SUPPORTING INFORMATION

The Palladium-Catalyzed Reaction of Aryl Iodides with Acetic Anhydride. A Carbon Monoxide Free Synthesis of Acetophenones

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Melting points were determined with a Büchi apparatus and are uncorrected. All of the reagents and the catalyst are commercially available and were used as purchased, without further purification. Reaction products were purified on axially compressed columns, packed with SiO₂ 25-40 µm (Macherey Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluting with *n*-hexane/ethyl acetate mixtures. ¹H NMR (200 MHz) and ¹³C NMR (50.3 MHz) spectra were recorded with a Bruker Avance 200 spectrometer. IR spectra were recorded with a Jasco FT/IR 430 spectrometer.

Table 2. Bases and Solvents in the Palladium-Catalyzed Reaction of *p*-Iodoanisole with Acetic Anhydride.^a

base	solvent	time (h)	T (°C)	yield % of recovered <i>p</i> -iodoanisole	yield % of <i>p</i> -methoxyacetophenone	yield % of the biaryl by-product
Et ₃ N ^b	DMF	2	80	16	32	16
Et ₃ N ^b	DMF	2	80	26	35,5	9
Et ₃ N	DMF	24	80	traces	54	43
DBU	DMF	24	80	85	-	-
DABCO	DMF	40	80	82	-	-
Pyridine	DMF	40	80	81	-	-
EtNPr ₂ ⁱ	DMF	40	80	traces	66	20
EtNPr ₂ ⁱ	DMF	15	100	traces	70	traces
EtNPr ₂ ⁱ	PhMe	24	100	/	47	8
EtNPr ₂ ⁱ	MeCN	24	100	53	25	2,4
K ₂ CO ₃	DMF	24	100	36	30	traces
EtNPr ₂ ⁱ	DMSO	15	100	70	-	-
EtNPr ₂ ⁱ	DMA	15	100	/	59	26
EtNPr ₂ ⁱ	THF	15	100	80	-	-

^a Unless otherwise stated, reactions were run by using 0.427 M solutions of *p*-iodoanisole with the following molar ratios: *p*-iodoanisole:acetic anhydride:base:LiCl: Pd₂(dba)₃ = 1:5:2:5:0.0125. ^b *p*-Iodoanisole:acetic anhydride = 1:2.

Table 3. Phosphine Ligands in the Palladium-Catalyzed Reaction of Ethyl *p*-Iodobenzoate with Acetic Anhydride.^a

phosphine	time (h)	yield % of <i>p</i> -ethoxycarbonylacetophenone	yield % of the biaryl by-product
PPh ₃	6	28	30
tris(<i>p</i> -Cl-C ₆ H ₄) ₃ P	1.5	31	54
tris(2,4,6-MeO ₃ -C ₆ H ₂) ₃ P	1.5	45	40
(<i>o</i> -tol) ₃ P	2	30	68
(2-furyl) ₃ P	6	14	38

^a Unless otherwise stated, reactions were run at 100 °C by using 0.427 M solutions of ethyl *p*-iodobenzoate with the following molar ratios: ethyl *p*-iodobenzoate:acetic anhydride:EtNPr₂:Pd₂(dba)₃:ligand = 1:5:2:0.0125:0.05.

Table 4. Salts in the Palladium-Catalyzed Reaction of Ethyl *p*-Iodobenzoate with Acetic Anhydride.^a

salt	equiv	concentration of the aryl iodide	time (h)	yield % of <i>p</i> -ethoxycarbonylacetophenone	yield % of the biaryl by-product
ⁿ Bu ₄ NCl	1	0.427 M	1	39	58
ⁿ Bu ₄ NCl	2	0.427 M	2	59	29
ⁿ Bu ₄ NCl	1	0.142 M	2	45	35
ⁿ Bu ₄ NCl	1	0.427 M	1	30	70
ⁿ Bu ₄ NBr	1	0.427 M	1	40	60
LiCl	3	0.427 M	1,5	60	22
LiCl	3	0.142 M	1,5	70	15
LiCl	5	0.142 M	1,45	70	10
LiCl	5	0.142 M	70	63	17

^a Reactions were run at 100 °C by using ethyl *p*-iodobenzoate (1 equiv), acetic anhydride (5 equiv), EtNPr₂ (2 equiv), Pd₂(dba)₃ (0.0125 equiv).

Typical procedure for the synthesis of acetophenones from aryl iodides and acetic anhydride (Table 1, entry 10): To a stirred solution of 9-iodophenanthrene (0.260 g, 0.855 mmol) in 6.0 mL of anhydrous DMF were added LiCl (0.181 g, 4.27 mmol), Pd₂(dba)₃ (0.0098 g, 0.0107 mmol), EtNPr₂ (0.298 mL, 1.71 mmol), and acetic anhydride (0.405 mL, 4.27 mmol). The flask was purged with argon and the mixture was stirred for 7 h at 100 °C. After cooling, the reaction mixture was diluted with diethyl ether and washed with water. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, 35 g; *n*-hexane/EtOAc 90/10 v/v) to give 0.151 g of the **3i** (80% yield): mp: 69-70 °C; IR (neat) 2923, 1665 cm⁻¹; ¹H NMR (CDCl₃) δ 8.83-8.65 (m, 3H), 8.20 (s, 1H), 7.96 (dd, *J*₁ = 7.9 Hz, *J*₂ = 1.6 Hz, 1H), 7.81-7.62 (m, 4H), 2.85 (s, 3H); ¹³C NMR (CDCl₃) δ 201.9, 134.8, 132.1, 130.9, 130.8, 130.1, 129.9, 129.0, 128.4, 127.7, 127.2, 126.9, 122.9, 122.8, 30.1; Anal Calcd for C₁₆H₁₂O, C, 87.25; H, 5.49; Found C, 87.32; H, 5.47.

3a; mp: oil; IR (neat): 2963, 2841, 1675, 1258, 1028 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.89 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (CDCl_3) δ 196.8, 163.5, 130.6, 130.3, 113.7, 55.5, 26.3; Anal Calcd for $\text{C}_9\text{H}_{10}\text{O}_2$, C, 71.98; H, 6.71; Found C, 71.91; H, 6.70.

3b; mp: oil; IR (neat) 2964, 2837, 1684 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.53-7.48 (m, 2H), 7.37 (t, J = 8.1 Hz, 1H), 7.14-7.13 (m, 1H), 3.86 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (CDCl_3) δ 198.0, 160.0, 138.5, 129.6, 121.2, 112.4, 119.6, 55.5, 26.8; Anal Calcd for $\text{C}_9\text{H}_{10}\text{O}_2$, C, 71.98; H, 6.71; Found C, 71.89; H, 6.69.

3c; mp: oil; IR (neat) 2963, 2837, 1681 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.72 (dt, J_1 = 5.0 Hz, J_2 = 2.1 Hz, 1H), 7.47 (dd, J_1 = 6.4 Hz, J_2 = 1.1 Hz, 1H), 7.09-6.91 (m, 2H), 3.94 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (CDCl_3) δ 199.9, 158.9, 133.7, 130.3, 128.2, 120.5, 111.6, 55.4, 31.8 Anal Calcd for $\text{C}_9\text{H}_{10}\text{O}_2$, C, 71.98; H, 6.71; Found C, 71.92; H, 6.73.

3d; mp: oil; IR (neat) 2922, 1682, 1268 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.89 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 2.61 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (CDCl_3) δ 198.0, 144.0, 134.8, 129.3, 128.5, 26.6, 21.7; Anal Calcd for $\text{C}_9\text{H}_{10}\text{O}$, C, 80.56; H, 7.51; Found C, 80.61; H, 7.49.

3e; mp: oil; IR (neat) 2924, 1680 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.71 (d, J = 7.7 Hz, 1H), 7.50-7.22 (m, 3H), 2.57 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (CDCl_3) δ 201.8, 138.5, 137.7, 132.1, 131.6, 129.5, 125.8, 29.6, 21.7; Anal Calcd for $\text{C}_9\text{H}_{10}\text{O}$, C, 80.56; H, 7.51; Found C, 80.49; H, 7.49.

3f; mp: oil; IR (neat) 2919, 1680 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.61 (s, 2H), 7.24 (s, 1H), 2.62 (s, 3H), 2.41 (s, 6H); ^{13}C NMR (CDCl_3) δ 198.6, 138.2, 137.2, 134.7, 126.1, 26.7, 21.2; Anal Calcd for $\text{C}_{10}\text{H}_{12}\text{O}$, C, 81.04; H, 8.16; Found C, 81.11; H, 8.14.

3g; mp: oil; IR (neat) 2962, 1741, 1685 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.98-7.93 (m, 2H), 7.62-7.50 (m, 2H), 5.19 (s, 2H), 2.67 (s, 3H), 2.15(s, 3H); ^{13}C NMR (CDCl_3) δ 199.1, 171.9, 138.4, 137.6, 133.7, 129.8, 129.1, 128.8, 66.2, 26.9, 21.1; Anal Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$, C, 68.74; H, 6.29; Found C, 68.79; H, 6.31.

3h; mp: oil; IR (neat) 2925, 1683 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.94 (d, J = 8.0 Hz, 2H), 7.68-7.32 (m, 3H), 2.58 (s, 3H); ^{13}C NMR (CDCl_3) δ 197.8, 137.2, 133.0, 128.6, 128.3, 26.5; Anal Calcd for $\text{C}_8\text{H}_8\text{O}$, C, 79.97; H, 6.71; Found C, 79.91; H, 6.70.

3j; mp: oil; IR (neat) 1685, 1231 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.06-7.99 (m, 2H), 7.30-7.12 (m, 2H), 2.63 (s, 3H); ^{13}C NMR (CDCl_3) δ 206.4, 196.6, 165.9 (d, J = 5.1 Hz), 131.0 (d, J = 9.3 Hz), 115.8 (d, J = 17.3 Hz), 26.6; ^{19}F NMR {H} (CDCl_3) δ -105.75; Anal Calcd for $\text{C}_8\text{H}_7\text{FO}$, C, 69.65; H, 5.11; Found C, 69.58; H, 5.10.

3k; mp: oil; IR (neat) 2928, 1687, 1233 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.92 (td, J_1 = 7.2 Hz, J_2 = 1.8 Hz, 1H), 7.62-7.51 (m, 1H), 7.31-7.13 (m, 2H), 2.69 (d, J = 4.9 Hz, 3H); ^{13}C NMR (CDCl_3) δ 197.3 (d, J = 3.2 Hz), 163.4 (d, J = 254.9 Hz), 135.6 (d, J = 9.1 Hz), 131.5 (d, J = 2.4 Hz), 126.6 (d, J = 12.8 Hz), 125.3 (d, J = 3.5 Hz), 117.5 (d, J = 23.8 Hz), 31.7 (d, J = 7.4 Hz); ^{19}F NMR {H} (CDCl_3) δ -109.83; Anal Calcd for $\text{C}_8\text{H}_7\text{FO}$, C, 69.65; H, 5.11; Found C, 69.69; H, 5.10.

3l; mp: oil; IR (neat) 2927, 1694, 1362 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.24 (s, 1H), 8.17 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 2.67 (s, 3H); ^{13}C NMR (CDCl_3) δ 196.6, 137.5, 131.4, 131.2 (q, J = 32.8 Hz), 129.4 (q, J = 3.8 Hz), 129.3, 125.1 (q, J = 3.8 Hz), 123.7 (q, J = 272.5 Hz), 26.6; ^{19}F NMR {H} (CDCl_3) δ -112.3; Anal Calcd for $\text{C}_9\text{H}_7\text{F}_3\text{O}$, C, 57.45; H, 3.75; Found C, 57.40; H, 3.74.

3m; mp: wax; IR (neat) 3004, 1685, 1094 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.91 (dd, J_1 = 6.7 Hz, J_2 = 2.0 Hz, 2H), 7.45 (dd, J_1 = 6.7 Hz, J_2 = 2.0 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR (CDCl_3) δ 195.9, 139.6, 135.5, 129.8, 129.0, 26.6; Anal Calcd for $\text{C}_8\text{H}_7\text{ClO}$, C, 62.15; H, 4.56; Found C, 62.21; H, 4.54.

3n; mp: 49-50 $^\circ\text{C}$; IR (KBr) 2992, 1709, 1684 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.14 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.5 Hz, 2H), 4.42 (q, J = 7.1, 2H), 2.65 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl_3) δ 197.5, 165.7, 140.1, 134.2, 130.0, 128.1, 61.4, 26.8, 14.2; Anal Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$, C, 68.74; H, 6.29; Found C, 68.80; H, 6.31.

3o; mp: 105-106°C; IR (neat) 3431, 1679, 648, 604 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.05 (s, 4H), 2.67 (s, 6H); ^{13}C NMR (CDCl_3) δ 197.5, 140.1, 128.5, 26.9; Anal Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$, C, 74.06; H, 6.21; Found C, 74.10; H, 6.22.

3p; mp: wax; IR (KBr) 3108, 1693, 1523, 1344 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.31 (d, $J = 8.5$ Hz, 2H), 8.13 (d, $J = 8.5$ Hz, 2H), 2.70 (s, 3H); ^{13}C NMR (CDCl_3) δ 196.4, 150.5, 141.6, 129.4, 123.9, 27.0; Anal Calcd for $\text{C}_8\text{H}_7\text{NO}_3$, C, 58.18; H, 4.27; N, 8.48; Found C, 58.25; H, 4.26; N, 8.46.