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Copper catalyzed synthesis of aryl/alkyl mixed phosphates from diphenylphosphoryl azides and aliphatic alcohols under mild conditions

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ABSTRACT

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1. Introduction

In the realm of chemistry, organophosphorus compounds are prominent motifs in terms of living systems and commercial applications, attracting increasing attention from academic as well as industrial researchers [1]. It has been proved that the introduction of a phosphate group could essentially change the chemical and physical properties, resulting in diversified polarization and intermolecular bonding characteristics of the parent structure. In particular, aryl/alkyl mixed phosphates are of great commercial importance [2] acting as versatile precursors in pesticides, fungicides, non-halogenated flame retardant, lubricants, pro-drugs [3], and so on (Scheme 1). For example, compound I, is a wellrecognized synthetic precursor in the preparation of ceftriaxone antibiotic [4]. Compounds II and III are investigated as nucleotide prodrug for the treatment of HIV [5] and novel flame retardant [6], respectively. Nevertheless, these kinds of compounds are costly due to their rare availability from natural sources.

In the last couple of years, tremendous efforts have been made on the preparation of aryl/alkyl mixed phosphates, and several organic phosphoric reagents **IV—VIII** have been extensively documented so

* Corresponding authors. E-mail addresses: lyjiao@nwu.edu.cn (L-Y. Jiao), maxym@nwu.edu.cn (X.-X. Ma). far (Scheme 2). As illustrated in Scheme 2a, the reaction between phosphorus chlorides IV and alcohols are always performed in the presence of Lewis acid and the starting material IV need to be prepared prior to use with different chlorides [7a-7d]. As for the diphenyl phosphite VI, however, since Atherton and Todd reported for the first time in 1940's, the sole example appeared so far was to convert diphenyl phosphite into corresponding diphenoxychlorophosphine chloride in situ [7e] (Scheme 2b). A more straightforward procedure was started with diphenyl phosphate V, which normally undergoes condensation with alcohols [8] to provide target phosphates (Scheme 2c). Disappointingly, however, diphenyl methyl phosphates were always generated with poor reactivities [8c,8d,8f]. Additionally, transesterification and oxidation can be viewed as alternatives. Very recently, the Kang group disclosed a key extension to prepare the target molecular through transesterification mediated by Tf₂O and pyridine, providing outstanding chemoselectivity to the existing methodology library [9] (Scheme 2d). In 2009, an interesting example for the photooxidation of phosphites was elucidated by Nishiyama and Ando under organotelluride catalysis, where O₂ was employed as terminal oxidant [10] (Scheme 2e). Besides, different other reagents such as phosphoric-sulfonic anhydrides [11a], N-phosphoryl oxazolidinone [11b,11c], benzotriazole-based phosphonyl reagents [11d] could also lead to desired product. In a word, some of the phosphoric

An efficient and convenient one-pot protocol is developed to prepare aryl/alkyl mixed phosphates in the presence of copper catalyst under exceptionally mild conditions. A series of versatile, ubiquitous, and inexpensive phosphoryl azides and aliphatic alcohols are combined for the first time ever. Diphenylphosphoryl azide is employed as novel phosphors reagent through an unexpected cleavage of P—N bond. The transformation is advantageous with respect to a broad of functional group compatibility and different esterification products are isolated in good to excellent results. This new catalytic system represents a superior platform towards a mild, operationally simple, practical, and scalability alternative to access target molecules. Furthermore, a plausible mechanism is proposed based on insightful mechanistic studies.

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Scheme 1. Representative examples of aryl/alkyl mixed phosphates.

reagents are corrosive, unstable, difficult to prepare and expensive. Apart from this, these reactions always suffer from drawbacks in terms of the requirements of excess additives, harsh reaction conditions, narrow substrate scope and low reactivity. From the viewpoint of synthesis application, it is highly desirable but challenging to develop a new synthetic method from a low cost and readily available phosphoric reagent.

Being recognized as an "energetic reagent", diphenylphosphoryl azide (DPPA) was widely used in many kinds of transformations due to its various reactivities under distinguished reaction conditions [12,13]. Generally, it could serve as an azido source through the cleavage of the P–N bond under base conditions [14] (Scheme 3a). On the other hand, an amino moiety could be delivered deriving from DPPA via the cleavage of N_{α} -- N_{β} bond in the presence of transition metals, such as Cu, Co, Ru, and Ir, followed by C-H bond insertion to afford aminadion products [15] (Scheme 3b). Enlightened by this, we envisioned that the DPPA, which are readily accessible and inexpensive, might act as potential phosphorylation reagents through the cleavage of P-N bonds through a different reaction setup.

Herein, we developed a novel and practical method to access a wide range of mixed phosphates from DPPA under mild reaction conditions, which serve as newly phosphorylatipon reagents through the unusual copper catalyzed cleavage of P-N bond (Scheme 3c).

2. Results and discussion

Then we concentrated on the establishment of reaction condition in a systematic manner. From the standpoint of simplicity

(a) substitution

OPh $O = \dot{P} - CI (IV)_{-}$

and economics, the diphenylphosphoryl azide (1a) was subjected to methanol (2a) to identify the catalytic system under air. As the results depicted in Table 1, methanol (2a) was in excess and served both as reactant and solvent. However, no conversion was observed initially (entry 1). Satisfyingly, the addition of 5 mol% CuCl led to the formation of desired product 3aa in almost full conversion and 87% isolated yield over a prolonged reaction time (entry 2). It is especially noteworthy that copper was chosen as the metal because of its square planar geometry reducing the impact of steric effects [16]. Interestingly, unlike classical transformations [15], the unexpected P–N bond rather than the N_{α} – N_{β} bond was activated in this transformation. Doubling the loading of copper salts led to exclusive increasing the isolated yield, yet at the same time, shorten reaction time significantly (entry 3). The effect of copper source on the reaction system was further investigated. As shown in Table 1, Cu(I) and Cu(II) were efficient to furnish the product with good yield in range of 78–95%, wheres a reduced yield was observed in case of Cu(0) (entries 4–12). It was found that the counterion has an influence on reactivity as well, replacement of CuCl with other copper source all reduced the yield to varying degree. We are pleased to find the reaction is not sensitive to the water, thus the reaction could be performed under air and in the presence of moisture, which exhibited the convenience of our protocol. Additional efforts was dedicated to promote the yields by screening the temperature and additives. A correlation between yields and temperature revealed the best result was obtained in 40 °C (entries 3, 13, 14). With this result in hand, we next explored the additives. The presence of base improved the yield, which might due to the generation of more nucleophilic alkoxyl aion under base condition (entries 15, 16). Considering the high cost and viscosity of aliphatic alcohols, we turned our attention to employ other reaction media. After a solvent screening (entries 17-22), the best result was outlined in entry 21, 96% yield was achieved in cyclohexane at 40 °C for 24 h, which represents a highly efficient and convenient approach for this transformation.

Inspired by this result, a variety of aliphatic alcohols were explored under optimized reaction conditions (Table 2). Alcohols bearing alkyl, aryl, and alkyene functionalities all undertaken the reaction smoothly, leading to the corresponding phosphates in excellent yields. The electron withdrawing substituted alkyl alcohol was inferior to electron donating substituents, affording the products in slightly lower yield $(2b \rightarrow 3ab vs 2c \rightarrow 3ac)$. The reactivity pattern may indicate the increased nucleophicility of alcohol would facilitate the reaction. It appeared that the steric effect has an important influence on the reactivity. In general, the primary alcohols were superior to the secondary ones $(2d \rightarrow 3ad, 2f \rightarrow$ **3af** vs $2e \rightarrow 3ae$, $2g \rightarrow 3ag$), however, almost no conversion was observed when tertiary alcohol with a *tert*-butyl substituent was employed $(2h \rightarrow 3ah)$. In addition, the diminished yields were obtained in case of cyclopentanol (2m) and cyclohexanol (2n), respectively. These results suggested the reaction might involve-

OPh



Scheme 2. Well developed methods to prepare aryl/alkyl mixed phosphates.





Scheme 3. Types of bond cleavage of DPPA under distinguishing conditions.





Entry	Catalyst (x)	Additive (y)	Solvent	T (°C)	t (h)	Yield (%) ^b
1	_	_	МеОН	40	15	nd ^c
2	CuCl (5)	—	MeOH	40	24	87
3	CuCl (10)	—	MeOH	40	3	95
4	Cul (10)	—	MeOH	40	3	traces
5	$CuCl_2 \cdot 2H_2O(10)$	—	MeOH	40	3	30
6	CuF ₂ (10)	—	MeOH	40	3	80
7	$Cu(OAc)_2$ (10)	—	MeOH	40	3	78
8	Cu(OTf) ₂ (10)	—	MeOH	40	3	82
9	Cu(NO ₃) ₂ ·3H ₂ O (10)	—	MeOH	40	3	93
10	$CuSO_4 \cdot 5H_2O(10)$	—	MeOH	40	3	36
11	CuO (10)	—	MeOH	40	3	traces
12	Cu powder (10)	—	MeOH	40	3	40
13	CuCl (10)	—	MeOH	rt	24	88
14	CuCl (10)	—	MeOH	60	2	93
15	CuCl (10)	NaOH (0.5)	MeOH	40	3	96
16	CuCl (10)	Na_2CO_3 (0.5)	MeOH	40	3	98
17	CuCl (10)	—	CH ₂ Cl ₂ :MeOH (9:1)	40	24	69
18	CuCl (10)	—	dioxane:MeOH (9:1)	40	24	46
19	CuCl (10)	—	MeCN:MeOH (9:1)	40	24	traces
20	CuCl (10)	—	Et ₂ O:MeOH (9:1)	40	24	67
21	CuCl (10)	_	cyclohexane:MeOH (9:1)	40	24	96
22	CuCl (10)	—	DMF:MeOH (9:1)	40	24	70

Reaction conditions: 1a (0.5 mmol, 1.0 equiv.), 2a (excess amount employed) with indicated amount of catalyst, additive in solvent under air atmosphere. а b Isolated yield after purification by flash column chromatography on silica gel.

nd = Not detected.

ment of SN₂ pathway. To our delight, the alcohols bearing a long alkyl chain (2q) which represents a useful building block in drug discovery showed high reactivity. Furthermore, it should be mentioned that the alcohols with a C1 to C7 alkyl chain were all well compatible, showing the potential applications of this transformation. Thus, it could be concluded that after reaching a certain level

of electron-richness required for the desired esterification, modification of the steric demand becomes more important than modulation of the length of carbon chain parameters.

Subsquently, a varity of phosphoryl azides were investigated as well. As shown in Table 3, various phosphoryl azides bearing methyl (1b-1d) and methoxyl (1e) substituents on aryl ring

Table 2

Variation of aliphatic alcohols under optimized reaction conditions to prepare aryl/ alkyl mixed phosphates with DPPA.^a



^aReaction conditions: **1a** (0.5 mmol, 1.0 equiv.), **2a-2q** (0.2 mL, excess amount), CuCl (10 mol%), Na₂CO₃ (0.5 equiv.) in cyclohexane (1.8 mL) as co-solvent at 40 °C for 24 h under air atmosphere. Data in the brackets refer to isolated yield after purification by flash column chromatography on silica gel. ^bWith out the addition of Na₂CO₃.

^cReactions conducted at 60 °C.

irrespective of the substituted positions were well compatible, affording the desired products in comparable high yields (**1b**-**1e** \rightarrow **3ba-3ea**). This result showed that the steric hindrance on DPPA had negligible effect on the reaction. Nevertheless, the halogen group was not tolerant, the yield was reduced dramatically in terms of a bromo substituted phosphoryl azide (**1f** \rightarrow **3fa**).

Table 3

Variation of phosphoryl azide under optimized reaction conditions to prepare aryl/ alkyl mixed phosphates with MeOH. $^{\rm a}$



^aReaction conditions: **1a–1f** (0.5 mmol, 1.0 equiv.), **2a** (excess amount), CuCl (10 mol%), in methanol (2.0 mL) at 40 °C for 3–15 h under air atmosphere. Data in the brackets refer to isolated yield after purification by flash column chromatography on silica gel.

^bIsolated yield after 3 h reaction time. ^cIsolated yield after 6 h reaction time.

^dIsolated yield after 15 h reaction time.

In order to further demonstrate the scalability and practicality of this catalytic system, a gram scale reaction was carried out by using 5.0 mmol of DPPA (**1a**) in methanol (**2a**). The product was generated in 93% yield (Scheme 4).

With respect to clarify the reaction mechanism, a number of control experiments were conducted to gain further insights. The competition experiments between propanol (**2d**) and isopropanol (**2e**) was conducted, resulting in the desired phosphates in an approximately 92:8 (**3ad**:**3ae**) ratio (Scheme 5), the data revealed the steric effect of alcohol play a crucial role in the reaction. The obvious steric effect of alcohol provide the evidence for the involvement the SN₂ pathway.

As far as we know, processes involving both copper salts and organic azides are Chan–Lam type reaction, in which sulfonyl azides or azidoformates could couple with aryl boronic aicd to furnish an amide group [17]. Considering the Chan–Lam intermediate would be involved, phenylboronic acid (4) was subjected to our reaction system. However, no typical Chan–Lam product **5** was detected, demonstrating that the formation of the corresponding pathway was not involved in our transformation (Scheme 6). Furthermore, previous reported Chan–Lam mechanism indicated that Cu(I), Cu(II), and Cu(III) were all involved in the catalytic cycle, in which O_2 serves as terminal oxidant. We then conducted our reaction under inert atmosphere whereas N_2 was tolerated and was even beneficial in this transformation (Scheme 7).

A comparable yield was obtained in the presence of 2,2,6,6-tet ramethylpiperidinooxy (TEMPO) as radical scavenger, demonstrating that the radical suspect [18] was ruled out (Scheme 8).

^d3.0 Equiv. of **2q** was used.



Scheme 4. Gram scale synthesis of diphenyl methyl phosphate 3aa.



Scheme 5. Intermolecular competition of 2d and 2e with DPPA.



Scheme 6. Chan-Lam type product 5 not detected.



Scheme 7. Atmosphere effect on the formation of mixed phoshate 3aa.

Additionally, we also referred to the density functional theory (DFT) calculations to understand our pathway, it has proved that the formation of the matal-azido adduct was quite plausible [17b,c,19]. Accordingly, a proposed mechanism for the coppercatalyzed esterification of diphenylphosphoryl azide compounds with alcohols was put forward in Scheme 9. The metal-azido



Scheme 8. The effect of TEMPO on the 3aa formation.



Scheme 9. Proposed mechanism for the transformation.

intermediate was generated in situ between the reaction of DPPA and [Cu] catalyst, followed by a SN_2 type nucleophilic attack with the alkoxyl anion. Afterwards, the desired phosphate was accomplished. At the same time, the released unstable [Cu—N₃] species was decomposed immediately to regenerate [Cu] catalyst and deliver a N₂ molecular. It was worth mentioning that the addition of base could accelerate the product formation through the deprotonation of alcohols. More detailed mechanistic studies is currently undertaken in our laboratory.

3. Conclusion

To sum up, the reaction of phosphoryl azides and aliphatic alcohols was accomplished efficiently under copper catalysis for the first time. The inexpensive and readily available phosphoryl azides served as phosphrous source through an unexpected cleavage of P—N bond. Our protocol was applicable for a broad substrate scope of aliphatic alcohols with high functional group tolerance under mild reaction conditions. A series of aryl/alkyl mixed phosphates was prepared in high yield. The employment of inexpensive reagents, together with the mild reaction condition, operational simplicity, and up-gradation possibility, making our approach amenable for technical applications. Some control experiments were launched to gain insight and a mechanism was proposed accordingly.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.09.014.

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