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Silver-Catalyzed Oxyphosphorylation of Unactivated Alkynes

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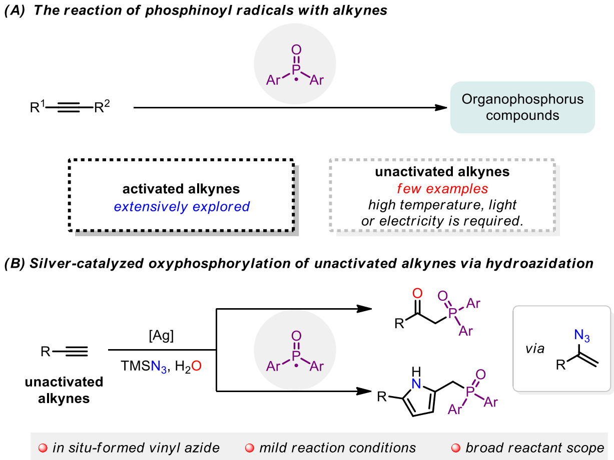
Abstract: Here, we describe an application of hydroazidation in the instant activation of alkynes for achieving the oxyphosphorylation of unactivated alkynes with diarylphosphinoyl radicals under mild reaction conditions. This reaction provides a method for accessing β-ketophosphine oxides and phosphorus-containing pyrroles.

Keywords: Alkynes; Silver-catalyzed; Hydroazidation; β-Ketophosphine oxides; Pyrroles

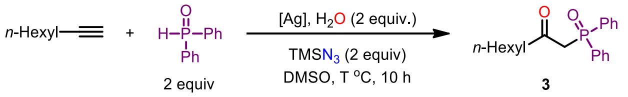
Organophosphorus compounds are of fundamental importance in synthetic and biological chemistry. They are widely found in natural products, nucleotides and pharmaceuticals, playing a central role in biology as structural elements and key mediators of biological processes and serving as vital materials for organic synthesis.[1] As a result, their preparation has received much attention, and the reaction of unsaturated hydrocarbons with phosphorus-centered radicals is an efficient, step-economic, and extensively used method for their preparation.[2] However, in contrast to the wide applicability of the reaction of alkenes with phosphorus-centered radicals, the reaction of alkynes with phosphorus-centered radicals is often limited to the use of activated alkynes or highly reactive phosphorus-centered radical (such as diethoxyphosponyl radical) precursors as raw materials.[2,3] For example, the reaction of dialkyl/diaryl *H*-phosphonate and alkynes can be easily catalyzed by transition metal, such as Cu,[3b,3d] Pd,[3i] and Ag,[3a] under mild conditions through dialkyloxyphosphonyl/diaryloxyphosphonyl radical intermediates. There have been few reports on the synthesis of organophosphorus compounds from unactivated alkynes and lowly reactive diarylphosphinoyl radicals, and all showed poor functional group tolerance because the reaction requires high temperature,[4] light[5] or electricity[6] (Scheme 1A). Therefore, the reaction between unactivated alkynes and lowly reactive phosphorus-centered radicals under mild reaction conditions is highly desirable to synthetic chemists.



Scheme 1. (A) The reaction of phosphinoyl radicals with alkynes; (B) Silver-catalyzed oxyphosphorylation of unactivated alkynes.

In the past years, our group has engaged in research on the activation and conversion of alkynes for the synthesis of nitrogen-containing molecules.[7] In this context, we have employed a strategy for activating terminal alkynes by employing silver catalysts, thus developing a general hydroazidation method for unactivated terminal alkynes to access vinyl azides.[8] Vinyl azides are highly reactive and versatile building blocks for many transformations. The azidyl group of vinyl azides can not only activate alkenes to facilitate their addition reaction with radicals[9] but also act as an amino source or a leaving group to promote the conversion of vinyl azides.[10] Combined with the above-mentioned properties of vinyl azides and the high efficiency and good compatibility of the silver-catalyzed hydroazidation of alkynes, we speculated that the silver-catalyzed hydroazidation of alkynes could provide an efficient strategy for the instant activation of alkynes. Given the importance of organophosphorus compounds in people’s daily lives and our continued research interest in the activation of alkynes, we herein establish a silver-catalyzed oxyphosphorylation of unactivated alkynes via hydroazidation under mild conditions. This reaction provides a simple and practical method for the preparation of β-ketophosphine oxides and phosphorus-containing pyrroles (Scheme 1B).

Table 1. Optimization of the reaction conditions.[a]



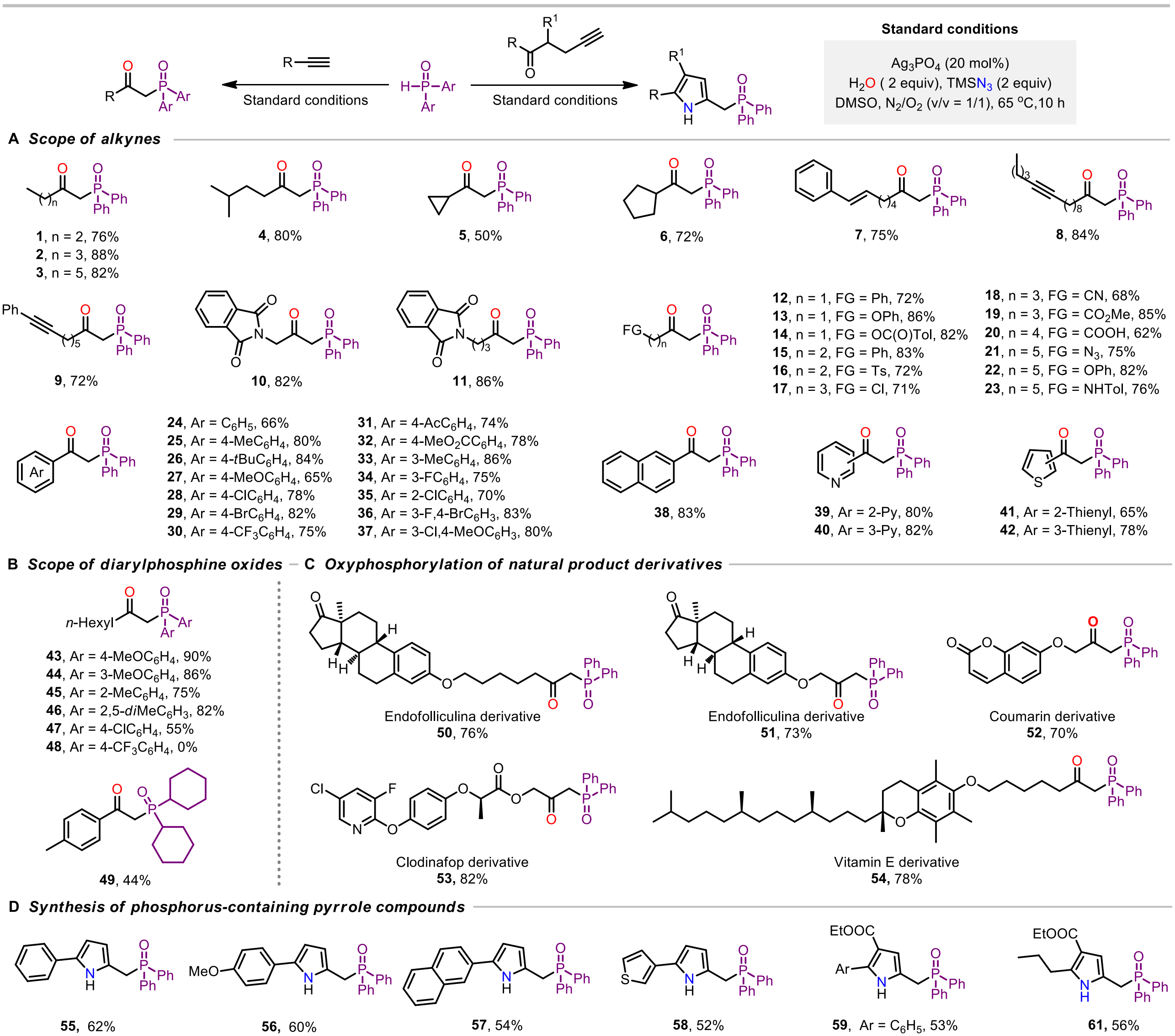
Entry	[Ag] (20 mol%)	T (°C)	Gas atmosphere	Yield (%)[b]
1	Ag_2CO_3	80	Air	47
2	AgN_3	80	Air	21
3	$AgNO_3$	80	Air	24
4	Ag_3PO_4	80	Air	61
5	Ag_3PO_4	65	Air	68
6	Ag_3PO_4	50	Air	57
7	Ag_3PO_4	65	N_2	56
8	Ag_3PO_4	65	N_2/O_2 (v/v = 1/1)	82
9	Ag_3PO_4	65	O_2	73
10[c]	Ag_3PO_4	65	N_2/O_2 (v/v = 1/1)	75
11[d]	Ag_3PO_4	65	N_2/O_2 (v/v = 1/1)	63

[a] Reaction conditions: 1-octyne (0.5 mmol), $Ph_2P(O)H$ (1.0 mmol), $TMSN_3$ (1.0 mmol), H_2O (1.0 mmol) and [Ag] (0.1 mmol) in DMSO (2 mL) at 65 °C under N_2/O_2 (v/v = 1/1) for 10 h; [b] Isolated yield; [c] Ag_3PO_4 (0.15 mmol); [d] Ag_3PO_4 (0.05 mmol).

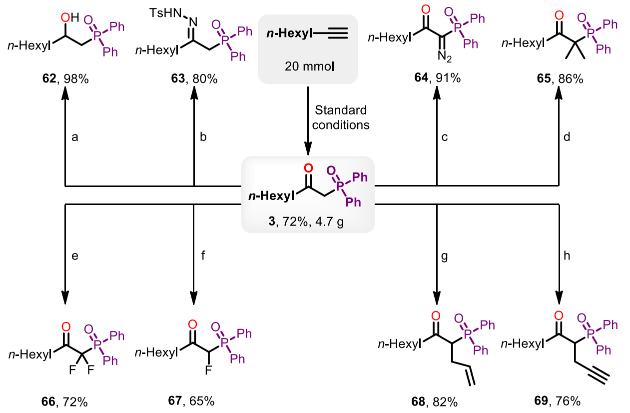
To verify the feasibility of the strategy for activating alkynes via hydroazidation, diphenylphosphine oxide was added to the standard reaction system for hydroazidation of 1-octyne (Table 1, entry 1).[8] This reaction gave β-ketophosphine oxide **3** in a yield of 47% after 10 h. To determine the optimal conditions for this reaction, the catalyst, temperature, and gaseous atmosphere were varied. The type of silver catalyst affected the efficiency of this reaction, and the reaction with silver phosphate as the catalyst gave the highest yield of compound **3** (entries 2-4). As the reaction temperature was decreased to 65 °C, the yield of compound **3** increased to 68% (entry 5). However, the yield of compound **3** decreased to 57% when the reaction temperature was further lowered to 50 °C (entry 6). The gas atmosphere had a considerable impact on the reaction (entries 7-9), and an aerobic environment was conducive to the reaction (entry 5 vs entry 7). To a certain extent, as the amount of oxygen increased, the yield of compound **3** increased (entry 6 vs entry 8). However, the yield of compound **3** under a pure oxygen atmosphere was not as high as that under a N_2/O_2 mixture (entry 8 vs entry 9), potentially because oxygen may directly/indirectly promote the generation of phosphinoyl radicals; thus, as the concentration of oxygen increases, the rate of phosphinoyl radical generation increases. Under an atmosphere of pure oxygen, the rate of phosphinoyl radical generation is so fast that the generated radicals are consumed, thereby reducing the yield of compound **3**. Finally, the effect of the amount of silver salt on the reaction efficiency was also investigated. The results listed in entries 10 and 11 showed that both increasing and decreasing the amount of silver salt reduced the yield of compound **3**.

With the optimal reaction conditions in hand, the scope of alkynes was next explored (Scheme 2A). Alkynes bearing either alkyl chains or cyclic alkyl groups could participate in this reaction, and the corresponding β-ketophosphine oxides (**1-6**) could be obtained in moderate to high yields. An alkyne with a three-membered tension ring could retain the three-membered ring (**5**) in this reaction. Notably, the functional groups in the alkyl-bearing alkynes were not altered in this reaction (**7-23**), and for alkynes with internal olefins or internal alkynyl groups, the reaction could occur selectively at the terminal alkynes (**7-9**). For aryl alkynes, the electronic effect and steric effect of substituents on the benzene ring had no obvious influence on the reaction, and the corresponding β-ketophosphine oxides could be obtained in good yield (**24-37**). Moreover, fused aryl- and heteroaryl-substituted alkynes also showed good tolerance to this reaction (**38-42**).

Next, we used 1-octyne as the raw material to examine the tolerance of diarylphosphine oxides in the oxyphosphorylation of alkynes (Scheme 2B). The electronic effect of substituents on the benzene ring of the diphenylphosphine oxides greatly affected this reaction. Electron-donating groups, such as methyl and methoxyl groups, were conducive to reaction (**43-46**), while electron-withdrawing groups, such as chloro and trifluoromethyl groups, were not conducive to reaction (**47** and **48**). This difference may result from the fact that electron-donating groups can increase the reactivity of diarylphosphine oxide radicals while electron-withdrawing groups can stabilize diarylphosphine oxide radicals.[2b,11] Notably, the reaction also showed good tolerance with dialkylphosphine oxide, and could give the desired product **49** with a yield of 44%. The application of oxyphosphorylation to the functionalization of alkynes in selected natural products afforded β-ketophosphine oxides **50-54** in good yields (Scheme 2C), showing functional group tolerance and potential for functionalizing more-complex molecules of biological relevance. In addition, when terminal alkynes with a carbonyl group at the γ position were used as raw materials, the reaction afforded phosphorus-containing pyrroles (**55-61**) in moderate yields (52-62%) (Scheme 2D). The structure of product **55** was further confirmed by single-crystal X-ray diffraction analysis.[12] This method can access 2,5-disubstituted or 2,3,5-trisubstituted phosphorus-containing pyrroles via a simple route.



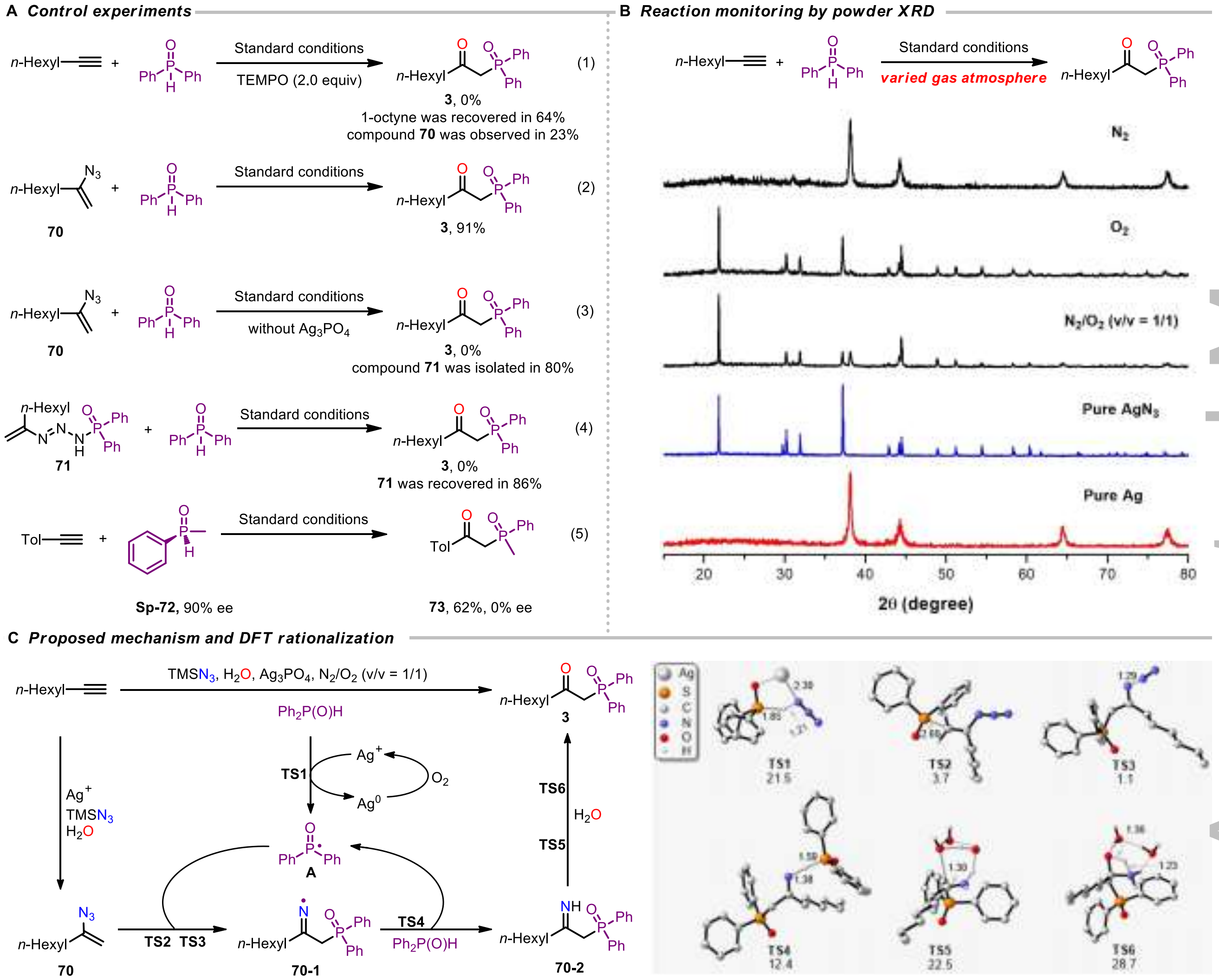
Scheme 2. Scope of the reaction of alkynes with diarylphosphine oxides.



Scheme 3. Gram-scale synthesis and further product transformations. (a) $NaBH_4$ (0.75 equiv), MeOH (2 mL), RT, 1 h; (b) $TsNHNH_2$ (1.2 equiv), CH_3COOH (3-5 drop), C_2H_5OH (2 mL), 70 °C, 12 h; (c) TsN_3 (1.0 equiv), DBU (1.5 equiv), MeCN (2 mL), 0 °C to RT, 12 h; (d) NaH (2.0 equiv), CH_3I (2.0 equiv), THF (5 mL), RT, 8 h; (e) selectfluor (3.0 equiv), H_2O / CH_3CN = 1:1 (2 mL), 40 °C, 24 h; (f) Selectfluor (1.1 equiv), H_2O / CH_3CN = 1:1 (2 mL), RT, 12 h; (g) NaH (2.0 equiv), allyl bromide (1.5 equiv), THF (5 mL), RT, 12 h; h) NaH (1.1 equiv), 3-bromopropyne (1.1 equiv), THF (5 mL), RT, 8 h.

β-Ketophosphine oxides are important phosphorus-containing compounds that have a wide range of applications in organic chemistry, coordination chemistry, and biochemistry.[13] To test the practicality of our method for the synthesis of β-ketophosphine oxides, a multigram-scale experiment was conducted. Compound **3** was obtained in a yield of 72% when 20 mmol of 1-octyne was added to the standard reaction system (Scheme 3), indicating that this method has the potential for scaled-up production. Subsequently, several transformations of β-ketophosphine oxide 3 were carried out. For example, the carbonyl group in compound **3** could be reduced to a hydroxyl group (**62**) almost quantitatively[14] and could also be converted into a sulfonyl hydrazone (**63**) in high yield.[15] The conversion could also occur at the methylene group of compound **3**, introducing a diazo group (**64**)[16] or selectively introducing one or two alkyl or other functional groups, for example (**65-69**).[17]

To understand the mechanism of this reaction, systemic control experiments were carried out. The oxyphosphorylation of the alkyne was completely suppressed in the presence of TEMPO, and a small amount of vinyl azide **70** was detected (Scheme 4A, eq. 1). Moreover, the reaction of **Sp-72** with 90% ee value and *p*-toluene acetylene under standard reaction conditions gave a racemic product **73** (eq. 5). The above results indicated that the reaction might involve a radical process and vinyl azide might be a reaction intermediate. The reaction involves a radical process was further confirmed by EPR analysis spectroscopy (Figure S3). The reaction in which vinyl azide **70** was added instead of an alkyne under standard reaction conditions afforded compound **3** in 91% yield (eq. 2), confirming that vinyl azide is an intermediate in this reaction. The reaction of vinyl azide **70** and diphenylphosphine oxide in the absence of silver salt under an N_2/O_2 atmosphere did not produce target product **3** but instead produced compound **71** (eq. 3), demonstrating that the diarylphosphine oxide radical was not produced by the oxidation of oxygen, but by the oxidation of the silver salt. The reaction of compound **71** under standard conditions did not afford target product **3** (eq. 4), indicating that compound **71** was not an intermediate. To verify that redox cycling of silver occurs in the reaction system, we used powder XRD to detect the changes in silver species in the reaction system under different gas atmospheres. As shown in Scheme 4B, we found that in the reactions under an N_2, O_2, or N_2/O_2 atmosphere, the silver species detected were elemental silver, silver azide, and a mixture of elemental silver and silver azide, respectively, indicating that the conversion of Ag(0) to Ag(I) in the reaction system depended on the oxidation of oxygen.



Scheme 4. Mechanistic investigation of the reaction to form β-ketophosphine oxide **3**. (A) Control experiments; (B) Reaction monitoring by powder XRD; (C) Proposed mechanism and DFT rationalization.

On the basis of the above investigations, a plausible mechanism for the oxyphosphorylation of alkynes is given in Scheme 4C, and the proposed mechanism was verified with density functional theory (DFT) calculations run at the PCM-M06-2X/6-311++G(d,p) level (for additional details, see Figure S5). Initially, vinyl azide **70** was generated from the hydroazidation of an alkyne, and diphenylphosphine oxide radical **A** was generated from the reaction of Ag(I) and diphenylphosphine oxide via TS1 ($\Delta G^{\ddagger}$ = 21.5 $kcal\cdot mol^{-1}$).[18] The transformation of Ag(0) to Ag(I) in the reaction system depended on the oxidation by oxygen. The reaction of vinyl azide **70** with diphenylphosphine oxide radical **A** gave imine radical **70-1** via **TS2** ($\Delta G^{\ddagger}$ = 3.7 $kcal\cdot mol^{-1}$) and **TS3** ($\Delta G^{\ddagger}$ = 1.1 $kcal\cdot mol^{-1}$). [19] Then, imine radical **70-1** was reduced by diphenylphosphine oxide to generate imine **70-2** and diphenylphosphine oxide radical **A** via **TS4** ($\Delta G^{\ddagger}$ = 12.4 $kcal\cdot mol^{-1}$). Finally, imine **70-2** was hydrolyzed to β-ketophosphine oxide **3** via **TS5** ($\Delta G^{\ddagger}$ = 22.5 $kcal\cdot mol^{-1}$) and **TS6** ($\Delta G^{\ddagger}$ = 28.7 $kcal\cdot mol^{-1}$). [7e,20] (The process of the generation of pyrrole see Figure S4 in Surpporting Information.)

In conclusion, we have described an effective reaction between unactivated alkynes and phosphinoyl radicals under mild reaction conditions, opening up a new application for the hydro-azidation of alkynes and providing a simple and practical method for the preparation of β-ketophosphine oxides and phospho-rus-containing pyrroles. In addition, the combination of control experiments, powder XRD analysis of the silver species in the system, and DFT calculations clearly reveals the specific reaction mechanism, which not only gives people a deeper understanding of the chemistry of vinyl azides and phosphorus radicals, but also provides a new means for the study of mechanism.

Experimental Section

General procedure for the synthesis of 3

To a 10 mL Schlenk reaction tube were added 1-octyne (55 mg, 0.5 mmol), dry DMSO (2 mL), then $TMSN_3$ (0.132 mL, 1.0 mmol), H_2O (0.018 mL, 1.0 mmol), Ag_3PO_4 (42 mg, 0.1 mmol), diphenylphosphine oxide (1.0 mmol, dissolved in 1 mL DMSO) were added. The mixture was then stirred at 65 ^{o}C for 8-12 h under two balloons with the same volume O_2 and N_2. Upon completion of the reaction, saturated NH_4Cl (aq.) was added to quench the reaction and the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with H_2O, brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting mixture was purified by silica gel column chromatography using (petroleum ether/ethyl acetate = 1:1) to afford **3** in 80% yield as a white solid.

Acknowledgements

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References

[1] a) L. D. Quin, *A Guide to Organophosphorus Chemistry*; Wiley Interscience: New York, **2000**; b) V. P. Kukhar, H. R. Hudson, Eds.; *Aminophosphonic and Aminophosphinic Acids: Chemistry and Biological Activity*; John Wiley & Sons: Chichester, **2000**; c) D. E. C. Corbridge, *Phosphorus: Chemistry, Biochemistry and Technology*, 6th ed.; CRC Press: London, **2013**; d) G. P. Horsman, D. L. Zechel, *Chem. Rev.* **2017**, *117*, 5704-5783.

[2] a) Y. Gao, G. Tang, Y. Zhao, *Phosphorus, Sulfur, and Silicon and the Related Elements*, **2017**, *192*, 589-596; b) D. Leca, L. Fensterbank, E. Lacôte, M. Malacria, *Chem. Soc. Rev.* **2005**, *34*, 858-865.

[3] a) X. Chen, X. Li, X. Chen, L. Qu, J. Chen, K. Sun, Z. Liu, W. Bi, Y. Xia, H. Wu, Y. Zhao, *Chem. Commun.* **2015**, *51*, 3846-3849; b) M. Zhou, M. Chen, Y. Zhou, K. Yang, J. Su, J. Du, Q. Song, *Org. Lett.* **2015**, *17*, 1786-1789; c) P. Zhang, L. Zhang, Y. Gao, J. Xu, H. Fang, G. Tang, Y. Zhao, *Chem. Commun.* **2015**, *51*, 7839-7842; d) N. Yi, R. Wang, H. Zou, W. He, W. Fu, W. He, *J. Org. Chem.* **2015**, *80*, 5023-5029; e) Y. Zeng, D. Tan, W. Lv, Q. Li, H. Wang, *Eur. J. Org. Chem.* **2015**, 4335-4339; f) W. Zhong, Q. Zhang, M. Li, D. Hu, M. Cheng, F. Du, J. Ji, W. Wei, *Synth. Commun.* **2016**, *46*, 1377-1385; g) M. Bu, G. Lu, C. Cai, *Catal. Sci. Technol.* **2016**, *6*, 413-416; h) W. Zhong, T. Tan, L. Shi, X. Zeng, *Synlett.* **2018**, *29*, 1379-1384; i) X. Li, G. Hu, P. Luo, G. Tang, Y. Gao, P. Xu, Y. Zhao, *Adv. Synth. Catal.* **2012**, *354*, 2427-2432.

[4] a) Y. Chen, W. Duan, *J. Am. Chem. Soc.* **2013**, *135*, 16754-16757; b) Y. Unoh, K. Hirano, T. Satoh, M. Miura, *Angew. Chem.* **2013**, *125*, 13213-13217; *Angew. Chem. Int. Ed.* **2013**, *52*, 12975-12979; c) W. Ma, L. Ackermann, S*ynthesis* **2014**, *46*, 2297-2304; d) T. Wang, S. Chen, A. Shao, M. Gao, Y. Huang, A. Lei, *Org. Lett.* **2015**, *17*, 118-121; e) S. Chen, P. Zhang, W. Shu, Y. Gao, G. Tang, Y. Zhao, *Org. Lett.* **2016**, *18*, 5712-5715; f) H. Guo, A. Yoshimura, T. Chen, Y. Saga, L. Han, *Green Chem.* **2017**, *19*, 1502.

[5] a) W. Liu, T. Lei, S. Zhou, X. Yang, J. Li, B. Chen, J. Sivaguru, C. Tung, L. Wu, *J. Am. Chem. Soc.* **2019**, *141*, 13941-13947; b) V. Quint, F. Morlet-Savary, J. Lohier, J. Lalevée, A. Gaumont, S. Lakhdar, *J. Am. Chem. Soc.* **2016**, *138*, 7436-7441; c) H. Wang, Y. Li, Z. Tang, S. Wang, H. Zhang, H. Cong, A. Lei, *ACS Catal.* **2018**, *8*, 10599-10605; d) T. Huang, Y. Saga, H. Guo, A. Yoshimura, A. Ogawa, L. Han, *J. Org. Chem.* **2018**, *83*, 8743-8749; e) H. Hou, Y. Xu, H. Yang, X. Chen, C. Yan, Y. Shi, S. Zhu, *Org. Lett.* **2020**, *22*, 1748-1753.

[6] V. V. Khrizanforova, K. V. Kholin, M. N. Khrizanforov, M. K. Kadirov, Y. H. Budnikova, *New J. Chem.* **2018**, *42*, 930-935.

[7] For reviews, see: a) P. Sivaguru, S. Cao, K. R. Babu, X. Bi, *Acc. Chem. Res.* **2020**, *53*, 662-675; See also: b) J. Liu, Z. Fang, Q. Zhang, Q. Liu, X. Bi, *Angew. Chem*. **2013**, *125*, 7091-7095; *Angew. Chem. Int. Ed.* **2013**, *52*, 6953-6957; c) J. Liu, Z. Liu, P. Liao, X. Bi, *Org. Lett.* **2014**, *16*, 6204-6207; d) Y. Ning, N. Wu, H. Yu, P. Liao, X. Li, X. Bi, *Org. Lett.* **2015**, *17*, 2198-2201; e) Y. Ning, Q. Ji, P. Liao, E. A. Anderson,

X. Bi, *Angew. Chem.* **2017**, *129*, 13993-13996; *Angew. Chem. Int. Ed.* **2017**, *56*, 13805-13808; f) J. Tang, P. Sivaguru, Y. Ning, G. Zanoni, X. Bi, *Org. Lett.* **2017**, *19*, 4026-4029; g) H. Wang, P. Mi, W. Zhao, R. Kumar, X. Bi, *Org. Lett.* **2017**, *19*, 5613-5616; h) B. Liu, Y. Ning, M. Virelli, G. Zanoni, E. A. Anderson, X. Bi, *J. Am. Chem. Soc.* **2019**, *141*, 1593-1598.

[8] a) Z. Liu, J. Liu, L. Zhang, P. Liao, J. Song, X. Bi, *Angew. Chem.* **2014**, *126*, 5409-5413; *Angew. Chem. Int. Ed.* **2014**, *53*, 5305-5309; b) Z. Liu, P. Liao, X. Bi, *Org. Lett.* **2014**, *16*, 3668-3671.

[9] For reviews, see: a) J. Fu, G. Zanoni, E. A. Anderson, X. Bi, *Chem. Soc. Rev.* **2017**, *46*, 7208-7228; b) H. Hayashi, A. Kaga, S. Chiba, *J. Org. Chem.* **2017**, *82*, 11981-11989; See also: c) W. Shu, A. Lorente, E. Gómez-Bengoa, C. Nevado, *Nat. Commun.* **2017**, *8*, 13832; d) Y. Ning, X. Zhao, Y. Wu, X. Bi, *Org. Lett.* **2017**, *19*, 6240-6243; e) W. Chen, X. Liu, E. Chen, B. Chen, J. Shao, Y. Yu, *Org. Chem. Front.* **2017**, *4*, 1162-1166; f) H. Qin, S. Wu, J. Liu, F, Liu, *Chem. Commun.* **2017**, *53*, 1696-1699; g) X. Wang, H. Li, G. Qiu, J. Wu, *Chem. Commun.* **2019**, *55*, 2062-2065; h) Y. Ning, A. Mekareeya, K. R. Babu, E. A. Anderson, X. Bi, *ACS Catal.* **2019**, *9*, 4203-4210.

[10] For reviews, see: a) B. Hu, S. G. DiMagno, *Org. Biomol. Chem.* **2015**, *13*, 3844-3855; b) H. Ni, G. Zhang, Y. Yu, *Curr. Org. Chem.* **2015**, *19*, 776-789; See also: c) V. Kanchupalli, S. Katukojvala, *Angew. Chem.* **2018**, *130*, 5531-5535; *Angew. Chem. Int. Ed.* **2018**, *57*, 5433-5437; d) J. R. Donald, S. L. Berrell, *Chem. Sci.*, **2019**, *10*, 5832-5836; e) X. Zhang, Z. Zhang, J. Song, Z. Wang, *Chem. Sci.* **2020**, *11*, 7921-7926; f) G. Zhang, H. Ni, W. Chen, J. Shao, H. Liu, B. Chen, Y. Yu, *Org. Lett.* **2013**, *15*, 5967-5969; g) H., Zou, H. Zhu, J. Shao, J. Wu, W. Chen, M. A. Giulianotti, Y. Yu, *Tetrahedron*, **2011**, *67*, 4887-4891; h) Y. Li, D. Hong, P. Lu, Y. Wang, *Tetrahedron Lett.* **2011**, *52*, 4161-4163.

[11] P. Peng, Q. Lu, L. Peng, C. Liu, G. Wang, A. Lei, *Chem. Commun.* **2016**, *52*, 12338-12341.

[12] CCDC 2035667 (**55**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

[13] a) B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863-927; b) S. K. Perumal, S. A. Adediran, R. F. Pratt, *Bioorg. Med. Chem.* **2008**, *16*, 6987-6994; c) T. Boesen, D. J. Fox, W. Galloway, D. S. Pedersen, C. R. Tyzack, S. Warren, *Org. Biomol. Chem.* **2005**, *3*, 630-637; d) S. V. Pronin, A. Martinez, K. Kuznedelov, K. Severinov, H. A. Shuman, S. A. Kozmin, *J. Am. Chem. Soc.* **2011**, *133*, 12172-12184; e) F. A. Cotton, R. A. Schunn, *J. Am. Chem. Soc.* **1963**, *85*, 2394-2402; f) C. Giorgio, O. Gianmauro, A. P. Gerard, *Tetrahedron.* **2003**, *59*, 9471-9515; g) W. Tang, X. Zhang, *Chem. Rev.* **2003**, *103*, 3029-3070.

[14] L. Shao, Y. Wu, J. Xu, J. He, Y. Zhao, L. Peng, Y. Li, Y. Yang, C. Xia, Q. Zhao, *Nat. Prod. Bioprospect.* **2014**, *4*, 181-188.

[15] T. Bzeih, D. Lamaa, G. Frison, A. Hachem, N. Jaber, J. Bignon, P. Retailleau, M. Alami, A. Hamze, *Org. Lett.* **2017**, *19*, 6700−6703.

[16] S. Fang, Y. Zhao, H. Li, Y. Zheng, P. Lian, X. Wan, *Org. Lett.* **2019**, *21*, 2356-2359.

[17] a) L. Tang, Z. Yang, J. Jiao, Y. Cui, G. Zou, Q. Zhou, Y. Zhou, W. Rao, X. Ma, *J. Org. Chem.* **2019**, *84*, 10449-10458; b) Y. Jiang, C. Park, T. Loh, *Org. Lett.* **2014**, *16*, 3432-3435.

[18] a) Y. Li, M. Sun, H. Wang, Q. Tian, S. Yang, *Angew. Chem.* **2013**, *125*, 4064-4068; *Angew. Chem., Int. Ed.* **2013**, *52*, 3972-3976; b) W. Kong, E. Merino, C. Nevado, *Angew. Chem.* **2014**, *126*, 5178-5182; *Angew. Chem. Int. Ed.* **2014**, *53*, 5078-5082; c) J. Sun, J. Qiu, Y. Wu, W. Hao, C. Guo, G. Li, S. Tu, B. Jiang, *Org. Lett.* **2017**, *19*, 754-757; d) T. Cai, J. Liu, H. Zhang, X. Wang, J. Feng, R. Shen, Y. Gao, *Org. Lett.* **2019**, *21*, 4605-4608.

[19] a) P. Tang, C. Zhang, E. Chen, B. Chen, W. Chen, Y. Yu, *Tetrahedron Lett.* **2017**, *58*, 2157-2161; b) H. I. Jung, D. Y. Kim, *Synth. Commun.* **2020**, *50*, 380-387.

[20] J. Ke, Y. Tang, H. Yi, Y. Li, Y. Cheng, C. Liu, A. Lei, *Angew. Chem.* **2015**, *127*, 6704-6707; *Angew. Chem. Int. Ed.* **2015**, *54*, 6604-6607.

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Silver-Catalyzed Oxyphosphorylation of Unactivated Alkynes

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