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Journal of Organometallic Chemistry 648 (2002) 297–301

Journal of Organometallic Chemistry

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Rhodium-catalyzed coupling of sodium tetraphenylborate with acid anhydrides in the presence or absence of norbornene

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Received 29 October 2001; accepted 9 November 2001

Abstract

Treatment of sodium tetraphenylborate with aliphatic or aromatic acid anhydrides in the presence of a rhodium catalyst gives the corresponding alkyl (or aryl) phenyl ketones in good yields. In the presence of norbornene, tandem three-component coupling products, 2-acyl-3-phenylnorbornanes are obtained. © 2002 Published by Elsevier Science B.V.

Keywords: Rhodium catalyst; Organoboron compounds; Acid anhydrides; Cross-coupling

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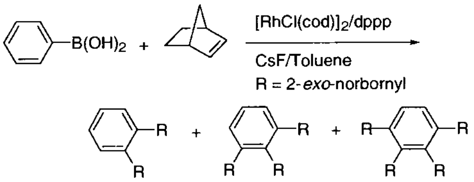
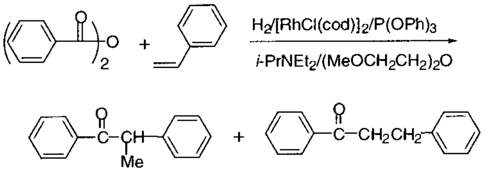
1. Introduction

Organoboron compounds are versatile reagents in the palladium-catalyzed coupling reaction with organic halides that is the well-known Suzuki–Miyaura reaction [1]. Recently, arylboron compounds including arylboronic acids and tetraaryl borates also have proved to be effective arylating reagents in rhodium catalysis. For example, polar alkenes such as enones [2], alkenylphosphonates [3] and nitroalkenes [4] undergo conjugate arylation. Mizoroki–Heck type coupling or hydroarylation occurs with styrenes or related alkenes [5]. The latter reaction proceeds with alkynes [6]. Aldehydes [7] and imines [8] are nucleophilically arylated.

We reported that arylboronic acids undergo a unique ‘merry-go-round’ type multiple alkylation up to four times upon treatment with norbornene (Scheme 1) [9]. The reaction involves mono- to tetraalkyl-substituted arylrhodium(I) species as the principal intermediates whose protonolysis leads to the products. On the other hand, we also found that alkenes react with acid anhydrides in the presence of a rhodium catalyst under hydrogen to give hydroacylated products (Scheme 2) [10]. The reaction proceeds via oxidative addition of the anhydrides to intermediary alkylrhodium(I) species. Thus, we considered that a new three-component coupling system via rhodium catalysis to produce certain aromatic ketones could be developed by adding acid anhydride to the reaction in Scheme 1. Consequently, we first examined the direct coupling of arylboron compounds with acid anhydrides in order to obtain appropriate conditions for the ketone synthesis, and then, the reaction in the presence of norbornene was investigated. It has been found that (a) the former reaction using sodium tetraphenylborate efficiently proceeds to afford the corresponding phenyl ketones (Scheme 3), and (b) the latter gives 2-acyl-3-phenylnorbornanes as the principal products along with the ketones (Scheme 4). These results are reported herein.



Scheme 1.



Scheme 2.

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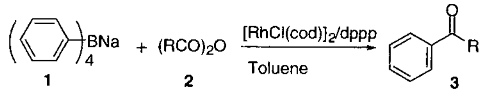
0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(01)01439-5

2. Results and discussion

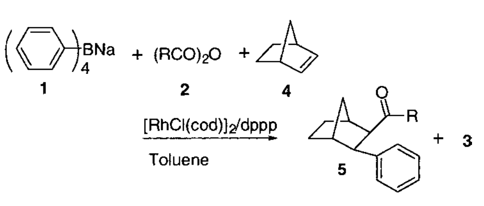
2.1. Reaction of sodium tetraphenylborate (1) with acetic anhydride (2a)

We first examined the reaction using phenylboronic acid, potassium phenyl(trifluoro)borate [11] and sodium tetraphenylborate (**1**) as phenylating reagents in the presence of acetic anhydride (**2a**). The former two species could not couple with **2a**, although during the performance of this work, related palladium-catalyzed coupling reactions of arylboronic acids with acid anhydrides [12,13], aryl trifluoroacetates [14] and benzoic acid thioesters [15] were reported. However, the borate **1** was found to react with **2a** efficiently to give acetophenone (**3a**).

Table 1 summarizes the results under different conditions. When **1** (1 mmol) was treated with **2a** (3 mmol) in the presence of $[RhCl(cod)]_2$ (0.01 mmol) and PPh_3 (0.04 mmol) in toluene at 100 °C for 2 h, the ketone **3a** was produced in 51% yield (entry 1). Using a bulky phosphine $P(t\text{-}Bu)_3$ in place of PPh_3 gave a somewhat better yield (entry 2). Bidentate ligands such as dppf and dppp further improved the reaction efficiency (entries 3 and 4). Thus, **3a** was obtained in 133% yield using dppp, suggesting that more than one phenyl group in **1** could be utilized. Dioxane and DMF as solvents were not effective (entries 5 and 6).

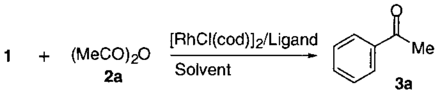


Scheme 3.



Scheme 4.

Table 1
Reaction of sodium tetraphenylborate (**1**) with acetic anhydride (**2a**) [a]



Entry	Ligand	Solvent	Yield of **3a** [b] (%)
1	PPh_3	Toluene	51
2	$P(t\text{-}Bu)_3$	Toluene	79
3	dppf	Toluene	91
4	dppp	Toluene	133
5	dppp	Dioxane	63
6	dppp	DMF	0

[a] The reaction was carried out at 100 °C for 2 h under N_2 using **1** (1 mmol), **2a** (3 mmol), $[RhCl(cod)_2]_2$ (0.01 mmol) and ligand (0.04 mmol for monodentate ligand or 0.02 mmol for bidentate ligand).

[b] Determined by GC analysis [(mmol of **3a**/mmol of **1**) × 100].

2.2. Reaction of 1 with various acid anhydrides 2

Shown in Table 2 are the results for the reaction of **1** (1 mmol) with anhydrides **2b**–**f** (2 mmol) using dppp as ligand in toluene. The reactions of **1** with linear aliphatic anhydrides **2b** and **2c** proceeded as well as that with **2a** to give ketones **3b** and **3c** in good yields. Isobutyric anhydride (**2d**) could also be used. Benzoic anhydrides **2e** and **2f** efficiently reacted to afford benzophenones **3e** and **3f**. Interestingly, using crotonic anhydride (**2g**) gave a mixture of (*E*)-1-phenyl-2-buten-1-one (**3g**) and 1,3-diphenylbutan-1-one (**3g′**). The formation of the diphenylated compound **3g′** implies that conjugate phenylation can also occur under the present conditions. By prolonging reaction time, **3g′** could be obtained as the major product.

2.3. Reaction of 1 with acid anhydrides 2 in the presence of norbornene (4)

When **1** (1 mmol) was treated together with **2a** (3 mmol) and **4** (1 mmol) in the presence of $[RhCl(cod)]_2$ and dppp in toluene at 100 °C for 2 h, *exo*-2-acetyl-*exo*-3-phenylbicyclo[2.2.1]heptane (**5a**) was produced in 47% yield as the three-component coupling product together with ketone **3a** (62%) (Scheme 4 and entry 1 in Table 3). Using **2a** (1 mmol) and **4** (3 mmol) selectively gave **5a**, but the yield was considerably low (entry 2). In this case, the formation of di-, tri- and tetranorbornylbenzenes was also observed (see Scheme 1). However, other possible compounds such as 1:1:2 coupling product of **1**, **2a** and **4** and further alkylated ketones were not detected. Increasing both the amounts of **2a** and **4** afforded more than 60% yield of **5a** (entries 3 and 5).

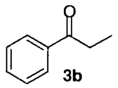
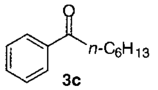
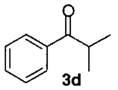
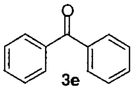
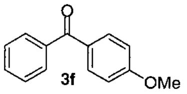
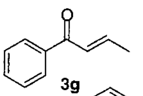
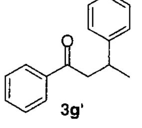
As expected, the reactions of **1** with **2b**, **2e** and **2f** gave the corresponding *exo*-2-acyl-*exo*-3-phenylbicyclo[2.2.1]heptane **5b**, **5e** and **5f**, respectively (entries 6–8). Note that **5f** was obtained with a high yield of 126%, although the reaction was relatively slow.

2.4. Reaction scheme

A plausible mechanism for the formation of ketones **3** and **5** is illustrated in Scheme 5. The first step may involve the generation of phenylrhodium(I) species **A** by transmetalation [16]. Then, oxidative addition of **2** to give acylphenylrhodium(III) intermediate **B** followed by reductive elimination affords **3**. In the presence of **4**, insertion of it into the phenyl–rhodium bond of **A** in an *exo*-fashion to produce alkylrhodium intermediate **C**. Then, oxidative addition of **2** to give acylalkylrhodium(III) intermediate **D** occurs and the subsequent reductive elimination affords **5** [17,18]. As proposed previously [9], intramolecular rhodation via C–H cleavage in **C** to give rhodacycle **E** and the successive reductive elimination affords 2-(2-norbornyl)-phenylrhodium species **F**. Subsequently, the insertion–cyclorhodation–reductive elimination process occurs up to three times, resulting in the formation of multiply alkylated benzenes (Scheme 1).

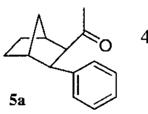
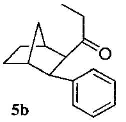
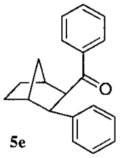
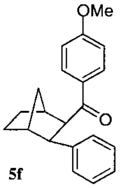
The formation of **5** along with **3** in the presence of **4** implies that the transformation of **A** to **C** competes with that to **B**. The lack of 1:1:2 coupling product of **1**, **2** and **4** and further alkylated ketones even using an excess amount of **4** (e.g. entry 4 in Table 3) suggests that the oxidative addition giving **D** is more favorable than the formation of **F** via **E**. The observed high selectivity of **5f** could be attributed to the fact that the oxidative addition of **2f** to **A** is relatively slow due to the presence of the electron-donating methoxy substituent. Even in this case, no trace of products derived from **F** or more alkylated species was observed. This leads us to deduce that another factor inhibiting the formation of them intervenes. However, the details are not clear at the present stage.

Table 2
Reaction of sodium tetraphenylborate **1** with various acid anhydride **2** [a]

Entry	Anhydride	Time (h)	Product	Yield[b] (%)
1	**2b**: R = Et	2	 **3b**	155
2	**2c**: R = *n*-Hexyl	24	 **3c**	133
3	**2d**: R = *i*-Pr	4	 **3d**	121
4	**2e**: R = Ph	20	 **3e**	150
5	**2f**: R = 4-$MeOC_6H_4$	24	 **3f**	142
6	**2g**: R = MeCH=CH	2 (24)	 **3g**  **3g'**	93 (43) 39 (77)

[a] The reaction was caried out at 100 °C under N_2 using **1** (1 mmol), **2a** (2 mmol), $[RhCl(cod)]_2$ (0.01 mmol) and dppp (0.02 mmol).
[b] Determined by GC analysis [(mmol of **3**/mmol of **1**) × 100].

Table 3
Reaction of sodium tetraphenylborate **1** with acid anhydride **2a**, **2b**, **2e**, and **2f** in the presence of norbornene (**4**) [a]

Entry	Anhydride	Ratio of 1:2:4	Products, % yield[b]	
			5	3
1	**2a**	1:3:1	 **5a** 47	**3a** 62
2[c]	**2a**	1:1:3	**5a** 27	**3a** 0
3	**2a**	1:3:3	**5a** 60 (55)	**3a** 68
4	**2a**	1:2:7	**5a** 42	**3a** 45
5	**2a**	1:5:7	**5a** 64	**3a** 65
6	**2b**	1:3:3	 **5b** 84 (46)	**3b** 86
7	**2e**	1:3:3	 **5e** 71 (52)	**3e** 45
8[d]	**2f**	1:3:3	 **5f** 126 (43)	**3f** 41

[a] The reaction was caried out at 100 °C for 2 h under N_2 using **1** (1 mmol), **2a** (2 mmol), $[RhCl(cod)]_2$ (0.01 mmol) and dppp (0.02 mmol).
[b] Determined by GC analysis [(mmol of product/mmol of **1**) × 100]. Value in parenthesis is yield after chromatographic purification.
[c] Di-, tri-, and tetranorbornylbenzenes were also produced in 33, 19 and 17% yields, respectively.
[d] Reaction for 24 h.

3. Experimental

3.1. General

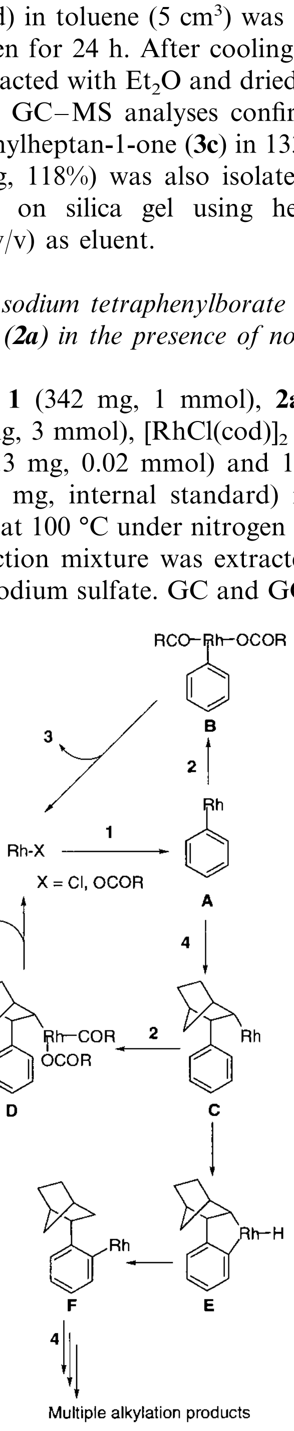
^1H- and ^{13}C-NMR spectra were recorded at 400 and 100 MHz, respectively, for $CDCl_3$ solutions. MS analysis was made by EI. GC analysis was carried out using a silicone OV-17 glass column (i.d. 2.6 mm × 1.5 m). All the starting materials were commercially available and used as received. The solvents employed were purified by standard methods before use. The following experimental procedure may be regarded as typical in methodology and scale.

*3.2. Reaction of sodium tetraphenylborate (**1**) with heptanoic anhydride (**2c**)*

A mixture of **1** (342 mg, 1 mmol), **2c** (484 mg, 2 mmol), $[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol), dppp (8.3 mg, 0.02 mmol) and 1-methylnaphthalene (ca. 100 mg, internal standard) in toluene (5 cm^3) was stirred at 100 °C under nitrogen for 24 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. GC and GC–MS analyses confirmed the formation of 1-phenylheptan-1-one (**3c**) in 133% yield. The product (224 mg, 118%) was also isolated by column chromatography on silica gel using hexane–diethyl ether (99.8:0.2, v/v) as eluent.

*3.3. Reaction of sodium tetraphenylborate (**1**) with acetic anhydride (**2a**) in the presence of norbornene (**4**)*

A mixture of **1** (342 mg, 1 mmol), **2a** (306 mg, 3 mmol), **4** (282 mg, 3 mmol), $[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol), dppp (8.3 mg, 0.02 mmol) and 1-methylnaphthalene (ca. 100 mg, internal standard) in toluene (5 cm^3) was stirred at 100 °C under nitrogen for 2 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. GC and GC–MS analyses confirmed the formation of *exo*-2-acetyl-*exo*-3-phenylbicyclo[2.2.1]heptane (**5a**) and acetophenone (**3a**) in 60 and 68% yields, respectively. The product mixture was fractionated by column chromatography on silica gel. Elution with hexane–Et_2O (99.2:0.8, v/v) gave compound **5a** (118 mg, 55%).



Scheme 5.

3.4. Products

Compounds **3a**, **3b**, **3d**–**f** were identified by comparison with the corresponding commercial samples. The analytical data of other products are given below.

1-Phenylheptan-1-one (**3c**) [19]: oil; ^{1}H-NMR δ 0.89 (t, 3H, $J = 7.0$ Hz), 1.27–1.42 (m, 6H), 1.70–1.77 (m, 2H), 2.96 (t, 2H, $J = 7.3$ Hz), 7.45 (t, 2H, $J = 7.3$ Hz), 7.55 (t, 1H, $J = 7.3$ Hz), 7.96 (d, 2H, $J = 7.3$ Hz); ^{13}C-NMR δ 14.00, 22.49, 24.30, 29.01, 31.63, 38.59, 128.00, 128.50, 132.81, 137.08, 200.56; MS *m*/*z* 190 (M^+).

(*E*)-1-Phenyl-2-buten-1-one (**3g**) [20]: oil; ^{1}H-NMR δ 2.00 (dd, 3H, $J = 1.5$, 6.6 Hz), 6.90 (qd, 1H, $J = 1.5$, 15.4 Hz), 7.08 (qd, 1H, $J = 6.6$, 15.4 Hz), 7.46 (t, 2H, $J = 7.3$ Hz), 7.55 (t, 1H, $J = 7.3$ Hz), 7.93 (d, 2H, $J = 7.3$ Hz); ^{13}C-NMR δ 18.58, 127.53, 128.48 (overlapped), 132.56, 137.90, 145.04, 190.78; MS *m*/*z* 146 (M^+).

1,3-Diphenylbutan-1-one (**3g′**) [21]: m.p. 71–72 °C; ^{1}H-NMR δ 1.34 (d, 3H, $J = 6.9$ Hz), 3.18 (dd, 1H, $J = 8.3$, 16.7 Hz), 3.30 (dd, 1H, $J = 5.8$, 16.3 Hz), 3.42–3.55 (m, 1H), 7.17–7.21 (m, 1H), 7.25–7.32 (m, 4H), 7.44 (t, 2H, $J = 7.3$ Hz), 7.54 (t, 1H, $J = 7.3$ Hz), 7.93 (d, 2H, $J = 8.0$ Hz); ^{13}C-NMR δ 21.85, 35.56, 47.02, 126.26, 126.85, 128.05, 128.51, 128.54, 132.95, 137.20, 146.56, 199.07: MS *m*/*z* 224 (M^+).

exo-2-Acetyl-*exo*-3-phenylbicyclo[2.2.1]heptane (**5a**) [22]: oil; ^{1}H-NMR δ 1.19–1.27 (m, 1H), 1.36–1.43 (m, 2H), 1.50 (s, 3H), 1.58–1.62 (m, 2H), 2.24 (d, 1H, $J = 10.3$ Hz), 2.36 (s, 1H), 2.55 (s, 1H), 3.00 (d, 1H, $J = 10.3$ Hz), 3.20 (d, 1H, $J = 10.3$ Hz), 7.16–7.18 (m, 3H), 7.22–7.26 (m, 2H); ^{13}C-NMR δ 28.43, 31.13, 31.24, 37.11, 38.42, 43.50, 52.63, 62.51, 126.40, 128.22, 128.33, 142.34, 209.82; MS *m*/*z* 214 (M^+).

exo-2-Phenyl-3-propionylbicyclo[2.2.1]heptane (**5b**): oil; ^{1}H-NMR δ 0.46 (t, 3H, $J = 7.0$ Hz), 1.22–1.26 (m, 1H), 1.35–1.43 (m, 2H), 1.58–1.65 (m, 2H), 1.75–1.96 (m, 2H), 2.29–2.34 (m, 1H), 2.35 (s, 1H), 2.52 (s, 1H), 2.99 (d, 1H, $J = 10.3$ Hz), 3.17 (d, 1H, $J = 10.3$ Hz), 7.12–7.16 (m, 3H), 7.20–7.26 (m, 2H); ^{13}C-NMR δ 7.00, 28.50, 31.21, 37.25, 37.41, 38.53, 43.38, 52.75, 61.31, 126.28, 128.23, 128.30, 142.46, 212.17; MS *m*/*z* 228 (M^+). Anal. Found: C, 84.16; H, 8.84. Calc. for $C_{16}H_{20}O$: C, 84.16; H, 8.83%.

exo-2-Benzoyl-*exo*-3-phenylbicyclo[2.2.1]heptane (**5e**) [17]: m.p. 87–88 °C; ^{1}H-NMR δ 1.40–1.52 (m, 3H), 1.69–1.75 (m, 2H), 2.42–2.48 (m, 2H), 2.69 (s, 1H), 3.29 (d, 1H, $J = 10.3$ Hz), 3.84 (d, 1H, $J = 10.3$ Hz), 6.88–6.96 (m, 5H), 7.21 (t, 2H, $J = 7.3$ Hz), 7.34 (t, 1H, $J = 7.3$ Hz), 7.54 (t, 2H, $J = 7.3$ Hz); ^{13}C-NMR δ 28.94, 31.14, 37.38, 39.16, 43.52, 53.87, 56.18, 125.80, 127.60, 127.84, 127.97, 128.38, 131.94, 138.49, 141.78, 201.68; MS m/z 276 (M^+).

3-(4-Methoxybenzoyl)-2-phenylbicyclo[2.2.1]heptane (**5f**): m.p. 150–151 °C; ^{1}H-NMR δ 1.46–1.50 (m, 3H), 1.69–1.73 (m, 2H), 2.42 (m, 1H), 2.48 (d, 1H, $J = 10.3$ Hz), 2.67 (s, 1H), 3.28 (d, 1H, $J = 10.3$ Hz), 3.78 (s, 3H), 3.76–3.78 (m, 1H), 6.71 (d, 2H, $J = 8.8$ Hz), 6.90–6.98 (m, 5H), 7.57 (d, 2H, $J = 8.8$ Hz). ^{13}C-NMR δ 29.05, 31.13, 37.38, 39.28, 43.48, 54.06, 55.29, 55.77, 113.02, 125.77, 127.57, 128.34, 130.24, 131.59, 141.94, 162.61, 200.04; MS m/z 306 (M^+). Anal. Found: C, 82.12; H, 7.15. Calc. for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24%.

4. Note added in proof

After this manuscript had been accepted for publication, the relevant reactions of aryl boronic acids with carboxylic acids using $Pd(PPh_3)_4$ [R. Kakino, H. Narahashi, I. Shimizu, A. Yamamoto, Chem. Lett. (2001) 1242] and with anhydrides using $[Rh(ethylene)Cl]_2$ [C.G. Frost, K.J. Wadsworth, Chem. Commun. (2001) 2316] have appeared.

Acknowledgements

This research was supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) “Exploitation of Multi-Element Cyclic Molecules” from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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