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The Palladium-Catalyzed Cross-Coupling Reaction of 9-(Organothio)-9-borabicyclo[3.3.1]nonanes with Organic Electrophiles: Synthesis of Unsymmetrical Sulfides

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Abstract

The synthesis of unsymmetrical sulfides was carried out in high yields by the palladium-catalyzed cross-coupling reaction of 9-(organothio)-9-borabicyclo[3.3.1]nonane (9-(RS)-9-BBN) with organic electrophiles, such as iodoarenes, 1-iodo-1-alkenes, allyl carbonate, and propargyl carbonate. Iodoarenes and 1-iodo-1-alkenes were smoothly converted into the corresponding sulfides at 50 °C in the presence of $PdCl_2$(dppf) (3 mol%) and K_3PO_4 (3 equivs) in DMF. On the other hand, the cross-couplings of 9-(RS)-9-BBN with allyl and propargyl carbonates proceeded in DMF without any assistance of bases. The both reactions catalyzed by a $Pd(dba)_2$-dppf catalyst regioselectively produced allyl and allenyl sulfides, respectively. The scope and limitation, as well as the effects of varying the reaction conditions, were discussed.

1. Introduction

The transition metal-catalyzed cross-coupling reaction of sulfur nucleophiles with organic electrophiles is an attractive and straightforward method to synthesize aryl and vinyl sulfides with high regio- and stereoselectivity. A number of metal thioalkoxides, including lithium,1 sodium,2 silicon,3 potassium,3a,4 and tin,5 has been successfully utilized, but the reaction of boron-sulfur reagents6 has not been yet investigated. We recently reported the palladium(0)-catalyzed thioboration7 of terminal alkynes with 9-(organothio)-9-borabicyclo[3.3.1]nonane (9-(RS)-9-BBN) derivatives8 (1) to provide (Z)-[b-(thiovinyl)]boranes and their cross-coupling reaction with organic halides to give 1-alkenyl sulfides. The reaction was carried out under mild conditions (at 50 °C) with high stereoselectivity, without catalyst poisoning, and was tolerated to a wide variety of functional groups.6b,9 Since 1 is readily available by the dehydrogenative condensation of 9-BBN with thiols, the results prompted us to examine other transition metal-catalyzed reactions of 1. We found that the cross-coupling reaction of 1 with organic electrophiles (2) readily catalyzed by PdCl2(dppf) under very mild conditions to afford unsymmetrical sulfides (3) in excellent yields (eq 1).

insert Eq 1

2. Results and discussion

2.1. Reaction conditions

The reaction conditions were optimized at 50 。C using 1 (R1 = Ph) and iodobenzene (Table 1). The cross-coupling reaction of organoboron reagents with organic halides proceeds in the presence of palladium catalyst and base.10 A suitable base is again essential for the present coupling reaction. The use of powdered K3PO4 suspended in DMF was recognized to be most effective (entry 1), because strong bases or weak bases, such as powdered KOH or K2CO3, resulted in low yields (entries 2 and 3). As for the ligand on the palladium catalyst, 1,1 ユ-bis(diphenylphosphino)ferrocene (dppf)11 revealed an extremely high catalyst activity. The reaction produced 3 in quantitative yields within 5 h when using PdCl2(dppf) or Pd(dba)2/2dppf as a catalyst (entries 1 and 4). Although Pd(PPh3)4 has been used as a catalyst for such coupling reaction of thioalkoxides,1-5 the activity was quite low for the present reaction presumably due to the slow rate of reductive elimination from PhS-Pd(II)-Ph intermediate (entry 5). Other bidentate phosphine ligands, such as dppb, dppp, and dppe, were ineffective (entries 6-8). For all these coupling reactions in the presence of K3PO4, the polar solvents accelerate the reaction rate: e.g., DMF > dioxane > toluene.

insert Table 1

2.2. A relative reactivity of the representative thioalkoxides

Various metal thioalkoxides have been used for the cross-coupling with organic halides.1-5 To examine the effect of metal ions on the reaction rate, iodobenzene was allowed to react with representative metal thiophenoxides under neutral conditions or in the presence of K3PO4 (Table 2). Under neutral conditions, the trimethylstannyl thiophenoxide revealed higher reactivity than the 9-BBN or the trimethylsilyl derivative; however, the reactions of lithium and sodium thiophenoxide were very slow, presumably due to the catalyst poisoning by coordination of sulfur anion to the palladium metal. In contrast, a dramatic rate enhancement was observed on the reactions of the boron, silicon, and tin reagents in the presence of K_3PO_4. Although the coupling reaction of stannyl thiophenoxides with organic halides have been carried out under neutral conditions at rather high temperatures (100-120 ℃),5 it is quite interesting that the presence of base extremely accelerated the rates of the reaction (entry 5). The base may increase the nucleophilicity of the thio groups by their coordination to the metals to accelerate the rate of transmetalation to the palladium(II) halides.12 The mechanism involving smooth transmetalation between these sulfur nucleophiles and oxopalladium(II) intermediate13 generated by the displacement of halide ligand on palladium with the base is considered as an alternative pathway.12,14 The presence of base similarly accelerates the palladium-catalyzed cross-coupling reaction of organoboron,10,12,14 -silicon,15 and -tin16 compounds.

insert Table 2

2.3. Reaction scope

A various (alkylthio)- or (arylthio)boron compounds can be used for the cross-coupling. A comparison of 9-(arylthio)- and 9-(alkylthio)-9-BBN during the coupling with iodobenzene in the presence of $PdCl_2$(dppf) and K_3PO_4 in DMF (Table 3) demonstrated that both reagents produce 3 in a range of 80-98 % yields (entries 1-6). The reaction with (arylthio)boranes having electron-withdrawing groups such as (4-chlorophenylthio)borane (entry 3), or sterically less hindered primary (alkylthio)boranes such as (butylthio)borane (entry 4) was very slow at 50 ℃, and they gave satisfactory yields at over 80 ℃. The coupling reaction of (benzylthio)borane was also very slow at 50 ℃ and provided a very low yield of benzyl phenyl sulfide (18 %) together with dibenzyl sulfide (7 %) at 120 ℃ (entry 7). Presumably, the benzyl phenyl sulfide undergoes oxidative addition17 to palladium(0) complexes to produce a $PhCH_2$-Pd(II)-SPh species; thus, such side reaction may consume the product and undergoes the further coupling with (benzylthio)borane leading to dibenzyl sulfide. The nickel(0)-catalyzed cross-coupling of thiolate anions with aryl halides has been also suffered from such by-product formation.4a insert Table 3

In Table 4, the representative results of the palladium-catalyzed cross-coupling reaction of 1 with 2 are summarized. The high yields were readily achieved for the representative iodoarenes, while the reactions with bromides resulted in low yields. There were no large difference in the yields and the reaction rates between aryl iodides having an electron-donating and an electron-withdrawing substituents, and both iodoarenes were completely consumed within 5 h at 50 。C (entries 1-4). 2-Iodotoluene quantitatively coupled with 1 (R1=tBu) at 50 。C (entry 5), but the reaction of iodomesitylene with 1 (R1=Ph) failed at 80 。C due to the steric hindrance. The reaction with 1-iodo-1-alkenes produced the corresponding 3 in high yields with retention of configuration (entries 7-9).

insert Table 4

We previously reported that the cross-coupling reaction of propargyl carbonates with organoboranes or organoboronates smoothly proceeds without any assistance of bases because the oxidative addition produces the alkoxopalladium(II) species able to transmetalate with boron reagents under neutral conditions.18 Indeed, geranyl carbonate smoothly coupled with 1 (R1 = Ph) in DMF at 80 。C in the presence of 3 mol% of Pd(dba)2/dppf to regioselectively provide the terminal coupling product in 93 % yield (eq 2). The oxidative addition of propargyl carbonate to palladium(0) through an allylic rearrangement led to the allenyl sulfide as the sole product under similar neutral conditions18 (eq 3).

insert Eqs 2 and 3

2.4. Reaction mechanism

The reaction may proceed through a mechanism19 similar to that of palladium-catalyzed coupling reactions of metal-sulfur compounds which involves (a) the oxidative addition of organic halide to palladium(0) complex to give X-Pd(II)-R2 (4), (b) the transfer of R1S group on boron to 4 in an aid of base, and (c) the reductive elimination of 3 from R1S-Pd(II)-R2 (5) (Figure 1).

insert Figure 1

Hartwig has recently demonstrated that the addition of sodium alkyl thiolates to 4 provided aryl alkyl thiolate complexes, [(dppe)Pd(StBu)(Ar)] (6) which corresponds to 5, were stable at room temperature.20 In contrast to C-C bond-forming reactions,21 the reductive elimination from 6 was accelerated by electron-withdrawing substituents on Ar group, suggesting a transition state that contains some character analogous to nucleophilic aromatic substitutions.22 The electron-withdrawing groups in haloarenes, in general, accelerate the oxidative addition step and presumably also the transmetalation step; thus, the presence of these groups may accelerate the overall catalytic cycle. However, the present reaction of 1 (R1=Ph) revealed no appreciable reaction rate difference between unsubstituted and substituted iodoarenes with 4-Me2N or 4-CO2Me (entries 1-3 in Table 4). The reaction rates were more strongly affected by the ligands on the palladium catalysts decreasing in a order of dppf >> dppb > dppp > dppe (entries 4, 6-8 in Table 1). Although the effect of these ligands on the oxidative addition or the transmetalation step has not been fully investigated, the relative activity can be parallel to the bond angles of L2PdCl2 (L2 = bidentate phosphine ligands) in which the large P-Pd-P bond angle and the small Cl-Pd-Cl bond angle favors the reductive elimination from 5.23

3. Experimental details

All the experiments were carried out under nitrogen atmosphere. IR spectra were taken on a Hitachi Perkin-Elmer Model 125 spectrometer. 1H NMR spectra were recorded in CDCl3 by a Hitachi R-90H (90 MHz) spectrometer using Me4Si as an internal standard. Mass spectra were obtained with a Finnigan ITD 800 for the GC-MS analyses and a JEOL JMS-DX303 for the high-resolution analyses. GC analyses were performed using a Hitachi 263 equipped with a stainless steel column (OV-17 on Uniport B, 2 m).

3.1. Materials and reagents

Solvents were purified by distillation from appropriate drying reagents. 9-(Organothio)-9-BBN derivatives were prepared by the dehydrogenative condensation of 9-BBN with the corresponding thiols.7,8 Lithium1b and sodium2d thiophenoxide were prepared by the reported procedures. (Phenylthio)trimethylsilane and -stannane were obtained by the reaction of lithium thiophenoxide with chlorotrimethylsilane and bromotrimethylstannane, respectively.3b Dichloro[1,1ユ-bis(diphenylphosphino)ferrocene]palladium(II) (PdCl2(dppf))23 and bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$)24 were prepared by using the literature procedures. 4-Iodo-N,N-dimethylaniline,25 2-iodo-1-octene,26 (E)-1-iodo-1-hexene,27 (E)-b-iodostyrene,27 and (E)-3,3-dimethyl-1-iodo-1-butene27 were synthesized by the reported procedures.

3.2. Reaction conditions (Table 1)

The best conditions for the preparation of diphenyl sulfide were determined by the following general procedure. Palladium complex (0.03 mmol) and a base (3 mmol) were added to a flask equipped with a reflux condenser, a septum inlet, and a magnetic stirring bar. The flask was flushed with nitrogen and charged with 6 mL of solvent. Iodobenzene (204 mg, 1.0 mmol) and 9-(phenylthio)-9-BBN (1, R^1=Ph) (253 mg, 1.1 mmol) were added by means of a hypodermic syringe through the septum inlet. The mixture was then stirred at 50 °C for 5 h. The product was extracted with benzene (20 mL), washed with water three times to remove DMF, and dried over magnesium sulfate. The yields based on iodobenzene were determined by GLC using hexadecane as an internal standard.

3.3. A relative reactivity of the representative thioalkoxides (Table 2)

To a flask were added $PdCl_2$(dppf) (22 mg, 0.03 mmol) and K_3PO_4 (636 mg, 3 mmol), and the flask was flushed with nitrogen. DMF (6 mL), iodobenzene (204 mg, 1.0 mmol), and metal thiophenoxide (1.1 mmol) were added, and the mixture was then stirred at 50 °C for 5 h. The coupling in the absence of K_3PO_4 was conducted under similar conditions.

3.4. General procedure for the coupling of 1 with aryl or 1-alkenyl iodides (Tables 3 and 4)

A flask, equipped with a magnetic stirring bar, a septum inlet, and a reflux condenser, was charged with $PdCl_2$(dppf) (22 mg, 0.03 mmol) and K_3PO_4 (636 mg, 3 mmol) and then flushed with nitrogen. DMF (6 mL), a halide (1.0 mmol), and 9-(organothio)-9-BBN (1.1 mmol) were successively added. After being stirred at 50 °C for 5 h, the reaction mixture was cooled to room temperature, diluted with benzene (20 mL), repeatedly washed with water to remove DMF (3 times), and finally dried over magnesium sulfate. The isolation of products was carried out by chromatography over silica gel.

The following compounds were prepared by the above general procedure.

3.4.1. Phenyl p-tolyl sulfide

n_D 1.6173; IR (film) 3050, 2930, 1590, 1490, 1480, 1440, 1090, 1020, 810, 740, 690 cm^{-1}; ^1H NMR d 2.34 (s, 3 H), 7.12 (d, 2 H, J = 8.1 Hz), 7.1-7.3 (m, 5 H), 7.30 (d, 2 H, J = 9.5 Hz); MS (ITD) m/e 51 (22), 65 (14), 77 (8), 91 (18), 185 (19), 200 (M^+, 100);

exact mass calcd for C13H12S 200.0660, found 200.0643.

3.4.2. 4-Chlorodiphenyl sulfide

nD 1.6344; IR (film) 3060, 1590, 1480, 1090, 1010, 820, 740, 690 cm-1; 1H NMR d 7.1-7.3 (m, 5 H), 7.2-7.4 (m, 4 H); MS (ITD) m/e 51 (50), 75 (16), 108 (12), 152 (6), 185 (50), 220 (M+, 100); exact mass calcd for C12H9SCl 220.0114, found 220.0097.

3.4.3. Butyl phenyl sulfide

nD 1.5483; IR (film) 3060, 2960, 2870, 1590, 1480, 1440, 1090, 1020, 740, 690 cm-1; 1H NMR d 0.92 (t, 3 H, J = 7.0 Hz), 1.2-1.8 (m, 4 H), 2.92 (t, 2 H, J = 7.0 Hz), 7.1-7.4 (m, 5 H); MS (ITD) m/e 51 (2), 57 (2), 65 (5), 110 (9), 123 (6), 166 (M+, 100); exact mass calcd for C10H14S 166.0816, found 166.0809.

3.4.4. sec-Butyl phenyl sulfide

nD 1.5393; IR (film) 3080, 2980, 2940, 1590, 1490, 1440, 1100, 1030, 740, 690 cm-1; 1H NMR d 1.01 (t, 3 H, J = 7.1 Hz), 1.27 (d, 3 H, J = 6.8 Hz), 1.4-1.8 (m, 2 H), 3.0-3.4 (m, 1 H), 7.1-7.5 (m, 5 H); MS (ITD) m/e 65 (2), 109 (3), 137 (1), 166 (M+, 100); exact mass calcd for C10H14S 166.0816, found 166.0801.

3.4.5. tert-Butyl phenyl sulfide

nD 1.5305; IR (film) 3080, 2960, 1480, 1440, 1370, 1170, 1030, 750, 690 cm-1; 1H NMR d 1.29 (s, 9 H), 7.2-7.4 (m, 3 H), 7.4-7.6 (m, 2 H); MS (ITD) m/e 57 (35), 65 (5), 110 (34), 166 (M+, 100); exact mass calcd for C10H14S 166.0816, found 166.0811.

3.4.6. 4-(Phenylthio)-N,N-dimethylaniline

mp 67 。C; IR (Nujol) 2930, 1600, 1510, 1460, 1380, 820, 740, 690 cm-1; 1H NMR d 2.97 (s, 6 H), 6.69 (d, 2 H, J = 9.0 Hz), 7.0-7.2 (m, 5 H), 7.38 (d, 2 H, J = 9.0 Hz); MS (ITD) m/e 51 (27), 77 (16), 109 (10), 136 (7), 152 (13), 196 (20), 229 (M+, 100); exact mass calcd for C14H15NS 229.0926, found 229.0923.

3.4.7. Methyl 4-(phenylthio)benzoate

mp 79 。C; IR (Nujol) 2950, 1720, 1600, 1460, 1380, 1280, 1120, 760, 690 cm-1; 1H NMR d 3.88 (s, 3 H), 7.20 (d, 2 H, J = 8.6 Hz), 7.3-7.6 (m, 5 H), 7.89 (d, 2 H, J = 8.6 Hz); MS (ITD) m/e 51 (22), 69 (10), 108 (8), 137 (4), 152 (7), 184 (23), 213 (49), 244 (M+, 100); exact mass calcd for C14H12O2S 244.0558, found 244.0541.

3.4.8. 4-(sec-Butylthio)bezonitrile

nD 1.5748; IR (film) 3070, 2980, 2940, 2240, 1600, 1490, 1460, 1090, 820 cm-1; 1H NMR d 1.03 (t, 3 H, J = 7.3 Hz), 1.34 (d, 3 H, J = 6.6 Hz), 1.5-1.8 (m, 2 H), 3.1-3.5 (m, 1 H), 7.34 (d, 2 H, J = 9.0 Hz), 7.53 (d, 2 H, J = 8.4 Hz); MS (ITD) m/e 50 (4), 57

(31), 63 (8), 75 (3), 90 (5), 135 (26), 162 (3), 191 (M+, 100); exact mass calcd for C11H13NS 191.0769, found 191.0769.

3.4.9. tert-Butyl o-tolyl sulfide

nD 1.5324; IR (film) 3070, 2970, 1480, 1360, 1170, 760 cm-1; 1H NMR d 1.29 (s, 9 H), 2.52 (s, 3 H), 7.0-7.3 (m, 3 H), 7.53 (d, 1 H, J = 5.9 Hz); MS (ITD) m/e 51 (5), 57 (73), 65 (4), 77 (6), 91 (52), 124 (74), 180 (M+, 100); exact mass calcd for C11H16S 180.0973, found 180.0962.

3.4.10. 2-(Phenylthio)-1-octene

nD 1.5314; IR (film) 3070, 2930, 2850, 1610, 1580, 1480, 1440, 1020, 750, 690 cm-1; 1H NMR d 0.88 (t, 3 H, J = 5.7 Hz), 1.1-1.8 (m, 8 H), 2.23 (t, 2 H, J = 7.1 Hz), 4.87 (s, 1 H), 5.14 (s, 1 H), 7.2-7.5 (m, 5 H); MS (ITD) m/e 59 (33), 69 (36), 81 (22), 110 (97), 135 (78), 150 (67), 221 (M+ + 1, 100); exact mass calcd for C14H20S 220.1285, found 220.1305.

3.4.11. (E)-1-(p-Tolylthio)-1-hexene

nD 1.5470; IR (film) 3030, 2940, 2860, 1490, 1470, 1100, 960, 800 cm-1; 1H NMR d 0.90 (t, 3 H, J = 6.5 Hz), 1.2-1.6 (m, 4 H), 2.15 (q, 2 H, J = 6.2 Hz), 2.32 (s, 3 H), 5.88 (dt, 1 H, J = 15.0 and 7.3 Hz), 6.13 (d, 1 H, J = 15.2 Hz), 7.11 (d, 2 H, J = 5.3 Hz), 7.22 (d, 2 H, J = 5.9 Hz); MS (ITD) m/e 55 (23), 65 (30), 79 (21), 91 (59), 124 (74), 130 (80), 148 (24), 163 (63), 206 (M+, 100); exact mass calcd for C13H18S 206.1130, found 206.1127.

3.4.12. (E)-1-(sec-Butylthio)-2-phenylethene

nD 1.5843; IR (film) 3040, 2980, 2940, 1600, 1450, 940, 740, 690 cm-1; 1H NMR d 1.02 (t, 3 H, J = 7.3 Hz), 1.36 (d, 3 H, J = 6.8 Hz), 1.5-1.8 (m, 2 H), 2.8-3.2 (m, 1 H), 6.54 (d, 1 H, J = 15.4 Hz), 6.78 (d, 1 H, J = 15.6 Hz), 7.0-7.4 (m, 5 H); MS (ITD) m/e 51 (9), 65 (7), 77 (5), 91 (34), 102 (3), 135 (78), 192 (M+, 100); exact mass calcd for C12H16S 192.0973, found 192.0987.

3.4.13. (E)-3,3-Dimethyl-1-(phenylthio)-1-butene

nD 1.5524; IR (film) 3070, 2960, 1590, 1480, 1440, 1370, 1030, 960, 740, 690 cm-1; 1H NMR d 1.08 (s, 9 H), 6.06 (s, 2 H), 7.2-7.4 (m, 5 H); MS (ITD) m/e 55 (9), 65 (7), 83 (16), 135 (6), 177 (33), 192 (M+, 100); exact mass calcd for C12H16S 192.0972, found 192.0990.

3.5. The coupling with ally and propargyl carbonates (Eqs 2 and 3)

A mixture of Pd(dba)2 (17 mg, 0.03 mmol), dppf (17 mg, 0.03 mmol), and DMF (6 mL) was stirred at room temperature for 30 min under nitrogen atmosphere. The carbonate (1.0 mmol) and 9-(phenylthio)-9-BBN (253 mg, 1.1 mmol) were added and the resulting solution was then stirred at 80 °C for 5 h. The product was isolated by column chromatography over silica gel.

3.5.1. (2E)-3,7-Dimethyl-1-(phenylthio)-2,6-octadiene

n_D 1.5527; IR (film) 3070, 2970, 2920, 1590, 1480, 1440, 1380, 730, 690 cm^{-1}; ^{1}H NMR d 1.58 (s, 6 H), 1.67 (s, 3 H), 1.8-2.1 (m, 4 H), 3.55 (d, 2 H, J = 7.7 Hz), 5.06 (m, 1 H), 5.31 (t, 1 H, J = 7.9 Hz), 7.0-7.4 (m, 5 H); MS (ITD) m/e 53 (13), 69 (100), 81 (56), 95 (11), 109 (20), 137 (17), 231 (3), 246 (M$^+$, 2); exact mass calcd for $C_{16}H_{22}S$ 246.1443, found 246.1457.

3.5.2. 7-Methyl-5-(phenylthio)-5,6-tridecadiene

n_D 1.5301; IR (film) 3070, 2930, 1960, 1590, 1480, 1440, 1020, 740, 690 cm^{-1}; ^{1}H NMR d 0.88 (t, 6 H, J = 6.8 Hz), 1.1-1.5 (m, 12 H), 1.64 (s, 3 H), 1.89 (t, 2 H, J = 6.6 Hz), 2.16 (t, 2 H, J = 6.7 Hz), 7.0-7.4 (m, 5 H); MS (ITD) m/e 55 (41), 67 (35), 81 (57), 93 (34), 109 (24), 123 (14), 193 (9), 225 (100), 302 (M$^+$, 22); exact mass calcd for $C_{20}H_{30}S$ 302.2069, found 302.2079.

Diphenyl sulfide, benzyl phenyl sulfide, and dibenzyl sulfide were directly compared with the corresponding authentic samples.

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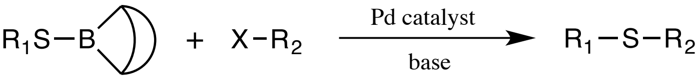
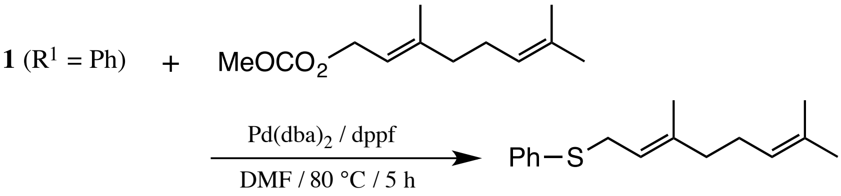


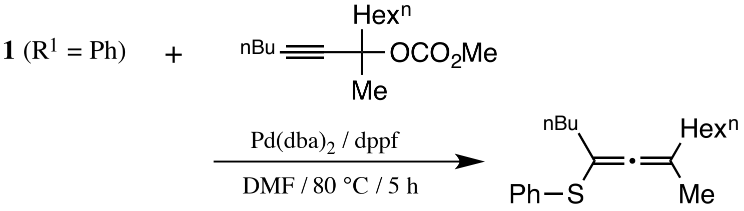
1 **2** **3**

(1)



(2)

93 % (E = 97 %)



(3)

86 %

Table 1. Reaction Conditions[a]

entry	catalyst	base	yield / %[b]
1	$PdCl_2(dppf)$	$K3PO_4$	99
2	$PdCl_2(dppf)$	KOH	64
3	$PdCl_2(dppf)$	$K2CO_3$	8
4	$Pd(dba)_2$ / 2dppf	$K3PO_4$	99
5	$Pd(PPh_3)_4$	$K3PO_4$	22
6	$Pd(dba)_2$ / 2dppb	$K3PO_4$	12
7	$Pd(dba)_2$ / 2dppp	$K3PO_4$	5
8	$Pd(dba)_2$ / 2dppe	$K3PO_4$	4

[a] The coupling between 9-(phenylthio)-9-BBN (1.1 mmol) and iodobenzene (1.0 mmol) was conducted at 50 °C for 5 h in DMF (6 mL) in the presence of catalyst (0.03 mmol) and base (3 mmol). [b] GLC yields based on iodobenzene.

Table 2. Cross-Coupling of Various Metal Thiophenoxides with Iodobenzene[a]

entry	PhS-m	none		K3PO$_4$[b]	
	m =	conv / %[c]	yield / %[d]	conv / %[c]	yield / %[d]
1	9-BBN	16	13	100	99
2	Li	3	2		
3	Na	3	2		
4	SiMe$_3$	18	13	81	78
5	SnMe$_3$	38	37	70	70

[a] Reactions were conducted at 50 °C for 5 h in DMF (6 mL) using a metal thiophenoxide (1.1 mmol), iodobenzene (1.0 mmol), and PdCl$_2$(dppf) (0.03 mmol).

[b] The same reaction with the above was carried out in the presence of K$_3$PO$_4$ (3 mmol).

[c] Conversion of iodobenzene.

[d] GLC yields based on iodobenzene.

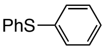
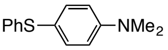
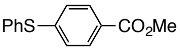
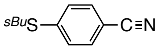
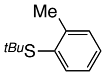
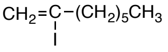
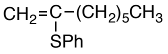
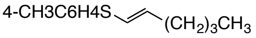
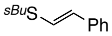
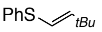
Table 3. Effect of Organothio Groups on the Reaction Rate[a]

entry	**1**, $\mathbf{R}^1$S =	temp / °C	yield / %[b]
1	PhS	50	87
2	4-MeC_6H_4S	50	98
3	4-ClC_6H_4S	80	91
4	nBuS	100	82
5	sBuS	50	84
6	tBuS	50	80
7	PhCH_2S	120	18

[a] All reactions were carried out for 5 h using of **1** (1.1 mmol), iodobenzene (1.0 mmol), $PdCl_2$(dppf) (0.03 mmol), K_3PO_4 (3 mmol) in DMF (6 mL).

[b] Isolated yields based on iodobenzene.

Table 4. Synthesis of Sulfides *via* Palladium-Catalyzed Coupling Reaction of **1** with Aryl and 1-Alkenyl Halides[a]

entry	**1**, R^1S =	halide	product	yield / %[b] (isomeric purity / %)[c]
1	PhS	Ph		87
2	PhS	$4\text{-IC}_6\text{H}_4\text{NMe}_2$		92
3	PhS	$4\text{-IC}_6\text{H}_4\text{CO}_2\text{Me}$		95
4	sBuS	$4\text{-IC}_6\text{H}_4\text{C}\equiv\text{N}$		99
5	tBuS	$2\text{-IC}_6\text{H}_4\text{Me}$		91
6	PhS	 $\text{CH}_2\text{=C(I)-(CH}_2)_5\text{CH}_3$	 $\text{CH}_2\text{=C(SPh)-(CH}_2)_5\text{CH}_3$	87
7	$4\text{-CH}_3\text{C}_6\text{H}_4\text{S}$	(E)-$\text{ICH=CH(CH}_2)_3\text{CH}_3$		99 (99)
8	sBuS	(E)-ICH=CHPh		93 (98)
9	PhS	(E)-ICH=CHBu^t		91 (99)

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[a] All reactions were conducted in DMF (6 mL) at 50 °C for 5 h using of 9-(organothio)-9-BBN (1.1 mmol) and organic halide (1.0 mmol) in the presence of PdCl_2(dppf) (0.03 mmol) and K_3PO_4 (3 mmol).

[b] Isolated yields based on the halides used. [c] Isomeric purity determined by GLC.

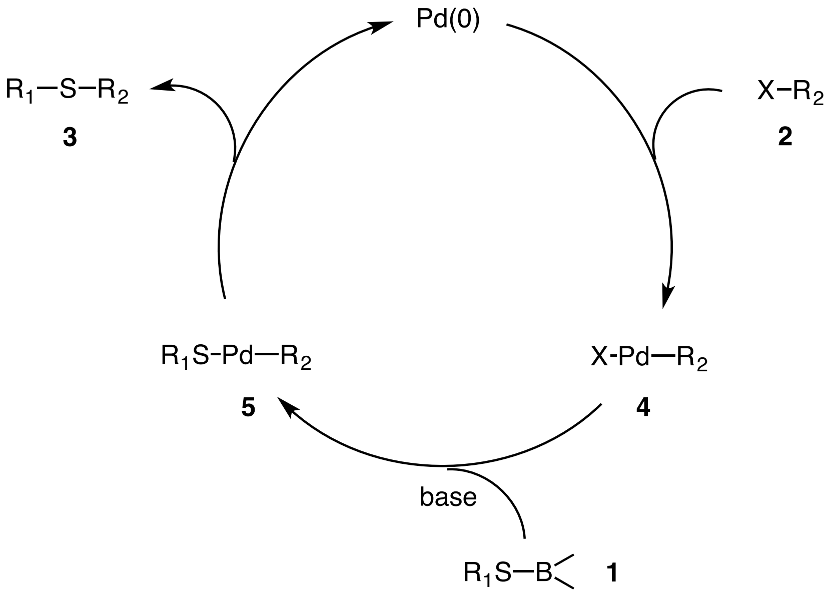

Figure 1. Catalytic Cycle for Coupling