

# Hypervalent Iodine in Synthesis Part 39.‡ Palladium-catalyzed Carbonylative Coupling of Iodonium Salts and Potassium Aryltrifluoroborates by Carbon Monoxide†

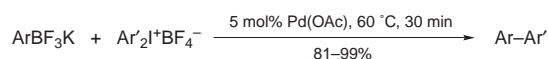
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Diaryl ketones and chalcones are obtained in good yields by palladium-catalyzed carbonylative coupling of diaryliodonium salts and (*E*)-phenylethenyl(phenyl)iodonium tetrafluoroborates with potassium aryltrifluoroborates in an atmosphere of carbon monoxide under mild conditions.

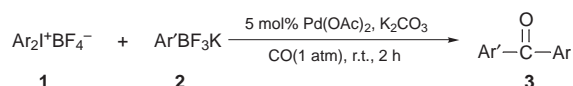
Cross-coupling reactions of organoboron compounds with organic halides and triflates catalyzed by palladium, known as the Suzuki reaction, have been shown to provide a versatile tool for the selective formation of C–C bonds.<sup>1</sup> Among the variety of organoboron compounds, potassium aryltrifluoroborates, ArBF<sub>3</sub>K, are very stable, water resistant and easily isolated. However, there has been little research on this type of organoboron compounds except for reports on their reactions with amino acids<sup>2</sup> and palladium-catalyzed cross-coupling reactions with arenediazonium tetrafluoroborates.<sup>3</sup>

We have recently reported<sup>4</sup> that palladium-catalyzed coupling of potassium aryltrifluoroborates with diaryliodonium tetrafluoroborates offered an efficient method for C–C bond formation on aromatic substrates (Scheme 1).



Scheme 1

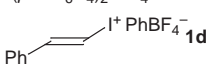
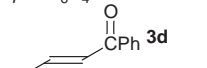
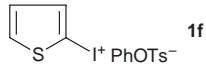
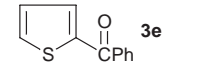
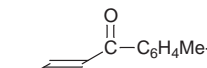
Recently, the alkoxyacylation and carbonylation of diaryliodonium salts in the presence of palladium to yield esters and ketones has been reported.<sup>5</sup> The facts suggested that diaryliodonium salts could serve as substrates for carbonylative cross-coupling reaction with potassium aryltrifluoroborates. Cross-coupling reactions were thus carried out under an atmosphere of carbon monoxide in the presence of an added base (Scheme 2).



Scheme 2

Results are given in Table 1. Unlike the palladium-catalyzed cross-coupling reaction of potassium aryltrifluoroborates with diaryliodonium tetrafluoroborates that we have reported, the palladium-catalyzed carbonylative coupling of potassium aryltrifluoroborates with diaryliodonium

Table 1 Palladium-catalyzed carbonylation of iodonium salts and potassium aryltrifluoroborates<sup>a</sup>

Entry	Iodonium salt	Potassium aryltrifluoroborate	Product	Yield(%) <sup>b</sup>
1	Ph <sub>2</sub> I <sup>+</sup> BF <sub>4</sub> <sup>-</sup> <b>1a</b>	PhBF <sub>3</sub> K <b>2a</b>	PhCOPh <b>3a</b>	92
2	( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> I <sup>+</sup> BF <sub>4</sub> <sup>-</sup> <b>1b</b>	<b>2a</b>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> COPh <b>3b</b>	90
3	( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> I <sup>+</sup> BF <sub>4</sub> <sup>-</sup> <b>1c</b>	<b>2a</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> COPh <b>3c</b>	84
4	 <b>1d</b>	<b>2a</b>	 <b>3d</b>	85
5	 <b>1f</b>	<b>2a</b>	 <b>3e</b>	80
6	<b>1b</b>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> BF <sub>3</sub> K <b>2b</b>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> COC <sub>6</sub> H <sub>4</sub> Me- <i>p</i> <b>3f</b>	83
7	( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> I <sup>+</sup> BF <sub>4</sub> <sup>-</sup> <b>1g</b>	<b>2b</b>	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> COC <sub>6</sub> H <sub>4</sub> Me- <i>p</i> <b>3g</b>	87
8	<b>1d</b>	<b>2b</b>	 <b>3h</b>	82
9	<b>1a</b>	<b>2b</b>	PhCOC <sub>6</sub> H <sub>4</sub> Me- <i>p</i> <b>3j</b>	88
10	<b>1c</b>	<b>2b</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> COC <sub>6</sub> H <sub>4</sub> Me- <i>p</i> <b>3j</b>	79
11	<b>1a</b>	<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> BF <sub>3</sub> K <b>2c</b>	PhCOC <sub>6</sub> H <sub>4</sub> OMe- <i>o</i> <b>3k</b>	80
12	<b>1b</b>	<b>2c</b>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> COC <sub>6</sub> H <sub>4</sub> OMe- <i>o</i> <b>3l</b>	83

<sup>a</sup> Reagents and conditions: 1 mmol iodonium salt, 1.2 mmol potassium aryltrifluoroborate, 1.5 mmol K<sub>2</sub>CO<sub>3</sub>, 5 mmol% Pd(OAc)<sub>2</sub> in 10 ml DME at room temperature and 1 atm CO for 2 h. <sup>b</sup> Isolated yield.

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

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tetrafluoroborates did not take place without added base and biaryls were the major products under such circumstances. Of added bases used (NaCO<sub>3</sub>, NaOAc, NaHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, KOAc, Et<sub>3</sub>N, Bu<sub>3</sub>N and Et<sub>2</sub>NH), the

best was  $K_2CO_3$  which suppressed the formation of biaryl byproducts (<10%) under an atmosphere of carbon monoxide.

Diphenyliodonium tetrafluoroborate **1a** reacted with potassium phenyltrifluoroborate **2a** in the presence of 5 mol%  $Pd(OAc)_2$  and  $K_2CO_3$  in DME at room temperature to give benzophenone **3a** in 92% yield. When diphenyliodonium chloride and tosylate were used in place of the tetrafluoroborate the reaction required a longer time of 6 h and gave a lower yield (57%) of product. This indicates that the tetrafluoroborate counter is superior to halide and tosylate counter ions in this reaction. This carbonylative coupling could be successfully applied to other potassium aryltrifluoroborates. With potassium *p*-methylphenyltrifluoroborate **2b** and *o*-methoxyphenyltrifluoroborate **2c**, *p*-methylbenzophenone **3i** and *o*-methoxybenzophenone **3k** were obtained in 88 and 80% yields, respectively. The reaction could also be extended to other iodonium salts **1b**, **1c** and **1g** under the same conditions. As for unsymmetric 2-thienylphenyliodonium tosylate **1f**, it could also undergo facile coupling with potassium phenyltrifluoroborate **2a** to give 2-benzoylthiophene **3e** as the single coupling product. Similarly, (*E*)-phenylethenyl(phenyl)iodonium tetrafluoroborate **1d** also underwent carbonylation with potassium phenyltrifluoroborate **2a** and potassium *p*-methylphenyltrifluoroborate **2b** under the same conditions to produce (*E*)-chalcone **3d** and (*E*)-*p*-methylchalcone **3h** in 85 and 82% yields, respectively.

It has been reported that hydroxy(tosyloxy)iodobenzene.  $PhI(OH)OTs$ , could be utilized in a coupling reaction with organoboron compounds in the presence of a palladium catalyst to give biaryls as products.<sup>6</sup> However, under the same conditions of this carbonylation in reaction with potassium phenyltrifluoroborate **2a** was not obtained and biphenyl was formed in 81% yield.

In summary, potassium aryltrifluoroborates are alternative organoboron compounds that can be applied to palladium-catalyzed carbonylative coupling of iodonium salts to give ketones under mild conditions in good yields.

## Experimental

*Typical Procedure for the Palladium-catalyzed Carbonylation of Iodonium Salts and Potassium Aryltrifluoroborates.*—Under an atmospheric pressure of carbon monoxide, 1.2 mmol potassium aryltrifluoroborate in 10 ml DME was injected into a mixture of 1 mmol iodonium salt, 1.5 mmol  $K_2CO_3$  and 5 mmol%  $Pd(OAc)_2$ . The resulting mixture was stirred at room temperature for 2 h, then diluted with saturated aqueous  $NH_4Cl$  and extracted with  $2 \times 5$  ml diethyl ether. The combined organic layer was dried over anhydrous  $MgSO_4$  and the solvent removed *in vacuo*. The residue was isolated by TLC (silica gel) with  $EtOAc$ -*n*-hexane (1:10) as developer to give ketone product which was purified by recrystallization from ethanol or light petroleum (bp 50–60 °C).

*Physical and Spectroscopic Data for the Products.*—**Benzophenone 3a**. Recrystallized from ethanol, mp 48–50 °C (lit.<sup>7</sup> 49–51 °C);  $\delta_H$  (60 MHz,  $CDCl_3$ ), 7.47 (s, 4H), 7.60 (m, 2H), 7.80 (m, 4H); IR (KBr) 3050, 1650, 1600, 1450, 1270, 760, 700, 640  $cm^{-1}$ .

**4-Methylbenzophenone 3b**. Recrystallized from light petroleum, mp 56–57 °C (lit.<sup>8</sup> 59.5 °C);  $\delta_H$  (60 MHz,  $CDCl_3$ ) 2.39 (s, 3H), 7.22 (m, 2H), 7.32–7.84 (m, 7H); IR (KBr) 3050, 1650, 1600, 1280, 730, 700  $cm^{-1}$ .

**4-Chlorobenzophenone 3c**. Recrystallized from ethanol, mp 74–76 °C (lit.<sup>9</sup> 75–77 °C);  $\delta_H$  (60 MHz,  $CDCl_3$ ) 7.33 (m, 2H), 7.30–7.70 (m, 5H), 7.66 (m, 2H); IR (KBr)  $\nu$  3030, 1650, 1590, 1280, 1090, 840, 790, 730, 700  $cm^{-1}$ .

**E-Chalcone 3d**. Recrystallized from light petroleum, mp 53–54 °C (lit.<sup>10</sup> 55–57 °C)  $\delta_H$  (60 MHz,  $CDCl_3$ ) 7.22–7.80 (m, 10H), 8.00 (m, 2H); IR (KBr)  $\nu$  3040, 1660, 1600, 1450, 1330, 1210, 1010, 750, 690  $cm^{-1}$ .

**2-Benzoylthiophene 3e**. Recrystallized from light petroleum mp 56–57 °C (lit.<sup>11</sup> 56–58 °C);  $\delta_H$  (60 MHz,  $CDCl_3$ ) 7.12 (m, 1H), 7.28–8.03 (m, 7H); IR (KBr)  $\nu$  1620, 1590, 1400, 1280, 830, 700, 640  $cm^{-1}$ .

**4,4'-Dimethylbenzophenone 3f**. Recrystallized from ethanol, mp 92–93 °C (lit.<sup>12</sup> 95 °C);  $\delta_H$  (60 MHz,  $CDCl_3$ ) 2.36 (s, 6H) 7.20 and 7.64 (AB q, 8H); IR (KBr)  $\nu$  1640, 1600, 1280, 1180, 750  $cm^{-1}$ .

**4-Methyl-4'-methoxybenzophenone 3g**. Recrystallized from ethanol, mp 102–103 °C (lit.<sup>13</sup> 105–107 °C);  $\delta_H$  (60 MHz,  $CDCl_3$ ) 2.40 (s, 3H), 3.86 (s, 3H), 6.90 (m, 2H), 7.21 (m, 2H), 7.64 (m, 2H), 7.74 (m, 2H); IR (KBr)  $\nu$  2980, 1650, 1600, 1450, 1260, 1020, 850, 760, 690  $cm^{-1}$ .

**E-4'-Methylchalcone 3h**. Recrystallized from light petroleum mp 56–57 °C (lit.<sup>14</sup> 59–60 °C)  $\delta_H$  (60 MHz,  $CDCl_3$ ) 2.36 (s, 3H), 7.15–7.75 (m, 9H), 7.98 (m, 2H); IR (KBr)  $\nu$  1665, 1610, 1340, 1210, 820, 760, 700  $cm^{-1}$ .

**4-Chloro-4'-methylbenzophenone 3j**. Recrystallized from light petroleum, mp 125–127 °C (lit.<sup>15</sup> 129–130 °C);  $\delta_H$  (60 MHz,  $CDCl_3$ ) 2.38 (s, 3H), 7.36 and 7.49 (AB q, 8H) IR (KBr)  $\nu$  3050, 1640, 1600, 1280, 840, 750, 700  $cm^{-1}$ .

**2-Methoxybenzophenone 3k**. Recrystallized from ethanol, mp 36–37 °C (lit.<sup>16</sup> 40 °C);  $\delta_H$  (60 MHz,  $CDCl_3$ ) 3.90 (s, 3H), 6.90 (m, 2H), 7.67 (m, 5H), 8.20 (m, 2H); IR (KBr)  $\nu$  3050, 2960, 1680, 1590, 1250, 1170, 1020, 840, 790, 740, 700  $cm^{-1}$ .

**2-Methoxy-4'-methylbenzophenone 3l**. Recrystallized from ethanol, mp 61–62 °C (lit.<sup>17</sup> 64–65 °C);  $\delta_H$  (60 MHz,  $CDCl_3$ ) 2.43 (s, 3H), 3.93 (s, 3H), 6.80–7.20 (m, 2H), 7.20–7.60 (m, 4H), 7.90–8.20 (m, 2H), IR (KBr)  $\nu$  3050, 2985, 1660, 1260, 1030, 825, 740, 690  $cm^{-1}$ .

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