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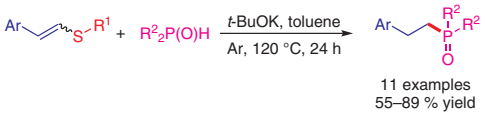
Potassium *tert*-Butoxide Mediated Reductive C–P Cross-Coupling of Arylvinyl Sulfides through C–S Bond Cleavage

Jie Feng[a]
Qiaoling Zhang[a]
Fuhai Li[a]
Lu Yang[b]
Ratnakar Reddy Kuchukulla[a]
Qingle Zeng*[a]

[a] State Key Laboratory of Geohazard Prevention and Geoenvironment Protection, College of Materials, Chemistry and Chemical Engineering, Chengdu University of Technology, Chengdu 610059, P. R. of China
qinglezeng@hotmail.com
[b] Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Azaaoba Aramaki, Aoba-ku, Sendai, 980-8578, Japan



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Abstract A transition-metal-free *t*-BuOK-mediated reductive C–P cross-coupling reaction of arylvinyl sulfides with diarylphosphine oxides through C–S bond cleavage has been developed. This protocol not only permits the synthesis of diaryl(2-arylethyl)phosphine oxides, but also achieves an unprecedented construction of a C–P bond through C–S bond cleavage and reduction of a C–C double bond in one pot.

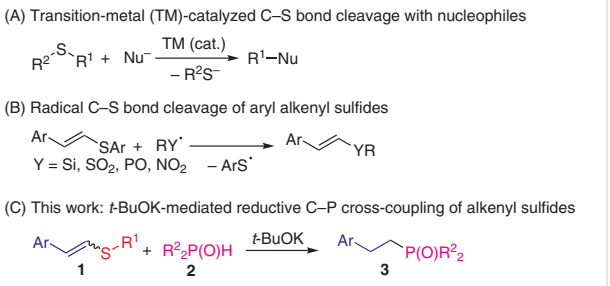
Key words alkenyl sulfides, C–S bond cleavage, C–P bond formation, potassium butoxide, transition-metal-free synthesis

Organophosphorus compounds have attracted considerable attention due to their broad range of applications in organic synthesis, materials science, bioorganic and medicinal chemistry, coordination chemistry, and catalysis, and as flame retardants.[1] In the 1980s, Hirao and colleagues reported the construction of C–P bonds by palladium-catalyzed reactions of aryl or alkenyl halides with dialkylphosphates.[2] Since then, a range of organic and organometallic compounds have been used to synthesize organophosphorus compounds, including organic halides,[3] derivatives of alcohols or phenols,[4] diazonium salts,[5] aryl hydrazines,[6] boric acids,[7] silanes,[8] sulfides,[9] aryl nitriles,[10] aryl or alkenyl carboxylic acids,[11] amides,[12] and aromatic esters.[13]

Conversion of C–X bonds into various C–Y bonds catalyzed by transition metals is an essential process in organic synthesis. Halogen compounds are commonly used in this method.[14] However, sulfur compounds have greater stability and better availability than the halides used in conventional methods.[15] Sulfur is widely present in natural products, pesticides, and proteins; moreover, sulfur-containing molecules can be precisely modified by highly selective activation or functionalization of the C–S bond.[16] The construction of carbon–carbon and carbon–heteroatom bonds by activation and cleavage of C–S bonds has attracted widespread attention.[15b,17] There have been reports on the cleavage of C–S bonds, with formation of carbon–heteroatom bonds, by transition metals such as Pt,[18] Rh,[19] Fe,[20] Co,[21] Ni,[9a,22] Pd,[23] and Cu[24] (Scheme 1A).

However, few transition-metal-free coupling reactions have been reported.[25] Only alkenylsilanes, sulfones, phosphine oxides, and nitroolefins have been prepared by radical-mediated C–S bond cleavage of arylvinyl sulfides (Scheme 1B);[26] the products of these reactions are important structural units in many natural products, pharmaceuticals, and organic light-emitting materials.[27]

During our researches in organosulfur chemistry[28] and coupling reactions,[29] we occasionally observed transition-metal-free, *t*-BuOK-promoted synthesis of diaryl(2-arylethyl)phosphine oxides **3** by C–S bond cleavage and reductive C–P cross-coupling of arylvinyl sulfides **1** and diarylphosphine oxides **2** (Scheme 1C).



Scheme 1 Methods for activating C–S bonds

Initially, the reductive cross-coupling of 4-methylphenyl styryl sulfide (**1a**) with diphenylphosphine oxide (**2a**) was chosen as a model system for optimizing the reaction conditions (Table 1). The effects of various solvents on the reaction were investigated in the presence of *t*-BuOK (Table 1,

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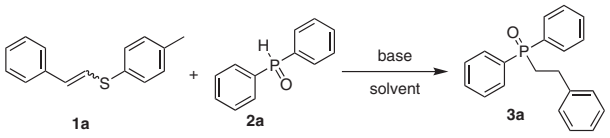
entries 1–9). The reaction did not proceed at room temperature under any of the reaction conditions tested, but after heating, some product **3a** was formed, except for the reactions in DMF, propane-1,3-diol, or DCE (Table 1). Screening of various solvents and bases at various temperatures revealed that the best yield of **3a** (82%) was obtained at 120 °C in toluene with *t*-BuOK as the base (entries 18 and 21). At lower temperatures, the reaction was significantly slower and lower yields were observed after 24 hours (entry 18 versus entries 2 and 15–17). Therefore, the optimal reaction conditions were found to involve toluene as solvent with 2.5 equivalents of *t*-BuOK as base under an argon atmosphere at 120 °C.[30,31]

Table 1 Screening of Reaction Conditions[a]

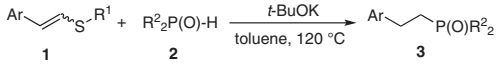


Entry	Base (equiv)	Solvent	Temp (°C)	Yield (%)
1	*t*-BuOK (2.0)	1,4-dioxane	110	23
2	*t*-BuOK (2.0)	toluene	110	51
3	*t*-BuOK (2.0)	DMSO	110	32
4	*t*-BuOK (2.0)	DMF	110	0
5	*t*-BuOK (2.0)	MeCN	80	10
6	*t*-BuOK (2.0)	propane-1,3-diol	110	0
7	*t*-BuOK (2.0)	xylene	110	43
8	*t*-BuOK (2.0)	DCE	80	0
9	*t*-BuOK (2.0)	EtOAc	80	12
10	*t*-BuONa (2.0)	toluene	110	13
11	K_2CO_3 (2.0)	toluene	110	0
12	KOH (2.0)	toluene	110	11
13	K_3PO_4 (2.0)	toluene	110	0
14	Et_3N (2.0)	toluene	110	0
15	*t*-BuOK (2.0)	toluene	40	0
16	*t*-BuOK (2.0)	toluene	60	0
17	*t*-BuOK (2.0)	toluene	80	42
18	*t*-BuOK (2.0)	toluene	120	65
19	*t*-BuOK (1.0)	toluene	120	0
20	*t*-BuOK (1.5)	toluene	120	31
21	*t*-BuOK (2.5)	toluene	120	82

[a] Reaction conditions: **1a** (1 mmol), **2a** (2 mmol), base, solvent (12 mL), 24 h.

With the optimized reaction conditions in hand, we next evaluated the scope of the substrate (Table 2). Various arylvinyl sulfides **1** successfully coupled with the diphenylphosphine oxides **2** to produce the corresponding (β-arylethyl)phosphine oxides **3a–i** in moderate to high yields (Table 2, entries 1–21). Because of electronic effects of the substituents on the aromatic ring, arylvinyl sulfides **1b** and **1c** (entries 2 and 3) with an electron-donating group afforded lower yields of the reductive cross-coupling products than did the electron-deficientyy substrates **1d–g** (entries 4–7). To our surprise, 2-pyridylethene (**1h**) with a hetaryl group afforded the target product **3h** in a yield as high as 87% (entry 8).

Table 2 Reaction of Alkenyl Sulfides **1** with Diarylphosphine Oxides **2**[a]



Entry	Ar	R^1	R^2	Product	Yield (%)
1	Ph	4-Tol	Ph (**2a**)	**3a**	82
2	4-Tol	4-Tol	Ph (**2a**)	**3b**	71
3	4-EtC_6H_4	4-Tol	Ph (**2a**)	**3c**	65
4	4-FC_6H_4	4-Tol	Ph (**2a**)	**3d**	86
5	3-FC_6H_4	4-Tol	Ph (**2a**)	**3e**	85
6	2-FC_6H_4	4-Tol	Ph (**2a**)	**3f**	83
7	4-ClC_6H_4	4-Tol	Ph (**2a**)	**3g**	85
8	2-pyridyl	4-Tol	Ph (**2a**)	**3h**	87
9	Ph	4-BrC_6H_4	Ph (**2a**)	**3a**	79
10	Ph	4-ClC_6H_4	Ph (**2a**)	**3a**	81
11	Ph	4-FC_6H_4	Ph (**2a**)	**3a**	89
12	Ph	3-FC_6H_4	Ph (**2a**)	**3a**	86
13	Ph	2-FC_6H_4	Ph (**2a**)	**3a**	81
14	Ph	4-MeOC_6H_4	Ph (**2a**)	**3a**	56
15	Ph	2-naphthyl	Ph (**2a**)	**3a**	73
16	Ph	*t*-Bu	Ph (**2a**)	**3a**	63
17	Ph	2-pentyl	Ph (**2a**)	**3a**	59
18	Ph	Bu	Ph (**2a**)	**3a**	51
19	Ph	cyclopentyl	Ph (**2a**)	**3a**	55
20	Ph	cyclohexyl	Ph (**2a**)	**3a**	69
21	Ph	4-Tol	3,5-$Me_2C_6H_3$ (**2b**)	**3i**	55

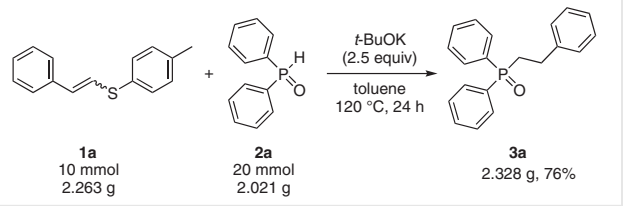
[a] Reaction conditions: **1** (1 mmol), **2** (2 mmol), *t*-BuOK (2.50 mmol), toluene (12 mL), 120 °C, 24 h.

We continued to investigate the effect on the yield of the reaction of alkyl or aryl substituents R^1 on substrate **1**. When R^1 was a substituted phenyl group, electronic effects of the substituents on the benzene ring were obvious. Electron-withdrawing substituents were beneficial to the reaction (Table 2, entries 9–13). Moreover, the more electronegative the halo group, the higher the yield (entries 9–11). An electron-donating methoxy group on the benzene ring sharply decreased the yield (entry 14). Overall, aromatic R^1 groups afforded higher yields than aliphatic R^1 groups (entries 9–15 versus 16–20). In this reaction, a styryl thioether provided moderate yields, regardless of whether the R^1

group was a bulky *tert*-butyl group or a smaller group, or was linear or cyclic (entries 16–20).

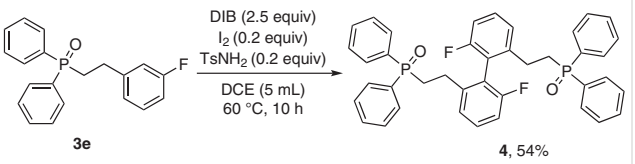
Finally, we carried out a reaction with bis(3,5-dimethylphenyl)phosphine oxide (**2b**) as the substrate under the same conditions, and the corresponding target product **3i** was obtained with a lower yield (Table 2, entry 21). This result might be due to the presence of the electron-donating methyl substituents on the benzene ring of **2b**.

This reaction was also carried out on a 10 mmol scale without a decrease in the reaction efficiency (Scheme 2). Thus, heating a mixture of **1a** (10 mmol), **2a** (20 mmol), and *t*-BuOK (25 mmol) in toluene (50 mL) at 120 °C for 24 hours gave product **3a** in 76% yield.



Scheme 2 Gram-scale experiment

A further transformation of product **3e** is shown in Scheme 3. In the presence of catalytic amounts of *p*-toluenesulfonamide and molecular iodine, [2-(3-fluorophenyl)ethyl](diphenyl)phosphine oxide and (diacetoxyiodo)benzene (DIB) in DCE at 60 °C gave the oxidative coupling product **4** in 54% yield.[32,33] This is a metal-free direct arylation of an aromatic C–H bond; in other words, a regiospecific dimerization of arenes through oxidative C–H bond activation, which has not been previously reported.

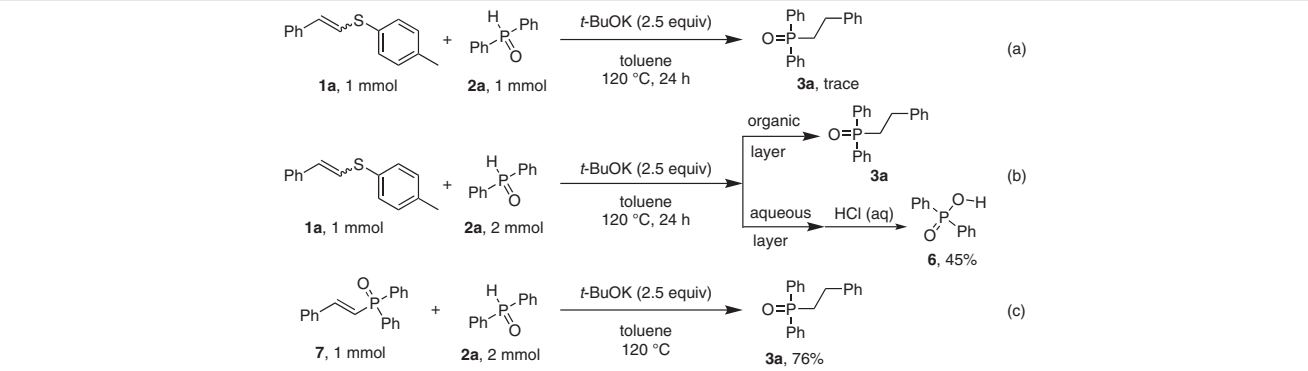


Scheme 3 Reaction expansion through oxidative cross-coupling

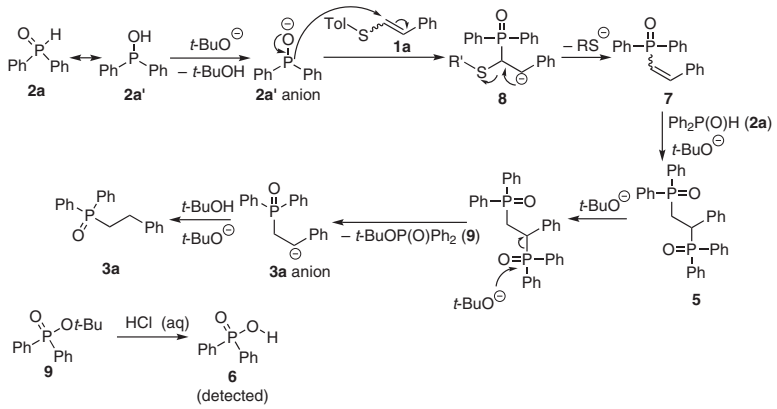
To explore the reaction mechanism, we designed a series of control experiments (Scheme 4). We found that when the ratio of the reaction starting materials was 1:1, the presence of the target product was barely detectable (Scheme 4a). We therefore believe that in this reaction, diphenylphosphine oxide acts as both a reactant and a reducing agent that can be oxidized to diphenylphosphinic acid (**6**) under alkaline conditions. We then repeated the experiment under the optimized conditions. After workup of the reaction, the aqueous phase was acidified with hydrochloric acid; subsequent extraction of the aqueous phase afforded a white solid confirmed to be diphenylphosphinic acid (**6**) by NMR and mass spectrometry (Scheme 4b). Furthermore, we presumed that the alkenyl(diphenyl)phosphine oxide **7** was the key intermediate before reduction, so we subjected compound **7** to the standard conditions and, as expected, we obtained the desired product **3a** in 76% yield (Scheme 4c).

Based on these experimental results, a plausible mechanism for the reductive C–P cross-coupling between arylvinyl sulfides and diarylphosphine oxides was proposed (Scheme 5). Tautomer **2a′** of **2a** is protonated by *t*-BuOK to give the **2a′** anion. Nucleophilic attack by the **2a′** anion on **1a** then produces sulfide **8**. Through electron transfer, **8** releases a TolS$^-$ anion and affords **7**. Addition of an excess of diphenylphosphine oxide (**2a**) to **7** generates **5**, which is attacked by *tert*-butoxide and then eliminates *t*-butyl diphenylphosphinate (**9**) to give an anion of product **3**. Finally, the anion of **3** is protonated by *tert*-butanol to produce the desired product **3a**. The diphenylphosphinic acid (**6**) mentioned above is generated from *tert*-butyl diphenylphosphinate (**9**) during the workup with aqueous HCl.

In summary, we have discovered a transition-metal-free *t*-BuOK-promoted C–S cleavage and, consequently, a reductive C–P cross-coupling reaction. Various diaryl(2-arylethyl)phosphine oxides were synthesized from a wide range of arylvinyl sulfides and diarylphosphine oxides in the presence of *t*-BuOK. The products can be synthesized on a gram scale and transformed further into other interesting mole-



Scheme 4 Control experiments



Scheme 5 Postulated reaction mechanism

cules. A reasonable mechanism is proposed based on control experiments.

Funding Information

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707319.

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(30) **Trisubstituted Phosphine Oxides 3a–i; General Procedure**

An oven-dried standard 25 mL ground-mouth test tube equipped with a stirrer bar was charged with the appropriate disubstituted phosphine oxide **2** (2.0 mmol, 2.0 equiv), alkenyl sulfide **1** (1.0 mmol, 1.0 equiv), *t*-BuOK (2.5 mmol, 2.5 equiv), and toluene (12 mL). The test tube was sealed with a sleeve rubber stopper and then evacuated and refilled with argon for three cycles. The mixture was stirred at 120 °C for 24 h, then cooled to r.t. The mixture was diluted with EtOAc and washed with H_2O, and the aqueous layer was extracted with EtOAc (×3). The combined organic layer was dried ($MgSO_4$) and concentrated under vacuum on a rotary evaporator, and the residue was purified by column chromatography (silica gel, PE–EtOAc gradient).

(31) **[2-(3-Fluorophenyl)ethyl](diphenyl)phosphine Oxide (3e)**

White crystals; yield: 276 mg (85%); mp 101–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.67 (m, 4 H), 7.54–7.39 (m, 6 H), 7.22–7.11 (m, 1 H), 6.98–6.87 (m, 1 H), 6.87–6.78 (m, 2 H), 2.97–2.81 (m, 2 H), 2.60–2.47 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.84 (d, J_{C-F} = 246.0 Hz), 143.57 (dd, J_{C-P} = 15.2 Hz, J_{C-F} =7.2 Hz), 132.50 (d, J_{C-P} = 98.7 Hz), 131.88 (d, J_{C-P} = 2.7 Hz), 130.70 (d, J_{C-P} = 9.3 Hz), 130.03 (d, J_{C-F} = 8.3 Hz), 128.73 (d, J_{C-P} = 11.6 Hz), 123.73 (d, J_{C-F} = 2.8 Hz), 114.92 (d, J_{C-F} = 21.2 Hz), 113.19 (d, J_{C-F} = 21.0 Hz), 31.53 (d, J_{C-P} = 70.0 Hz), 27.30 (dd, J_{C-P} = 2.9, 1.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –113.15. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.22. HRMS (ESI-MS): *m/z* [M + Na]$^+$ calcd for $C_{20}H_{18}FNaOP$: 347.0972; found: 347.0951.

(32) **[(6,6′-Difluorobiphenyl-2,2′-diyl)bis(ethane-2,1-diyl)]bis(diphenylphosphine) Dioxide (4)**

An oven-dried standard 25 mL ground-mouth test tube equipped with a stirrer bar was charged with phosphine oxide **3e** (0.324 g, 1.0 mmol), (diacetoxyiodo)benzene (0.805 g, 2.5 mmol), I_2 (0.051 g, 0.2 mmol), *p*-toluenesulfonamide (0.034 g, 0.2 mmol), and DCE (5 mL). The test tube was sealed with a sleeve rubber stopper and then evacuated and refilled with argon for three cycles. The mixture was stirred at 60 °C for 10 h, then cooled to r.t. The reaction was quenched with aq $Na_2S_2O_3$, and the mixture was extracted with EtOAc and washed with H_2O. The aqueous layer was extracted with EtOAc (×3), and the combined organic layer was dried ($MgSO_4$) and concentrated in vacuum on a rotary evaporator. The residue was purified by column chromatography (silica gel, PE–EtOAc gradient) to give a white solid; 349 mg (54%); mp 101–102 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.73 (m, 8 H), 7.67 (dd, *J* = 8.7, 5.7 Hz, 2 H), 7.58–7.41 (m, 12 H), 6.96 (dd, *J* = 9.4, 3.0 Hz, 2 H), 6.62 (td, *J* = 8.3, 3.0 Hz, 2 H), 3.06–2.92 (m, 4 H), 2.54 (ddd, *J* = 10.8, 8.9, 4.7 Hz, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.05 (d, J_{C-F} = 248.2 Hz), 145.84 (dd, J_{C-P} = 14.9 Hz, J_{C-F} =7.2 Hz), 140.55 (d, J_{C-F} = 7.8 Hz), 132.74 (s), 131.95 (d, J_{C-F} = 2.8 Hz), 131.75 (s), 130.84 (d, J_{C-P} = 9.5 Hz), 128.70 (d, J_{C-P} = 11.7 Hz), 116.83 (d, J_{C-F} = 22.2 Hz), 115.68 (d, J_{C-F} = 21.7 Hz), 32.97 (s), 30.10 (d, J_{C-P} = 69.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –113.56 to –113.67 (m). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.46 (s). HRMS (ESI-MS): *m/z* [M + Na + I_2]$^+$ calcd for $C_{40}H_{34}F_2I_2NaO_2P_2$: 922.9984; found: 922.9956.