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Direct phosphorylation of benzylic C–H bonds under transition metal-free conditions forming $sp^3C–P$ bonds†

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Direct phosphorylation of benzylic C–H bonds was achieved in a biphasic system under transition metal-free conditions. A selective radical/radical $sp^3C–H/P(O)–H$ cross coupling was proposed, and various substituted toluenes were applicable. The transformation provided a promising method for constructing $sp^3C–P$ bonds.

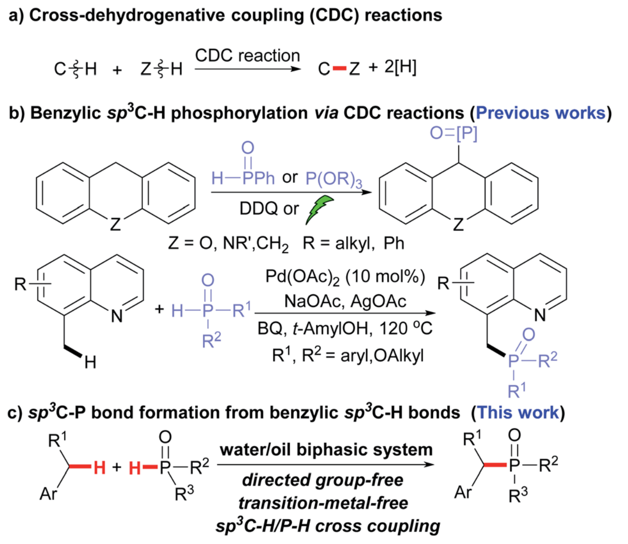
To construct C–P bonds is of great significance in modern organic synthesis,[1] because organophosphorus compounds play varied roles in medical,[2,3] materials,[4] and synthetic chemistry fields.[5] Traditionally, the C–P bonds were formed from P–Cl species *via* nucleophilic substitutions with organometallic reagents,[6] P–OR species *via* Michaelis–Arbusov reactions,[7] or P–H species *via* the alkylation in the present of a base or a transition metal.[8]

Over the past decades, cross dehydrogenative coupling reactions (CDC reactions) have become a powerful and atom-economic methodology for constructing chemical bonds.[9] By using this strategy, C–H bonds can couple with Z–H bonds without prefunctionalization and thus short-cut the synthetic procedures (Scheme 1a).

A similar construction of C–P bonds *via* CDC was also realized.[10,11] Among these methods, the phosphorylation of $sp^3C–H$ having an adjacent N or O atom, or the carbonyl group was well-developed.[11] Relatively, the formation of benzylic $sp^3C–P$ bond was less reported,[11w] which was mainly limited to the $sp^3C–H$ of xanthene or 8-methylquinoline (Scheme 1b).[12] In these reported processes, transition metal catalysts or photo-, electro-catalysts were usually involved,[11v] and an excess of P(O)–H compounds was usually employed.[11,13] To the best of our knowledge, the phosphorylation of non-active benzylic C–H bonds has scarcely been reported.

Considering both benzylic and phosphorus radicals could be generated by oxidation,[14] which might subsequently couple, the phosphorylation of benzylic $sp^3C–H$ bonds would be achieved (Scheme 1c). Herein, we disclosed the construction of benzylic C–P bonds from toluene and P–H species. The reaction was carried out under transition metal-free reaction conditions,[15] and exhibited high regio-selectivity. The aromatic C–H remained intact during the reaction.

We began our investigation by exploring the reaction of toluene **1a** and diphenylphosphine oxide **2a** in the presence of an oxidant (Table 1). When **2a** was stirred in toluene at 120 °C for 3 h in the presence of 2 equiv. potassium persulfates, a trace amount of diphenylbenzylphosphine oxide **3a** (<1%) was detected (entry 1). In a mixed solvent of toluene/water (1 : 1), the yield of **3a** was increased to 12% (entry 2). It should be noted that the homocoupled product 1,2-diphenylethane **4** was formed in 16 : 84 ratio (**3a**/**4**). Further addition of 1 equiv. phase transfer reagent (sodium dodecyl sulfate, SDS) led to produce **3a**



Scheme 1 Cross dehydrogenative coupling reactions and direct phosphorylation of benzylic C–H bonds.

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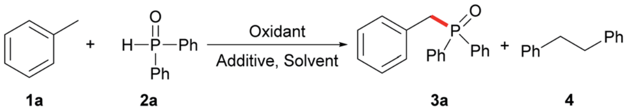
Table 1 Optimization of the reaction conditions[a]



Entry	Oxidant	Toluene/water (v/v)	Additive	**3a** yield[b] (%)	**3a**/**4**[c]
1	$K_2S_2O_8$	1 : 0	—	Trace	—
2	$K_2S_2O_8$	1 : 1	—	12	16 : 84
3	$K_2S_2O_8$	1 : 1	SDS	37	26 : 74
4	$Na_2S_2O_8$	1 : 1	SDS	31	27 : 73
5	$(NH_4)_2S_2O_8$	1 : 1	SDS	27	23 : 77
6	Oxone	1 : 1	SDS	None	—
7	—	1 : 1	SDS	None	—
8	—	1 : 1	—	None	—
9	$K_2S_2O_8$	1 : 1	SDBS	41	36 : 64
10	$K_2S_2O_8$	1 : 2	SDBS	46	28 : 72
11	$K_2S_2O_8$	1 : 3	SDBS	35	24 : 76
12[d]	$K_2S_2O_8$	1 : 2	SDBS	46	32 : 68
13[e]	$K_2S_2O_8$	1 : 2	SDBS	26	21 : 79
14[f]	$K_2S_2O_8$	1 : 2	SDBS	29	26 : 74
15[g]	$K_2S_2O_8$	1 : 2	SDBS	48	38 : 62
16[g,h]	$K_2S_2O_8$	1 : 2	SDBS	0	—

[a] Reaction condition: **1a** (1 mL), **2a** (0.2 mmol), oxidant (2 equiv.), additive (1 equiv.) and H_2O, 120 °C, 3 h. under N_2. [b] GC yields using *n*-dodecane as an internal standard. [c] The ratio of **3a**/**4** was determined by GC analysis. [d] 50 mol% SDBS was used. [e] 20 mol% SDBS was used. [f] At 100 °C. [g] **1** (0.8 mL) and H_2O (1.6 mL), 3 equiv. $K_2S_2O_8$ was used, 120 °C for 15 min. [h] 3 equiv. TEMPO was added.

in 37% yield (entry 3).[16] Other persulfates could also be used as an oxidant albeit with decreasing yields (Table 1, entries 4 and 5). No desired products were detected when the reaction was carried out with oxone or in the absence of oxidants (entries 6–8). By using sodium 4-dodecylbenzenesulfonate (SDBS) instead of SDS as the phase transfer reagent, a higher yield was afforded (entry 9). A higher percent of water (toluene/water = 1 : 2) gave **3a** in 46% yield. However, further increasing the percent of water led to a decrease of the yield (entries 10 and 11). The yield was not changed with a decreased load of SDBS to 50 mol%. Further reducing the amount of SDBS to 20 mol% resulted in a poorer yield (entries 12 and 13). At lower temperature, the yield of **3a** was also decreased to 29% (entry 14). Worth noting is that the reaction could be complete within 15 min when 3 equiv. of $K_2S_2O_8$ was used, producing **3a** in 48% yield (entry 15).

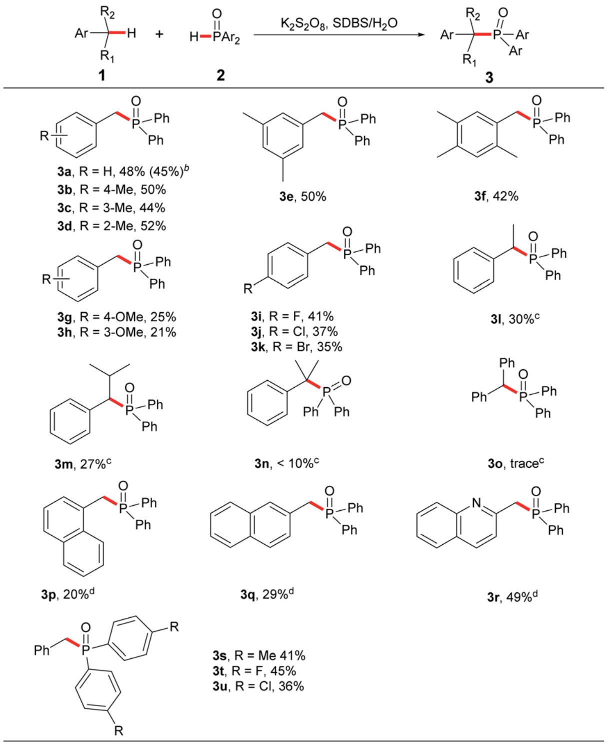
Based on the above results, we can easily find that a serious amount of 1,2-diphenylethane **4** was formed. These results suggest that the homocoupling rate of **1a** was very quick. Thus, the choice of the phase transfer reagent and oxidant is the key to cross-coupling of toluene and diphenylphosphine oxide in this biphasic solvent system.

Excessive P–H species were usually employed in reported CDC reactions to form C–P bonds, because of their facile oxidation.[13] In our procedure, toluene was excessive, thus the yields were calculated based on **2a**. The yields looked like low, which did not indicate the poorer conversion rate of P–H species. With the optimized conditions in hand, the substrate scope of the CDC reactions was explored (Table 2). Toluene and variously substituted toluene reacted with secondary phosphine oxides to afford corresponding **3**. The phosphorylation of sp^2C–H was not detected, and only mono-phosphorylation product was formed, which exhibited excellent chemo- and regioselectivity.

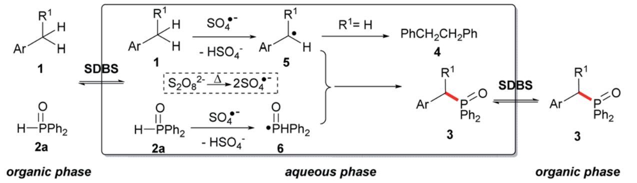
In addition to toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, and 1,2,4,5-tetramethylbenzene all coupled with **2a** to give the expected **3b–f** in moderate yields. Methoxy substituted toluene gave relatively lower yields of **3g** and **3h**. *para*-Halo substituted toluene exhibited good reactivity, furnishing the coupling products **3i** and **3j** in moderate yields. Comparing to toluene, a decreasing order of reactivity was observed for ethyl benzene (**3l**, 30% yield), isobutyl benzene (**3m**, 27% yield), isopropyl benzene (**3n**, <10% yield), and diphenyl methane (**3o**, trace). The order was probably controlled by the steric hindrance around the benzylic carbon. 1-Methylnaphthalene and 2-methylnaphthalene also gave low yields (**3p** and **3q**). However, 2-methylquinoline served well and coupled with **2a**, affording the product **3r** in 49% yield, which could be ascribed to the activation of the nitrogen atom. Besides of **2a**, diaryl phosphine oxides having methyl, F, and Cl substituents could also be employed as the substrate, producing **3s–3u** in moderate yields under similar reaction conditions.

Although the mechanism of the direct phosphorylation of benzyl C–H bond in aqueous solution is not quite clear, some

Table 2 Transition-metal-free benzylic C–H phosphorylation[a]



[a] Reaction conditions: **1** (0.8 mL), **2** (0.2 mmol), $K_2S_2O_8$ (3 equiv.), SDBS (50%) and H_2O (1.6 mL), 120 °C, under N_2, the reactions were monitored by TLC and/or GC until **2** work out. [b] 1 mmol scale, 30 min. [c] 130 °C. [d] 100 °C.



Scheme 2 Proposed mechanism for the direct phosphorylation of benzylic C–H bonds under transition metal-free reaction conditions.

aspects could be grasped based on experimental results. Firstly, the desired product **3a** was not detected when the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added, implying that a radical pathway might be possible in this reaction (entry 16). Secondly, the reaction only occurred in aqueous phase, and relied on the presence of PTC (phase transfer catalyst), as seen in that **3a** was difficultly formed in entries 1 and 2 of Table 1. In most cases, 1,2-diphenylethane **4** was detected, which showed benzyl radical **5** should be involved.[17]

We supposed **1** is converted to benzyl radical **5** by SO_4^- radical that is generated *via* hemolytic cleavage of potassium persulfates.[18] Meanwhile, phosphorus radical **6** is similarly formed from **2.** Because potassium persulfate was water soluble, both **1** and **2** had to be transferred into aqueous solution to react with potassium persulfates.[19] This proposal is also in accord with the experimental results that no products of sp^2C–H phosphorylation are detected, which are the main products in the previous radical systems.[20] Finally, cross couplings between **5** and **6** produce **3** (Scheme 2).

Conclusions

In summary, we have achieved the first direct phosphorylation of benzylic C–H bonds with secondary phosphine oxides in a biphasic system under the transition metal-free reaction conditions *via* radical/radical sp^3C–H/P(O)–H cross coupling. This transformation is applicable to various toluene derivatives, affording a new atom-economic protocol for sp^3C–P bond formation. Compared with the previous reports, this novel process based on a readily available reaction system exhibits exclusive chemo- and regioselectivity.

Conflicts of interest

There are no conflicts to declare.

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20 Those reactions proceed via a process involving electrophilic addition of phosphorus radical to aromatic cycles, single-electron transfer and subsequent deprotonation, see ref. 10*c*–*h*.