RSC Advances



PAPER

View Article Online



Cite this: RSC Adv., 2022, 12, 18072

I₂-mediated Csp²-P bond formation via tandem cyclization of o-alkynylphenyl isothiocyanates with organophosphorus esters†

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Received 16th May 2022 Accepted 7th June 2022

DOI: 10.1039/d2ra03072a

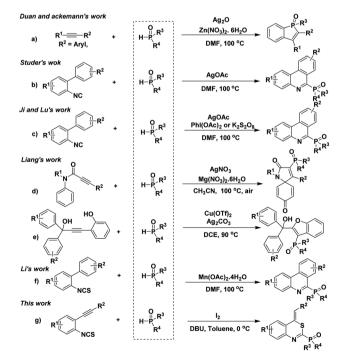
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A novel, I_2 -mediated tandem cyclization of o-alkynylphenyl isothiocyanates with organophosphorus esters has been developed under mild conditions. Different kinds of 4H-benzo[d][1,3]thiazin-2-ylphosphonate could be synthesized in moderate to excellent yields. This method has the advantages of easy access to raw materials, free-metal catalyst, simple operation, high yield and high functional group tolerance.

As an important class of organic products, organophosphorus compounds have received considerable attention because they have broad application in the field of materials science,1 medicinal chemistry,2 organic synthesis,3 natural products,4 and ligand chemistry.5 Phosphorus-containing compounds are valuable precursors of many biologically active molecules which can act as antibiotics,6 anti-tumor agents7 and enzyme inhibitors.8 Traditionally, the preparation of organophosphorus compounds relies on a transition-metal-catalyzed crosscoupling of phosphine reagents with electrophilic aryl halides (Ar-X), aryl boronic acids (Ar-B), aryl diazonium salts (Ar-N), aryl diazo and so on.¹² Recently, the construction of a Csp²-P bond on heterocycles is another powerful method to synthesize the organophosphorus compounds. 13 For instance, the Duan group and the Ackermann group reported a Ag-mediated C-H/P-H functionalization method to construct a Csp²-P bond by using arylphosphine oxides and internal alkynes as the substrates 13a,b (Scheme 1a). In 2014, Studer and co-workers reported a pioneering radical cascade reaction for the synthesis of 6-phosphorylated phenanthridines from 2-isocyanobiphenyls and diphenylphosphine oxides (Scheme 1b).13c Before long, Ji and Lu's group described two similar radical process with excess of PhI(OAc)₂ or K₂S₂O₈ as the oxidant (Scheme 1c). ^{13d,e} Recently, Liang and co-works developed two cases of cascade functionalization to construct phosphorylated heterocycles via the ionic pathway (Scheme 1d and 1e).13fg Meanwhile, Li and coworkers reported a Mn(II)-promoted tandem cyclization reaction of 2biaryl isothiocyanates with phosphine oxides which went through the same mechanism(Scheme 1f).13h Despite the usefulness of the above methods, common problems, such as complex reaction substrates, relatively high temperature, excess amounts of oxidants, limited their applications. Furthermore,

transition metals are required in these reactions, thereby resulting in limitations in reactants. Therefore, the development of a simple and transition-metal-free method for the formation of the Csp²-P bond from easily prepared starting materials is highly desirable.

o-Alkynylphenyl isothiocyanates are easily prepared organic synthons with versatile chemical reactivity,14 and they could be used as electrophiles,15 nucleophiles,16 and radical receptors17 due to the N=C=S moiety in the structure. Recently, the rapid development of the transition-metal-catalyzed cascade cycloadof o-alkynylphenyl isothiocyanates with various



Scheme 1 Synthesis of P-containing heterocycles through Csp²-P bond formation.

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† Electronic supplementary information available. https://doi.org/10.1039/d2ra03072a

nucleophiles provides a new and powerful synthetic strategy to synthesize different heterocycles. Very recently, we have developed a tandem cyclization process for the synthesis of 4*H*-benzo [*d*][1,3]thiazin-2-yl)phosphonates by using this strategy. As part of our continuing interest in the transformation of *o*-alkynylphenyl isothiocyanates, we describe herein a novel I₂-promotedtandem reaction to construct Csp²-P bond from *o*-alkynylphenyl isothiocyanates and phosphine oxides(Scheme 1g).

The starting o-alkynylphenyl isothiocyanates were prepared via the Sonogashira coupling of 2-iodoanilines with terminal alkynes, 20 followed by the treatment with thiophosgene according to the literature procedure.21 We commenced our studies with the reaction of o-phenylethynylphenyl isothiocyanate (1a, 0.2 mmol) and diethyl phosphonate (2a, 0.6 mmol) in the presence of I₂ (0.5 equiv.) as the catalyst, 8diazabicyclo[5,4,0]undec-7-ene (DBU, 3.0 equiv.) as the base, in dichloromethane (DCM, 2 mL) at 0 °C for 12 h in air atmosphere. Gratifyingly, the desired product diethyl (Z)-(4-benzylithiazin-2-yl)phosphonate 3a dene-4*H*-benzo[d][1,3] obtained in 75% yield (Table 1, entry 1). Next, different iodized salts, no better results can be obtained (Table 1, entries 2-4). It is worth noting that no product was obtained in the absence of base (Table 1, entry 5). This result indicated that a base is indispensable to afford the target product. Subsequently, we

Table 1 Optimization of the reaction conditions^a

Entry	Catalyst	Base	Solvent	Temp.	Yield (%)
1	I_2	DBU	DCM	0 °C	75
2	ΚΙ	DBU	DCM	0 °C	64
3	NaI	DBU	DCM	0 °C	50
4	ZnI_2	DBU	DCM	0 °C	55
5	I_2	_	DCM	0 °C	NR
6	${\bf I_2}$	DABCO	DCM	0 °C	Trace
7	I_2	KOAc	DCM	0 °C	NR
8	${\bf I_2}$	NaOAc	DCM	0 °C	NR
9	I_2	K_2HPO_4	DCM	0 °C	NR
10	${\bf I_2}$	Cs_2CO_3	DCM	0 °C	Trace
11	${\bf I_2}$	NaOH	DCM	0 °C	Trace
12	I_2	DBU	DCE	0 °C	28
13	${\bf I_2}$	DBU	$CHCl_3$	0 °C	32
14	I_2	DBU	DMF	0 °C	Trace
15	${\bf I_2}$	DBU	1,4-Dioxane	0 °C	50
16	I_2	DBU	MeCN	0 °C	35
17	${\bf I_2}$	DBU	Toluene	0 °C	84
18	${\bf I_2}$	DBU	Toluene	$25~^{\circ}\mathrm{C}$	70
19	\mathbf{I}_2	DBU	Toluene	$40~^{\circ}\mathrm{C}$	52
20	${\rm I}_2$	DBU	Toluene	80 °C	42
21	I_2	DBU	Toluene	$-10~^{\circ}\mathrm{C}$	66

^a Reaction was performed with 1a (0.2 mmol), 2a (0.6 mmol), catalyst (0.1 mmol), base (0.6 mmol), in solvent (2 mL) for 12 h. ^b Isolated yield based on o-phenylethynylphenyl isothiocyanate 1a.

examined the base effect on the reaction (Table 1, entries 6–11). The reaction can hardly proceed when other bases such as DABCO, KOAc, NaOAc, K_2HPO_4 , Cs_2CO_3 and NaOH were employed. We next examined the solvent effect (Table 1, entries 12–17). When toluene was employed as the solvent, the highest yield of 84% was obtained. Then, we examined the effect of temperature on the reaction. When the reaction temperature was increased to room temperature, the reaction was completed with a yield of 70% (Table 1, entry 18). Increasing the reaction temperature to 80 °C or reducing the reaction temperature to -10 °C resulted in a diminished yield (Table 1, entries 19–21) (Schemes 1–4)

In order to further demonstrate the substrate scope, different o-alkynyl phenylisothiocyanates were then explored and the results are summarized in Table 2. All reactions proceeded smoothly, leading to the desired 4H-benzo[d][1,3]thiazin-2-yl phosphonates in moderate to good yields. For example, the reactions of o-alkynyl phenylisothiocyanates 1b-1f completed at 0 °C in 12 h to give corresponding products 3b-3f in 70-85% yields. Among them, substrates 1 with an electron-rich aryl group such as p-MeOC $_6$ H $_4$ and p-MeC $_6$ H $_4$ at the R 2 position, showed good results (81% and 85%, 3e and 3f). As reported in our other

 ${\bf Table~2} \quad {\bf Tandem~cyclization~of~o-alkynylphenyl~isothiocyanates~with~diphenylphosphines}^{a,b}$

 $[^]a$ Reactions were performed with o-alkynylphenyl isothiocyanates 1 (0.2 mmol), phosphite or diphenylphosphines 2 (0.6 mmol), $\rm I_2$ (0.1 mmol), DBU (0.6 mmol), in toluene (2 mL) under 0 °C for 12 h. b Isolated yield based on o-phenylethynylphenyl isothiocyanate 1.

articles, 19 no desired products were obtained when the R² group in the substrate o-alkynylphenyl isothiocyanates 1 was an alkyl group, such as n-butyl, t-butyl, and n-hexyl. Similarly, when the R² group in the substrate o-alkynylphenyl isothiocyanates 1 was the cyclopropyl group, the desired desired 4H-benzo[d][1,3]thiazin-2-yl phosphonate 3g was obtained in 70% yield. On the other hand, the reactions of o-alkynylphenyl isothiocyanates bearing various substituents such as fluoro, chloro, bromo, trifluoromethyl, methyl and methoxy groups on the aryl rings at the R¹ position, regardless of their electronic properties and substitution positions, gave the desired products 3h-3r in moderate to good yields. Particularly, p-Br substituted 1j and 1o appeared excellent reactivity and the corresponding products 3j and 3o were obtained in 92% and 90% yield, respectively. In order to further expand the substrate scope, we moved on to examine the P-reagents under the optimal conditions. The reaction of dimethyl phosphate and diphenylphosphine oxide with 1a under the standard conditions, the corresponding products dimethyl (Z)-(4-benzylidene-4H-benzo[d][1,3]thiazin-2-yl)phosphonate and (*Z*)-(4-benzylidene-4*H*-benzo[d][1,3]thiazin-2-yl)diphenyl phine oxide (3s and 3t) were obtained in 81% yield and 79% yield, respectively. It is noteworthy that the corresponding target products (3u and 3v) with excellent yield (96% and 99% yield) are obtained when we replace diphenylphosphine oxide with di-ptolylphosphine oxide and bis(4-methoxyphenyl)phosphine oxide. Similarly, all products were uniformly formed as the Z-isomer, which might be due to a kinetic effect according to Baldwin's rules and a smaller steric effect compared to the E-isomer.²²

Next, we examined the reaction of 2-isothiocyanato-3-(phenylethynyl)pyridine $\mathbf{1x}$ with $\mathbf{2a}$ under the standard conditions (Scheme 2). Not surprisingly, the corresponding product $\mathbf{3x}$ diethyl (Z)-(4-benzylidene-4H-pyrido[2,3-d][1,3]thiazin-2-yl) phosphonate was obtained in 47% yield.

Scheme 2 The reaction of 2-isothiocyanato-3-(phenylethynyl)pyridine with 2a.

Scheme 3 Two control experiments for mechanism.

Scheme 4 Proposed mechanism.

Two control experiments were carried out to obtain some mechanism insight into the reaction. Firstly, 3.0 equiv. of 2,2,6,6 tetramethylpiperidine N-oxide (TEMPO) was added in the reaction of *o*-alkynylphenyl isothiocyanate **1a** with diethyl phosphonate **2a**, and product **3a** could be isolated in 75% yield (Scheme 3, 1). Similarly, the yield of **3a** was not influenced when we added 3.0 equiv. of 2,6-di-*tert*-butyl-4-methylphenol (BHT) in the reaction (Scheme 3, 2). These results probably suggested that the reaction may not follow a radical pathway.

Base on the above results and previous reports, 23 a possible mechanism was proposed for this reaction (Scheme 4). Firstly, in the presence of DBU as the base, the nucleophilic addition of P-anion to an isothiocyanate moiety in compound 1 would occur to produce the intermediate **A**. Then, Intermediate **A** could undergo isomerization to afford intermediate **B**. Next, molecular iodine serves as a π -acid to react with triple bond, giving iodocyclized intermediates **C** which followed by an intramolecular nucleophilic addition to give the intermediate **D**. Finally, intermediate **D** underwent the protodeiodination to give the target product 3.

Conclusions

In summary, we have developed molecular-iodine-catalyzed cyclization reactions of o-alkynylphenyl isothiocyanates and organophosphorus esters as a mild synthetic method of organophosphorus compounds. Different kinds of 4H-benzo[d] [1,3]thiazin-2-ylphosphonate could be synthesized in moderate to good yields. Avoiding the use of metal catalysts and the availability of raw materials are the advantages of this approach which provided a simple and direct pathway to construct organophosphorus compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the Natural Science Foundation of China (NSFC) (grant number 22061021, 21762023) and the

Scientific Research Fund of Jiangxi Provincial Education Department are gratefully acknowledged.

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