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I_2-mediated Csp^2–P bond formation *via* tandem cyclization of *o*-alkynylphenyl isothiocyanates with organophosphorus esters†

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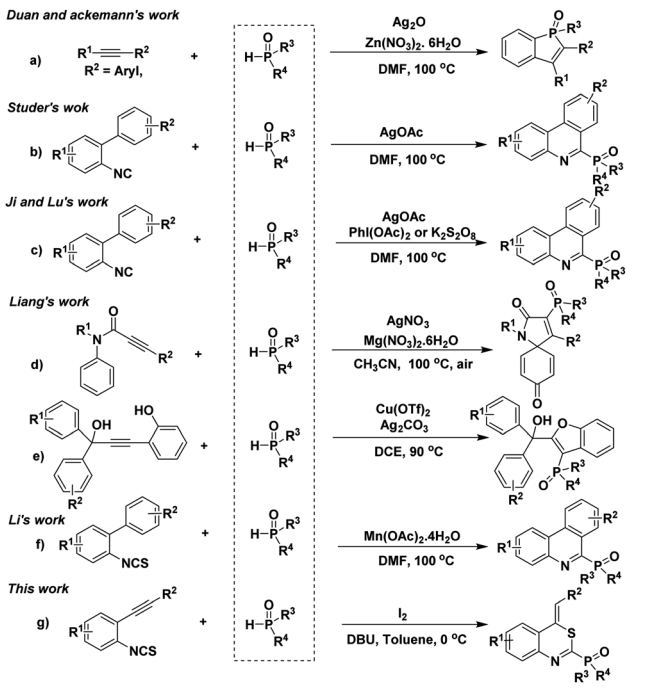
A novel, I_2-mediated tandem cyclization of *o*-alkynylphenyl isothiocyanates with organophosphorus esters has been developed under mild conditions. Different kinds of 4*H*-benzo[*d*][1,3]thiazin-2-ylphosphonate could be synthesized in moderate to excellent yields. This method has the advantages of easy 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 agents[7] and enzyme inhibitors.[8] Traditionally, the preparation of organophosphorus compounds relies on a transition-metal-catalyzed cross-coupling of phosphine reagents with electrophilic aryl halides (Ar-X),[9] aryl boronic acids (Ar-B),[10] aryl diazonium salts (Ar-N),[11] and so on.[12] Recently, the construction of a Csp^2–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 Csp^2–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 $K_2S_2O_8$ 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).[13f,g] Meanwhile, Li and coworkers reported a Mn(II)-promoted tandem cyclization reaction of 2-biaryl 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 Csp^2–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 receptors[17] due to the N=C=S moiety in the structure. Recently, the rapid development of the transition-metal-catalyzed cascade cycloaddition of *o*-alkynylphenyl isothiocyanates with various



Scheme 1 Synthesis of P-containing heterocycles through Csp^2–P bond formation.

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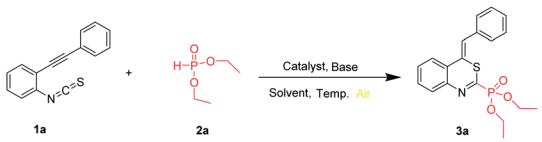
nucleophiles provides a new and powerful synthetic strategy to synthesize different heterocycles. Very recently, we have developed a tandem cyclization process for the synthesis of 4*H*-benzo[*d*][1,3]thiazin-2-yl)phosphonates by using this strategy.[18] As part of our continuing interest in the transformation of *o*-alkynylphenyl isothiocyanates,[19] we describe herein a novel I_2-promotedtandem reaction to construct Csp^2–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 I_2 (0.5 equiv.) as the catalyst, 8-diazabicyclo[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-benzylidene-4*H*-benzo[*d*][1,3] thiazin-2-yl)phosphonate **3a** was 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 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 4*H*-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*-$MeOC_6H_4$ and *p*-MeC_6H_4 at the R^2 position, showed good results (81% and 85%, **3e** and **3f**). As reported in our other

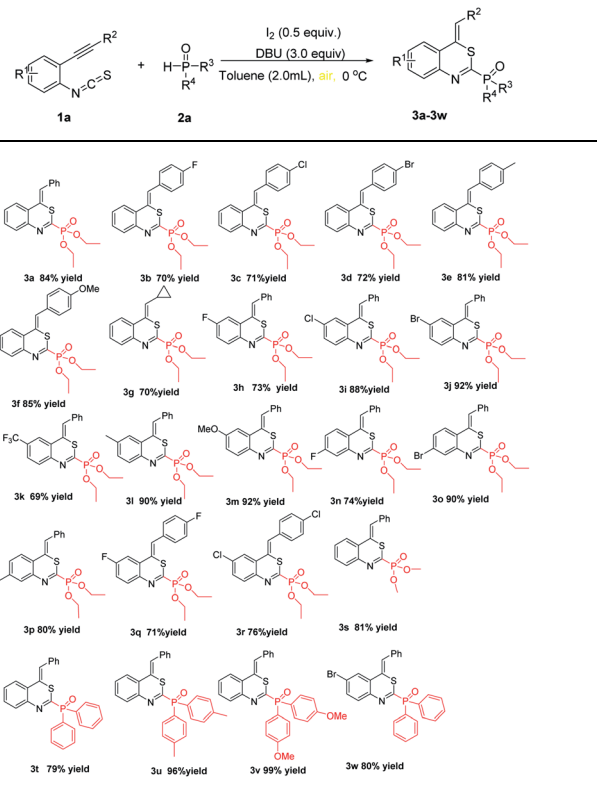
Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst	Base	Solvent	Temp.	Yield (%)[b]
1	I_2	DBU	DCM	0 °C	75
2	KI	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	I_2	DABCO	DCM	0 °C	Trace
7	I_2	KOAc	DCM	0 °C	NR
8	I_2	NaOAc	DCM	0 °C	NR
9	I_2	K_2HPO_4	DCM	0 °C	NR
10	I_2	Cs_2CO_3	DCM	0 °C	Trace
11	I_2	NaOH	DCM	0 °C	Trace
12	I_2	DBU	DCE	0 °C	28
13	I_2	DBU	$CHCl_3$	0 °C	32
14	I_2	DBU	DMF	0 °C	Trace
15	I_2	DBU	1,4-Dioxane	0 °C	50
16	I_2	DBU	MeCN	0 °C	35
17	I_2	DBU	Toluene	0 °C	84
18	I_2	DBU	Toluene	25 °C	70
19	I_2	DBU	Toluene	40 °C	52
20	I_2	DBU	Toluene	80 °C	42
21	I_2	DBU	Toluene	−10 °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**.

Table 2 Tandem cyclization of *o*-alkynylphenyl isothiocyanates with diphenylphosphines[a,b]

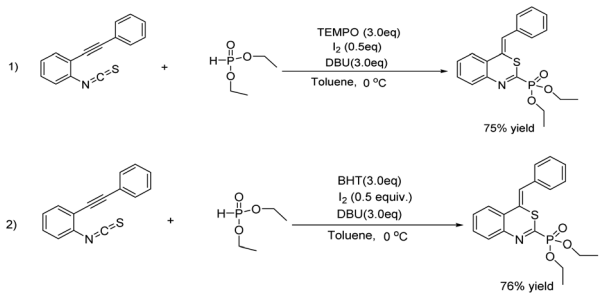


[a] Reactions were performed with *o*-alkynylphenyl isothiocyanates **1** (0.2 mmol), phosphite or diphenylphosphines **2** (0.6 mmol), I_2 (0.1 mmol), DBU (0.6 mmol), in toluene (2 mL) under 0 °C for 12 h. [b] Isolated yield based on *o*-phenylethynylphenyl isothiocyanate **1**.

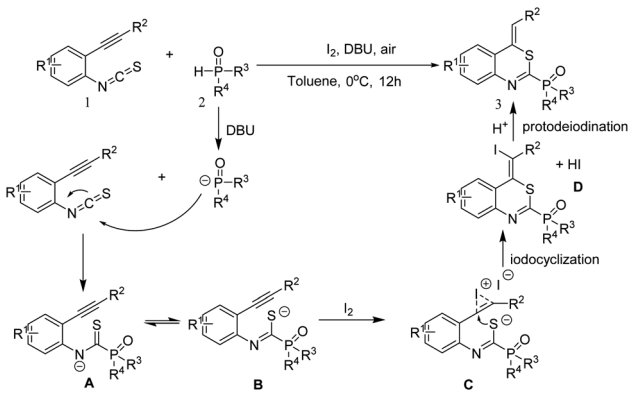
articles,[19] no desired products were obtained when the R^2 group in the substrate *o*-alkynylphenyl isothiocyanates **1** was an alkyl group, such as *n*-butyl, *t*-butyl, and *n*-hexyl. Similarly, when the R^2 group in the substrate *o*-alkynylphenyl isothiocyanates **1** was the cyclopropyl group, the desired desired 4*H*-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 R^1 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-4*H*-benzo[*d*][1,3]thiazin-2-yl)phosphonate and (*Z*)-(4-benzylidene-4*H*-benzo[*d*][1,3]thiazin-2-yl)diphenyl phosphine 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-*p*-tolylphosphine 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 **1x** with **2a** under the standard conditions (Scheme 2). Not surprisingly, the corresponding product **3x** diethyl (*Z*)-(4-benzylidene-4*H*-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 4*H*-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.

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