A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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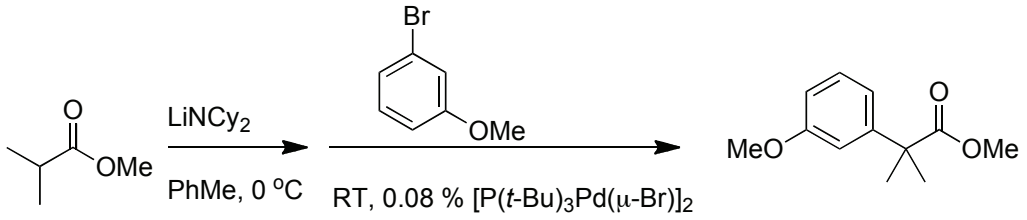
September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

α-ARYLATION OF ESTERS CATALYZED BY THE Pd(I) DIMER [P(*t*-Bu)$_3$Pd(μ-Br)]$_2$



Submitted by David S. Huang, Ryan J. DeLuca, and John. F. Hartwig.[1]
Checked by David Hughes.

1. Procedure

A 500-mL, 3-necked, round-bottomed flask (Note 1) equipped with a 3-cm oval Teflon-coated magnetic stir bar is fitted with a gas inlet adapter connected to a nitrogen line and a gas bubbler. The other two necks are capped with rubber septa; a thermocouple probe is inserted through one of the septa. (Note 2) To the flask is added anhydrous toluene (100 mL, Note 3) and dicyclohexylamine (9.96 g, 54.9 mmol, 1.3 equiv). The flask is placed in an ice-water bath and cooled with stirring to +2 °C. *n*-Butyllithium (2.36 M in hexanes, 22.0 mL, 15.2 g, 51.9 mmol, 1.23 equiv) is added over 10 min to the cooled solution of dicyclohexylamine via a 50-mL disposable syringe (Notes 4 and 5). The reaction mixture is stirred for 20 min at 0–5 °C. To the resulting lithium dicyclohexylamide suspension is added methyl isobutyrate (5.40 mL, 4.80 g, 47.0 mol, 1.11 equiv) over 20 min via a disposable 10-mL syringe (Note 6). The reaction mixture is stirred for an additional 30 min at 0–5 °C. 3-Bromoanisole (5.40 mL, 7.90 g, 42.2 mol, 1.00 equiv) is then added over 1 min via a 10-mL disposable syringe. The mixture is degassed by two vacuum-nitrogen purge cycles (Note 7). A septum is removed, [P(*t*-Bu)$_3$Pd(μ-Br)]$_2$ (12.4 mg, 0.0160 mmol, 0.00038 equiv) is added under a flow of nitrogen, and then the septum is replaced (Note 8). The flask is removed from the ice-water bath, allowed to warm to ambient temperature, and the reaction mixture is stirred for one hour (Note 9). A septum is removed and additional [P(*t*-Bu)$_3$Pd(μ-Br)]$_2$ (13.8 mg, 0.0180 mmol, 0.00042 equiv) is added under a flow of nitrogen (Note 10). The reaction mixture is stirred at ambient temperature for 4 h. After

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confirming reaction completion (Note 9), *t*-butyl methyl ether (100 mL) is added. One septum is removed and replaced with a 100-mL dropping funnel. Aqueous HCl (1N, 70 mL) is added to the reaction mixture over 10 min via the dropping funnel, resulting in a temperature rise to 30 °C and formation of a thick slurry (Note 11). The resulting suspension is stirred for 10 min and then is filtered through a 600-mL coarse-porosity sintered glass funnel. The precipitate is washed with *t*-butyl methyl ether (4 x 25 mL). The resulting mixture is transferred to a 500-mL separatory funnel, and the organic layer is separated, washed sequentially with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL), and then is vacuum-filtered through a bed of Na_2SO_4 (50 g) in a 350-mL medium porosity sintered glass funnel. The cake is rinsed with *t*-butyl methyl ether (3 x 25 mL). The filtrate is concentrated by rotary evaporation (40 °C bath, 100 mmHg initial, lowered to 20 mmHg) to afford the crude product (10.2 g), which is purified by silica gel column chromatography (Note 12) to furnish methyl 2-(3-methoxyphenyl)-2-methylpropanoate (7.14–7.59 g, 81–86 % yield) as a clear yellow oil (Notes 13-15).

2. Notes

1. All glassware was dried in an oven at 130 °C prior to use.
2. The internal temperature is monitored using a J-Kem Gemini digital thermometer with a Teflon-coated T-Type thermocouple probe (12-inch length, 1/8 inch outer diameter, temperature range –200 to +250 °C).
3. The following reagents and solvents were obtained from Sigma-Aldrich and used without further purification: toluene (ACS reagent, >99.5%, dried over 3A pelleted molecular sieves), 2.5 M BuLi in hexanes, dicyclohexylamine (99%), methyl isobutyrate (99%), 3-bromoanisole (98%), *t*-butyl methyl ether (ACS reagent, >99%), ethyl acetate (ACS reagent, >99.5%), and hexanes (ACS reagent, >98.5%). $[P(t\text{-}Bu)_3Pd(\mu\text{-}Br)]_2$ was obtained from Strem and stored in a glove box freezer at –35 °C. Deionized tap water was used throughout.
4. The mass of *n*-BuLi added was determined by weighing the syringe before and after addition. *n*-BuLi was titrated using diphenylacetic acid as described in Davies, S. G.; Fletcher, A. M.; Roberts, P. M. *Org. Synth*, **2010,** *87,* 143-160.

5. The reaction mixture warmed to 7 °C during the addition and became a yellow slurry as $LiNCy_2$ precipitated when the enolate was formed.

6. Adding the ester slowly is crucial to avoid the Claisen condensation product, which is difficult to remove from the product by flash chromatography. The mixture warmed to 6 °C during the addition.

7. The purge cycle was carried out by slowly drawing a vacuum in the flask, which results in bubbling as the mixture is degassed. After 2 minutes the bubbling nearly ceases and the flask is back-filled with nitrogen. The cycle is repeated to ensure all dissolved oxygen, which may be present, is removed.

8. The quality of the catalyst is vital to the reaction. The catalyst should be a dark metallic green. If there is concern about the quality of the catalyst, a ^{31}P NMR spectrum should be obtained. $^{31}P\{^{1}H\}$NMR (500 MHz,C_6H_6, H_3PO_4) δ: 87.0 (s). Poorly performing catalyst is brown/black in color and contains species that appear in the ^{31}P NMR spectrum at δ: 107 (s). $[P(t\text{-}Bu)_3Pd(\mu\text{-}Br)]_2$ decomposes to $[Pd(P(t\text{-}Bu)_3)_2(C(CH_3)_2CH_2)(\mu\text{-}Br)]_2$ over time.[2]

9. The mixture warms to 20 °C over 20 minutes and changes from a brown mixture to yellow. The progress of the reaction is monitored by ^{1}H NMR (checker) or GC analyses (submitter). At the one-hour reaction point after the first catalyst addition, the reaction proceeds only 5-10 %. For the NMR analysis, a sample of the reaction mixture is quenched into a mixture of 1 mL of 1N HCl and 1 mL of $CDCl_3$. The bottom organic layer is filtered through a plug of sodium sulfate into an NMR tube. The methyl resonances of the methyl ester and methoxy group are diagnostic (OMe product resonance at 3.85 ppm, starting material at 3.84 ppm; CO_2Me product resonance at 3.70 ppm, starting material at 3.72 ppm). GC analyses were obtained on an Agilent 6890 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μm film) and an FID detector. The temperature program: hold at 80 °C for 1.5 min, ramp from 80 °C to 300 °C at 100 °C /min, hold at 300 °C for 3 min. t_R (3-bromoanisole) = 3.33 min, t_R (methyl 2-(3-methoxyphenyl)-2-methylpropanoate) = 3.89 min.

10. After the second charge of catalyst the mixture slowly warms from 23 °C to 33 °C over 30 min and then returns to room temperature over the next hour. The reaction is generally complete within an hour of the second charge. The checker found the double catalyst charge protocol provided optimum results, where the first charge is largely sacrificial. When added as

a single charge, the reaction times were variable (10-30 hours) and generally stalled at 90% completion. For stalled reactions, a second catalyst charge even after one-day reaction time will drive the reaction to completion.

11. The ^{1}H NMR spectrum of the precipitate matched the spectrum of dicylohexylammonium chloride.[3]

12. A 6-cm glass column is wet-packed (4% EtOAc/hexanes) with SiO_2 (250 g) topped with 0.5 cm sand. The crude reaction product is loaded neat on the column and eluted with 4% EtOAc/hexanes (2.5 L), collecting 100 mL fractions. TLC (UV visualization) is used to follow the chromatography. The R*f* value of the title compound is 0.4 (10% EtOAc/hexanes). Fractions 15-22 are concentrated by rotary evaporation (40 °C bath, 20 mmHg), then held under vacuum (20 mmHg) at 22 °C for 20 h to constant weight (7.14–7.59 g).

13. Methyl 2-(3-methoxyphenyl)-2-methylpropanoate has the following physical and spectroscopic data: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.59 (s, 6 H), 3.67 (s, 3 H), 3.81 (s, 3 H), 6.79 (ddd, *J* = 8.2, 2.5, 0.8 Hz, 1 H), 6.91–6.89 (m, 1 H), 6.93 (ddd, *J* = 7.8, 1.8, 0.8 Hz, 1 H), 7.26 (t, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.7, 46.7, 52.3, 55.3, 111.7, 112.4, 118.3, 129.5, 146.6, 159.8, 177.3; IR (thin film): 2978, 2953, 2838, 1729, 1601, 1584, 1490, 1466, 1434, 1263, 1149, 1050 cm^{-1}. LC-MS calcd for $[M + H]^+$ 209.2; found 209.1; GC-MS (EI): 208 (M^+) (25 %), 149 ($[M–CO_2Me]^+$)(100 %). HPLC >99 area % purity at 215 nm detection (HPLC conditions, Zorbax extend C18 column (3 x 150 mm), 3.5 μM particle size; 0.75 mL/min flow; gradient eluent from 5/95 MeCN/ aq. pH 3.5 buffer to 100% MeCN over 9.5 min, hold for 3 min; 35 °C; product elutes at 8.5 min). An analytical sample was prepared by dissolving 100 mg of the product in 3 mL of hexanes, filtering through a 0.45 micron PTFE syringe filter, and concentrating to dryness under vacuum for 20 h. Anal. calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74; found: C, 68.97; H, 7.73.

14. The product after chromatographic purification contains 0.5-1.0 % of the Claisen condensation product of methyl isobutyrate (methyl 2,2,4-trimethyl-3-oxopentanoate; NMR match with the literature, Mloston, G.; Romanski, J.; Linden, A.; Heimgartner, H. *Helv. Chim. Acta* **1999**, *82*, 1302-1310) as assessed by peak integration of the ^{13}C-^{1}H satellite resonances (0.55 %) corresponding to the OMe and CO_2Me protons of the product against the ^{1}H resonances corresponding to gem-dimethyl (δ 1.39) and $\underline{Me_2}CH$ (δ 1.09) protons of the Claisen impurity. For more details on using ^{13}C satellites for quantitative analysis of low level impurities, see Claridge, T. D. W.; Davies,

S. G.; Polywka, M. E. C.; Roberts, P. M.; Russell, A. J.; Savory, E. D.; Smith, A. D. *Org. Lett.* **2008**, *10*, 5433. This impurity was not detected by GC-MS or LC-MS.

15. The major by-product generated in the reaction (2-6 % yield) is *N*, *N*-dicyclohexyl-3-methoxyaniline arising from the C-N cross-coupling reaction between dicyclohexylamine and 3-bromoanisole. This impurity elutes prior to the main fraction in the column chromatography and is readily removed. A pure sample was obtained by combining early fractions from several reactions and re-chromatographing as follows. A 5-cm glass column is wet-packed (3% EtOAc/hexanes) with SiO_2 (150 g) topped with 0.5 cm sand. The crude amine (1.0 g) is loaded neat and eluted with 3% EtOAc/hexanes (700 mL), taking 50 mL fractions. Fractions 16-18 are concentrated by rotary evaporation (40 °C bath, 20 mmHg) to afford *N*, *N*-dicyclohexyl-3-methoxyaniline (0.68 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.11-1.17 (m, 2 H), 1.28-1.36 (m, 4 H), 1.55-1.66 (m, 6 H), 1.75-1.82 (m, 8 H), 3.26 (tt, J = 3.3, 11.6 Hz, 2 H), 3.79 (s, 3 H), 6.36 (dd, J = 2.3, 8.2 Hz, 1 H), 6.50 (t, J = 2.3 Hz, 1 H), 6.57 (dd, J = 2.3, 8.3 Hz, 1 H), 7.09 (t, J = 8.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 26.2, 26.6, 32.2, 55.3, 58.0, 103.2, 106.7, 113.3, 128.9, 150.4, 160.1.

Safety and Waste Disposal Information

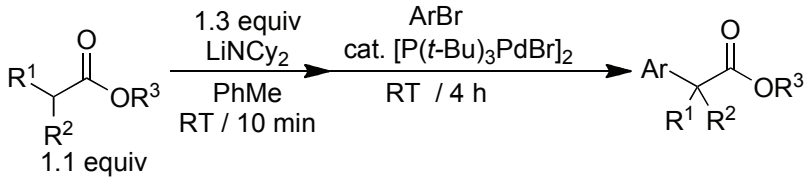
All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

The palladium-catalyzed coupling of carbonyl compounds and aryl halides is a convenient method for the synthesis of the aryl C-C bond in α-aryl carboxylic acid derivatives.[4-9] The α-arylation of esters proceeds in high yields and tolerates a variety of functional groups on both the ester and the aryl halide.[5] The α-arylation of esters with aryl bromides is reported in the literature to proceed at ambient temperature for catalyst systems containing tri-*tert*-butylphosphine as ligand.[5d, 5f, 5i, 5j] The catalyst for these systems is either generated by treating a Pd^0 precursor with tri-*tert*-butylphosphine or from the palladium (I) dimer, $[(P(t\text{-}Bu)_3Pd(\mu\text{-}Br)]_2$. $[(P(t\text{-}Bu)_3Pd(\mu\text{-}Br)]_2$ is

an effective catalyst for a number of different cross-coupling reactions.[5f, 5h-5j, 6c, 10-15] The α-arylation of esters with aryl bromides has been studied with the $[(P(t\text{-}Bu)_3Pd(\mu\text{-}Br)]_2$ as the catalyst (Table 1). The coupling of esters with aryl bromides containing different functional groups and heteroatoms proceeds in moderate to high yield with low catalyst loadings.[5h] This catalyst is advantageous because it can be weighed in air, even though tri-*tert*-butylphosphine is pyrophoric. $[(P(t\text{-}Bu)_3Pd(\mu\text{-}Br)]_2$ is a more active catalytic system for the coupling of esters and aryl bromides than other catalytic systems based on tri-*tert*-butylphosphine.[5d, 5h]

Table 1. α-Arylation of ester with aryl bromides catalyzed by $[(P(t\text{-}Bu)_3Pd(\mu\text{-}Br)]_2$.[5h]



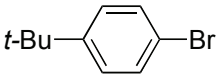
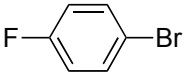
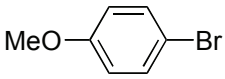
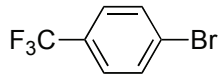
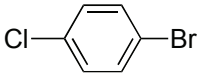
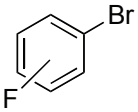
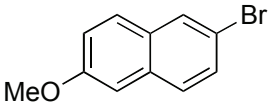
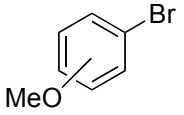
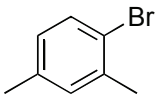
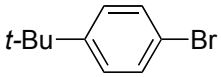
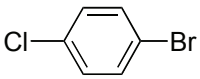
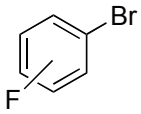
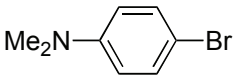
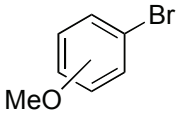
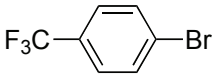
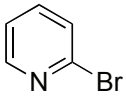
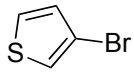
Entry	R^1	R^2	R^3	ArBr		Cat. loading	Yield[a]
1	H	H	*t*-Bu			0.2%	83%
2						0.4%	82%
3						0.2%	86%
4						0.4%	73%
5	Me	H	*t*-Bu			0.2%	83%
6					*p*-F	0.2%	88%
7					*m*-F	0.2%	90%
8						0.2%	75%
9					*p*-OMe	0.25%	87%
10					*m*-OMe	0.25%	84%
11					*o*-OMe	0.25%	87%

Table 1. (continued)

Entry	R^1	R^2	R^3	ArBr		Cat. loading	Yield[a]
12						0.05%	72%
13	Me	Me	Me			0.05%	72%
14						0.5%	89%
15					*p*-F	0.5%	85%
16					*m*-F	0.5%	72%
17						0.05%	88%
18					*p*-OMe	0.5%	85%
19					*m*-OMe	0.5%	88%
20					*m*-OMe	0.075%	77%[b]
21						0.5%	60%
22						0.5%	71%
23						0.5%	75%

a) Isolated yields (average of two runs) for reaction of 1 mmol of bromorarene in 3 mL toluene. b) This work

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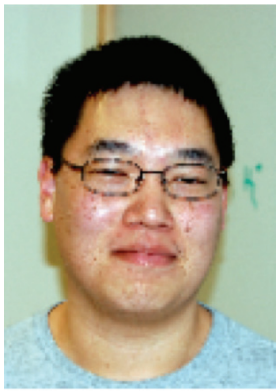
Appendix
Chemical Abstracts Nomenclature; (Registry Number)

Dicyclohexylamine: Cyclohexanamine, *N*-cyclohexyl-; (101-83-7)
n-Butyllithium: Lithium, butyl-; (109-72-8)
Methyl isobutyrate: Propanoic acid, 2-methyl-, methyl ester; (547-63-7)
3-Bromoanisole: Benzene, 1-bromo-3-methoxy-; (2398-37-0)
Di-μ-bromobis(tri-*tert*-butylphosphine)dipalladium; (185812-86-6)
Methyl 2-(3-methoxyphenyl)-2-methylpropanoate: Benzeneacetic acid, 3-methoxy-α,α-dimethyl-, methyl ester; (32454-33-4)

John F. Hartwig received his A. B. degree from Princeton in 1986 and his Ph.D. from the University of California, Berkeley in 1990 before conducting postdoctoral research at the Massachusetts Institute of Technology. He began his independent career at Yale University in 1992 and joined the faculty at Illinois in July 2006. Professor Hartwig's research focuses on the discovery and mechanistic understanding of organic reactions catalyzed by organometallic complexes. He has developed palladium-catalyzed cross-coupling reactions to form carbon-heteroatom bonds, palladium-catalyzed couplings of enolates, the functionalization of C-H bonds with boron reagents, asymmetric iridium-catalyzed allylic substitution, and catalysts for olefin hydroamination.

Ryan DeLuca was born in 1984 in Salt Lake City, Utah. He graduated from Southern Utah University with a B.S. degree in chemistry in 2007. He spent a year at the University of Illinois Urbana-Champaign working under the guidance of Professor John F. Hartwig. He is currently pursuing his Ph.D. at the University of Utah with Prof. Matthew Sigman.



David Huang was born in 1983 in Ames, Iowa. He received his B.S. from UC Berkeley in 2006, where he preformed undergraduate research in the Toste lab. David joined the Hartwig group at the University of Illinois in the fall of 2006 as a graduate student. His research focuses on the palladium-catalyzed coupling with enolates.

2010-118
fr 18-26
nmr400b h-1

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Current Data Parameters
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PROCNO                 1

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TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
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FIDRES          0.200774 Hz
AQ             2.4904180 sec
RG                 406.4
DW                76.000 usec
DE                 7.00 usec
TE                299.9 K
D1           0.10000000 sec
TD0                    1

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PL1                 6.00 dB
SFO1        399.8724694 MHz

F2 - Processing parameters
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WDW                   no
SSB                    0
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GB                     0
PC                1.00
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3	7.2583	2902.3765	1.47
4	7.2384	2894.4191	0.91
5	6.9395	2774.8979	0.57
6	6.9368	2773.8183	0.68
7	6.9353	2773.2185	0.72
8	6.9177	2766.1808	0.70
9	6.9017	2759.7828	0.88
10	6.8959	2757.4636	1.24
11	6.8910	2755.5042	0.82
12	6.8082	2722.3950	0.59
13	6.8069	2721.8752	0.61
14	6.8022	2719.9958	0.57
15	6.8010	2719.5159	0.55
16	6.7868	2713.8378	0.54
17	6.7814	2711.6785	0.50
18	3.8148	1525.4241	11.72
19	3.6661	1465.9634	12.07
20	1.5792	631.4747	20.00
21	1.5670	626.5963	0.39
22	1.3897	555.6994	0.16