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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 $Pd_2(dba)_3$ ·CHCl₃ (5 mol%) and NaOMe (5 equiv.) in CH₃CN 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 known³ that CoBr₂(1.5 equiv.)-mediated carbonylation of organozinc reagents leads to symmetrical polyfunctional ketones. Here we report the palladium-catalyzed carbonylation of organolead acetates⁴ leading to symmetrical ketones (Scheme 1).

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$$2\text{RPb}(\text{OAc})_3 + \text{CO}(1 \text{ atm}) \xrightarrow{\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3 (5 \text{ mol }\%)}_{\text{NaOMe} (5 \text{ equiv}), \text{CH}_3\text{CN}, \text{ rt}} \text{RCOR}$$

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 $Pd_2(dba)_3$ ·CHCl₃(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 2f⁸ 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 PdCl₂ (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 $Pd_2(dba)_3$ CHCl₃ (26 mg, 0.026 mmol), and NaOMe (138 mg, 2.56 mmol) in dry CH₃CN (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

Entry	Organolead Compounds	Product	Isolated Yield (%)
1	Pb(OAc) ₃ 1a		70
2	Pb(OAc) ₃ 1b		70
3	MeO- Pb(OAc) ₃ 1c	MeO 2c OMe	72
4	MeO- OMe 1d	MeO O OMe MeO O OMe 2d	69
5	S Pb(OAc) ₃ 1e	$\sim 2e^{O}$	85
6	$\begin{pmatrix} O \\ Pb(OAc)_2 \end{pmatrix}$		74z
7	Ph Pb(OAc) ₃ 1g	Ph Ph 2g	71 ^a

Table 1. The Palladium Catalyzed Carbonylative Coupling of Organolead Acetates

^aPdCl₂ (5 mol%) was used as a catalyst.

at room temperature for 3 h and extracted with diethyl ether ($20 \text{ mL} \times 3$). The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo. The crude product was separated by SiO₂ column chromatography (EtOAc/hexanes 1:10, R_f = 0.38) to afford the coupled product **2e** (42 mg, 85%). TLC, SiO₂, EtOAc/hexanes 1:10, R_f=0.38.

m.p. $90^{\circ} \sim 90.5^{\circ}$ C¹H NMR (400 Hz, CDCl₃) 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, SiO₂, EtOAc/hexanes 1:10, $R_f = 0.40$. m.p. $90^{\circ} \sim 93^{\circ}C^{-1}H$ NMR (400 Hz, CDCl₃) 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, SiO₂, EtOAc/hexanes 1:10, $R_f = 0.25$. m.p. $141^{\circ}-143^{\circ}C$ ¹H NMR (400 Hz, CDCl₃) 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, SiO₂, EtOAc/hexanes 1:10, $R_f = 0.26$. ¹H NMR (400 Hz, CDCl₃) 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, SiO₂, EtOAc/hexanes 1 : 10, $R_f = 0.34$. m.p. $30^{\circ} \sim 32^{\circ}C^{-1}H$ NMR (400 Hz, CDCl₃) 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).

SYMMETRICAL KETONES

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

TLC, SiO₂, EtOAc/hexanes 1:10, $R_f = 0.33$. m.p. $104^{\circ} \sim 107^{\circ}C$ ¹H NMR (400 Hz, CDCl₃) 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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