31 (2H, sextet, J = 7.6 Hz), 1.52 (2H, quintet, J = 7.2 Hz), 1.62 (2H, sextet, J = 7.2 Hz), 3.12-3.19 (2H, m), 7.66 (6H, dd, J = 12.4, 7.2 Hz), 7.72 (6H, dt, J = 7.2, 3.6 Hz), 7.83 (3H, dt, J = 7.2, 1.6 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 13.5, 21.9, 22.1 (d, J = 4.6 Hz), 22.3 (d, J = 50.8 Hz), 32.3 (d, J = 15.1 Hz), 117.9 (d, J = 85.7 Hz), 119.9 (q, J = 318.2 Hz), 130.6 (d, J = 12.9 Hz), 133.3 (d, J = 9.8 Hz), 135.3 (d, J = 3.0 Hz). ³¹P-NMR (162 MHz, CDCl₃) δ 23.1. IR (KBr) 3064, 2969, 1238, 1440, 1354, 1201, 1048, 788 cm⁻¹. MS (FAB) m/z 333 (M^+ -Tf₂N). Anal. Calcd. for C₂₅H₂₆F₆NO₄PS₂: C, 48.94% H, 4.27% N, 2.28% S, 10.45%. Found: C, 48.85% H, 4.21% N, 2.27% S, 10.45%.

1-Hexyltriphenylphosphonium Bis(trifluoromethanesulfonyl)imide (Table 2, entry 5). 20 equivalents of 1-hexene were reacted. Colorless solid. Mp 90.0–90.5 °C (EtOH : Et₂O = 2 : 1). ¹H-NMR (400 MHz, CDCl₃) δ 0.84 (3H, t, J = 7.2 Hz), 1.24-1.28 (4H, m), 1.52-1.58 (2H, m), 1.59-1.64 (2H, m), 3.12-3.19 (2H, m), 7.66 (6H, dd, J = 12.4, 7.2 Hz), 7.72 (6H, dt, J = 7.2, 3.6 Hz), 7.83 (3H, dt, J = 7.2, 1.6 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 13.8, 22.2, 22.3 (d, J = 52.3 Hz), 22.4 (d, J = 4.6 Hz), 30.0 (d, J = 15.1 Hz), 31.0, 117.9 (d, J = 85.6 Hz), 119.9 (q, J = 319.7 Hz), 130.6 (d, J = 12.1 Hz), 133.3 (d, J = 9.8 Hz), 135.3 (d, J = 3.0 Hz). ³¹P-NMR (162 MHz, CDCl₃) δ 23.0. IR (KBr) 3065, 2935, 2872, 1352, 1195, 1058 cm⁻¹. MS (FAB) m/z 347 (M^+ -Tf₂N). Anal. Calcd. for C₂₆H₂₈F₆NO₄PS₂: C, 49.76% H, 4.50% N, 2.23% S, 10.22%. Found: C, 49.72% H, 4.60% N, 2.13% S, 10.33%.

Ethyltris(*p*-chlorophenyl)phosphonium Bis(trifluoromethanesulfonyl)imide (Table 2, entry 6). Colorless solid. Mp 84.5–85.5 °C (EtOH : Et₂O = 2 : 1). ¹H-NMR (400 MHz, CDCl₃) δ 1.35 (3H, dt, J = 20.8, 7.2 Hz), 3.25-3.37 (2H, m), 7.62 (6H, dd, J = 12.4, 8.0 Hz), 7.70 (6H, dd, J = 8.0, 2.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 6.3, 16.1 (d, J = 51.5 Hz), 115.3 (d, J = 88.6 Hz), 119.8 (q, J = 319.8 Hz), 131.2 (d, J = 12.9 Hz), 134.6 (d, J = 11.4 Hz), 142.9. ³¹P-NMR (162 MHz, CDCl₃) δ 25.5. IR (KBr) 3087, 2954, 1579, 1487, 1354, 1192, 1055 cm⁻¹. MS (FAB) m/z 393 (M^+ -Tf₂N). Anal. Calcd. for C₂₂H₁₇Cl₃F₆NO₄PS₂: C, 39.16% H, 2.54% N, 2.08% Cl, 15.76% S, 9.50%. Found: C, 39.15% H, 2.54% N, 2.08% Cl, 15.65% S, 9.35%.

1-Propyltris(*p*-chlorophenyl)phosphonium Bis(trifluoromethanesulfonyl)imide (Table 2, entry 7). Colorless solid. Mp 148.5–149.0 °C (EtOH : Et₂O = 2 : 1). ¹H-NMR (400 MHz, CDCl₃) δ 1.16 (3H, t, J = 7.2 Hz), 1.63 (2H, septet, J = 7.2 Hz), 3.14-3.21 (2H, m), 7.62 (6H, dd, J = 12.4, 8.0 Hz), 7.69 (6H, dd, J = 8.0, 3.2 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 14.8 (d, J = 17.4 Hz), 16.3 (d, J

= 4.5 Hz), 23.7 (d, $J = 50.0$ Hz), 115.6 (d, $J = 88.7$ Hz), 119.8 (q, $J = 319.7$ Hz), 131.2 (d, $J = 12.8$ Hz), 134.6 (d, $J = 11.4$ Hz), 142.9 (d, $J = 3.0$ Hz). ^{31}P -NMR (162 MHz, CDCl_3) δ 23.1. IR (KBr) 3091, 2974, 1579, 1486, 1351, 1201, 1055, 822, 760 cm^{-1} . MS (FAB) m/z 407 ($\text{M}^+ - \text{Tf}_2\text{N}$). Anal. Calcd. for $\text{C}_{23}\text{H}_{19}\text{Cl}_3\text{F}_6\text{NO}_4\text{PS}_2$: C, 40.10% H, 2.78% N, 2.03% Cl, 15.44% S, 9.31%. Found: C, 40.26% H, 2.83% N, 1.89% Cl, 15.26% S, 9.17%.

1-Butyltris(*p*-chlorophenyl)phosphonium Bis(trifluoromethanesulfonyl)imideate (Table 2, entry 8). 20 equivalents of 1-butene were reacted. Colorless solid. Mp 144.0–145.0 °C (EtOH : Et₂O = 2 : 1). ^1H -NMR (400 MHz, CDCl_3) δ 0.92 (3H, t, $J = 7.2$ Hz), 1.48–1.62 (4H, m), 3.18–3.25 (2H, m), 7.62 (6H, dd, $J = 12.4, 8.0$ Hz), 7.70 (6H, dd, $J = 8.0, 3.2$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 13.3, 21.8 (d, $J = 50.8$ Hz), 23.5 (d, $J = 16.7$ Hz), 24.3 (d, $J = 4.6$ Hz), 115.6 (d, $J = 88.7$ Hz), 119.8 (q, $J = 319.0$ Hz), 131.2 (d, $J = 13.6$ Hz), 134.6 (d, $J = 10.7$ Hz), 143.0. ^{31}P -NMR (162 MHz, CDCl_3) δ 23.6. IR (KBr) 3092, 2966, 1579, 1352, 1199, 1056, 819, 759 cm^{-1} . MS (FAB) m/z 421 ($\text{M}^+ - \text{Tf}_2\text{N}$). Anal. Calcd. for $\text{C}_{24}\text{H}_{21}\text{Cl}_3\text{F}_6\text{NO}_4\text{PS}_2$: C, 41.01% H, 3.01% N, 1.99% Cl, 15.13% S, 9.12%. Found: C, 40.81% H, 3.02% N, 1.97% Cl, 14.95% S, 8.90%.

1-Pentyltris(*p*-chlorophenyl)phosphonium Bis(trifluoromethanesulfonyl)imideate (Table 2, entry 9). In a two-necked flask equipped with a reflux condenser were placed tris(*p*-chlorophenyl)phosphine (1 mmol, 365 mg), $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (1 mol%, 10.4 mg), bis(trifluoromethanesulfonyl)imide (1.1 mmol, 310 mg), and 1-pentene (5 mmol, 0.55 mL) in chlorobenzene (3 mL) under an argon atmosphere. The solution was heated at 65 °C for 24 h, and concentrated. The residue was washed with ether/hexane, and recrystallized from ethanol : ether = 2 : 1 giving the title compound (648.4 mg, 91%) as colorless solid. Mp 85.5–86.0 °C (EtOH : Et₂O = 2 : 1). ^1H -NMR (400 MHz, CDCl_3) δ 0.84 (3H, t, $J = 7.2$ Hz), 1.31 (2H, septet, $J = 7.6$ Hz), 1.49–1.57 (4H, m), 3.15–3.22 (2H, m), 7.61 (6H, dd, $J = 12.4, 8.0$ Hz), 7.68 (6H, dd, $J = 8.0, 2.0$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 13.7, 22.05, 22.06 (d, $J = 50.0$ Hz), 22.2 (d, $J = 4.5$ Hz), 32.3 (d, $J = 16.7$ Hz), 115.5 (d, $J = 87.9$ Hz), 119.7 (q, $J = 318.2$ Hz), 131.1 (d, $J = 12.8$ Hz), 134.4 (d, $J = 11.4$ Hz), 142.8 (d, $J = 3.8$ Hz). ^{31}P -NMR (162 MHz, CDCl_3) δ 23.4. IR (KBr) 3090, 2957, 2872, 1580, 1353, 1201, 1065, 1012, 817, 760 cm^{-1} . MS (FAB) m/z 435 ($\text{M}^+ - \text{Tf}_2\text{N}$). Anal. Calcd. for $\text{C}_{25}\text{H}_{23}\text{Cl}_3\text{F}_6\text{NO}_4\text{PS}_2$: C, 41.88% H, 3.23% N, 1.95% Cl, 14.84% S, 8.95%. Found: C, 41.72% H, 3.30% N, 1.92% Cl, 14.78% S, 8.80%.

1-Hexyltris(*p*-chlorophenyl)phosphonium Bis(trifluoromethanesulfonyl)imideate (Table 2, entry 10). 5 equivalents of 1-hexene were reacted. Colorless solid. Mp 80.0–81.0 °C (EtOH). ^1H -NMR (400 MHz, CDCl_3) δ 0.85 (3H, t, $J = 7.2$ Hz), 1.23–1.28 (4H, m), 1.53–1.57 (4H, m), 3.20–3.28 (2H, m), 7.61 (6H, dd, $J = 12.4, 8.0$ Hz), 7.71 (6H, dd, $J = 8.0, 2.4$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 13.7, 22.0 (d, $J = 51.3$ Hz), 22.2, 22.3 (d, $J = 4.5$ Hz), 29.9 (d, $J = 16.7$ Hz), 30.9, 115.6 (d, $J = 87.9$ Hz), 119.8 (q, $J = 319.0$ Hz), 131.2 (d, $J = 12.9$ Hz), 134.6 (d, $J = 10.6$ Hz), 142.9 (d, $J = 3.8$ Hz). ^{31}P -NMR (162 MHz, CDCl_3) δ 23.7. IR (KBr) 3090, 2957, 2871, 1580, 1353, 1202, 1065, 760 cm^{-1} . MS (FAB) m/z 449 ($\text{M}^+ - \text{Tf}_2\text{N}$). Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{Cl}_3\text{F}_6\text{NO}_4\text{PS}_2$: C, 42.72% H, 3.45% N, 1.92% Cl, 14.55% S, 8.77%. Found: C, 42.76% H, 3.37% N, 1.84% Cl, 14.53% S, 8.51%.

Reaction of (*E*)-2-hexene. In a two-necked flask equipped with a reflux condenser were placed tris(*p*-chlorophenyl)phosphine (1 mmol, 365 mg), $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (1 mol%, 10.4 mg),

bis(trifluoromethanesulfonyl)imide (1.1 mmol, 310 mg), and (*E*)-2-hexene (5 mmol, 0.625 mL) in chlorobenzene (3 mL) under an argon atmosphere. The solution was heated at 65 °C for 24 h, and then was concentrated. The residue was washed with ether/hexane. ¹H-NMR analysis using 1,1,2-trichloroethane as internal standard indicated formation of hexyltris(*p*-chlorophenyl)phosphonium bis(trifluoromethanesulfonyl)imide in 91% yield. The reaction of (*E*)-3-hexene proceeded analogously.