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Silver-mediated direct phosphorylation of benzothiazoles and thiazoles with diarylphosphine oxides†

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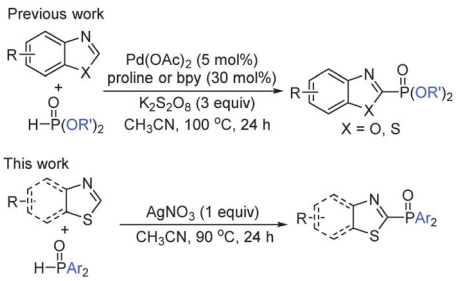
A silver nitrate-mediated, efficient phosphorylation of benzothiazoles and thiazoles with diarylphosphine oxides was developed. This process provides a convenient route for the synthesis of a variety of 2-diarylphosphoryl benzothiazoles and thiazoles which are promising precursors of a series of hemilabile P,N-ligands with small bite angles.

The construction of C(sp^2)–P bonds represents an important transformation in synthetic chemistry because of its prevalence in a wide range of biologically active molecules, pharmaceuticals, phosphine-containing ligands, and functional materials.[1,2] Transition metal-catalyzed phosphonation of aryl (pseudo)halides has provided a useful tool for the synthesis of aromatic organophosphorus compounds.[3] Recently, palladium-catalyzed cross dehydrogenative coupling reaction of (het)aromatic compounds with phosphites has emerged as an economically attractive alternative, which avoids the need for prefunctionalization of (het)Ar–H to aryl (pseudo)halides.[4] However, in most cases, a large excess of silver salts or $K_2S_2O_8$ had to be used as an oxidant. Moreover, to avoid the deactivation of the palladium catalysts by H-phosphonates, a relatively large amount of ligand should be used.[4c,d] In 2012, Li *et al.* reported the first example of palladium-catalyzed direct 2-phosphonation of azoles with dialkyl phosphites (Scheme 1).[4c] In this transformation, the addition of 30 mol% proline or 2,2′-bipyridine as a ligand and 3 equiv. of $K_2S_2O_8$ as an oxidant was necessary. In addition, rather than H-phosphonates, the direct coupling of diarylphosphine oxides with azoles, which may provide a direct route to the synthesis of a variety of 2-diarylphosphoryl azoles, was not involved in their work.[4c]



Scheme 1 Phosphonation of benzothiazoles.

On the other hand, since the pioneering work of Jason and Fields in 1962,[5] radical phosphonation of (hetero)arenes has attracted significant attention. Several metal salts were found to be effective for the generation of phosphonyl radicals.[6,7] In 2006, Ishii developed a Mn(II)/Co(II)/O_2-catalyzed phosphonation reaction of arenes with dialkyl phosphites.[6c] Subsequently, Zou and Zhang *et al.* reported a $Mn(OAc)_3$-promoted phosphonation of heterocycles, such as thiazoles, furans, and pyrroles, with diethyl phosphites.[6d] However, for these two strategies, aliphatic acid was normally used as solvent, which is not suitable for acid sensitive substrates. Recently, a silver-catalyzed dehydrogenative cross-coupling reaction of dialkyl phosphites with heteroarenes was developed by Huang and his coworkers based on the previous work of Effenberger.[7a,b] Peroxodisulfate was used to oxidize silver(I) to silver(II) which may further oxidize the dialkyl phosphite to an electrophilic cation radical.[7b] Notably, the phosphorus substrates in these transformations were limited to dialkyl phosphites. Recently, Yang reported a silver-catalyzed carbon–phosphorus functionalization of alkenes using $Ph_2P(O)H$.[8] Duan also developed a silver-mediated C–H/P–H functionalization reaction of arylphosphine oxides with internal alkynes.[9] It is believed that a nucleophilic phosphoryl radical was generated from the reaction between silver salts and diarylphosphine oxides through the formation of silver diarylphosphine oxides. In this context, with our continued interest in the synthesis of 2-substituted benzothiazoles and also encouraged by Chang's work on silver-mediated direct amination of azoles,[10,11]

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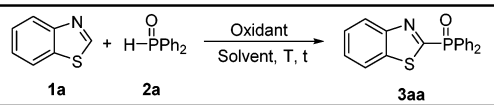
† Electronic supplementary information (ESI) available: General and experimental information on optimization studies and procedures for phosphorylation of benzothiazoles, characterization data (^{1}H NMR, ^{13}C NMR, ^{31}P NMR, HRMS) for all new compounds, single crystal X-ray structure analysis of **3ia** and complex **6**. CCDC 1039491 and 1038973. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc10017d

Table 1 Optimization of the reaction conditions[a]



Entry	Oxidant	Solvent	t (h)	Yield[b] (%)
1	AgOAc	MeCN	24	39
2	Ag_2O	MeCN	24	35
3	Ag_2CO_3	MeCN	24	33
4	AgOTf	MeCN	24	8
5	$AgNO_3$	MeCN	24	65
6[c]	$AgNO_3$	MeCN	24	32
7[d]	$AgNO_3$	MeCN	24	48
8	$AgNO_3$	MeCN	12	55
9	$AgNO_3$	MeCN	36	56
10[e]	$AgNO_3$	MeCN	24	72
11	$AgNO_3$	DCE	24	44
12	$AgNO_3$	DMF	24	57
13	$AgNO_3$	1,4-Dioxane	24	39
14	$AgNO_3$	PhMe	24	29
15	$AgNO_3$	EtOAc	24	34

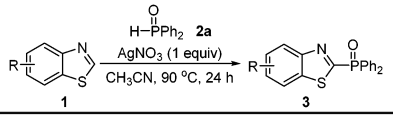
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), oxidant (0.2 mmol), solvent (1.5 mL), 90 °C. [b] Isolated yield. [c] In air. [d] 1.5 equiv. of $AgNO_3$. [e] 3 equiv. of **2a**.

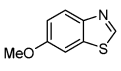
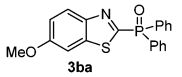
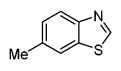
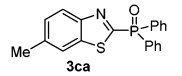
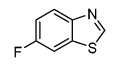
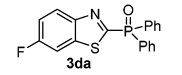
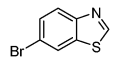
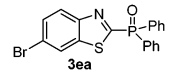
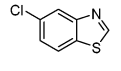
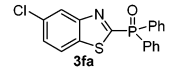
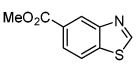
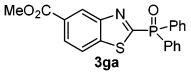
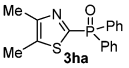
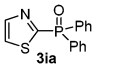
we envisioned that the nucleophilic addition of phosphoryl radicals to benzothiazoles followed by oxidative aromatization may lead to the formation of 2-phosphorylated benzothiazoles. Herein, we introduce a silver-mediated direct phosphorylation of benzothiazoles and thiazoles with diaryl phosphine oxides under mild conditions without the addition of any other oxidants (Scheme 1).

In an initial experiment, benzothiazole **1a** was treated with diphenylphosphine oxide ($Ph_2P(O)H$, **2a**) in the presence of 1 equiv. of AgOAc in acetonitrile at 90 °C (Table 1, entry 1). To our delight, the desired 2-diphenylphosphinyl benzothiazole **3aa** was obtained in 39% yield after 24 h. Then several silver salts were tested and $AgNO_3$ was proved to be the best oxidant (entries 2–5). The desired product **3aa** was obtained in 65% yield in the presence of 1 equiv. of $AgNO_3$ (entry 5). Notably, a similar reaction performed in air gave the desired product in only 32% yield (entry 6). The addition of 1.5 equiv. of $AgNO_3$ resulted in a lower yield of 48% (entry 7). Moreover, lower yields were also observed after 12 or 36 h indicating that the reaction time is also crucial for the coupling (entries 8 and 9). Delightedly, when 3 equiv. of **2a** was used, the yield of **3aa** increased to 72% (entry 10). Furthermore, a range of solvents were screened and acetonitrile was proved to be the most suitable solvent (entries 11–15). Other metal salts, such as $Mn(OAc)_3$, $Cu(OAc)_2$, $CuCl_2$ and $FeCl_3$, were also tested and none of them gave better results (see the ESI†).

With the optimized conditions in hand, we examined the reactions of diphenylphosphine oxide with various benzothiazoles (Table 2). Both electron-rich and electron-deficient substituents on the phenyl rings of benzothiazoles were tolerated. Phosphorylation of both 6-methoxy and 6-methyl-substituted benzothiazoles afforded the corresponding products **3ba** and **3ca** in high yields (entries 1 and 2). Several electron-withdrawing groups, such as fluoro-, bromo-, chloro-, and methoxycarbonyl-groups, on the

Table 2 Investigation of the scope in benzothiazoles[a]



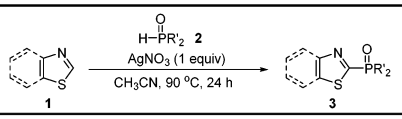
Entry	Substrate	Product	Yield[b] (%)
1		 **3ba**	86 (89)[c]
2		 **3ca**	63
3		 **3da**	74
4		 **3ea**	69
5		 **3fa**	85
6		 **3ga**	90 (92)[c]
7		 **3ha**	72
8		 **3ia**	23

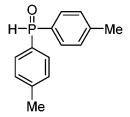
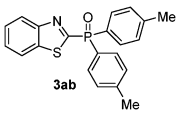
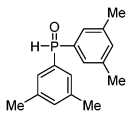
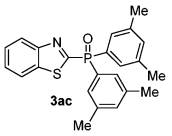
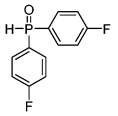
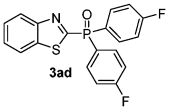
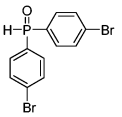
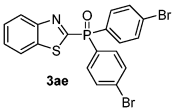
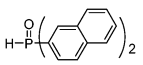
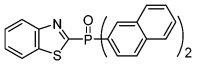
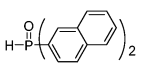
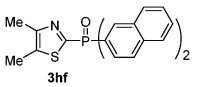
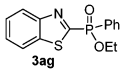
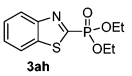
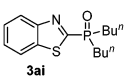
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $AgNO_3$ (0.2 mmol), MeCN (1.5 mL), 90 °C. [b] Isolated yield. [c] Yields of 2.00 mmol scale reactions (0.65 g of **3ba** and 0.72 g of **3ga**).

benzothiazoles survived well in this transformation (entries 3–6). Interestingly, 4,5-dimethylthiazole could also react with $Ph_2P(O)H$ under the standard conditions affording the desired product **3ha** in 72% yield (entry 7). In addition, treatment of the simple thiazole with diphenylphosphine oxide gave the corresponding product **3ia** in only 23% yield perhaps due to the formation of other regioisomers (entry 8). We have also tested the scalability of this transformation with 2.00 mmol scale synthesis of **3ba** in 89% yield (0.65 g) and **3ga** in 92% yield (0.72 g), respectively. Furthermore, the reaction of benzoxazole with diphenylphosphine oxide under the optimized conditions was also performed. Disappointingly, the desired phosphorylation product was not observed.

Subsequently, different diarylphosphine oxides were subjected to the established reaction conditions (Table 3). Both *para*- and *meta*-methyl substituents on the phenyl ring have little effect on the reaction and the corresponding products (**3ab** and **3ac**) were obtained in high yields (entries 1 and 2; 71% and 82%). The electron-withdrawing *para*-fluoro group was also compatible and the corresponding product **3ad** was isolated in 51% yield (entry 3). However, treatment of the diarylphosphine oxide involving a *para*-bromo substituent with benzothiazole **1a** afforded the desired product **3ae** in only 23% yield (entry 4). In addition, di(naphthalen-2-yl)phosphine oxide could react with both benzothiazole and 4,5-dimethylthiazole and lead to the corresponding product in moderate yields (entries 5 and 6).

Table 3 Investigation of the scope in diarylphosphine oxides[a]

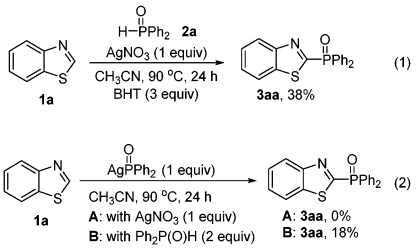


Entry	Substrate	Product	Yield[b] (%)
1		 3ab	71
2		 3ac	82
3		 3ad	51
4		 3ae	23
5		 3af	39
6		 3hf	63
7		 3ag	42
8		 3ah	19
9		 3ai	92

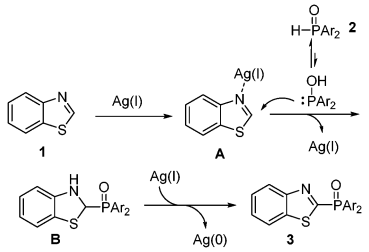
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $AgNO_3$ (0.2 mmol), MeCN (1.5 mL), 90 °C. [b] Isolated yield.

Furthermore, the reaction between ethyl phenylphosphinate and benzothiazole **1a** produced **3ag** in 42% yield (entry 7). Notably, under the standard conditions, the phosphorylation of benzothiazoles with diethyl phosphonate produced **3ah** in only 19% yield (entry 8). To our surprise, the reaction between dibutylphosphine oxide **2i** and benzothiazole **1a** gave the desired product **3ai** in 92% yield (entry 9).

In order to gain insight into the mechanism, several control experiments were carried out (Scheme 2). Firstly, an efficient radical scavenger BHT was introduced into the reaction between **1a** and **2a**, which afforded the phosphorylation product **3aa** in only 38% yield (eqn (1)). Moreover, it is known that diphenylphosphine oxide could react with $AgNO_3$ leading to the formation of silver complex $Ph_2(O)PAg$ (**4**).[8] In this regard, $Ph_2(O)PAg$ was prepared according to a previous report[8a] and added to the reaction of **1a** in the presence of $AgNO_3$ at 90 °C (eqn (2)). It was supposed that the 2-phosphoryl benzothiazoline radical intermediate derived from the nucleophilic addition of the corresponding phosphoryl radical on the



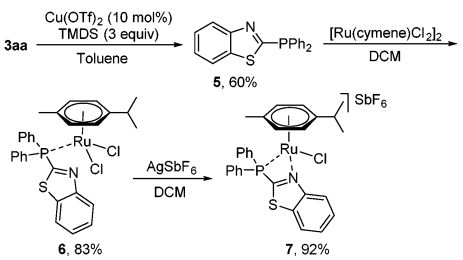
Scheme 2 Investigation on the reaction mechanism.



Scheme 3 Proposed mechanism.

benzothiazole **1a** could be further oxidized by $AgNO_3$ to form the desired product **3aa**. To our surprise, no phosphorylation product was detected after 24 h, which suggested that perhaps the phosphoryl radical was not involved in the reaction process. Afterwards, the reaction of **1a** with $Ph_2(O)PAg$ and $Ph_2(O)PH$ was also performed, which only led to the formation of **3aa** in 18% yield (eqn (2)). Furthermore, different from Yang's results,[8a] addition of several nitrates, such as $Mg(NO_3)_2$ and $Zn(NO_3)_2$, as additives could not promote the reaction (see the ESI†). Based on these experiments, a plausible mechanism for the dehydrogenative cross-coupling is proposed as shown in Scheme 3. Firstly, the thiazole ring is activated through the coordination of N atoms with the Ag(I) salt to form intermediate **A**.[12] Then the nucleophilic addition of the diphenylphosphine oxide to **A** leads to the formation of intermediate **B**, which undergoes oxidative aromatization in the presence of Ag(I) to give the final product **3**.[11a]

Furthermore, to explore the potential utility of benzo[*d*]thiazol-2-yldiarylphosphines as versatile ligands in coordination chemistry, several experiments were performed (Scheme 4).[2c,13] Using Beller's method,[14] 2-diphenylphosphinyl benzothiazole **3aa** could be reduced with tetramethyldisiloxane in the presence of 10 mol% $Cu(OTf)_2$ affording the corresponding phosphine ligand **5** in 60% yield. Treatment of $[Ru(cymene)Cl_2]_2$ with excess of **5** led to the



Scheme 4 Preparation of ruthenium complex **7**.

formation of a neutral P-coordinated ruthenium(II) complex **6**.[15] Further treatment of complex **6** with $AgSbF_6$ gave rise to the additional coordination of the benzothiazole nitrogen atom to ruthenium to afford the corresponding cationic ruthenium complex **7**. Complexes **6** and **7** are potential catalyst precursors for hydrogenation of olefins.[16,17]

In summary, we have developed a facile and efficient method for the preparation of various benzo[*d*]thiazol-2-yldiarylphosphine oxides through silver mediated direct phosphorylation of benzothiazoles and thiazoles. This method is compatible with the reported Pd-catalyzed reactions,[4c] which may produce a more convenient route to the synthesis of a series of novel P,N-ligands. Further investigations on the scope and exact mechanism of this method and the applications of the P,N ligands are underway in our laboratory.

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