Chinese Chemical Letters xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Direct synthesis of α-hydroxyketone phosphates from terminal alkynes and *H*-phosphine oxides in the presence of $PhI(OAc)_2$ and H_2O

Dong-Yan Hu [a,c], Meng-Shun Li [a,c], Wen-Wu Zhong [b,c], Jian-Xin Ji [b], Jin Zhu [a], Wei Wei [d], Qiang Zhang [b,*], Ming Cheng [b,*]

[a] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China
[b] Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, China
[c] University of the Chinese Academy of Sciences, Beijing 100049, China
[d] School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, China

ARTICLE INFO

Article history:
Received 1 April 2016
Received in revised form 4 May 2016
Accepted 10 May 2016
Available online xxx

Keywords:
α-Hydroxyketone phosphates
Alkynes
H-Phosphine oxides
Water
Phenyliodine diacetate

ABSTRACT

A simple and highly efficient one-pot method for the construction of α-hydroxyketone phosphates from terminal alkynes and *H*-phosphine oxides has been developed in the presence of $PhI(OAc)_2$ and H_2O. The present protocol provides an attractive approach to α-hydroxyketone phosphates in good to high yields, with the advantages of operation simplicity, the use of commercially available materials, broad substrate scope, high atom efficiency and good tolerance to scale-up synthesis.

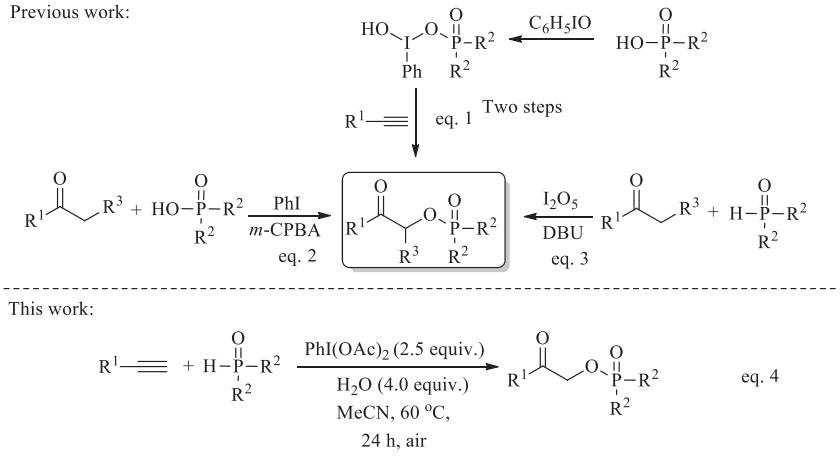
1. Introduction

Organophosphates have attracted increasingly synthetic pursuit of chemists because of their widely applications in many major physiological processes [1], drug discovery [2], organic synthesis [3] and agrochemicals [4]. Particularly, α-hydroxy-ketone phosphates can be used as sugar analogues [5] and important intermediates for the construction of phospholipid and oligonucleotide through the selective hydrolytic removal of the ketoxide motif [6]. As such, the development of general and efficient methods to access α-hydroxyketone phosphates is of great interest. Traditionally, α-hydroxyketone phosphates are synthesized by the α-phosphoryloxylation of ketones with the [hydroxy(phosphoryloxy)iodo]arenes [7], the reaction of 2,2,2-trialkoxy-1,3,2-dioxaphospholen with hydrogen chloride [5], and the oxyphosphorylation of silyl enol ethers with phosphoric acid and *p*-(difluoroiodo) toluene [8]. An alternative method for the construction of α-hydroxyketone phosphates has also been developed *via* the addition of terminal alkynes with unstable hypervalent iodine compound intermediate, which was preformed from the reaction of phosphonic acid with iodosobenzene (Scheme 1, Eq. (1)) [9]. However, all these methods suffer from limitations such as unreadily available starting materials, tedious work-up procedures, relatively harsh reaction conditions, toxic chemical wastes, the poor substrate scope, or low yields. Therefore, it is still highly desirable to develop a simple, convenient and efficient approach to α-hydroxyketone phosphates.

In 2012, Yan [10] and co-workers reported iodobenzene/*m*-chloroperbenzoic acid (*m*-CPBA) mediated the α-phosphoryloxylation of ketones with $(RO)_2PO_2H$ (Scheme 1, Eq. (2)). Very recently, Wang *et al.* [11] reported a new method for the construction of α-hydroxyketone phosphates through I_2O_5/DBU mediated direct α-phosphoryloxylation of ketones with H-phosphonates (Scheme 1, Eq. (3)). Nevertheless, stoichiometric amount of potentially dangerous peroxide oxidant or base are still required in the two well developed reactions. Here, we wish to report a simple, convenient and highly efficient $PhI(OAc)_2$ mediated procedure for the construction of α-hydroxyketone phosphates from alkynes and *H*-phosphine oxides in the presence of water under mild conditions (Scheme 1, Eq. (4)). The present protocol provides an alternative and highly attractive route to various α-hydroxyketone phosphates from the commercially available starting materials, and especially it avoids the use of

* Corresponding authors.
E-mail addresses: zhangqiang@cib.ac.cn (Q. Zhang), chengming198101@163.com (M. Cheng).

http://dx.doi.org/10.1016/j.cclet.2016.05.029
1001-8417/



Scheme 1. Methods for the synthesis of α-hydroxyketone phosphates.

unstable reagents, and stoichiometric amounts of bases, toxic or potentially dangerous oxidants.

2. Experimental

All chemicals and solvents were purchased from Aldrich, J&K and Alfa Aesar Chemical Company as reagent grade and used without further purification unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were collected in $CDCl_3$ on a Bruker Avance 400 spectrometer with TMS as internal standard at room temperature, ^{31}P NMR spectra were recorded at 162 MHz, and chemical shifts (δ) reported relative to external 85% phosphoric acid (δ = 0.0 ppm), the chemical shifts (δ) were expressed in parts per million (ppm) and *J* values were given in hertz (Hz). HRMS were performed on a Brucker Daltonics Bio-TOF-Q mass spectrometer by the ESI method and LC–MS were obtained on a on a Waters Xevo TQ (Waters, Manchester, UK) equipped with an ESI source. The products were purified by flash column chromatography on silica gel (200–300 mesh).

2.1. General procedure for the synthesis of α-hydroxyketone phosphates **3**

To a solution of diarylphosphine oxides **2** (0.5 mmol) in acetonitrile (3.0 mL) were added $PhI(OAc)_2$ (1.25 mmol), H_2O (2.0 mmol) and alkynes **1** (0.75 mmol). The reaction mixture was then stirred for 24 h at 60 °C in air. After the reaction, the solvents were removed under vacuum. The residue was purified by flash chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (1:1) as eluent to give the desired product **3**.

2.2. The procedure of gram-scale reaction for the synthesis of ***3aa***

To a solution of diphenylphosphine oxide **2a** (2.02 g, 10.0 mmol) in acetonitrile (60.0 mL) were added $PhI(OAc)_2$ (8.05 g, 25.0 mmol), H_2O (720.0 μL, 40.0 mmol) and phenylacetylene **1a** (1.53 g, 15.0 mmol). The reaction mixture was then stirred for 24 h at 60 °C in air. After the reaction, the solvents were removed under vacuum. Water (60.0 mL) was added to the reaction mixture, and then the mixture was extracted with EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (1:1) as eluent to give the desired product **3aa** (2.99 g, 89%).

2.3. The reaction of diphenylphosphine oxide ***2a*** with $PhI(OAc)_2$

To a solution of diphenylphosphine oxide **2a** (1.0 mmol) in acetonitrile (6.0 mL) were added $PhI(OAc)_2$ (1.0 mmol) and H_2O (4.0 mmol). The reaction mixture was then stirred for 24 h at 60 °C in air. After the reaction, the solvents were removed under vacuum. The residue was purified by flash chromatography on silica gel using a mixture of dichloromethane and methanol (5:1) with addition of AcOH (1‰) as eluent to give the desired product **6a** (209.0 mg, 96%).

2.4. The reaction of phenylacetylene ***1a*** with diphenylphosphinic acid ***6a***

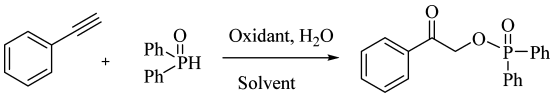
To a solution of diphenylphosphinic acid **6a** (0.5 mmol) in acetonitrile (3.0 mL) were added $PhI(OAc)_2$ (1.25 mmol), H_2O (2.0 mmol) and phenylacetylene **1a** (0.75 mmol). The reaction mixture was then stirred for 24 h at 60 °C in air. After the reaction, the solvents were removed under vacuum. The residue was purified by flash chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (1:1) as eluent to give the desired product **3aa** (153.0 mg, 91%).

3. Results and discussion

At the outset of our investigation, the reaction of phenylacetylene **1a** and diphenylphosphine oxide **2a** was chosen as the model reaction to optimize the reaction conditions. Gratifyingly, the desired product **3aa** was obtained in 26% yield when the model reaction was performed in the presence of $PhI(OAc)_2$ (1.0 equiv.)/H_2O (1.0 equiv.) at 60 °C in air for 24 h (Table 1, entry 1). It was found that the reaction gave a better yield 40% when the loading of H_2O was increased to 4.0 equiv. (Table 1, entry 4). Further optimization suggested that the reaction efficiency was obviously improved with the increasing of $PhI(OAc)_2$ loading, the best yield was obtained when 2.5 equivalent of $PhI(OAc)_2$ was used (Table 1, entry 9). The screening of other oxidants, such as $K_2S_2O_8$, *m*-CPBA, TBHP and H_2O_2 could not improve the reaction efficiency (Table 1, entries 11–14). Subsequent investigation on the effect of solvents showed that the reaction performed in MeCN was found to be superior for the formation of **3aa** (Table 1, entries 15–20). In addition, we found that the reaction temperature also played an important role in this transformation (Table 1, entries 9, 21–23). The desired product **3aa** was isolated in only 36% yield when the model reaction was carried out at room temperature (Table 1, entry 21), and the best yield was obtained when the reaction was

Please cite this article in press as: D.-Y. Hu, et al., Direct synthesis of α-hydroxyketone phosphates from terminal alkynes and *H*-phosphine oxides in the presence of $PhI(OAc)_2$ and H_2O, Chin. Chem. Lett. (2016), http://dx.doi.org/10.1016/j.cclet.2016.05.029

Table 1
Optimization of reaction conditions.[a]

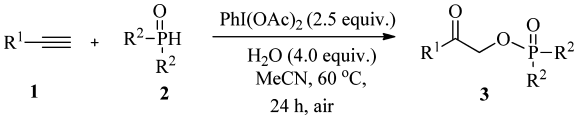


1a **2a** **3aa**

Entry	H_2O (equiv.)	Oxidant (equiv.)	Solvent	T (°C)	Yield (%)[b]	Entry	H_2O (equiv.)	Oxidant (equiv.)	Solvent	T (°C)	Yield (%)[b]
1	1.0	$PhI(OAc)_2$ (1.0)	MeCN	60	26	13	4.0	TBHP (2.5)	MeCN	60	0
2	2.0	$PhI(OAc)_2$ (1.0)	MeCN	60	33	14	4.0	H_2O_2 (2.5)	MeCN	60	0
3	3.0	$PhI(OAc)_2$ (1.0)	MeCN	60	38	15	4.0	$PhI(OAc)_2$ (2.5)	1,4-dioxane	60	0
4	4.0	$PhI(OAc)_2$ (1.0)	MeCN	60	40	16	4.0	$PhI(OAc)_2$ (2.5)	THF	60	0
5	5.0	$PhI(OAc)_2$ (1.0)	MeCN	60	39	17	4.0	$PhI(OAc)_2$ (2.5)	Toluene	60	79
6	6.0	$PhI(OAc)_2$ (1.0)	MeCN	60	36	18	4.0	$PhI(OAc)_2$ (2.5)	DCE	60	81
7	4.0	$PhI(OAc)_2$ (1.5)	MeCN	60	61	19	4.0	$PhI(OAc)_2$ (2.5)	EtOH	60	12
8	4.0	$PhI(OAc)_2$ (2.0)	MeCN	60	82	20	4.0	$PhI(OAc)_2$ (2.5)	DMF	60	21
9	4.0	$PhI(OAc)_2$ (2.5)	MeCN	60	90	21	4.0	$PhI(OAc)_2$ (2.5)	MeCN	25	36
10	4.0	$PhI(OAc)_2$ (3.0)	MeCN	60	88	22	4.0	$PhI(OAc)_2$ (2.5)	MeCN	40	55
11	4.0	$K_2S_2O_8$ (2.5)	MeCN	60	0	23	4.0	$PhI(OAc)_2$ (2.5)	MeCN	70	84
12	4.0	*m*-CPBA (2.5)	MeCN	60	0	24	0	$PhI(OAc)_2$ (2.5)	MeCN	60	0

[a] Reaction conditions: Phenylacetylene **1a** (0.75 mmol), diphenylphosphine oxide **2a** (0.5 mmol), H_2O (0–6 equiv.), oxidant (1–3 equiv.), solvent (3.0 mL), air, 24 h.
[b] Isolated yields based on **2a**.

Table 2
Results for the synthesis of α-hydroxyketone phosphates from terminal alkynes and *H*-phosphine oxides.[a]



1 **2** **3**

Entry	R^1	R^2	Product	Yield (%)	Entry	R^1	R^2	Product	Yield (%)
1	C_6H_5	C_6H_5	**3aa**	90	15	4-$(CH_2CN)C_6H_4$	C_6H_5	**3oa**	85
2	2-MeC_6H_4	C_6H_5	**3ba**	65	16	1-naphthyl	C_6H_5	**3pa**	64
3	3-MeC_6H_4	C_6H_5	**3ca**	83	17	3-thienyl	C_6H_5	**3qa**	78
4	4-MeC_6H_4	C_6H_5	**3da**	80	18	2-phenylethyl	C_6H_5	**3ra**	83
5	4-EtC_6H_4	C_6H_5	**3ea**	75	19	Cyclohexyl	C_6H_5	**3sa**	73
6	4-$MeOC_6H_4$	C_6H_5	**3fa**	69	20	*n*-Butyl	C_6H_5	**3ta**	74
7	4-FC_6H_4	C_6H_5	**3ga**	79	21	*t*-Butyl	C_6H_5	**3ua**	68
8	4-BrC_6H_4	C_6H_5	**3ha**	82	22	Cyclopentylmethyl	C_6H_5	**3va**	70
9	4-ClC_6H_4	C_6H_5	**3ia**	80	23	3-Cyano-*n*-Propyl	C_6H_5	**3wa**	69
10	2-ClC_6H_4	C_6H_5	**3ja**	69	24	C_6H_5	4-$MeOC_6H_4$	**3ab**	68
11	3-ClC_6H_4	C_6H_5	**3ka**	82	25	C_6H_5	4-MeC_6H_4	**3ac**	65
12	4-$CF_3C_6H_4$	C_6H_5	**3la**	81	26	C_6H_5	4-FC_6H_4	**3ad**	87
13	4-$NO_2C_6H_4$	C_6H_5	**3ma**	75	27	C_6H_5	4-ClC_6H_4	**3ae**	91
14	4-$(CO_2Me)C_6H_4$	C_6H_5	**3na**	76					

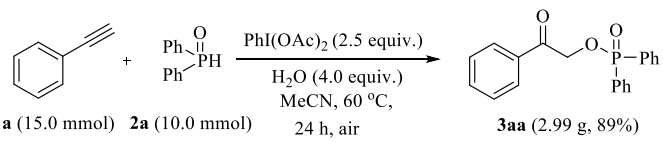
[a] Reaction conditions: **1** (0.75 mmol), **2** (0.5 mmol), $PhI(OAc)_2$ (1.25 mmol), H_2O (2.0 mmol), MeCN (3.0 mL), 60 °C, air, 24 h. Isolated yields based on **2**.

conducted at 60 °C. It should be noted that none of desired product **3aa** was detected when the reaction performed in the absence of H_2O, suggesting that H_2O could play the key role in the synthesis of α-hydroxyketone phosphates (Table 1, entry 24).

With the optimal conditions in hand, we next examined the substrate scope of this transformation. In general, both electron-rich and electron-deficient aromatic alkynes were all suitable for this reaction to afford α-hydroxyketone phosphates in good to high yields under the standard conditions (Table 2, **3aa**–**3oa**). The substituent groups on the *ortho*-position of aromatic ring led to a negative effect on the reaction efficiency, which might be caused by the steric hindrance (Table 2, **3ba** and **3ja**). Also, functional groups such as halogen, trifluoromethyl, nitro, cyano, and carboxylic ester were all well tolerated, whose corresponding products can be applied in further modifications (Table 2, **3ga**–**3oa**). It was observed that 1-ethynylnaphthalene and heteroaromatic alkenes such as 3-ethynylthiophene were also tolerated to afford the product **3pa** and **3qa** in 64% and 78% yields, respectively. Notably, when aliphatic alkynes were used as the substrates, the corresponding products were also obtained in good yields (Table 2, **3ra**–**3wa**). With respect to the *H*-phosphine oxides, in addition to diphenylphosphine oxide **2a**, other diarylphosphine oxides bearing both electron-donating and electron-withdrawing groups were all suitable substrates, leading to the corresponding products in good to excellent yields (Table 2, **3ab**–**3ae**).

Furthermore, the synthetic applicability of this method was investigated on a gram scale by using the model reaction between **1a** and **2a**. As shown in Scheme 2, the reaction could afford 2.99 g of **3aa** in 89% yield without any significant loss of its efficiency. Thus, this reaction could serve as a practical and efficient protocol to synthesize α-hydroxyketone phosphates.

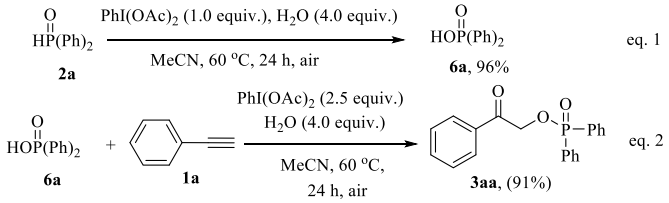
In order to gain some insights into this reaction mechanism, two control experiments were conducted (Scheme 3). When diphenylphosphine oxide **2a** was independently treated with $PhI(OAc)_2$ (1.0 equiv.)/H_2O (4.0 equiv.) in the absence of phenylacetylene, the diphenylphosphinic acid **6a** was obtained in 96%



1a (15.0 mmol) **2a** (10.0 mmol) **3aa** (2.99 g, 89%)

Scheme 2. Gram scale reaction.

Please cite this article in press as: D.-Y. Hu, et al., Direct synthesis of α-hydroxyketone phosphates from terminal alkynes and *H*-phosphine oxides in the presence of $PhI(OAc)_2$ and H_2O, Chin. Chem. Lett. (2016), http://dx.doi.org/10.1016/j.cclet.2016.05.029



Scheme 3. Control experiments.

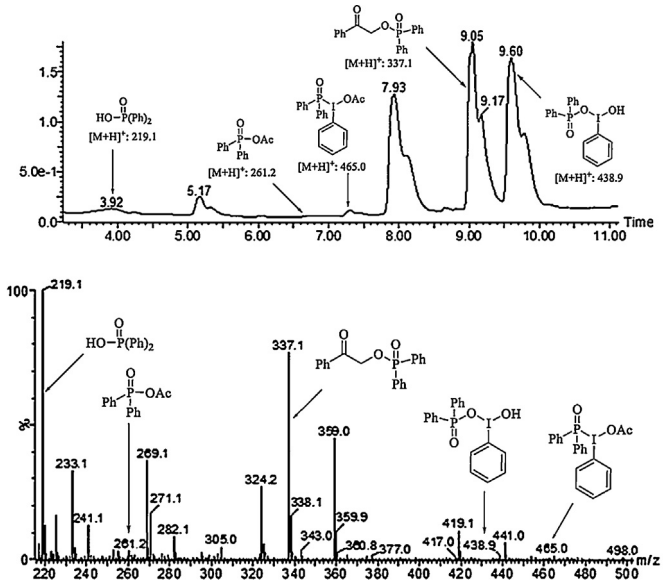


Fig. 1. LC–MS spectrum of **4a**, **5a**, **6a**, **7a** and **3aa**.

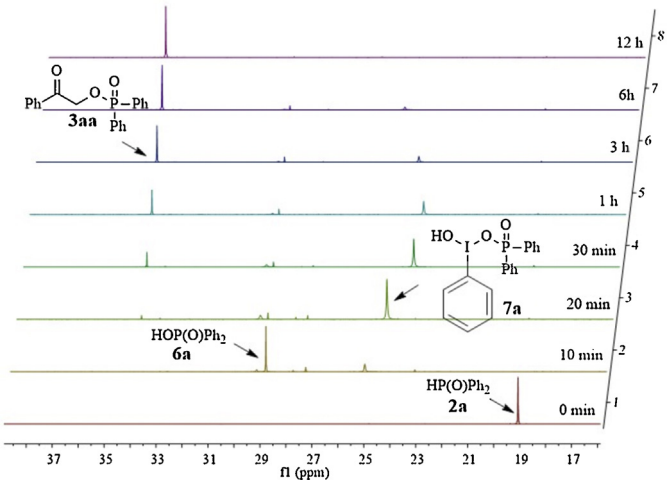
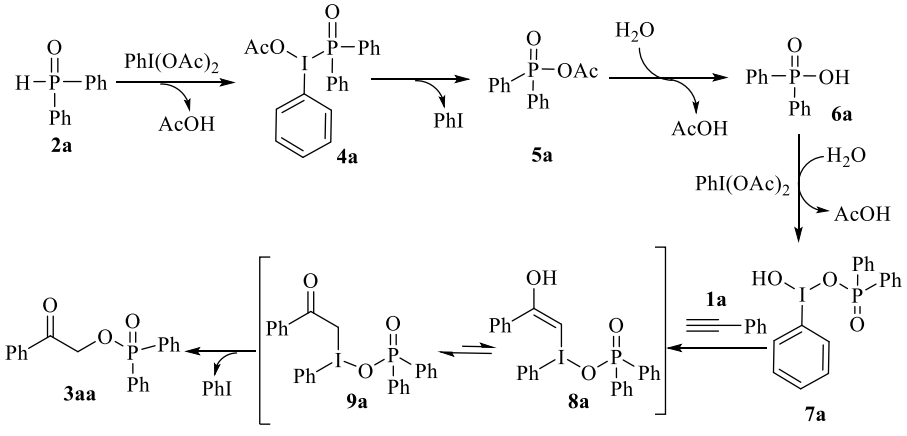


Fig. 2. ^{31}P NMR spectral changes during the reaction process.

yield (Scheme 3, Eq. (1)). Furthermore, the desired product **3aa** could be isolated in 91% yield when the reaction of diphenylphosphinic acid **6a** and phenylacetylene **1a** was performed under standard conditions (Scheme 3, Eq. (2)). The above results indicated that diphenylphosphinic acid **6a** might be a key intermediate in the present reaction system.

On the basis of the above results and previous reports [9,12–14], a tentative reaction pathway was proposed in Scheme 4. Initially, diphenylphosphine oxide **2a** was oxidized by phenyliodine diacetate to give diphenylphosphinic acid **6a** through the consecutive transformation of the intermediate **4a** and **5a** [12]. Subsequently, the resulting diphenylphosphinic acid **6a** reacted with phenyliodine diacetate to form the unstable hypervalent iodine intermediate **7a** [13]. Next, the selective addition of hypervalent iodine reagent **7a** to phenylacetylene **1a** would lead to the formation of **8a**, which underwent isomerization to give hypervalent iodine intermediate **9a** [9,14]. Finally, the reductive elimination of hypervalent iodine intermediate **9a** produced the desired product **3aa** with the release of indobenzene [9]. To our delight, the proposed intermediate **4a**, **5a**, **6a**, and **7a** were all detected by LC–MS analysis when the model reaction was performed at 1.5 h (Fig. 1 and Supporting information for detailed description of LC–MS analysis experiment).

To gain further understanding of the detailed reaction process, the model reaction was monitored by ^{31}P NMR spectroscopy (Fig. 2). In a round-bottom flask, a mixture of diphenylphosphine oxide **2a**, PhI(OAc)$_2$, phenylacetylene **1a** and H_2O was added into CD_3CN. The sample was immediately drawn off and tested by ^{31}P NMR spectrum. The spectrum showed a signal at 19.06 ppm, which was assigned as the starting material diphenylphosphine oxide **2a** [15]. After being heated at 60 °C for 10 min, the signal of **2a** disappeared, while two new signals at 29.02 and 25.20 ppm appeared, which were assigned to be diphenylphosphinic acid **6a** [16] and intermediate **7a** [9,13], respectively. Then, after being heated for 20 min, the signal of diphenylphosphinic acid **6a** slumped while the signal of intermediate **7a** increased dramatically. Moreover, a signal at 34.09 ppm was simultaneously observed, corresponding to signals of the final product **3aa** [9]. With the progress of the reaction, the ^{31}P NMR signal of intermediate **7a** disappeared gradually and the signal of **3aa**



Scheme 4. Possible reaction pathway.

Please cite this article in press as: D.-Y. Hu, et al., Direct synthesis of α-hydroxyketone phosphates from terminal alkynes and *H*-phosphine oxides in the presence of PhI(OAc)$_2$ and H_2O, Chin. Chem. Lett. (2016), http://dx.doi.org/10.1016/j.cclet.2016.05.029

increased. Thus, these data support the mechanistic hypothesis described in Scheme 4.

4. Conclusion

In conclusion, a new and simple method has been developed for the one-pot construction of α-hydroxyketone phosphates from terminal alkynes and *H*-phosphine oxides in the presence of $PhI(OAc)_2/H_2O$. This protocol provides a convenient and efficient approach to various α-hydroxyketone phosphates in good to high yields from commercially available starting materials with high regioselectivity and excellent functional group tolerance. Such an attractive synthesis methodology for α-hydroxyketone phosphates would find the potential applications in the fields of synthetic and pharmaceutical chemistry. The detailed scope, mechanism, and synthetic application of this reaction are currently underway in our laboratory.

Acknowledgments

We gratefully acknowledge financial support from the National Natural Science Foundation of China (Nos. 21172213, 21302109, 21402184, and 21572217).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2016.05.029.

References

[1] M.W. Bowler, M.J. Cliff, J.P. Waltho, G.M. Blackburn, Why did nature select phosphate for its dominant roles in biology, N. J. Chem. 34 (2010) 784–794.
[2] (a) C. Schultz, Prodrugs of biologically active phosphate esters, Bioorg. Med. Chem. 11 (2003) 885–898;
(b) C. Ducho, U. Gorbig, S. Jessel, et al., Bis-cycloSal-d4T-monophosphates: drugs that deliver two molecules of bioactive nucleotides, J. Med. Chem. 50 (2007) 1335–1346;
(c) S.J. Hecker, M.D. Erion, Prodrugs of phosphates and phosphonates, J. Med. Chem. 51 (2008) 2328–2345.
[3] (a) S. Protti, M. Fagnoni, Phosphate esters as "tunable" reagents in organic synthesis, Chem. Commun. 31 (2008) 3611–3621;
(b) A. Parra, S. Reboredo, A.M. Martin Castro, J. Aleman, Metallic organophosphates as catalysts in asymmetric synthesis: a return journey, Org. Biomol. Chem. 10 (2012) 5001–5020.
[4] (a) R. Neumann, H.H. Peter, Insecticidal organophosphates: nature made them first, Experientia 43 (1987) 1235–1237;
(b) H.W. He, The use of OP and development of new organophosphorus agrochemicals in China, Phosphorus Sulfur Silicon Relat. Elem. 183 (2008) 266–279;
(c) J. Wink, F.R. Schmidt, G. Seibert, W. Aretz, Cyclipostins: novel hormone-sensitive lipase inhibitors from *Streptomyces* sp. DSM 13381, I. Taxonomic studies of the producer microorganism and fermentation results, J. Antibiot. 55 (2002) 472–479;
(d) L. Vîrtesy, B. Beck, M. Bronstrup, et al., Cyclipostins, novel hormone-sensitive lipase inhibitors from *Streptomyces* sp. DSM 13381, II. Isolation, structure elucidation and biological properties, J. Antibiot. 55 (2002) 480–494.
[5] F. Ramirez, J. Bauer, C.D. Telefus, Introduction of the amide function into 1, 3, 2-dioxaphospholenes with pentavalent phosphorus, J. Am. Chem. Soc. 92 (1970) 6935–6942.
[6] (a) F. Ramirez, B. Hansen, N.B. Desai, Kinetics and mechanisms of the rapid alkaline hydrolysis of dimethylphosphoacetoin, J. Am. Chem. Soc. 84 (1962) 4588;
(b) H. Witzel, A. Botta, K. Dimroth, Mechanismus der alkalischen hydrolyse von dialkyl-[2-oxo-alkyl]-phosphaten, Chem. Ber. 98 (1965) 1465–1469;
(c) R. Kluger, S.D. Taylor, Mechanisms of carbonyl participation in phosphate ester hydrolysis and their relationship to mechanisms for the carboxylation of biotin, J. Am. Chem. Soc. 113 (1991) 996–1001;
(d) F. Ramirez, J.F. Marecek, Synthesis of phosphodiesters: the cyclic enediol phosphoryl (CEP) method, Synthesis (1985) 449–488.
[7] (a) F. Ramirez, N.B. Desai, Crystalline 1:1 adducts from the reaction of tertiary phosphate esters with ortho-quinones and with alpha-diketones. New routes to quinol-monophosphates and to ketol-monophosphates, J. Am. Chem. Soc. 82 (1960) 2652–2653;
(b) F. Ramirez, S.L. Glaser, A.J. Bigler, J.F. Pilot, Synthesis of sugar-like phosphates by the oxyphosphorane condensation. Reaction of glyoxal with trialkyl phosphites and preparation of phosphate esters of glycolaldehyde, a-hydroxy b-keto aldehydes, and hydroxy malon-aldehyde chloride, J. Am. Chem. Soc. 91 (1969) 496–500;
(c) F. Ramirez, S.B. Bhatia, A.J. Bigler, C.P. Smith, New syntheses of β-keto-α-hydroxy acid chlorides, of α-hydroxy β-diketones, and of their phosphate esters, J. Org. Chem. 33 (1968) 1192–1196;
(d) G.F. Koser, J.S. Lodaya, D.G. Ray, P.B. Kokil, Direct α-phosphoryloxylation of ketones and phosphoryloxylactonization of pentenoic acids with [hydroxy((bi-s(pheny1oxy)phosphory1)oxy)-ido]benzene, J. Am. Chem. Soc. 110 (1988) 2987–2988;
(e) T. Nabana, H. Togo, Reactivities of novel [hydroxy (tosyloxy)iodo]-arenes and [hydroxy(phosphoryloxy)iodo]arenes for α-tosyloxy lation and α-phosphoryloxylation of ketones, J. Org. Chem. 67 (2002) 4362–4365.
[8] G.F. Koser, K.C. Chen, Y.L. Huang, C.A. Summers, Oxyphosphorylation of carbon with phosphoric acid and *p*-(dif1uoroiodo)toluene: synthesis of tris-ketol phosphates and their conversion into lithium bis-ketol phosphates, J. Chem. Soc. Perkin Trans. 1 (1994) 1375–1376.
[9] R.M. Morisrty, C. Condeiu, A. Tao, O. Prskash, New organohyper-valent iodine reagents for α-methylphosphonylations and α-diphenyl- and α-dimethylphosphinylations, Tetrahedron Lett. 38 (1997) 2401–2404.
[10] Y. Pu, L.M. Gao, H.J. Liu, J. Yan, An effective catalytic α-phosphoryloxylation of ketones with iodobenzene, Synthesis 44 (2011) 99–103.
[11] C.L. Liu, W. Wei, D.S. Yang, et al., I_2O_5/DBU mediated direct α-phosphoryloxylation of ketones with H-phosphonates leading to α-hydroxyketone phosphates, Tetrahedron 71 (2015) 6901–6906.
[12] A. Hubacz, S. Makowiec, Direct conversion of secondary phosphine oxides and *H*-phosphinates with [di(acyloxy)iodo]benzenes to phosphinic and phosphonic amides, Heteroatom Chem. 20 (2009) 81–86.
[13] S.A. Moteki, A. Usui, T. Zhang, C.R. Solorio Alvarado, K. Maruoka, Site-selective oxidation of unactivated C_{sp3}-H bonds with hypervalent iodine (III) reagents, Angew. Chem. Int. Ed. 125 (2013) 8819–8822.
[14] S. Khamarui, R. Maiti, R.R. Mondal, D.K. Maiti, Reactant cum solvent water: generation of transient λ^3-hypervalent iodine, its reactivity, mechanism and broad application, RSC Adv. 5 (2015) 106633–106643.
[15] (a) A. Christiansen, C. Li, M. Garland, et al., On the tautomerism of secondary phosphane oxides, Eur. J. Org. Chem. 14 (2010) 2733–2741;
(b) A.A. Bobrikova, M.P. Koroteev, A.M. Koroteev, Y.V. Nelyubina, E.E. Nifant'ev, Phosphorylation of N-glycosides derived from para-substituted aromatic amines, Russ. Chem. Bull 57 (2008) 2021–2027.
[16] O.I. Artyushin, E.V. Sharova, P.V. Petrovskii, I.L. Odinets, N-Alkylation of amidothiophosphoryl compounds under phase-transfer catalysis conditions. Synthesis and properties of 1, 3, 2-thiazaphos-phacyclanes, Russ. Chem. Bull. 58 (2009) 216–222.

Please cite this article in press as: D.-Y. Hu, et al., Direct synthesis of α-hydroxyketone phosphates from terminal alkynes and *H*-phosphine oxides in the presence of $PhI(OAc)_2$ and H_2O, Chin. Chem. Lett. (2016), http://dx.doi.org/10.1016/j.cclet.2016.05.029