Palladium-Catalyzed Heck and Carbonylation Reactions of a Dinaphthaleneiodonium Salt Forming Functionalized 2-Iodo-1,1′-binaphthyls

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Abstract: The Heck-type olefination and carbonylation of a binaphthaleneiodonium salt **1** in the presence of a palladium catalyst gave high yields of the corresponding 2-iodo-2′-functionalized-1,1′-binaphthyls with high selectivity.

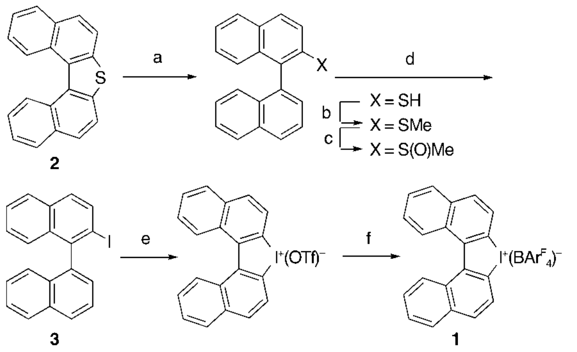
Keywords: binaphthyl; carbonylation; Heck reaction; iodonium salt; palladium catalyst

Introduction

Axially chiral 1,1′-binaphthyls bearing two identical substituents at the 2 and 2′ positions, which are represented by BINOL and BINAP, have found wide applications in catalytic asymmetric reactions.[1] Recently, those bearing two different substituents at the 2 and 2′ positions have also attracted increasing attention.[2] We have previously reported a nickel-catalyzed Grignard cross-coupling of a dinaphthothiophene, which proceeds through oxidative addition of one of the two carbon-sulfur bonds to a nickel(0) species to lead to axially chiral 1,1′-binaphthyls substituted with an alkyl group at the 2 position while leaving a carbon-sulfur bond at the 2′ position.[3] Unfortunately, the thiophene carbon-sulfur bond is not reactive towards oxidative addition to palladium(0) species, which makes it difficult to extend this type of catalytic ring opening reaction to the palladium-catalyzed reactions which involve the oxidative addition as one of the key steps in the catalytic cycle. Diaryliodonium salts[4] attracted our attention, because the carbon-iodonium bond is known to undergo oxidative addition to palladium(0) and hence they are reactive substrates for some of the typical palladium-catalyzed reactions, for example, cross-coupling,[5] Heck,[6] and carbonylation.[7] Herein we report the use of the dinaphthaleneiodonium salt **1** for palladium-catalyzed reactions, which provides a new route to 2-substituted 1,1′-binaphthyls containing iodide at the 2′ position.

Results and Discussion

Scheme 1 summarizes the preparation of the dinaphthaleneiodonium salt **1**, which has a 1,1′-binaphthyl backbone,[8] by way of 2-iodo-1,1′-binaphthyl (**3**)[9] as a key intermediate. We have developed a new efficient route to the iodide **3**, whose preparation by the Sandmeyer reaction of 2-amino-1,1′-binaphthyl had been previously reported.[9] Our route starts with dinaphthothiophene **2**,[10] which was subjected to nickel-catalyzed reductive



Scheme 1. Preparation of iodonium (**1**). *Conditions and reagents*: (a) Ni(acac)$_2$ (5 mol %), *i*-PrMgBr (1.15 equivs.), THF, reflux, 9 h (78%); (b) MeI (1.2 equivs.), K_2CO_3 (3 equivs.), acetone, rt, 15 h (100%); (c) *m*CPBA (1.5 equivs.), CH_2Cl_2, 0 °C, 90 min (77%); (d) 1) EtMgBr (1.5 equivs.), THF, rt, 20 min, 2) I_2 (1.6 equivs.), rt, 10 h (83%); (e) 1) $NaBO_3 \cdot 4\,H_2O$ (10 equivs.), $MeCO_2H$, 70 °C, 4.5 h, 2) TfOH (1.2 equivs.), CH_2Cl_2, 0 °C to rt, 5 h (24%, 2 steps); (f) Na-BAr$^F_4$ [Ar^F = 3,5-bis(trifluoromethyl)phenyl, 1.0 equiv.], CH_2Cl_2/MeOH/H_2O, 3 h (95%).

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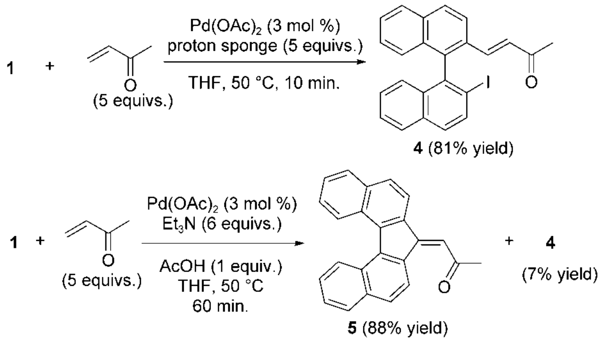


Scheme 2. Heck reaction with iodonium salt **1**.

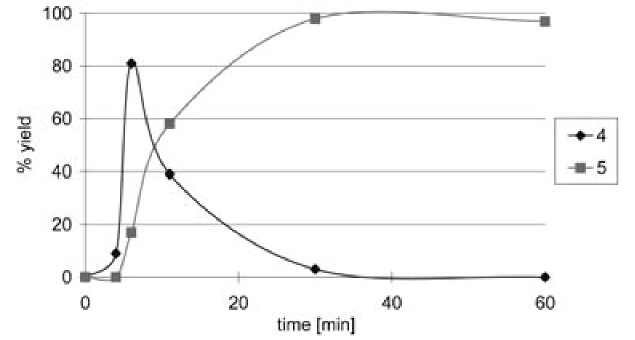
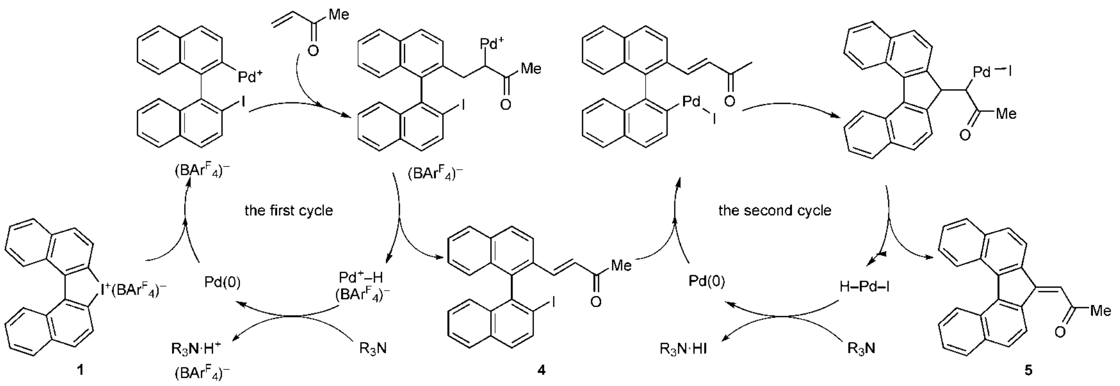


Figure 1. Heck reaction of iodonium salt **1** in the presence of Et_3N and AcOH.



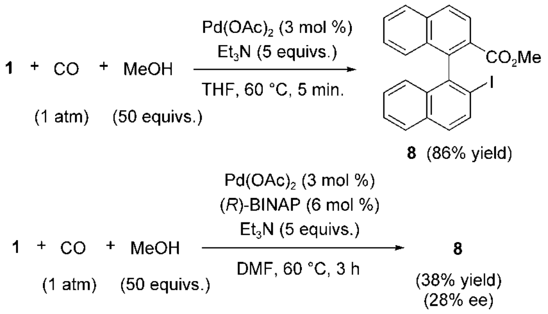
Scheme 3. Catalytic cycle for the Heck reaction of iodonium species **1**.

cleavage[3] with 2-propylmagnesium bromide giving 2-mercapto-1,1′-binaphthyl. Methylation of the thiol with methyl iodide and oxidation of the methyl sulfide with *m*-CPBA gave methyl sulfoxide. Treatment of the sulfoxide with ethylmagnesium bromide followed by addition of iodine to the generated binaphthylmagnesium species[3] gave the iodide **3** in 50% yield (4 steps from thiophene **2**). Oxidation of **3** with sodium perborate in acetic acid[11] followed by addition of trifluoromethanesulfonic acid to the resulting diacetoxyiodonium salt[12] gave the cyclized diaryliodonium triflate. To improve the solubility of the iodonium salt, its counteranion was replaced by tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($BAr^F{}_4{}^-$) to give the cyclic diaryliodonium **1**.

The diaryliodonium salt **1** was found to have high reactivity towards the Heck-type olefination (Scheme 2).[13] Thus, the reaction of **1** with methyl vinyl ketone (5 equivs.) and proton sponge (5 equivs.) in the presence of 3 mol % of palladium acetate in THF at 50 °C was completed within 10 min to give an 81% yield of the ring opening olefination product **4**, that is, a 1,1′-binaphthyl functionalized at the 2 and 2′ positions with an alkenyl group and iodide. Under the same reaction conditions or even at elevated temperatures, dinaphthothiophene **2** or 2,2′-bis(trifluoromethanesulfonyloxy)-1,1′-binaphthyl did not undergo the Heck-type reaction, demonstrating the higher reactivity of iodonium salt **1**.

It is remarkable that the use of triethylamine (6 equivs.) in place of proton sponge brought about the second intramolecular Heck reaction[14] leading to the dinaphthofulvene derivative **5** as a major product. The second intramolecular reaction was promoted by the addition of acetic acid (1 equiv.) to give 88% yield of **5** together with a minor amount (7% yield) of **4** in the reaction at 50 °C for 60 min. The reaction in the presence of triethylamine and acetic acid was monitored by ^{1}H NMR analysis, which is shown in Figure 1. The starting iodonium salt **1** was first all converted into the iodobinaphthyl **4** in 7 min, and the second intramolecular Heck reaction of **4**, which is slower than the first intermolecular reaction, produced **5** in high yield.

The catalytic cycle, which consists of the first intermolecular reaction of the iodonium salt **1** with methyl vinyl ketone and the second intramolecular reaction of iodide **4** forming fulvene **5**, is shown in Scheme 3. The reaction is initiated by oxidative addition of diaryliodonium **1** to a palladium(0) species. Insertion of methyl vinyl ketone into a cationic binaphthylpalladium intermediate followed by β-hydride elimination gives **4**. The second intramolecular Heck reaction which starts with the oxida-



Scheme 4. Carbonylation of iodonium salt **1**.

tive addition of binaphthyl iodide **4** to palladium(0) is promoted by triethylamine. The role of base on the reactivity remains to be clarified.

Iodonium salt **1** also showed high reactivity towards the palladium-catalyzed carbonylation reaction (Scheme 4).[7] The reaction with atmospheric carbon monoxide and triethylamine in methanol at 60 °C was completed within 5 min to give an 86% yield of 2-iodo-2′-methoxycarbonyl-1,1′-binaphthyl **6**. The second carbonylation giving diester was not observed at all.

The yield of the carbonylation product **6** was generally lower in the presence of photon ligands. As a result, attempted asymmetric carbonylation using chiral phosphine ligands did not give us a satisfactory result. One of the best results is the reaction in the presence of (*R*)-BINAP in *N,N*-dimethylformamide, which gave a 38% yield of ester **6** in 28% ee.

Conclusion

In conclusion, we have succeeded in the use of a binaphthaleneiodonium salt **1** for the palladium-catalyzed Heck and carbonylation reactions, which gave high yields of 2-iodo-2′-functionalized-1,1′-binaphthyls with high selectivity.

Experimental Section

All moisture-sensitive manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR and chloroform-*d* (δ 77.0 ppm) for ^{13}C NMR. Dinaphthothiophene **2**[10] and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[15] were prepared according to the reported procedures. Characterization data for the compounds obtained here are provided in the Supporting Information.

1,1′-Binaphthyl-2-thiol[3b]

To a solution of dinaphthothiophene **2** (2.84 g, 10.0 mmol) and Ni(acac)$_2$ (257 mg, 1.00 mmol) in tetrahydrofuran (200 mL) was added *i*-propylmagnesium bromide in diethyl ether (8.0 mL, 12 mmol) at 0 °C. The reaction mixture was refluxed for 9 h, before 10% hydrochloric acid was added. The mixture was extracted with chloroform three times. The combined organic layer was washed with saturated aqueous sodium bicarbonate and aqueous sodium chloride, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexane = 1/19) to give 1,1′-binaphthyl-2-thiol; yield: 4.48 g (78%).

2-Iodo-1,1′-binaphthyl (3)[9]

To a suspension of 1,1′-binaphthyl-2-thiol (3.56 g, 12.4 mmol) and potassium carbonate (5.15 g, 37.3 mmol) in acetone (100 mL) was added methyl iodide (0.85 mL, 14 mmol). The reaction mixture was stirred at room temperature for 12 h, before water was added. The mixture was extracted with chloroform three times. The combined organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to give 2-methylthio-1,1′-binaphthyl (yield: 3.35 g, 100%), which was used for the next step without further purification.

To a solution of the methyl sulfide obtained above (1.50 g, 5.00 mmol) in dichloromethane (42 mL) was added *m*-chloroperbenzoic acid (0.95 g, 5.5 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 4.5 h, before saturated aqueous sodium bicarbonate was added. The mixture was extracted with chloroform three times. The combined organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexane = 1/1) to give 2-methylsulfinyl-1,1′-binaphthyl (yield: 1.21 g, 77%) as a diastereomeric mixture (1.8/1), which was used for the next step without separation.

To a solution of the sulfoxide obtained above (1.21 g, 3.82 mmol) in tetrahydrofuran (130 mL) was added dropwise ethylmagnesium bromide (1.9 M in diethyl ether, 3.0 mL, 5.7 mmol) at 0 °C. The mixture was stirred at room temperature for 35 min, before iodine (1.94 g, 7.64 mmol) was added. The resulting mixture was stirred at room temperature for additional 6 h, and then quenched with saturated aqueous sodium thiosulfate. The mixture was extracted with ethyl acetate three times. The combined organic layer was washed with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexane = 1/49) to give iodide **3**; yield: 1.20 g (83%).

Iodonium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1)

The reported procedures for the oxidation of an aryl iodide,[11] and the formation of a diaryliodonium triflate[12b] were modified. To a stirred solution of iodide **3** (1.14 g, 3.00 mmol) in acetic acid (30 mL) was added portionwise sodium perborate tetrahydrate (4.62 g, 30.0 mmol) at 70 °C. The mixture was stirred at 70 °C for 4.5 h. The solution was concentrated to half its volume by removal of acetic acid by evaporation under reduced pressure, and water was added. The solid was filtered, washed with water, and dried under reduced pressure. To its solution in dichloromethane (30 mL) was added dropwise trifluoromethanesulfonic acid (0.32 mL, 3.6 mmol) at 0 °C. The mixture was stirred at room temperature for 5 h, before water was added. The organic layer was extracted with dichloromethane three times. The combined organic layer was washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was chromatographed on silica gel (methanol/chloroform = 1/10) to give the iodonium triflate; yield: 397 mg (24%).

To a solution of the iodonium triflate (1.06 g, 2.00 mmol) in dichloromethane (40 mL) and water (20 mL) was added a solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1.77 g, 2.00 mmol) in methanol (20 mL). The mixture was stirred at room temperature for 3 h. The mixture was diluted with chloroform, washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give the iodonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **1**; yield: 2.47 g (95%).

Heck Reaction of Iodonium Salt 1 in the Presence of Proton Sponge

To a solution of iodonium salt **1** (100 mg, 80.5 μmol), palladium acetate (0.54 mg, 2.4 μmol) and proton sponge (86.3 mg, 402 μmol) in tetrahydrofuran (0.80 mL) was added methyl vinyl ketone (52 μL, 402 μmol). The mixture was stirred at 50 °C for 10 min, before 10% hydrochloric acid was added. The mixture was extracted with chloroform three times, the extract washed with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexane = 1/6) to give Heck product **4**; yield: 29.2 mg (81%).

Heck Reaction of Iodonium Salt 1 in the Presence of Triethylamine and Acetic Acid

To a solution of iodonium salt **1** (100 mg, 80.5 μmol), palladium acetate (0.54 mg, 2.4 μmol), triethylamine (67 μL, 0.48 mmol), and acetic acid (5 μL, 0.08 mmol) in tetrahydrofuran (0.80 mL) was added methyl vinyl ketone (52 μL, 402 μmol). The mixture was stirred at 50 °C for 1 h. Aqueous work-up followed by silica gel chromatography in a similar manner to that for the reaction with proton sponge gave a mixture of cyclic product **5** and **4** (14/1) (25.2 mg, 88% yield for **5**, 7% yield for **4**).

For the monitoring experiment shown in Figure 1, 1,3-dimethoxybenzene (11.1 mg, 10.5 μL, 80.5 μmol) was added as an internal standard, and the yields of **4** and **5** were determined by ^{1}H NMR.

Carbonylation of Iodonium Salt 1

A solution of iodonium salt **1** (100 mg, 80.5 μmol), palladium acetate (0.54 mg, 2.4 μmol), and triethylamine (57 μL, 0.40 mmol) in methanol (0.8 mL) was stirred at 60 °C under a CO atmosphere (1 atm) for 5 min, before water was added. The mixture was extracted with chloroform three times, and the chloroform layer was washed with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexane = 1/6) to give methyl ester **6**; yield: 30.4 mg (86%).

Asymmetric Carbonylation of Iodonium Salt 1

The reaction of iodonium salt **1** (50.0 mg, 40.2 μmol), palladium acetate (0.45 mg, 2.0 μmol), (*R*)-binap (2.5 mg, 4.0 μmol), triethylamine (35 μL, 0.25 mmol), and methanol (82 μL, 2.0 mmol) in *N,N*-dimethylformamide (0.4 mL) at 60 °C under a CO atmosphere (1 atm) for 3 h gave methyl ester **6**; yield: 6.7 mg (38%). The enantiomeric excess was determined to be 28% ee by HPLC analysis with a chiral stationary phase column, Chiralpak AD (hexane/2-propanol = 49/1).

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