Rapid catalyst-free carbon–carbon bonds coupling reaction under ambient conditions and ultrasonic irradiation

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The catalyst-free coupling reaction of sodium tetraphenylborate with hypervalent iodine compounds was achieved under ultrasonic irradiation in water without a base, providing a convenient and rapid method for the formation of carbon–carbon bonds in good yield.

Keywords: coupling reaction, sodium tetraphenylborate, hypervalent iodine compounds, ultrasound

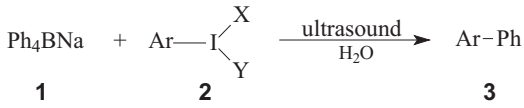
The formation of carbon–carbon bonds is very important in organic synthesis. The Suzuki reaction (palladium-catalysed cross-coupling of aryl halides with boronic acids) is one of the most versatile and utilised reactions for the selective construction of carbon–carbon bonds, in particular for the formation of biaryls.[1] In order to improve and simplify the Suzuki reaction, a wide range of metal complexes has been used as catalyst in these coupling reactions, attention particularly being focused on palladium. Since the use of metal catalysts leads to the generation of waste which can have a number of problems associated with it, the eradication of the catalyst from the Suzuki reaction offers significant advantages. Recently, Leadbeater and Marco first reported a catalyst-free Suzuki coupling reaction: aryl halides reacted with arylboronic acids under microwave irradiation without catalyst in water at 150°C and afforded biaryls in good yields.[2] However, due to the development of pressure using water as solvent and the need for specialised sealed vessels, this method is not suitable for organic reactions carried out at atmospheric pressure. In order to find an alternative to halides, Yan *et al.* focused their attention on hypervalent iodine compounds due to their high reactivity and excellent yields in Suzuki reactions under mild conditions,[3] their readily availability and their nontoxic properties. They found that when iodanes were mixed with sodium tetraphenylborate, they reacted smoothly in water at room temperature and provided good yields of coupling products.[4] They also investigated the coupling reaction under microwave irradiation, and found that the microwave irradiation could shorten the reaction times greatly.[5] Because temperature control is some difficult in microwave irradiation reactions at atmospheric pressure and in order to develop a fast and efficient catalyst-free coupling reaction at ambient temperature, I have investigated the reaction of hypervalent iodine compounds with sodium tetraphenylborate under ultrasonic irradiation. Here, I report for the first time a fast catalyst-free coupling reaction at ambient temperature in water under ultrasonic irradiation, which can extend the scope of catalyst-free Suzuki coupling reactions.

The sonochemical reaction was carried out in a thermostatted (25°C) ultrasonic cleaning bath of frequency 50 kHz in air.

Initially molar equivalents of sodium tetraphenylborate and hydroxy(tosyloxy)iodobenzene were mixed. It was found that after only 3 min an 85% yield of biphenyl was obtained under ultrasonic irradiation. Then, reaction with different molar equivalents of sodium tetraphenylborate to hydroxy(tosyloxy) iodobenzene were carried out, and it was found that all these reactions occurred easily and gave good yields of the same product. Equal equivalents of sodium tetraphenylborate and hypervalent iodine compound was chosen as the most suitable ratio. Under the optimal reaction conditions, the reactions of sodium tetraphenylborate (**1**) with a series of hypervalent iodine compounds (**2**) to produce coupling products (**3**) were investigated. They are shown in Scheme 1 and the results are summarised in Table 1.

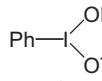
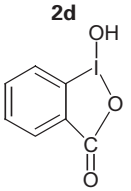
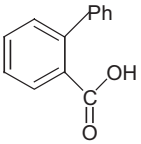
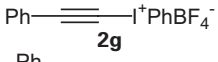
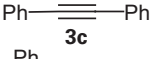
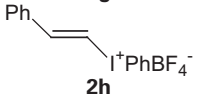
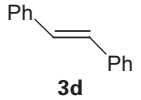
From Table 1, it is noteworthy that except for iodosylbenzene **2d** (entry 4)**,** all hypervalent iodine compounds reacted with sodium tetraphenylborate smoothly under ultrasonic irradiation and reaction completed in 5 min, giving products in good yields (Entries **1** to **5**). Iodanes **2a** and **2c** in the reaction needed shorter time and gave higher yields of product compared with **2b** and **2e,** which meant that iodanes with strongly acidic anions were more effective in the reaction (Entries **1** and **3**). The hypervalent iodonium salts **2f**–**2h** also reacted with sodium tetraphenylborate easily and **2h** gave a stereoselective product **3d**, which showed that ultrasound enhanced the reaction rates greatly compared with the result reported by Yan (that the reaction did not occur in a normal manner).[6]

In summary, a rapid and efficient method for formation of carbon–carbon bonds is afforded by the catalyst-free coupling reaction under ultrasonic irradiation in a water



Scheme 1

Table 1 The results of the coupling reactions of sodium tetraphenylborate with hypervalent iodine compounds under ultrasonic irradiation.

Entry	Hypervalent iodine compounds	Product	Time/ min	Yield/ %[a]
1	 **2a**	Ph–Ph **3a**	3	85
2	$PhI(OAc)_2$ **2b**	**3a**	5	72
3	$PhI(OCOCF_3)_2$ **2c**	**3a**	3	82
4	PhI=O **2d**	**3a**	10	50
5	 **2e**	 **3b**	5	70
6	$Ph_2I^+Cl^-$ **2f**	**3a**	5	72
7	 **2g**	 **3c**	3	75
8	 **2h**	 **3d**	5	70

[a]Isolated yield.

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medium. This method has advantages over other procedures in that it is simple, mild, high-yielding, and occurs at ambient temperature. Furthermore, the utility of hypervalent iodine compounds in organic syntheses was extended.

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 VARIAN-400 spectrometer, and mass spectra were determined on MS-EI instrument (FINNIGAN Trace DSQ) mass spectrometer. Ultrasonic irradiation was carried out with an ultrasonic cleaning bath (50 kHz).

Hydroxy(tosyloxy)iodobenzene (**2a**),[7] (diacetoxyiodo)benzene (**2b**),[8] [bis(tifluoroacetoxy)iodo]benzene (**2c**),[9] iodosylbenzene (**2d**),[10] 1-hydroxy-1,2-benziodoxol-3(*1H*)-one (**2e**)[11] diphenyliodonium chloride (**2f**),[12] alkynyliodonium salt (**2g**),[13] alkenylliodonium salt (**2h**)[13] were prepared according to the literature procedures. Sodium tetraphenylborate is commercially available.

The reaction of sodium tetraphenylborate with hypervalent iodine compounds: general procedure

Sodium tetraphenylborate (**1**) (85.5 mg, 0.25 mmol, 1.0 equiv), the hypervalent iodine compound (**2**) (0.25 mmol, 1.0 equiv), and H_2O (3 ml) were placed in a glass flask and irradiated for several minutes (shown in Table 1) in an ultrasonic cleaning bath (50 kHz). The mixture was extracted with diethyl ether (20 ml × 3), the organic layer was dried over anhydrous $MgSO_4$ and then evaporated under reduced pressure. The crude product was purified on a silica gel plate and the products **3** were obtained in good yields.

Biphenyl (**3a**): M.p. 68–69°C (Lit.[14] 69–72°C). ^{1}H NMR ($CDCl_3$): δ = 7.35 (m, 2H), 7.44 (m, 4H), 7.60 (m, 4H); IR (KBr): ν = 3035, 1569, 1481, 730 cm^{-1}; MS (70eV, EI) *m/z* (%): 154 (M^+, 100).

2-Biphenycarboxylic acid (**3b**): M.p. 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 (70eV, EI) *m/z* (%): 198 (M^+, 100).

Diphenylacetylene (**3c**): M.p. 58–59°C (Lit.[3d] 60°C). ^{1}H NMR ($CDCl_3$): δ = 7.22–7.41 (m, 6H), 7.51 (m, 4H); IR (KBr) ν = 3064, 3032, 1600,1500, 1262, 757, 691 cm^{-1}; MS (75eV, EI) *m/z* (%): 178 (M^+, 100).

E-1, 2-diphenylethylene (**3d**): M.p. 120–121°C (Lit.[3d] 122–124°C). ^{1}H NMR ($CDCl_3$): δ = 7.15 (s, 2H), 7.21 (m, 2H), 7.34 (m, 4H), 7.48 (m, 4H); IR (KBr) ν = 3079, 3034, 1698, 1496, 1073, 966, 767, 693 cm^{-1}; MS (75eV, EI) *m/z* (%): 180 (M^+, 100).

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