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A catalyst- and solvent-free Suzuki coupling reaction of sodium tetraphenylborate with hypervalent iodanes

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The catalyst- and solvent-free Suzuki coupling reaction of sodium tetraphenylborate with hypervalent iodanes was achieved under microwave irradiation in the absence of base. A rapid and convenient method for the formation of carbon–carbon bonds resulted in good yields.

Keywords: Suzuki reaction, sodium tetraphenylborate, iodane, microwave irradiation

The Suzuki reaction is one of the most versatile and utilised reactions for the selective construction of carbon–carbon bonds, in particular, for the formation of biaryls.[1] In the reaction, organoboranes are generally used to react with aryl halides or triflates in organic solvents in the presence of base although sometimes long reaction times and high reaction temperatures are required.[2] In order to improve and simplify the reaction protocol, hypervalent iodine compounds have been focused on as alternatives to aryl halides or triflates due to their high reactivity, especially iodonium salts,[3] in reactions with nucleophiles. This is generally explained by the "hyperleaving group" properties of the phenyliodanyl group, which is a remarkably good nucleofuge with a leaving group ability about 10^6 times greater than that of triflate,[3g] and a number of publications of using iodonium salts in Suzuki reactions have been reported in recent years.[4] Recently, Leadbeater and Marco reported a catalyst-free Suzuki coupling reaction,[5] in which aryl halides reacted with arylboronic acids under microwave irradiation without catalyst and afforded biaryls in good yields.

This report was very interesting, and we were inspired to find other catalyst-free Suzuki-type coupling reactions to extend the scope of this reaction. As part of a programme to investigate the catalyst-free Suzuki reaction, we used hypervalent iodanes in place of aryl halides and explored the catalyst-free coupling of sodium tetraphenylborate with iodanes in water at room temperature; an efficient catalyst- and base-free Suzuki-type coupling reaction was found giving good yields.[6] (Figure 1).

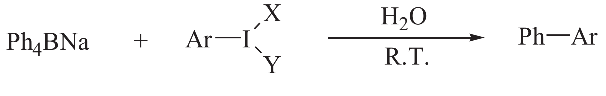
Taking advantage of above results, we checked the reaction under microwave irradiation because microwave-assisted organic syntheses have some advantages such as large reaction rates, high purity of products, and ease of manipulation.[7] In particular, microwave-irradiated procedures in water or in the absence of solvents for organic synthesis have attracted considerable interest in recent years due to their efficient and environmentally benign conditions.[4,8]

We report here a rapid and efficient catalyst- and solvent-free microwave-assisted Suzuki coupling reaction of sodium tetraphenylborate with hypervalent iodanes.

We used a readily available iodane PhI(OH)OTs,[9] referred to as Koser's reagent, to react with the same molar quantity of sodium tetraphenylborate under microwave irradiation, and biphenyl was afforded in 50% yield in 3 min. To improve the yield, a series of experiments was performed on the coupling of sodium tetraphenylborate with Koser's reagent. It was found that when the molar ratio of sodium tetraphenylborate to Koser's reagent reached 3: 1, 85% yield of biphenyl was afforded under microwave irradiation for 2 min. The result prompted us to investigate the reactions of sodium tetraphenylborate **(1)** with a series of iodanes **(2)** under the optimised conditions to afford products **(3)**. They are shown in Scheme **1** and the results are summarised in Table 1. The products were characterised by ^{1}H NMR, IR, MS spectra and melting points, which were consistent with the literature data.

It is clear from Table 1 that hypervalent iodanes can be used as powerful electrophilic agents in Suzuki reactions, all the reactions could be completed in 2 min and most gave products in good to excellent yields (entries **1–6**). It is well known that iodonium salts have been widely used in Suzuki reactions. However, reports of the use of iodanes in the coupling reactions are few[4a,10] and to our knowledge they have been no reports on catalyst- and solvent-free Suzuki reactions of sodium tetraphenylborate with iodanes under microwave irradiation.

In summary, a rapid and simple method with good yields for formation of carbon–carbon bonds is afforded by the microwave-promoted catalyst- and solvent-free Suzuki reaction and the scope of catalyst-free Suzuki coupling reactions has been extended.



$$Ph_4BNa + Ar{-}I\begin{smallmatrix}X\\Y\end{smallmatrix} \xrightarrow[R.T.]{H_2O} Ph{-}Ar$$

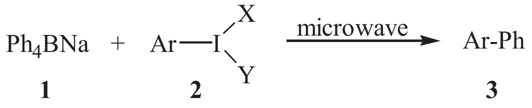
Figure 1

Experimental

M.p.s were determined on a digital m.p. apparatus and were not corrected. IR spectra were recorded on a FT-170 SX instrument, ^{1}H NMR spectra were measured on a Bruker AM-400 FT-NMR spectrometer and mass spectra were determined on HP5989A mass spectrometer. Microwave irradiation was carried out with an LWMC-201 microwave synthesiser (Nanjing Sanle Microwave Equipment Corporation) at full power (650W). Hydroxy(tosyloxy)iodobenzene (**2a**),[9] (diacetoxyiodo)benzene (**2b**),[11] [bis(tifluoroacetoxy)iodo] benzene (**2c**),[12] iodosobenzene tetrafluoroborate (**2d**),[13] iodosylbenzene (**2e**),[14] hydroxy(tosyloxy)*p*-chloroiodobenzene (**2f**)[15] and 1-hydroxy-1,2-benziodoxol-3(*1H*)-one (**2g**)[16] were prepared according to the literature procedures. Sodium tetraphenylborate was commercially available.

The reaction of sodium tetraphenylborate with iodanes general procedure

Sodium tetraphenylborate (1) (513 mg, 1.5 mmol) and iodane (2) (0.5 mmol) were mixed in a 10 ml glass tube. The mixture tube was placed inside an alumina bath and irradiated for 1–2 min (shown in Table 1) in a microwave synthesiser (LWMC-201) at full power (650W). After cooling to room temperature the mixture was extracted with diethyl ether (20 ml × 3). The organic layer was dried over



$$\underset{\mathbf{1}}{Ph_4BNa} + \underset{\mathbf{2}}{Ar{-}I\begin{smallmatrix}X\\Y\end{smallmatrix}} \xrightarrow{microwave} \underset{\mathbf{3}}{Ar\text{-}Ph}$$

Scheme 1

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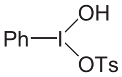
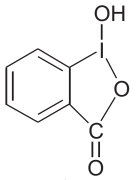
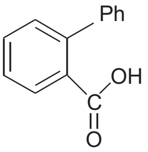
Table 1 Coupling reactions of sodium tetraphenylborate with iodanes under microwave irradiation

Entry	Iodane	Product	Time/min	Yield/%[a]
1	 **2a**	Ph–Ph **3a**	2	85
2	$PhI(OAc)_2$ **2b**	**3a**	2	91
3	$PhI(OCOCF_3)_2$ **2c**	**3a**	1	84
4	$Ph\text{-}I^+\text{-}O\text{-}I^+\text{-}Ph$ $2BF_4^-$ **2d**	**3a**	1	80
5	PhI=O **2e**	**3a**	1	68
6	$p\text{-}ClC_6H_4I(OAc)_2$ **2f**	$p\text{-}Cl\text{-}C_6H_4\text{-}Ph$ **3b**	2	78
7	 **2g**	 **3c**	1	56

[a]Isolated yield.

anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated on a silica gel plate using hexane as developer and afforded the pure product **3** in good yields.

Biphenyl (**3a**): M.p. 68–69°C (Lit.[17] 69–72°C). ^{1}H NMR (400 MHz, $CDCL_3$) δ: 7.32–7.36 (m, 2H), 7.42-7–46 (m, 4H), 7.58–7.61 (m, 4H); IR (KBr) ν = 3035, 1569, 1481, 730 cm^{-1}; MS (70eV, EI) *m/z* (%): 154 (M$^+$, 100).

p-Chlorobiphenyl (**3b**): M.p. 74–75°C (Lit.[18] 77°C). ^{1}H NMR (400 MHz, $CDCL_3$) δ: 7.32–7.34 (m, 1H), 7.36–7.39 (m, 2H), 7.40–7.44 (m, 2H), 7.46–7.50 (m, 2H), 7.51–7.55 (m, 2H); IR (KBr) ν = 3067, 3035, 1479, 1099,1005, 833, 760 cm^{-1}; MS (70eV, EI) *m/z* (%): 188 (M$^+$, 100).

2-Biphenylcarboxylic acid (**3c**): M.p. 108–110°C (Lit.[19] 112°C). ^{1}H NMR (400 MHz, $CDCL_3$) δ: 7.29–7.48 (m, 7H), 7.52–7.55 (m, 1H), 7.89–7.95 (m, 1H), 11.0 (br, 1H); IR (KBr) ν = 3400–2400 (br), 1700, 1685, 1306, 1296 cm^{-1}; MS (70eV, EI) *m/z* (%): 198 (M$^+$, 100).

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