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Radical phosphinylation of α,α-diaryl allylic alcohols with concomitant 1,2-aryl migration†

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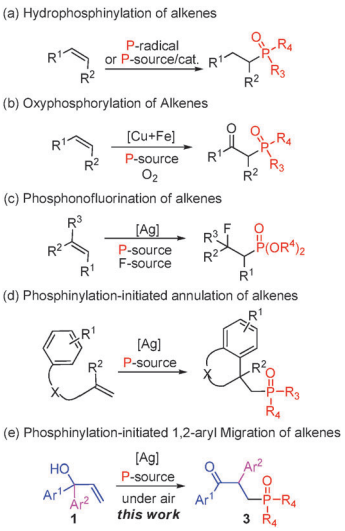
A novel radical phosphinylation of α,α-diaryl allylic alcohols with arylphosphine oxides was described for the direct preparation of α-aryl-β-phosphinylated carbonyl ketones in medium to good yields *via* 1,2-aryl migration. In this reaction, formation of new C(Ar)–C(sp^3) and C(sp^3)–P bonds was observed.

Organophosphorus compounds are privileged and important, which have attracted considerable attention because of their wide applications in pharmaceuticals[1] and agrochemicals,[2] organic synthesis,[3] as well as materials science.[4] They have also been utilized as excellent ligands for transition-metal catalysis and organocatalysts.[5] As such, intense research interests have been paid to explore practical synthesis *via* C–P bond construction.

The addition of P(O)–H bonds to alkenes (hydrophosphination) represents one of the most important processes (Scheme 1a), which is often promoted by radical initiators,[6] strong bases,[7] acids,[8] UV- or microwave-irradiation.[9,10] Although diverse C(sp^3)–P,[11] C(sp^2)–P[12] bond forming reactions *via* transition metal-catalyzed phosphination have proven to be efficient in the past few decades, new types of C–P formation are still highly desirable and present a considerable challenge. In 2011, Ji and coworkers established a copper/iron cocatalyzed oxidative synthesis of β-ketophosphonates (Scheme 1b).[13] Recently, Li's group described a silver-mediated C–P and C–F bond formation reaction of unactivated alkenes *via* condensation with diethyl phosphite and selectfluor (Scheme 1c).[14] Very recently, Yang *et al.* found that the active [$Ph_2P(O)Ag$] complexes can be employed to the phosphorylation-initiated cascade annulation of functionalized alkenes (Scheme 1d).[15] In addition, there are a series of studies devoted to incorporate the phosphonic functionality.[16] To the best of our knowledge, a neophyl-type rearrangement[17] driven by



Scheme 1 Phosphinylation of alkenes.

P-centered radical[18] addition to allylic alcohols **1**, leading to a variety of α-aryl-β-phosphinylated carbonyl compounds has never been previously reported (Scheme 1e). As a continuation of our interest in the radical pathway transformations,[19] herein, we describe a novel reaction of radical phosphinylation of α,α-diaryl allylic alcohols, which is emerging as a versatile and powerful tool for C(sp^3)–C and C(sp^3)–P bond formation.

Previous studies[14–16] revealed that phosphonyl radicals can be generated from $Ph_2P(O)H$ with silver salts. Based on this assumption, we initiated our work by using allylic alcohol **1a** and diphenyl phosphine oxide **2a** as a model reaction in the presence of AgOAc as an oxidant in toluene at 120 °C under air (Table 1, for more details, see ESI†). Gratifyingly, phosphinylation with concomitant 1,2-migration of a phenyl group was achieved, and the targeted α-aryl-β-phosphinylated carbonyl compound **3aa** was obtained in 35% LC-yield after 2 h (Table 1, entry 1). Note that a silver mirror was formed during the reaction. Encouraged by the results, we further optimized the reaction conditions. Solvent screening showed that 1,4-dioxane was optimal, providing **3aa** in

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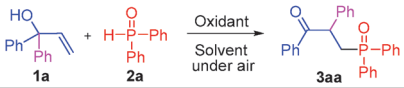
Table 1 Optimization of the reaction conditions[a]



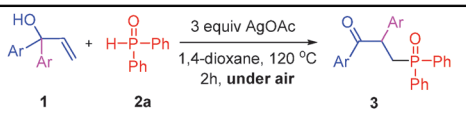
Entry	Oxidant (equiv.)	Solvent	LC-yield (%)[b]
1	AgOAc (2)	Toluene	35
2	AgOAc (2)	$ClCH_2CH_2Cl$	Trace
3	AgOAc (2)	1,4-Dioxane	79
4	$AgNO_3$ (2)	1,4-Dioxane	36
5	$AgCO_3$ (2)	1,4-Dioxane	Trace
6	AgOAc (1)	1,4-Dioxane	21
7	AgOAc (3)	1,4-Dioxane	88 (86)[c]
8	AgOAc (0.2) + $Cu(OAc)_2$ (0.5)	1,4-Dioxane	16
9	AgOAc (0.2) + $K_2S_2O_8$ (2)	1,4-Dioxane	Messy
10	AgOAc (0.2) + DTBP[d] (3)	1,4-Dioxane	47
11	AgOAc (0.2) + $PhI(OAc)_2$(2)	1,4-Dioxane	Messy
12	AgOAc (0.2) + TBHP[e] (3)	1,4-Dioxane	24 (29)[f]
13	AgOAc (0.2) + TBPB[g] (3)	1,4-Dioxane	37 (39)[f]
14	—	1,4-Dioxane	0

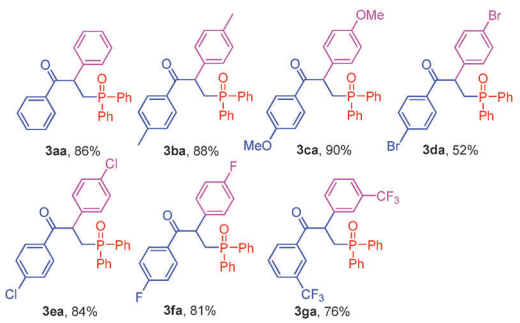
[a] All reactions were carried with **1a** (0.3 mmol), **2a** (0.45 mmol), and oxidant in solvent (2 mL) at 120 °C under air for 2 h. [b] Yields were determined by LC-MS with an internal standard (biphenyl) as the ratio between the formed products and the initial amount of limiting reactant. [c] Isolated yields. [d] DTBP = di-*tert*-butyl peroxide. [e] TBHP = *tert*-butyl hydroperoxide (70% in aqueous solution). [f] The reaction was carried out under Ar. [g] TBPB = *tert*-butylperoxybenzoate.

79% LC-yield (Table 1, entries 1–3). Next, changing AgOAc to other silver salts such as $AgNO_3$ or Ag_2CO_3 just led to lower yields (Table 1, entries 4–5). Additionally, higher oxidant loading (3 equiv.) improved the LC-yield of the model reaction to 88%, along with an isolated yield of 86% (Table 1, entry 7), while an attempt to decrease the oxidant loading was unsuccessful (Table 1, entry 6). Furthermore, a variety of oxidants in the presence of 20 mol% AgOAc were evaluated over whether they have potential for generation of P-radicals,[14–16] but the reactions did not give better results even under an argon atmosphere (Table 1, entries 8–13). Besides, no product was formed without AgOAc (Table 1, entry 14).

Having established the optimal conditions, we next examined other symmetrical and asymmetrical substrates of α,α-diaryl allylic alcohols, and the results were shown in Tables 2 and 3.

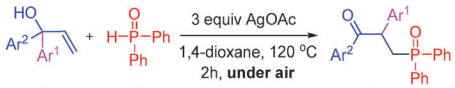
Table 2 Phosphinylation of symmetrical α,α-diaryl allylic alcohols[a]

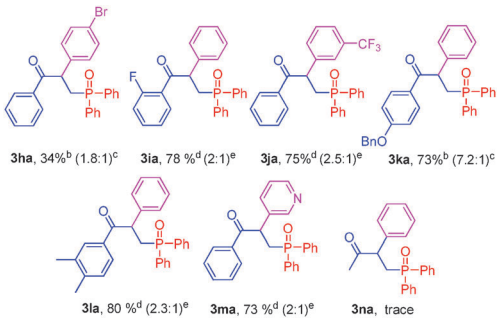




[a] All reactions are carried out under the optimal conditions; yields of isolated products.

Table 3 Phosphinylation of asymmetrical α,α-diaryl allylic alcohols[a]



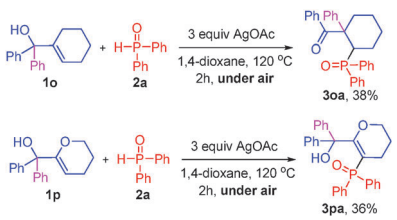


[a] All reactions are carried out under the optimal conditions; yields of isolated products. [b] Yields only of major products. [c] The ratio of **3** to its isomer was determined by ^{1}H NMR of the crude product. [d] Yields of **3** and its isomer, only major products are shown. [e] The ratio of **3** to its isomer was determined by ^{1}H NMR analysis of the isolated product.

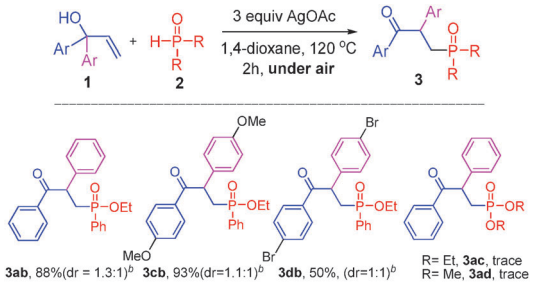
The current method was applied for symmetrical compounds **1** bearing methyl (**1b**) and methoxyl (**1c**) groups on the aromatic ring, affording the desired α-aryl-β-phosphinyl ketones **3ba** and **3ca** in 88% and 90% yields, respectively. Although the electronic effect on the aryl ring reduced the yields to some extent, still good yields of **3da**, **3ea** and **3fa** were obtained. Meanwhile, the *meta*-substituted aryl group also worked as a migrating group and product **3ga** was isolated in 76% yield.

To gain further insight into the selectivity of the aryl migration in this silver-promoted rearrangement reaction, allylic alcohols containing two different aryl groups were used, and the results are listed in Table 3. To our delight, ketone **3ha** was detected as a major product in 34% yield, and the ratio of **3ha** and its isomer was 1.8 : 1. For substrates **1j–l** and heterocyclic **1m**, it was also found that electron-poor aryl groups migrate preferentially. Importantly, this chemoselective manner suggested that the reaction might be a radical ("neophyl") rearrangement route[17] to the observed products. On the other hand, *ortho*-substituted aryl rings (**1i**) migrated less effectively, indicating that steric hindrance had a detrimental effect on the migration. Notably, the mono-aryl-type allylic alcohol **1n** was almost inert under our conditions.

During the course of our studies, cyclic allylic alcohols were chosen as the substrates as well (Scheme 2). It was demonstrated that **1o** also worked under the standard conditions, the desired migrated product **3oa** was obtained in 38% yield. However, when **1p**,



Scheme 2 Reaction of cyclic α,α-diaryl allylic alcohols with **2a**.



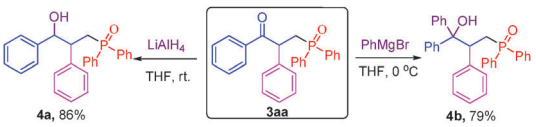
Scheme 3 Phosphinylation of α,α-diaryl allylic alcohols.

a structurally similar heterocyclic allylic alcohol to **1o** was introduced into the reaction with **2a**, no migrated product was observed, a γ-C–H bond phosphinylated product **3pa** was isolated in 36% yield. We supposed that the reaction, after diarylphosphonyl radical attack to the γ-position of **1p**, was more prone to direct oxidation/deprotonation[11d,12g] than aryl rearrangement due to the presence of an oxygen atom.

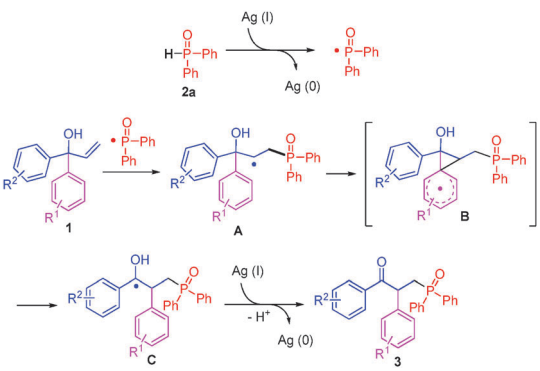
With respect to the diphenyl phosphine oxides, in addition to dialkyl phosphonates **2c** and **2d**, ethyl phenylphosphinate **2b** was a suitable candidate for this transformation, also underwent smoothly addition/rearrangement to afford the corresponding products **3ab**, **3cb** and **3db** in medium to good yields, respectively (Scheme 3).

Further synthetic transformations of the α-aryl-β-phosphinyl ketone products were investigated (Scheme 4). With the reduction of lithium aluminium hydride, **3aa** can be converted into the corresponding γ-benzoyl phosphine oxide **4a**, which was an important class of intermediates in the synthesis of the cyclopropane ring[20] and P-ligands.[21] Moreover, the tertiary alcohol **4b** was obtained in 79% yield by the reaction of the ketone with an aryl Grignard reagent.

On the basis of above results, we proposed a plausible reaction mechanism in Scheme 5. First, a P-centered radical



Scheme 4 Further transformations of the α-aryl-β-phosphinyl ketones.



Scheme 5 Proposed reaction mechanism.

is generated from diphenylphosphine oxide **2a** with Ag(I) salt,[14–16] and reacts with allylic alcohol **1** affording an alkyl radical **A**. Subsequently, an intramolecular addition of the radical to the aromatic ring to generate the spiro[2,5]octadienyl radical **B**, followed by migration of the electron-deficient aryl group preferentially, releases radical **C**. Note that *ortho*-substituted groups are reluctant to migrate owing to a sterically congested radical **B** was not favorable to the energy.[17d] Finally, single-electron transfer (SET) from **C** to silver(I) produces the desired product **3** along with loss of a proton.

In summary, we have developed a novel phosphinylation of α,α-diaryl allylic alcohols *via* 1,2-aryl migration of an aryl group involving new C(Ar)–C(sp^3) and C(sp^3)–P bond formation in one step. A variety of α-aryl-β-phosphinylated carbonyl ketones were obtained in moderate to excellent yields. In addition, chemoselective migration of the two different aryl groups was observed in the reaction. Currently, experiments toward enlarging the scope of the system to the synthesis of other phosphinylated compounds and further mechanistic studies are underway in our laboratory.

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