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Metal catalyst-free Suzuki-type coupling reaction in water

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Abstract—The catalyst-free Suzuki-type coupling reaction of sodium tetraphenylborate with iodanes was achieved in good yields in water at room temperature. Similarly, the coupling of sodium tetraphenylborate with iodonium salts easily occurred in acidic water medium at 50 °C in good yields. Both coupling reactions were also promoted by microwave irradiation in water in short time.

1. Introduction

The Suzuki reaction is one of the most versatile and utilized reactions for the selective construction of carbon–carbon bonds, in particular for the formation of biaryls.[1] For the development of improved conditions for the Suzuki reaction, a wide range of metal complexes have been used as catalysts in these coupling reactions, attention has particularly been focused on palladium. Recently, N. E. Leadbeater and M. Marco first reported a catalyst-free Suzuki coupling reaction,[2] in which aryl halides reacted with arylboronic acids under microwave irradiation without catalyst and afforded biaryls in good yields (Fig. 1). It was also reported that sodium tetraphenylborate could be used in place of phenylboronic acid as a phenylating agent in the reaction. Due to the development of pressure and the need for specialized sealed vessels for this method, the development of mild and efficient catalyst-free reaction conditions are required.

In order to improve and extend the scope of this reaction, especially to improve the coupling reaction using sodium tetraphenylborate as a phenylating agent, we focused our attention on hypervalent iodonium compounds. As powerful electrophilic reagents, hypervalent iodine compounds, in particular, iodonium salts have found synthetic application in the reactions with various nucleophiles,[3] they have also been used in Suzuki reaction to replace aryl halides and triflates affording products in excellent yields under mild reaction conditions.[4] Using hypervalent iodonium compounds as alternative for aryl halides and triflates, we investigated the coupling reaction of them with sodium tetraphenylborate. Here we would like to report the metal catalyst-free Suzuki-type coupling reaction of sodium tetraphenylborate with hypervalent iodonium compounds in water.

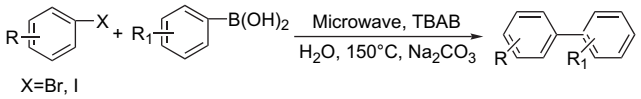
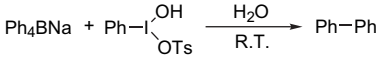


Figure 1.

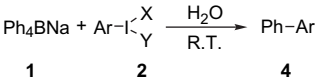
2. Results and discussion

2.1. The coupling reaction of sodium tetraphenylborate with iodanes in water

At the beginning, a readily available iodane, hydroxy(tosyloxy)iodobenzene,[5] referred to as Koser's reagent was used to couple with sodium tetraphenylborate in water at room temperature, the product of a biphenyl in good yield was obtained after the mixture was stirred for a short period of time (Scheme 1). To determine suitable reaction conditions, a series of experiments were performed on the coupling of sodium tetraphenylborate (**1**) with Koser's reagent (**2a**) to form biphenyl (**4a**), we found that when 2 equiv of **1** were used to react with **2a** in water for 0.5 h at room temperature, nearly quantitative **4a** was formed. Under the optimal reaction conditions, we checked the reactions of a series of typical iodanes stable in water with sodium tetraphenylborate (Scheme 2), the results were summarized in Table 1.[6]



Scheme 1.



Scheme 2.

Keywords: Suzuki-type reaction; Sodium tetraphenylborate; Iodanes; Iodonium salts; Microwave irradiation.
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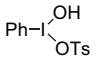
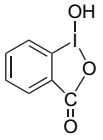
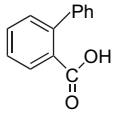
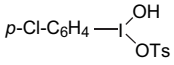
Table 1. The results of the Suzuki reaction of sodium tetraphenylborate with iodanes

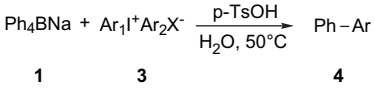
Entry	Iodane	Product	Yield (%)[a]
1	**2a** 	**4a** Ph–Ph	97
2	**2b** $PhI(OAc)_2$	**4a**	78
3	**2c** $PhI(OCOCF_3)_2$	**4a**	90
4	**2d** $Ph–I^+–O–I^+–Ph$ $2BF_4^-$	**4a**	91
5	**2e** PhI=O	**4a**	55[b]
6	**2f** p-MeO–$C_6H_4I(OAc)_2$	**4b** p-MeO–C_6H_4–Ph	99
7	**2g** p-Cl–$C_6H_4I(OAc)_2$	**4c** p-Cl–C_6H_4–Ph	47
8	**2h** 	**4d** 	90
9	**2i** 	**4c**	84

[a] Isolated yields.
[b] The reaction was run with sodium tetraphenylborate (2 equiv), iodosylbenzene (1 equiv), and p-TsOH (2 equiv) in water for 0.5 h.

It was shown that when Ar was a phenyl with electron-donating group, the yield of **4b** was almost quantitative (entry 6) and when Ar was a phenyl with electron-withdrawing group, the yields of **4c** were somewhat lower (entries 7 and 9) compared to **4b** (entry 6) and **4a** (entry 1), respectively. When iodosylbenzene (**2e**) was treated with **1** under the same reaction conditions, the reaction did not occur even when the reaction mixture was stirred for longer time at room temperature or in heating conditions, but after adding 2 equiv of p-TsOH and stirred for 0.5 h, product **4a** was obtained in 55% yield.[7]

2.2. The coupling reaction of sodium tetraphenylborate with iodonium salts in acidic water

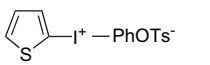
Analogous to iodanes, iodonium salts have high reactivity to sodium tetraphenylborate. However, we found that the catalyst-free Suzuki reaction did not occur when iodonium salts were used to react with sodium tetraphenylborate in water in the presence or absence of base at room temperature or higher temperatures. Then, we explored the coupling reaction in acidic conditions, a quite different result was obtained: the mixture of diphenyliodonium chloride (**3a**) with **1** was only stirred for a short time at 50 °C in acidic water, a product of biphenyl (**4a**) was obtained in good yield. Prompted by the result, a series of experiments were performed on the coupling of **1** with **3a** to determine the suitable reaction conditions. It was found that p-TsOH was the most efficient acid and the reaction of 4 equiv of sodium tetraphenylborate, 2 equiv of p-TsOH, and 1 equiv of diphenyliodonium chloride in water at 50 °C for 30 min afforded biphenyl in 95% yield. We extended this protocol to other iodonium salts, the symmetrical and unsymmetrical biaryls were readily available in high yields as shown in Scheme 3 and the results were summarized in Table 2.



Scheme 3.

From Table 2, it was shown that except iodonium salt **3c** (entry 3), all iodonium salts worked well in the reaction providing products in good to excellent yields. Iodonium salt **3f** with electron-withdrawing substituent in phenyl gave a somewhat lower yield product **4g** (entry 6) than electron-rich phenyliodonium salts **3b**, **3d**, and **3e** (entries 2, 4, and 5). It was also observed that the anions of iodonium salts affected the yield greatly: with **3b** the reaction was completed after only 0.5 h affording **4e** in 92% yield (entry 2); when **3h** was used in place of **3b** under the same reaction conditions, the reaction was not completed even after 28 h and the product was obtained in poor 29% yield. To try to improve the yield, we increased the amount of acid to 6 equiv and found that the coupling reaction was completed after 1 h, giving the desired product in a much improved 78% yield (entry 8). Similarly, **3i** was also mixed with 6 equiv of p-TsOH and 4 equiv of **1**, the reaction could give 72% product (entry 9), compared to a yield of 20% after a reaction time of 35 h under the standard conditions. With a tosylate iodonium salt **3g**, the reaction time was somewhat longer

Table 2. The results of the coupling reaction of sodium tetraphenylborate with iodonium salts

Entry	Iodonium salt	Product	Time (h)	Yield (%)[a]
1	**3a** $Ph_2I^+Cl^-$	**4a**	0.5	95
2	**3b** $(p$-Me–$C_6H_4)_2I^+Br^-$	**4e** p-Me–C_6H_4–Ph	0.5	92
3	**3c** $(p$-Br–$C_6H_4)_2I^+Br^-$	**4f** p-Br–C_6H_4–Ph	1	61
4	**3d** p-Me–C_6H_4–I^+–$PhBr^-$	**4e**	1	94
5	**3e** p-MeO–C_6H_4–I^+–$PhBr^-$	**4b**	1	92
6	**3f** $(m$-NO_2–$C_6H_4)_2I^+Br^-$	**4g** m-NO_2–C_6H_4–Ph	1	80
7	**3g** 	**4h** 	2	81
8	**3h** $(p$-Me–$C_6H_4)_2I^+BF_4^-$	**4e**	1	78[b]
9	**3i** $(p$-MeO–$C_6H_4)_2I^+BF_4^-$	**4b**	2	72[b]

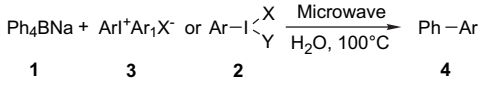
[a] Isolated yields.
[b] The reaction was run with sodium tetraphenylborate (4 equiv), iodonium salt (1 equiv), and p-TsOH (6 equiv) in water.

and the yield was somewhat lower compared with **3a** due to the influence of the anion (entry 7).

2.3. The coupling reaction of sodium tetraphenylborate with iodonium salts and iodanes under microwave irradiation in water

Taking advantage of the above results, we further checked the coupling reaction under microwave irradiation because microwave-assisted organic syntheses have some advantages such as fast reaction rates, high purity of products, and ease of manipulation.[8] In particular, the microwave-irradiated procedures in water medium for organic synthesis have attracted considerable interest in recent years due to their efficient and environmentally benign conditions.[9]

We used diphenyliodonium chloride (**3a**) to investigate the coupling reaction with sodium tetraphenylborate (**1**) under microwave irradiation in water, we found that the coupling was easy to be carried out and when the molar ratio of **1** to **3a** reached 2:1, the best result of 90% biphenyl was afforded under microwave irradiation for 4 min at 100 °C. Under the optimized conditions, the coupling reactions of iodonium salts **3** with **1** were shown in Scheme 4 and the good results were given in Table 3.



Scheme 4.

It was shown that most reactions could be completed in 4 min affording products in good to excellent yields (entries 1–6). However, iodonium salt **3f** with electron-withdrawing substituent in phenyl only provided **4g** in 37% yield after 5 min (entry 7). We also observed that the anions of iodonium salts affected the yield strongly: with **3b** the reaction was completed after only 3 min and afforded **4e** in 93% yield (entry 2); when **3h** was used in place of **3b** under the same reaction conditions, even after a prolonged reaction time of 15 min, **4e** was obtained in a poor 41% yield (entry 8).

Under the same reaction conditions, we found that iodanes (**2**) could react with sodium tetraphenylborate (**1**) and afforded products **4** in good yields only in 2 min (Scheme 4, Table 3).

Table 3. The results of the Suzuki reaction under microwave irradiation

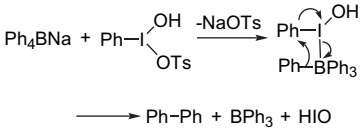
Entry	Iodonium salt and iodanes	Product	Time (min)	Yield (%)[a]
1	**3a**	**4a**	4	90
2	**3b**	**4e**	3	93
3	**3c**	**4f**	3	91
4	**3d**	**4e**	2	74
5	**3e**	**4b**	4	77
6	**3g**	**4h**	3	80
7	**3f**	**4g**	5	37
8	**3h**	**4e**	15	41
9	**2a**	**4a**	2	83
10	**2b**	**4a**	2	87
11	**2c**	**4a**	1	82
12	**2d**	**4a**	1	80
13	**2e**	**4a**	1	65
14	**2g**	**4c**	2	73
15	**2h**	**4d**	1	67

[a] Isolated yield.

The reaction with iodanes needed shorter reaction time than with iodonium salts meant that iodanes had more activity towards sodium tetraphenylborate. However, it may be due to their stability in water, in particular, under microwave irradiation part of them could be decomposed.

3. Conclusions

In summary, we have presented here our observations that the metal catalyst-free Suzuki-type coupling reaction of sodium tetraphenylborate with hypervalent iodonium compounds can be performed in water. The mechanism probably involved first a nucleophilic substitution of acid radical of iodonium salts or iodanes by Ph_4B^-, then, an intramolecular coupling reaction was accompanied to yield biaryls as shown by the coupling of sodium tetraphenylborate with Koser's reagent (Scheme 5). This coupling reaction provided fast and efficient method for preparation of biaryls, it had some advantages such as mild reaction conditions, simple procedure, and good yields. Furthermore, the scope of the catalyst-free Suzuki coupling reactions could be extended.



Scheme 5.

4. Experimental

4.1. General

Mps were determined on a digital mp 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 reaction was carried out with a single-mode cavity Sanle WHL70S-01 Microwave Synthesizer (Nanjing Sanle Microwave Equipment Corporation). Iodonium salts were prepared according to the literature procedures.[10] Iodanes were prepared according to the literature procedures.[5,11] Sodium tetraphenylborate is commercially available.

4.2. The general procedure for reaction of sodium tetraphenylborate with iodanes in water

Sodium tetraphenylborate (**1**) (342 mg, 1.0 mmol) and iodane (**2**) (0.5 mmol) were added in 5 mL of H_2O. The mixture was stirred for 0.5 h at room temperature and quenched with brine (5 mL). The mixture was extracted with diethyl ether (20×3 mL), and the organic layer was dried over anhydrous $MgSO_4$, and then evaporated in vacuo. The crude product was separated by a silica gel plate using hexane as developer to afford the pure product **4** in good yields.

4.3. The general procedure for reaction of sodium tetraphenylborate with iodonium salts in water

Sodium tetraphenylborate (**1**) (137 mg, 0.4 mmol, 4.0 equiv), iodonium salt (**3**) (0.1 mmol), and *p*-TsOH (38 mg, 0.2 mmol, 2.0 equiv) were added in 5 mL of H_2O. The mixture was stirred at 50 °C until it was complete. After cooling to room temperature the mixture was extracted with diethyl ether (20×3 mL), and the organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was separated by a silica gel plate using hexane as developer to afford the pure product **4** in good yields.

4.4. The general procedure for reaction of sodium tetraphenylborate with iodonium salts and iodanes under microwave irradiation in water

Sodium tetraphenylborate (**1**) (513 mg, 1.5 mmol), iodonium salt (**3**) or iodane (**2**) (0.75 mmol), and 5 mL of water were added to a 50 mL flask with a condenser. The vessel was placed inside the center of the microwave synthesizer and then exposed to microwave irradiation (250 W) to heat it at reflux for 1–15 min at 100 °C. After irradiation, the reaction mixture was cooled to room temperature and extracted with diethyl ether (20×3 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was separated by a silica gel plate using hexane as eluent and the pure product **4** was afforded.

4.4.1. Biphenyl (4a). Mp 68–69 °C (lit.[12] 69–72 °C). ^{1}H NMR ($CDCl_3$): 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 (70 eV, EI) *m*/*z* (%): 154 (M^+, 100).

4.4.2. *p*-Methoxybiphenyl (4b). Mp 86–87 °C (lit.[13] 88 °C). ^{1}H NMR ($CDCl_3$): δ=3.83 (s, 3H), 6.96–6.98 (m, 2H), 7.27–7.31 (m, 1H), 7.38–7.42 (m, 2H), 7.51–7.55 (m, 4H); IR (KBr): ν=3068, 3033, 1262, 1035, 835, 761 cm^{-1}; MS (70 eV, EI) *m*/*z* (%): 184 (M^+, 100).

4.4.3. *p*-Chlorobiphenyl (4c). Mp 74–75 °C (lit.[14] 77 °C). ^{1}H NMR ($CDCl_3$): 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 (70 eV, EI) *m*/*z* (%): 188 (M^+, 100).

4.4.4. 2-Biphenylcarboxylic acid (4d). Mp 108–110 °C (lit.[15] 112 °C). ^{1}H NMR ($CDCl_3$): δ=7.30–7.39 (m, 7H), 7.53 (m, 1H), 7.93 (m, 1H), 11.0 (br, 1H); IR (KBr): ν=3400–2400 (br), 1700, 1685, 1306, 1296 cm^{-1}; MS (70 eV, EI) *m*/*z* (%): 198 (M^+, 100).

4.4.5. *p*-Methylbiphenyl (4e). Mp 43–46 °C (lit.[16] 44–47 °C). ^{1}H NMR ($CDCl_3$): δ=2.39 (s, 3H), 7.23–7.26 (m, 2H), 7.30–7.34 (m, 1H), 7.40–7.44 (m, 2H), 7.48–7.51 (m, 2H), 7.56–7.59 (m, 2H); IR (KBr): ν=3067, 3033, 1488, 1007, 823, 766, 690 cm^{-1}; MS (70 eV, EI) *m*/*z* (%): 168 (M^+, 100).

4.4.6. *p*-Bromobiphenyl (4f). Mp 83–85 °C (lit.[16] 85–87 °C). ^{1}H NMR ($CDCl_3$): δ=7.33–7.37 (m, 1H), 7.42–7.46 (m, 4H), 7.52–7.57 (m, 4H); IR (KBr): ν=3064, 3031, 1477, 1393, 1080, 830, 767, 691 cm^{-1}; MS (75 eV, EI) *m*/*z* (%): 234 (M+1), 233 (M^+, 13.3), 232 (100).

4.4.7. *m*-Nitrobiphenyl (4g). Mp 56–58 °C (lit.[16] 58–60 °C). ^{1}H NMR ($CDCl_3$): δ=7.40–7.67 (m, 6H), 7.83–7.95 (m, 1H), 8.11–8.23 (m, 1H), 8.40–8.45 (m, 1H); IR (KBr): ν=3064, 3036, 1536, 1362, 877, 772, 733 cm^{-1}; MS (75 eV, EI) *m*/*z* (%): 199 (M^+, 100).

4.4.8. 2-Phenylthiophene (4h). Oil.[4a] ^{1}H NMR ($CDCl_3$): δ=7.10–7.13 (m, 1H), 7.30–7.34 (m, 2H), 7.37–7.40 (m, 1H), 7.46–7.49 (m, 2H), 7.62–7.66 (m, 2H); IR (KBr) ν=3103, 3062, 3036, 1496, 1451, 747 cm^{-1}; MS (70 eV, EI) *m*/*z* (%): 160 (M^+, 100).

Acknowledgements

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