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PALLADIUM-CATALYZED CARBONYLATIVE COUPLING OF ORGANOLEAD COMPOUNDS: SYNTHESIS OF SYMMETRICAL KETONES

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ABSTRACT

Organolead acetates can be carbonylated in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (5 mol%) and NaOMe (5 equiv.) in CH_3CN under atmospheric pressure of carbon monoxide at room temperature to afford symmetrical ketones.

The palladium-catalyzed carbonylative coupling of electrophiles with organometallic compounds, such as organostannanes, boron, aluminium, and zinc is an important method for the synthesis of ketones.[1] Recently, Jackson et al.[2] reported the synthesis of symmetrical ketones via palladium-catalyzed carbonylation of organozinc species. It is known[3] that $CoBr_2$(1.5 equiv.)-mediated carbonylation of organozinc reagents leads to symmetrical polyfunctional ketones. Here we report the palladium-catalyzed carbonylation of organolead acetates[4] leading to symmetrical ketones (Scheme 1).

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$$2\mathrm{RPb(OAc)_3} \quad + \quad \mathrm{CO\ (1\ atm)} \quad \xrightarrow[\mathrm{NaOMe\ (5\ equiv),\ CH_3CN,\ rt}]{\mathrm{Pd_2(dba)_3 \cdot CHCl_3\ (5\ mol\ \%)}} \quad \mathrm{RCOR}$$

Scheme 1.

The palladium-catalyzed carbonylative coupling of organolead acetates is summarized in Table 1. When the phenyllead triacetate (**1a**) reacted with carbon monoxide (1 atm) in the presence of $Pd_2(dba)_3 \cdot CHCl_3$(5 mol%) and NaOMe (5 equiv.) in acetonitrile for 3 h at room temperature, benzophenone (**2a**) was afforded in 70% yield (entry 1 in Table 1). The addition of NaOMe is critical.[5] Under the same conditions the reaction of *p*-tolyllead triacetate (**1b**) gave the dimerized ketone **2b** in 70% yield (entry 2). The *p*-methoxyphenyllead triacetate (**1c**) was readily coupled with carbon monoxide (1 atm) to provide the symmetrical ketone **2c**[6] in 72% yield (entry 3). The 2,4-dimethoxyphenyllead triacetate (**1d**) and 2-thienyllead triacetate (**1e**) were subjected to carbonylative coupling to afford the symmetrical ketones **2d** and **2e**[7] in 69% and 85% yields, respectively (entries 4 and 5). For di(2-furyl)lead diacetate (**1f**) the carbonylative coupling gave the ketone **2f**[8] in 74% yield (entry 6). This method was extended to alkenyllead triacetate (**1g**) and treatment of **1g** with carbon monoxide (1 atm) in the presence of $PdCl_2$ (5 mol %) as catalyst afforded the *trans*,*trans*-dibenzylideneacetone (**2g**) in 71% yield (entry 7).

Although the detailed mechanism for the formation of diaryl ketones remains obscure, it is presumed that organolead trimonoxide $RPb(OMe)_3$ is formed and drives facile oxidative addition with Pd(0) to give polar and reactive intermediate $RPdPb(OMe)_3$, followed by carbonylation reaction to furnish $RCOPdPb(OMe)_3$, which allows the transmetallation with $RPb(OMe)_3$ to afford RCOR. In summary, the palladium-catalyzed carbonylative coupling of organolead compounds afforded the symmetrical ketones.

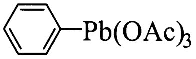
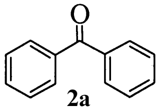
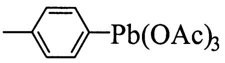
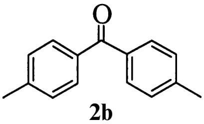
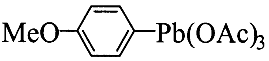
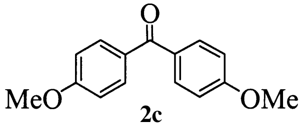
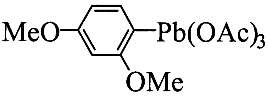
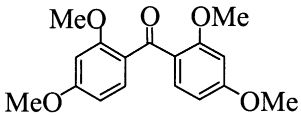
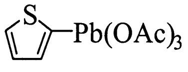
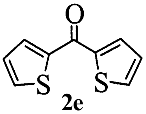
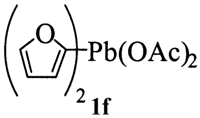
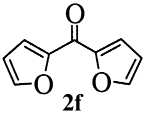
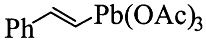
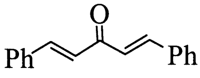
EXPERIMENTAL

Typical Procedures

Preparation of Bis-2-thiophenylmethanone (**2e**)

To a stirred solution of $Pd_2(dba)_3$ $CHCl_3$ (26 mg, 0.026 mmol), and NaOMe (138 mg, 2.56 mmol) in dry CH_3CN (25 mL) under atmospheric pressure of carbon monoxide was added 2-thienyllead triacetate (**1e**) (240 mg, 0.52 mmol) at room temperature. The reaction mixture was stirred

Table 1. The Palladium Catalyzed Carbonylative Coupling of Organolead Acetates

Entry	Organolead Compounds	Product	Isolated Yield (%)
1	 **1a**	 **2a**	70
2	 **1b**	 **2b**	70
3	 **1c**	 **2c**	72
4	 **1d**	 **2d**	69
5	 **1e**	 **2e**	85
6	 **1f**	 **2f**	74z
7	 **1g**	 **2g**	71[a]

[a] $PdCl_2$ (5 mol%) was used as a catalyst.

at room temperature for 3 h and extracted with diethyl ether (20 mL × 3). The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 10, $R_f = 0.38$) to afford the coupled product **2e** (42 mg, 85%). TLC, SiO_2, EtOAc/hexanes 1 : 10, $R_f = 0.38$.

m.p. 90° ~ 90.5°C ^{1}H NMR (400 Hz, CDCl$_3$) δ 7.18 (dd, 2H, J = 4.2, 0.7 Hz), 7.69 (dd, 2H, J = 4.2, 0.7 Hz), 7.89 (dd, 2H, J = 2.7, 1.1 Hz). IR (KBr) 3055, 2986, 1650, 1617, 1412, 1265 cm^{-1}. MS (EI) m/e (relative intensity) = 195 (M$^+$), 194 (73), 95 (100), 78 (11).

Di-*p*-tolyl-methanone (**2b**)

TLC, SiO$_2$, EtOAc/hexanes 1 : 10, R$_f$ = 0.40. m.p. 90°~93°C ^{1}H NMR (400 Hz, CDCl$_3$) δ 2.44 (s, 3H), 7.26 (d, 2H, J = 1.5 Hz), 7.70 (dd, 2H, J = 5.0, 1.5 Hz). IR (KBr) 3055, 2986, 1652, 1607, 1418, 1266 cm^{-1}. MS (EI) m/e (relative intensity) = 210 (M$^+$), 195 (21), 119 (100), 91 (30).

Bis-(4-methoxyphenyl)methanone (**2c**)

TLC, SiO$_2$, EtOAc/hexanes 1 : 10, R$_f$ = 0.25. m.p. 141°–143°C ^{1}H NMR (400 Hz, CDCl$_3$) δ 3.88 (s, 3H), 6.97 (m, 2H), 7.78 (m, 2H). IR (KBr) 3052, 1650, 1408 cm^{-1}. MS (EI) m/e (relative intensity) = 242 (12), 135 (100), 92 (20), 77 (25).

Bis-(2,4-dimethoxyphenyl)methanone (**2d**)

TLC, SiO$_2$, EtOAc/hexanes 1 : 10, R$_f$ = 0.26. ^{1}H NMR (400 Hz, CDCl$_3$) δ 3.60 (s, 3H), 3.82 (s, 3H), 6.42 (d, 1H, J = 2.2 Hz), 6.49 (dd, 1H, J = 2.2, 8.4 Hz), 7.49 (d, 1H, J = 8.4 Hz). IR (KBr) 3117, 3056, 2934, 1630, 1603, 1408, 1265 cm^{-1}. MS (EI) m/e (relative intensity) = 302 (M$^+$, 33), 284 (59), 164 (100), 150 (28). HRMS calcd for $C_{17}H_{18}O_5$: 302.1147, found: 302.1154.

Bis-2-furylmethanone (**2f**)

TLC, SiO$_2$, EtOAc/hexanes 1 : 10, R$_f$ = 0.34. m.p. 30°~32°C ^{1}H NMR (400 Hz, CDCl$_3$) δ 6.60 (dd, 2H, J = 3.0, 1.7 Hz), 7.55 (dd, 2H, J = 3.0, 0.6 Hz), 7.68 (dd, 2H, J = 1.7, 0.6 Hz). IR (KBr) 3134, 1633, 1467, 1402 cm^{-1}. MS (EI) m/e (relative intensity) = 163 (M$^+$), 162 (73), 95 (100), 78 (11).

1,5-Diphenyl-penta-1,4-dien-3-one (**2g**)

TLC, SiO_2, EtOAc/hexanes 1 : 10, $R_f = 0.33$. m.p. 104°~107°C ^1H NMR (400 Hz, $CDCl_3$) δ 7.10 (d, 1H, $J = 16$ Hz), 7.41 (m, 3H), 7.60 (m, 2H), 7.55 (d, 1H, $J = 16$ Hz). IR (KBr) 3055, 2987, 2860, 1654, 1620, 1265 cm^{-1}. MS (EI) m/e (relative intensity) = 235 (M^+), 234 (100), 233 (90), 131 (39), 103 (57), 77 (48).

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