Palladium-Catalyzed Carbonylative Cyclization of Unsaturated Aryl Iodides and Dienyl Triflates, Iodides and Bromides to Indianones and 2-Cyclopentenones

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Supporting Information

1-(2-Iodophenyl)-1-phenylethene (9). Methyltriphenylphosphonium bromide (5.5 mmol) was suspended in THF (10 mL) and n-BuLi (5.5 mmol of a 2.5 M soln) was added dropwise with stirring under N₂ at 0 °C. After 30 min at 0 °C, 2-iodobenzophenone (5 mmol) in THF (5 mL) was added dropwise and stirred for 1 h. The reaction was quenched with H₂O (20 mL) and extracted with ether (3 x 20 mL). The extracts were dried (Na₂SO₄), concentrated under vacuum and chromatographed on a silica gel column using 10:1 hexane/ethyl acetate to afford 9 as a clear oil in an 84% yield: ¹H NMR (CDCl₃) δ 5.28 (s, 1 H), 5.89 (s, 1 H), 7.07 (dt, J = 2.0, 7.6 Hz, 1 H), 7.33-7.77 (m, 7 H), 7.93 (dd, J = 0.8, 7.6 Hz, 1 H); ¹³C NMR (CDCl₃) δ 99.16, 116.09, 126.96, 127.89, 128.19, 128.48, 129.04, 130.77, 139.32, 139.56, 146.70, 151.63; IR (neat) 3080, 3027, 1493 cm⁻¹; HRMS calcd for C₁₄H₁₁I, found 305.99113, 305.99113.

1-Iodo-4,5-dimethoxy-2-vinylbenzene (13). This compound was prepared by the same method used for the preparation of 9, but 4,5-dimethoxy-2-iodobenzaldehyde was employed. Removal of the solvent afforded a 90% yield of compound 13 as a clear oil: ¹H NMR (CDCl₃) δ 3.84 (s, 3 H), 3.87 (s, 3 H), 5.20 (dd, J = 0.9, 10.3 Hz, 1 H), 5.50 (dd, J = 0.9, 17.4 Hz, 1 H), 6.79 (dd, J = 10.8, 17.4 Hz, 1 H), 7.00 (s, 1 H), 7.20 (s, 1 H); ¹³C NMR (CDCl₃) δ 56.18, 56.38, 88.65, 108.71, 115.10, 121.55, 133.34, 140.46, 149.63, 149.71; IR (neat) 3053, 2985, 1594 cm⁻¹; HRMS calcd for C₁₀H₁₁O₂, 289.98038, found 289.98079.
2-iodo-3,4,5-trimethoxy-1-vinylbenzene (15). This compound was prepared by the same method used for the preparation of 9, but 2-iodo-3,4,5-trimethoxybenzaldehyde was employed. Removal of the solvent afforded a 66% yield of compound 15 as a clear oil: $^1$H NMR (CDCl$_3$) $\delta$ 3.84 (s, 3 H), 3.85 (s, 3 H), 3.86 (s, 3 H), 5.23 (dd, $J = 0.8$, 10.8 Hz, 1 H), 5.50 (d, $J = 17.2$ Hz, 1 H), 6.88 (s, 1 H), 6.91 (dd, $J = 10.8$, 17.2 Hz, 1 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 56.19, 60.77, 61.09, 88.05, 105.65, 116.06, 136.62, 140.82, 141.99, 153.04, 153.84; IR (neat) 3050, 2950, 1555 cm$^{-1}$; HRMS calcd for $C_{11}H_{13}IO_3$ 319.99095, found 319.99136.

3-iodo-5-trimethylsilyl-2-vinylfuran (17). 3-Iodo-5-trimethylsilyl-2-furoic acid (8 mmol) was dissolved in dry THF (135 mL) and treated with BH$_3$•THF (16 mmol). The resulting cloudy white soln was heated at reflux for 4 h, cooled and carefully quenched with H$_2$O (270 mL). The mixture was extracted with ether (3 x 25 mL). The combined organic layers were washed with NaHCO$_3$ (2 x 100 mL), H$_2$O (100 mL), dried (Na$_2$SO$_4$), concentrated under vacuum and chromatographed on a silica gel column using 10:1 hexane/ethyl acetate to afford 2-(hydroxymethyl)-3-iodo-5-(trimethylsilyl)furan as a clear oil in a 90% yield.

2-(Hydroxymethyl)-3-iodo-5-(trimethylsilyl)furan (5 mmol), MnO$_2$ (100 mmol), and CH$_2$Cl$_2$ (75 mL) were placed in a 250 mL round bottom flask and flushed with Ar. The mixture was stirred overnight and filtered through Celite. The solvent was evaporated affording 3-iodo-5-(trimethylsilyl)furan-2-carbaldehyde as a clear oil in a 91% yield.

Methyltriphenylphosphonium bromide (4.4 mmol) was suspended in THF (10 mL) and n-BuLi (4.4 mmol of a 2.5 M soln) was added dropwise with stirring under N$_2$ at 0 °C. After 30 min at 0 °C, 3-iodo-5-(trimethylsilyl)furan-2-carbaldehyde (4 mmol) in THF (5 mL) was added dropwise and stirred for 1 h. The reaction was quenched with H$_2$O (20 mL) and extracted with ether (3 x 20 mL). The extracts were dried (Na$_2$SO$_4$), concentrated under vacuum and chromatographed on a silica gel column using 10:1 hexane/ethyl acetate to afford 17 as a clear oil in a 61% yield: $^1$H NMR (CDCl$_3$) $\delta$ 0.28 (s, 9 H), 5.25-5.30 (m, 1
H), 5.78-5.84 (m, 1 H), 6.61 (ddd, J = 0.6, 11.4, 17.4 Hz, 1 H), 6.67 (d, J = 0.6 Hz, 1 H);
\(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 1.52, 65.92, 115.08, 123.88, 128.17, 156.28, 161.72; IR (neat)
3053, 2985, 1422 cm\(^{-1}\); HRMS calcd for C\(_9\)H\(_{13}\)IOSi 291.97805, found 291.97866.

**2-Vinyl-1-cyclopentenyl trifluoromethanesulfonate (19).** This compound
was prepared by the same method used for the preparation of 21, but ethyl 2-
oxocyclopentanecarboxylate was employed (20 mmol): \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.98-2.08
(m, 2 H), 2.49-2.56 (m, 2 H), 2.73 (t, J = 7.5 Hz, 2 H), 5.21-5.31 (m, 2 H), 6.60 (dd, J =
10.8, 17.4 Hz, 1 H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 19.42, 27.76, 31.67, 118.62, 118.66 (q, J =
320.6 Hz), 126.86, 129.86, 144.75; IR (neat) 3110, 2955, 1664 cm\(^{-1}\); HRMS calcd for
C\(_8\)H\(_9\)F\(_3\)O\(_3\)S 242.07245, found 242.02280.

**2-Vinyl-1-cyclohexenyl trifluoromethanesulfonate (21).** To a soln of ethyl 2-
oxocyclohexanecarboxylate (20 mmol) in CH\(_2\)Cl\(_2\) (50 mL) was added i-Pr\(_2\)NEt (17.5 mL)
at -78 °C. The mixture was stirred for 10 min during which Tf\(_2\)O (24 mmol) was added
dropwise, followed by slow warming to room temp overnight. The mixture was washed
with H\(_2\)O (50 mL) and a 10% aq citric acid soln (2 x 75 mL). The organic layer was dried
(Na\(_2\)SO\(_4\)), concentrated under vacuum, and chromatographed on a silica gel column with
10:1 hexane/ethyl acetate to produce ethyl 2-trifluoromethanesulfonyloxy-1-
cyclohexenecarboxylate as a clear oil in a 99% yield.

To a cold (0 °C) magnetically stirred solution of ethyl 2-trifluoromethane-sulfonyloxy-
1-cyclohexenecarboxylate (8 mmol) in anhydrous ether (20 mL) was added DIBAl-H (24
mmol, 1 M soln in hexanes). The reaction was stirred at 0 °C for 30 min and quenched with
ethyl acetate (20 mL), followed by sufficient HCl (1 M aq soln) to dissolve all of the
precipitated solid. The separated aq phase was extracted with ether (3 x 50 mL) and the
combined organic extracts were washed with 1 M HCl (3 x 50 mL), dried (Na\(_2\)SO\(_4\)), and
concentrated under vacuum. The resulting residue was chromatographed on a silica gel
column with 10:1 hexane/ethyl acetate to produce 2-(hydroxymethyl)cyclohex-1-enyl
trifluoromethanesulfonate as a clear oil in an 85% yield.
2-(Hydroxymethyl)cyclohex-1-enyl trifluoromethanesulfonate (5 mmol), MnO₂ (100 mmol), and CH₂Cl₂ (75 mL) were placed in a 250 mL round bottom flask and flushed with Ar. The mixture was stirred overnight and filtered through Celite. The solvent was evaporated giving 2-trifluoromethanesulfonyloxy-1-cyclohexene-carbaldehyde as a pale yellow oil in an 85% yield. The aldehyde formed decomposes rapidly. Therefore, it was immediately used in the next step.

Methyltribenzylphosphonium bromide (6.6 mmol) was suspended in THF (15 mL) and n-BuLi (6.6 mmol of a 2.5 M soln) was added dropwise with stirring under nitrogen at 0 °C. After 30 min at 0 °C, 2-trifluoromethanesulfonyloxy-1-cyclohexencarbaldehyde (6 mmol) in THF (10 mL) was added dropwise and stirred for 1 h. The reaction was quenched with H₂O (20 mL) and extracted with ether (3 x 20 mL). The extracts were dried (Na₂SO₄), concentrated under vacuum and chromatographed on a silica gel column using 10:1 hexane/ethyl acetate to yield 2-vinyl-1-cyclohexenyl trifluoromethanesulfonate as a clear oil in a 25% yield: ¹H NMR (CDCl₃) δ 1.65-1.82 (m, 4 H), 2.31-2.36 (m, 2 H), 2.42-2.44 (m, 2 H), 5.24 (d, J = 11.1 Hz, 1 H), 5.34 (dt, J = 0.9, 17.4 Hz, 1 H), 6.78 (dd, J = 10.8, 17.4 Hz, 1 H); ¹³C NMR (CDCl₃) δ 21.53, 23.06, 24.52, 28.36, 116.52, 120.69, 127.17, 129.90, 145.90; IR (neat) 3099, 2945, 1664 cm⁻¹; HRMS calcd for C₉H₁₁F₃O₃S
256.03810, found 256.03848.

1-Bromo-2-vinylcyclohexene (23). Dry DMF (150 mmol) was cooled to 0 °C in dry CHCl₃ (220 mL) and PBr₃ (125 mmol) was added dropwise. The mixture was stirred at 0 °C for 1 h to give a yellow suspension. A soln of cyclohexanone (50 mmol) in CHCl₃ (50 mL) was added and the mixture was heated under reflux for 1 h. The reaction was cooled to 0 °C and aq NaHCO₃ was added slowly until the effervescence subsided. The mixture was extracted with CH₂Cl₂ (3 x 50 mL). The extracts were dried (Na₂SO₄), concentrated under vacuum and chromatographed on a silica gel column using 10:1 hexane/ethyl acetate to afford 2-bromocyclohex-1-enecarbaldehyde as a yellow oil in a 30% yield.
Methyltriphenylphosphonium bromide (11 mmol) was suspended in THF (15 mL) and n-BuLi (11 mmol of a 2.5 M soln) was added dropwise with stirring under nitrogen at 0 °C. After 30 min at 0 °C, 2-bromocyclohex-1-enecarbaldehyde (10 mmol) in THF (10 mL) was added dropwise and stirred for 1 h. The reaction was quenched with H₂O (20 mL) and extracted with ether (3 x 20 mL). The extracts were dried (Na₂SO₄), concentrated under vacuum and chromatographed on a silica gel column using 10:1 hexane/ethyl acetate to afford 1-bromo-2-vinylcyclohexene as a clear oil in an 82% yield: ¹H NMR (CDCl₃) δ 1.70-1.74 (m, 4 H), 2.25-2.29 (m, 2 H), 2.62-2.64 (m, 2 H), 5.13 (dq, J = 0.6, 8.1 Hz, 1 H), 5.25 (dq, J = 0.6, 12.9 Hz, 1 H), 6.91 (dd, J = 8.1, 12.9 Hz, 1 H); ¹³C NMR (CDCl₃) δ 22.31, 24.97, 27.01, 37.81, 114.60, 125.39, 132.45, 137.28; IR (neat) 3050, 2975, 1421 cm⁻¹. The remaining spectral properties match those previously reported in the literature.¹

1-Iodo-2-vinylcyclohexene (24). To a 25 mL round bottom flask was added 1-bromo-2-vinylcyclohexene (3.5 mmol), Mg (4.2 mmol), dry THF (6 mL), and one drop of CH₂I₂. The mixture was refluxed for 2 h, at which time a soln of I₂ (7 mmol) in THF (10 mL) was added and stirred for 1 h at room temperature. The reaction mixture was hydrolyzed with 2 N HCl and the product was extracted with ether. The ethereal soln was washed with satd aq NaCl, dried (Na₂SO₄), concentrated under vacuum, and chromatographed on a silica gel column using 10:1 hexane/ethyl acetate to afford 24 as a pale yellow oil in a 63% yield (95% percent pure, 5% of the corresponding bromide remained): ¹H NMR (CDCl₃) δ 1.64-1.70 (m, 2 H), 1.74-1.80 (m, 2 H), 2.30-2.34 (m, 2 H), 2.78-2.81 (m, 2 H), 5.10 (dq, J = 0.6, 8.1 Hz, 1 H), 5.25 (dq, J = 0.6, 12.9 Hz, 1 H), 6.69 (dd, J = 8.1, 12.9 Hz, 1 H); ¹³C NMR (CDCl₃) δ 22.45, 26.17, 27.50, 43.15, 105.28, 115.28, 137.30, 142.8; IR (neat) 3053, 2986, 1421 cm⁻¹; HRMS calcd for C₁₀H₁₅I, 233.99055, found 233.98562.

1-Vinyl-2-iodo-3,4-dihydonaphthalene (25). This compound was prepared by the same method used for the preparation of 24, but β-tetralone was employed: ¹H NMR (CDCl₃) δ 2.81-2.84 (m, 2 H), 2.92-2.96 (m, 2 H), 5.42 (dd, J = 0.8, 17.9 Hz, 1 H), 5.51 (dd, J = 1.2, 11.2 Hz, 1 H), 6.59 (dd, J = 11.6, 18.0 Hz, 1 H), 7.14-7.21 (m, 3 H),
7.42-7.44 (m, 1 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \(\delta\) 30.22, 40.33, 100.44, 120.61, 125.92, 126.38, 127.43, 127.62, 133.45, 136.22, 139.00, 140.07; IR (neat) 3010, 2950, 1450 cm\textsuperscript{-1}; HRMS calcd for C\textsubscript{12}H\textsubscript{11}I 281.99055, found 281.99094.

**2-Vinyl-1-iodo-3,4-dihyronaphthalene (27).** This compound was prepared by the same method used for the preparation of 24, but \(\alpha\)-tetralone was employed: \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \(\delta\) 2.60-2.63 (m, 2 H), 2.82-2.87 (m, 2 H), 5.37 (d, \(J = 11.1\) Hz, 1 H), 5.54 (d, \(J = 17.1\) Hz, 1 H), 7.01-7.30 (m, 4 H), 7.70 (d, \(J = 7.5\) Hz, 1 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \(\delta\) 26.38, 28.31, 117.67, 126.77, 126.96, 127.12, 128.29, 132.51, 136.62, 136.73, 141.27, 142.99; IR (neat) 3086, 2945, 2885, 2829, 1480 cm\textsuperscript{-1}; HRMS calcd for C\textsubscript{12}H\textsubscript{11}I 281.99055, found 281.99094.

**1-Bromo-2-vinylcycloheptene (29).** This compound was prepared by the same method used for the preparation of 23, but cycloheptanone was employed: \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \(\delta\) 1.45-1.51 (m, 2 H), 1.53-1.62 (m, 2 H), 1.72-1.80 (m, 2 H), 2.39-2.43 (m, 2 H), 2.85-2.88 (m, 2 H), 5.14 (dd, \(J = 0.9\), 11.1 Hz, 1 H), 5.26 (d, \(J = 17.4\) Hz, 1 H), 6.81 (dd, \(J = 10.8\), 17.1 Hz, 1 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \(\delta\) 25.28, 25.39, 27.95, 31.53, 41.78, 114.44, 127.68, 137.85, 138.76; IR (neat) 3085, 2880, 1480 cm\textsuperscript{-1}; HRMS calcd for C\textsubscript{9}H\textsubscript{13}Br 200.02006, found 200.02036.

**2-(2,2-Dideuteriovinyl)-1-iodobenzene (34).** (Methyl-\textsuperscript{d3})triphenylphosphonium iodide (5.5 mmol) was suspended in THF (10 mL) and \(\pi\)-BuLi (5.5 mmol of a 2.5 M soln) was added dropwise with stirring under N\textsubscript{2} at 0 °C. After 30 min at 0 °C, 2-iodobenzaldehyde (5 mmol) in THF (5 mL) was added dropwise and stirred for 1 h. The reaction was quenched with H\textsubscript{2}O (20 mL) and extracted with ether (3 x 20 mL). The extracts were dried (Na\textsubscript{2}SO\textsubscript{4}), concentrated under vacuum and chromatographed on a silica gel column using 10:1 hexane/ethyl acetate to afford 34 as a clear oil in an 60% yield with 93% deuterium incorporation: \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \(\delta\) 5.31-5.35 (m, 0.07 H), 5.61-5.66 (m, 0.07 H), 6.91 (s, 1 H), 6.96 (dt, \(J = 1.6\), 7.6 Hz, 1 H), 7.31-7.35 (m, 1 H), 7.53 (dd, \(J = 1.6\), 7.6 Hz, 1 H), 7.86 (dd, \(J = 1.2\), 8.0 Hz, 1 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \(\delta\) 99.77, 126.43,
128.46, 129.33, 139.49, 140.51, 140.79 (one sp² carbon mixing due to overlap); IR (neat) 3055, 2985, 1485 cm⁻¹; HRMS calcd for C₈H₅D₂I 231.97181, found 231.97230.

1-Indanone (6). The product was isolated in a 100% yield as a yellow oil after an 8 h reaction time. The spectral properties match those previously reported in the literature.²³

3-Methyldindan-1-one (8). The product was isolated in a 100% yield as a yellow oil after a 12 h reaction time. The spectral properties match those previously reported in the literature.⁴

3-Phenylindan-1-one (10). The product was isolated in a 60% yield as a yellow oil after a 72 h reaction time. The spectral properties match those previously reported in the literature.⁵

5,6-Dimethoxyindan-1-one (14). The product was isolated in an 82% yield as a pale yellow solid after a 24 h reaction time: lit mp⁶ 114-116 °C, found 110-113 °C. The spectral properties match those previously reported in the literature.⁷

5,6,7-Trimethoxyindan-1-one (16). The product was isolated in a 45% yield as a pale yellow solid after a 24 h reaction time: lit mp⁷ 75-77 °C, found 74-75 °C. The spectral properties match those previously reported in the literature.⁷

5-Trimethylsilyl-2-vinyl-3-furoic acid (18). The product was isolated in a 61% yield as a pale yellow solid after a 24 h reaction time: mp 100-103 °C; ¹H NMR (CDCl₃) δ 0.27 (s, 9 H), 5.47 (dd, J = 1.2, 11.2 Hz, 1 H), 6.02 (dd, J = 1.2, 17.6 Hz, 1 H), 6.93 (s, 1 H), 7.25 (dd, J = 11.2, 17.6 Hz, 1 H); ¹³C NMR (CDCl₃) δ -1.76, 113.80, 118.48, 121.39, 124.38, 160.38, 161.09, 169.30; IR (neat) 3500, 3053, 1683 cm⁻¹; HRMS calcd for C₁₀H₁₄O₃Si 210.07122, found 210.07159.

2-Vinylcyclopent-1-enecarboxylic acid (20). The product was isolated in an 89% yield as a pale yellow solid after a 24 h reaction time: lit mp⁹ 98-101 °C, found 100 °C; HRMS calcd for C₈H₁₀O₂ 138.06808, found 138.06828. The remaining spectral properties match those previously reported in the literature.⁹
2-Vinylcyclopent-1-enecarboxylic acid (20). The product was isolated in an 89% yield as a pale yellow solid after a 24 h reaction time: lit mp\(^9\) 98-101 °C, found 100 °C; HRMS calcd C\(_9\)H\(_{10}\)O\(_2\) 138.06808, found 138.06828. The remaining spectral properties match those previously reported in the literature.\(^9\)

4,5,6,7-Tetrahydroindan-1-one (22). The product was isolated in a 95% yield as a clear oil after a 12 h reaction time: \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 20.24, 21.92, 22.35, 28.79, 30.29, 34.69, 138.94, 173.85, 209.36. The remaining spectral properties match those previously reported in the literature.\(^10\)

1,2,4,5-Tetrahydrocyclopenta[a]naphthalen-3-one (26). The product was isolated in an 85% yield as a pale yellow solid after a 72 h reaction time: lit mp\(^11\) 75-78 °C, found 78-79 °C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 2.49 (tt, \(J = 1.8, 6.3, 12.3\) Hz, 2 H), 2.59-2.61 (m, 2 H), 2.87-2.93 (m, 4 H), 7.24-7.40 (m, 4 H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 18.39, 25.16, 28.16, 35.50, 124.39, 127.04, 128.45, 131.02, 132.22, 137.87, 138.83, 166.14, 207.97; IR (neat) 3053, 2937, 2595, 1688, 1630 cm\(^{-1}\); HRMS calcd for C\(_{13}\)H\(_{12}\)O 184.08882, found 184.08922.

2,3,4,5-Tetrahydrocyclopenta[a]naphthalen-1-one (28). The product was isolated in a 98% yield as a pale yellow solid after a 72 h reaction time: mp 112-113 °C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 2.55-2.58 (m, 2 H), 2.62-2.67 (m, 4 H), 2.94 (t, \(J = 6.0\) Hz, 2 H), 7.16-7.26 (m, 3 H), 8.23 (t, \(J = 5.7\) Hz, 1 H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 27.29, 27.85, 29.49, 36.13, 124.13, 126.94, 127.76, 128.02, 129.34, 134.65, 135.09, 175.32, 206.41; IR (neat) 3053, 2985, 1696 cm\(^{-1}\); HRMS calcd for C\(_{13}\)H\(_{12}\)O 184.08882, found 184.08972.

3,4,5,6,7,8-Hexahydro-2\(^H\)-azulen-1-one (30). The product was isolated in a 98% yield as a yellow oil after a 48 h reaction time. The spectral properties match those previously reported in the literature.\(^12\)

2,3-Di-\(n\)-propyclclopent-2-enone (32). The product was isolated in a 70% yield as a yellow oil after a 24 h reaction time: HRMS calcd for C\(_{11}\)H\(_{18}\)O 166.13577, found 166.13600. The spectral properties match those previously reported in the literature.\(^13\)
References

2-Vinylcyclohexenyl trifluoromethylsulfonylate

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