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.

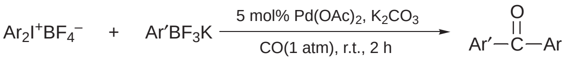
Cross-coupling reactions of organoboron compounds with organic halides and triflates catalyzed by palladium, known as the Suzuki reaction, have been shown to provide a versatile tool for the selective formation of C–C bonds.[1] Among the variety of organoboron compounds, potassium aryltrifluoroborates, $ArBF_3K$, 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[2] and palladium-catalyzed cross-coupling reactions with arenediazonium tetrafluoroborates.[3]

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

$$ArBF_3K + Ar'_2I^+BF_4^- \xrightarrow[\text{81–99\%}]{\text{5 mol\% Pd(OAc), 60 °C, 30 min}} Ar\text{–}Ar'$$

Scheme 1

Recently, the alkoxycarbonylation and carbonylation of diarylidonium salts in the presence of palladium to yield esters and ketones has been reported.[5] 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).

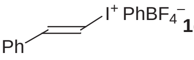
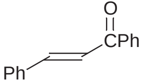
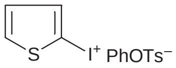
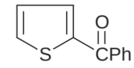
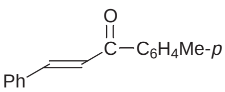


$$\underset{\mathbf{1}}{Ar_2I^+BF_4^-} + \underset{\mathbf{2}}{Ar'BF_3K} \xrightarrow[\text{CO(1 atm), r.t., 2 h}]{\text{5 mol\% Pd(OAc)}_2\text{, K}_2\text{CO}_3} \underset{\mathbf{3}}{Ar'\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}Ar}$$

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 tetrafluoroborates did not take place without added base and biaryls were the major products under such circumstances. Of added bases used ($NaCO_3$, NaOAc, $NaHCO_3$, K_2CO_3, KOAc, Et_3N, Bu_3N and Et_2NH), the

Table 1 Palladium-catalyzed carbonylation of iodonium salts and potassium aryltrifluoroborates[a]

Entry	Iodonium salt	Potassium aryltrifluoroborate	Product	Yield(%)[b]
1	$Ph_2I^+BF_4^-$ **1a**	$PhBF_3K$ **2a**	PhCOPh **3a**	92
2	(p-$MeC_6H_4)_2I^+BF_4^-$ **1b**	**2a**	p-MeC_6H_4COPh **3b**	90
3	(p-$ClC_6H_4)_2{}^+BF_4^-$ **1c**	**2a**	p-ClC_6H_4COPh **3c**	84
4	 **1d**	**2a**	 **3d**	85
5	 **1f**	**2a**	 **3e**	80
6	**1b**	p-$MeC_6H_4BF_3K$ **2b**	p-$MeC_6H_4COC_6H_4Me$-p **3f**	83
7	(p-$MeOC_6H_4)_2{}^+BF_4^-$ **1g**	**2b**	p-$MeOC_6H_4COC_6H_4Me$-p **3g**	87
8	**1d**	**2b**	 **3h**	82
9	**1a**	**2b**	$PhCOC_6H_4Me$-p **3j**	88
10	**1c**	**2b**	p-$ClC_6H_4COC_6H_4Me$-p **3j**	79
11	**1a**	o-$MeOC_6H_4BF_3K$ **2c**	$PhCOC_6H_4OMe$-o **3k**	80
12	**1b**	**2c**	p-$MeC_6H_4COC_6H_4OMe$-o **3l**	83

[a] *Reagents and conditions*: 1 mmol iodonium salt, 1.2 mmol potassium aryltrifluoroborate, 1.5 mmol K_2CO_3 5 mmol% $Pd(OAc)_2$ in 10 ml DME at room temperature and 1 atm CO for 2 h. [b] Isolated yield.

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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 phenytrifluoroborate **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.[6] However, under the same conditions of this carbonylation in reaction with potassium phenyltrilluoroborate **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 × 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.[7] 49–51 °C); δ_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.[8] 59.5 °C); δ_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.[9] 75–77 °C); δ_H (60 MHz, $CDCl_3$) 7.33 (m, 2H, 7.30–7.70 (m, 5H), 7.66 (m, 2H); IR (KBr) ν 3030, 1650, 1590, 1280, 1090, 840, 790, 730, 700 cm^{-1}.

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

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

4,4′-*Dimethylbenzophenone* **3f**. Recrystallized from ethanol, mp 92–93 °C (lit.[12] 95 °C); δ_H (60 MHz, $CDCl_3$) 2.36 (s, 6H) 7.20 and 7.64 (AB q, 8H); IR (KBr) ν 1640, 1600, 1280, 1180, 750 cm^{-1}.

4-*Methyl*-4′-*methoxybenzophenone* **3g**. Recrystallized from ethanol, mp 102–103 °C (lit.[13] 105–107 °C); δ_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) ν 2980, 1650, 1600, 1450, 1260, 1020, 850, 760, 690 cm^{-1}

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

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

2-*Methoxybenzophenone* **3k**. Recrystallized from ethanol, mp 36–37 °C (lit.[16] 40 °C); δ_H (60 MHz, $CDCl_3$) 3.90 (s, 3H), 6.90 (m, 2H), 7.67 (m, 5H), 8.20 (m, 2H); IR (KBr) ν 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.[17] 64–65 °C); δ_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) ν 3050, 2985, 1660, 1260, 1030, 825, 740, 690 cm^{-1}.

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