Visible-Light-Catalyzed Phosphonation–Annulation: An Efficient Strategy to Synthesize β-Phosphonopyrrolidines and β-Phosphonolactones†

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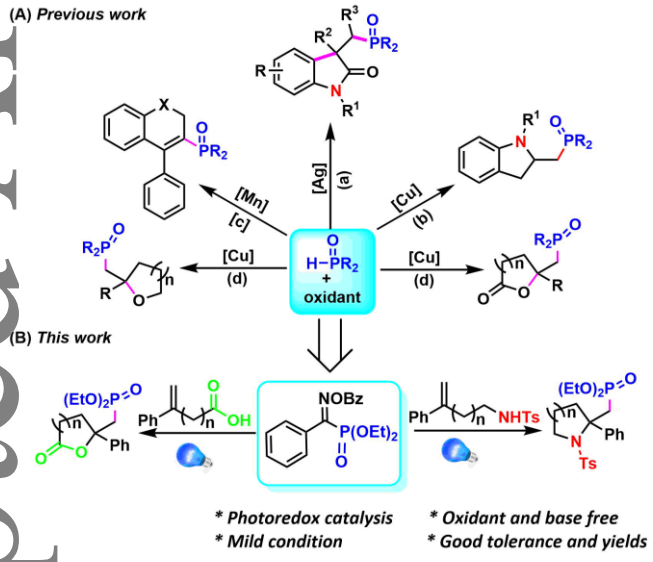
ABSTRACT A new type of phosphine radical precursor for C-P bond formation has been developed and successfully used in visible-light-catalyzed phosphonation-annulation of unsaturated sulfonamides and carboxylic acids. The catalytic process is simple and green accessible, and no additional oxidant or base is needed. Mechanistic studies suggest that the reaction proceeds via a single electron transfer pathway.

KEYWORDS Phosphine radical, Photocatalysis, Pyrrolidines, Lactones, Phosphonation-annulation

Introduction

Pyrrolidines and lactones are very important organic compound frameworks that are widely found in natural products, pharmaceuticals, organic materials, and concerned by chemists increasingly [1]. Therefore, methods of synthesizing pyrrolidines and lactones have been extensively studied, including Lewis acid or Lewis base catalysis [2], BrØnsted acid catalysis[3], transition metal catalysis[4], and electrophilic halides reaction[5]. With the rise of radical chemistry, radical reaction has also become a crucial method for the synthesis of such compounds[4a, 6].

Scheme 1. Phosphonation-annulation via phosphine radicals.



Organophosphorus compounds are used in agriculture[7], biochemistry[8], medicinal chemistry[9], materials[10], and organic synthesis[11]. Taking their multifunctional applications into consideration, design and synthesis of novel organophosphorus compounds have been extensively received attention in recent years[12]. Recently, there are heightened concerns about phosphine radicals for synthesizing organophosphorus compounds[13]. However, there is no denying that the production of phosphine radicals is often accompanied by stoichiometric amounts of a radical initiator, external oxidants and higher equivalent phosphine radical precursor[13], all of which remain as a challenge in current C-P bond formation via phosphine radicals (**A, Scheme 1**)[13f-i]. Exploring the new strategy to synthesize organophosphorus compounds has become an important topic in this field[14]. Visible light as a sustainable energy has played an important role in chemistry since the pioneering researches reported by MacMillan, Yoon, and Stephenson[15]. The accomplishment on synthesis of organophosphorus compounds via photo-redox catalysis has been documented since 2011[16], examples for the synthesis of phosphorylated pyrrolidines and lactones are still very rare to date[13i, 17]. In the past several years, our group has been working on exploring concise and efficient methodologies of phosphine radicals and made significant progress[13d-g]. Herein, we wish to report our latest advance in the synthesis of phosphorylated pyrrolidines and lactones (**B, Scheme 1**). In this transformation, a new type of phosphine radical precursor had been synthesized and used in the visible light catalyzed phosphonation-annulation reaction firstly. Meanwhile, this catalytic process is simple and green accessible, and no additional oxidant or base is needed.

Results and Discussion

Our investigation began with unsaturated sulfonamide **1a** and phosphine radical precursor **2a** in the presence of 1.0 mol % **PC** (photocatalyst) in DCM under argon atmosphere at room temperature (**Table 1, entry 1**). Fortunately, diethyl-((2-phenyl-1-tosylpyrrolidin-2-yl)-methyl)-phosphonate (**3a**) was isolated in 73 % yield when *fac*-Ir(ppy)$_3$ (ppy = 2-phenylpyridine) as photocatalyst. Which might mean that phosphine radicals can be produced smoothly under this condition. Then, the amount of phosphine radical precursor was changed, to our delight, when **2a** loading to 1.2 to 1.5 equivalent increased the yield to 82 % and 95 % (**Table 1, entry 2-3**). Different protecting groups for phosphine radical precursors have been investigated, including Me, Ac, *p*-NBz (**Table 1, entry 4-6**), only Bz as phosphine radical precursor's protecting group could give an excellent yield, and Ac protecting group also get product **3a** in 32 % yield. When Me and *p*-NBz served as protecting group, no product was detected under existing conditions. Following other solvents such as DCE, DME, toluene and CH_3CN were also screened, DCM was found to be the best solvent (**Table 1, entry 7-10**). After that, a further exploring the reaction condition by changing the photocatalyst, such as Eosin Y, Rhodamine B, Rose Bengal, and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ was found ineffective on catalysis, with *fac*-Ir(ppy)$_3$ serving as the best choice (**Table 1, entry 3, entry 11-14**). Furthermore, a control experiments revealed that photocatalyst and light were all necessary for phosphonation-annulation (**Table 1, entry 15-16**).

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† Dedicated to Professor Xiyan Lu on the occasion of his 90th birthday.

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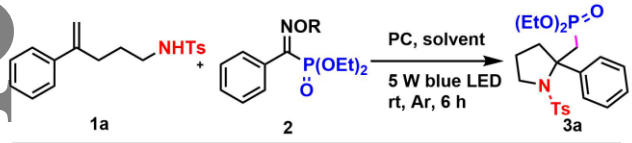
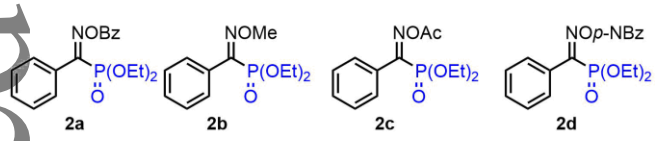
Next, we tested the influence of reaction atmosphere (**Table 1, entry 17**). It indicated that there were only trace products in air atmosphere. Finally, no desired products were formed when other phosphine radical precursors were used, such as $HP(O)Ph_2$ and $HP(O)(OEt)_2$ (**Table 1, entry 18**).

With the optimized reaction conditions in hand, we next shifted our attention to investigate the scope of various unsaturated

Table 1. Optimization of Reaction Conditions [a,b]



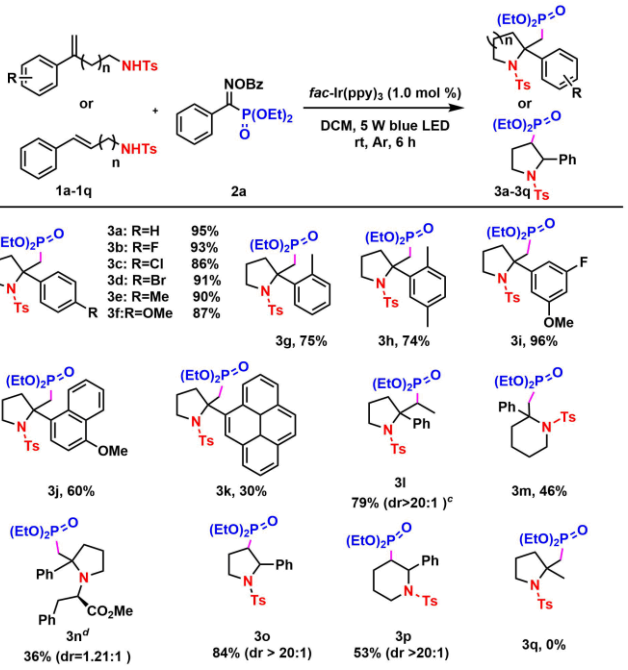
entry	PC (mol %)	solvent	2	yield(%)[b]
1[c]	*fac*-Ir(ppy)$_3$ (1.0)	DCM	2a	73
2[d]	*fac*-Ir(ppy)$_3$ (1.0)	DCM	2a	82
3	***fac*-Ir(ppy)$_3$ (1.0)**	**DCM**	**2a**	**95**
4	*fac*-Ir(ppy)$_3$ (1.0)	DCM	2b	N.D.[e]
5	*fac*-Ir(ppy)$_3$ (1.0)	DCM	2c	32
6	*fac*-Ir(ppy)$_3$ (1.0)	DCM	2d	N.D.
7	*fac*-Ir(ppy)$_3$ (1.0)	DCE	2a	84
8	*fac*-Ir(ppy)$_3$ (1.0)	DME	2a	73
9	*fac*-Ir(ppy)$_3$ (1.0)	Toluene	2a	N.D.
10	*fac*-Ir(ppy)$_3$ (1.0)	MeCN	2a	58
11	Eosin Y (5.0)	DCM	2a	N.D.
12	Rhodamine B (5.0)	DCM	2a	N.D.
13	Rose Bengal (5.0)	DCM	2a	N.D.
14	$Ru(bpy)_3Cl_2•6H_2O$ (2.0)	DCM	2a	N.D.
15	——	DCM	2a	n.r.[f]
16[g]	*fac*-Ir(ppy)$_3$ (1.0)	DCM	2a	n.r.
17[h]	*fac*-Ir(ppy)$_3$ (1.0)	DCM	2a	trace
18[i]	*fac*-Ir(ppy)$_3$ (1.0)	DCM	2a	n.r.



[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), **PC** (1.0 mol %) in 2 mL solvent was irradiated by 5 W blue LED for 6 h at room temperature under Ar. [b] Isolated yield based on **1a**. [c] **2a** (0.2 mmol). [d] **2a** (0.24 mmol). [e] N.D. = none detected. [f] n.r.= no reaction. [g] No light. [h] Under air atmosphere. [i] **2a**=$HP(O)Ph_2$ or $HP(O)(OEt)_2$.

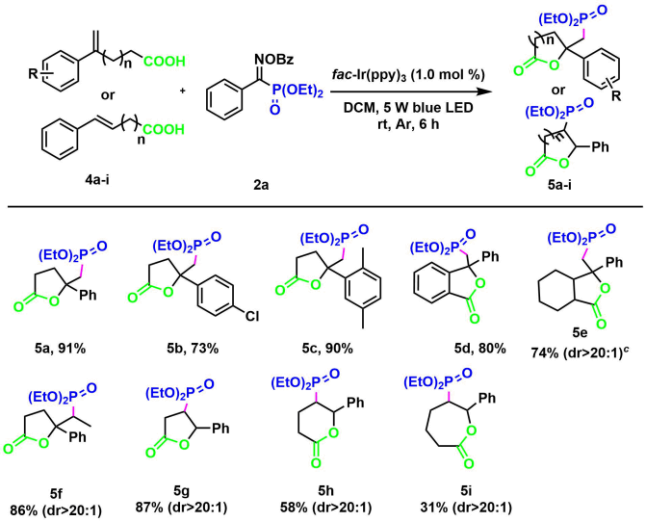
sulfonamides (**1b-1q**) with **2a** (**Scheme 2**). To our delight, substrates bearing various substituents led to the desired β-phosphonopyrrolidines in moderate to good yields (30%–96%), when unsaturated sulfonamides were explored in the presence 1.0 mol % *fac*-Ir(ppy)$_3$. In general, a series of unsaturated sulfonamides, with various substituents on the aromatic ring were proven to adapt to this reaction condition and provided the corresponding product in moderate to excellent yield (30%-96%, **3b-3k**). The efficient formation of **3b-3f** illustrated that not only electron-donating Me, OMe but also electron-withdrawing F, Cl, Br substituents were tolerated on the aryl ring. The steric bulk on the aromatic ring could affect the reaction. The lower yields were obtained with the larger steric bulk (**3j, 3k**). Moreover, for *meta*-substituted sulfonamides **1g** and **1h,** phosphonation-annulation reaction was occurred with moderate yield (75%, 74%), these lower yields might be affected by steric hindrance slightly. When the N-protecting group was a chiral group, we could get a chiral atropoisomeric product (**3n**) in 36% yield and low diastereomeric ratios (dr =1.21:1). What's more, non-terminal olefins **1l** could also achieve good yield (79%) and high diastereomeric ratios (dr >20:1). β-phosphonopiperidine (**3m**) were accessible obtained under the standard reaction conditions in moderate yield (46%). Notably, *endo*-selective phosphonocycloamination for internal β- or γ-aminoxyalkenes (**1o, 1p**) with **2a** gave the corresponding

Scheme 2. Scope of the Phosphonation-Annulation Reaction of Unsaturated Sulfonamides [a,b]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.3 mmol), *fac*-Ir(ppy)$_3$ (1.0 mol %) in 2 mL DCM was irradiated by 5 W blue LED for 6 h at room temperature under Ar. [b] Isolated yield based on **1**. [c] The dr value was determined by ^{31}P NMR without column chromatography. [d] 1.5 equiv. K_3PO_4 was added under standard reaction conditions.

Scheme 3. Scope of the Phosphonation-Annulation Reaction of Unsaturated Carboxylic Acids [a,b]



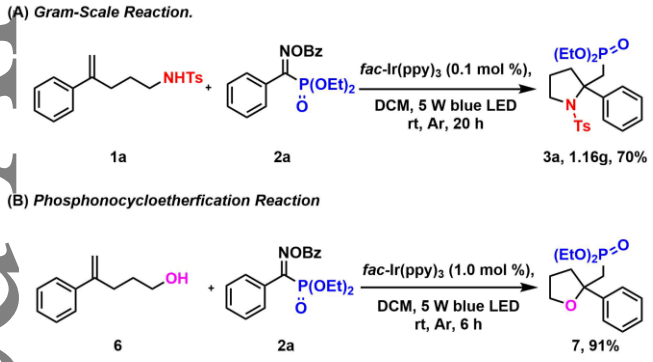
[a] Reaction conditions: **4** (0.2 mmol), **2a** (0.3 mmol), *fac*-Ir(ppy)$_3$ (1.0 mol %) in 2 mL DCM was irradiated by 5 W blue LED for 6 h at room temperature under Ar. [b] Isolated yield based on **4**. [c] The dr value was determined by ^{31}P NMR without column chromatography.

endo-products (**3o, 3p**) in good yields (84%, 53%) and high diastereomeric ratios (dr >20:1). Unfortunately, unsaturated sulfonamides **1q** could not react in our condition, which might be due to the fact that the tertiary carbon cation is not as stable as the benzyl carbon cation.

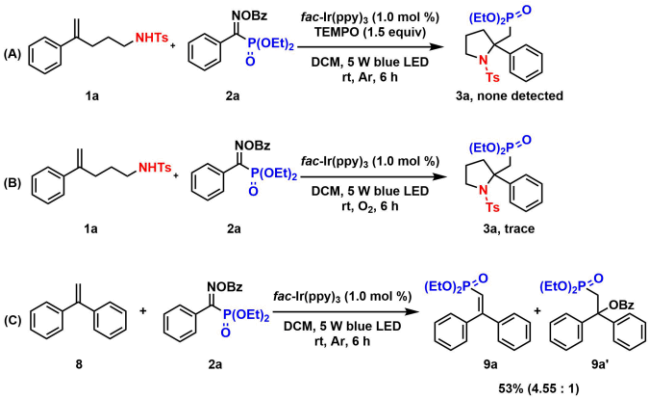
To further explore the scope of application of **2a**, various unsaturated carboxylic acids were tested. As shown in **scheme 3**, aromatic-substituted lactones **5b** and **5c** were generated in good yields with 73% and 90%. In addition, substrates with alkyl chain substituted could also obtain better yields (**5d, 5e**). Non-terminal olefins **4f** achieved good yield in 86% and high diastereomeric ratios (dr >20:1). Moreover, *endo*-selective phosphonolactonization for internal carboxy alkenes gave the corresponding *endo*-product (**5g-5i**) in moderate to good yields and high diastereomeric ratios (dr >20:1). However, the longer the alkyl chain of the substrate is (**4g-4i**) , the lower the yield is.

More importantly, a gram-scale reaction was performed to explore the utility of our strategy in organic synthesis. Diethyl-((2-phenyl-1-tosylpyrrolidin-2-yl)-methyl)-phosphonate (**3a**) 1.16g was obtained when decreasing the load of *fac*-Ir(ppy)$_3$ (0.1 mol %) (**A**, **Scheme 4**). Furthermore, phosphonocycloetherfication product **7** was isolated with 91% yield under the optimal reaction condition (**B**, **Scheme 4**).

Scheme 4. Gram-Scale Reaction and Phosphonocycloetherfication Reaction.

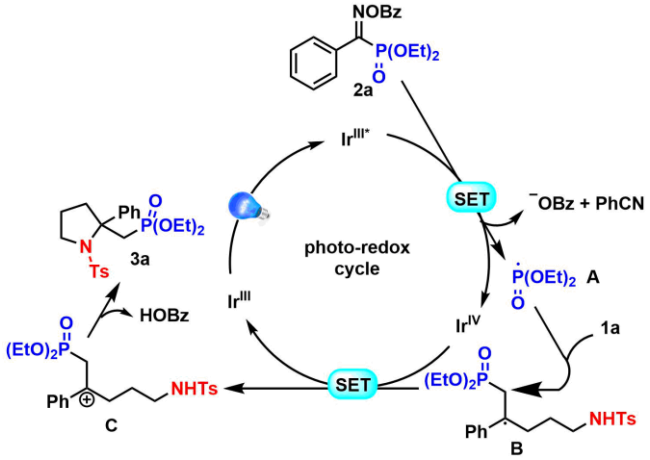


Scheme 5. Mechanism Experiments



To gain insight into the mechanism, the typical radical inhibitor TEMPO (2,2,6,6-tetramethyl-1-piper-idinyloxy) inhibited the reaction completely (**A, Scheme 5**). When **1a** was replaced by radical scavenger 1,1-diphenylethylene (**8**) under standard conditions, coupling-product: phosphondifunctionalized-product (**9a:9a'**=4.55:1) was obtained 53% yield totally (**C, Scheme 5**). This indicated that $^{\cdot}P(O)(OEt)_2$ and $^{\cdot}OBz$ were generated in the system. Trace product was detected when O_2 was instead of Ar (**B, Scheme 5**). The above experiments showed that the reaction might have experienced a free radical pathway.

Scheme 6. A Plausible Reaction Mechanism.



Base on the analysis of mechanism experiments and published literatures[18], a mechanism was proposed for the phosphonation-annulation reaction (**Scheme 6**). Upon blue light photoexcitation, Ir^{III} is excited to a photoexcited state Ir^{III*}. Ir^{III*} oxidatively quenched by **2a** to generate Ir^{IV} ($E_{1/2}^{IV/III*}$ = -1.73 V vs. SCE)[19] and P-radical **A**. Then P-radical **A** is rapidly trapped by unsaturated substrates **1a** to form a radical intermediate **B**, which undergoes a single electron transfer (SET) oxidation to generate benzyl cation intermediate **C** and regenerate Ir^{III} photocatalyst simultaneously. Subsequently, benzyl cation is nucleophilic attacked to form desired products.

Conclusions

In summary, a new type phosphine radical precursor has been developed to generate phosphine radical through photo-redox catalysis without additional oxidant and base. This phosphine radical precursor offers a straightforward and efficient strategy to C-P bond formation via visible light photocatalysis. The significant transformation exhibits a great value in organic synthesis and medicine formation which is oxidant sensitive. As well as sundry β-Phosphonopyrrolidines and β-Phosphonolactones were formed smoothly.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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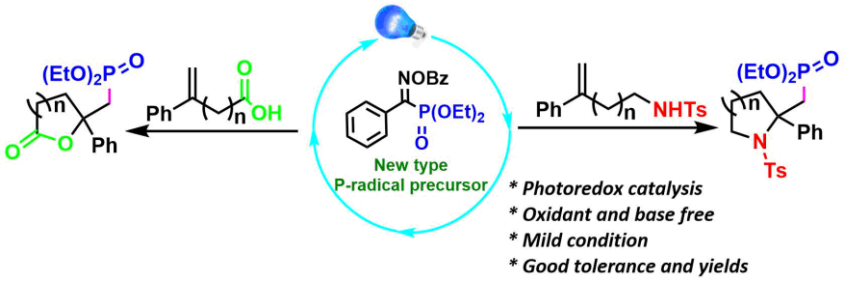
Visible-Light-Catalyzed Phosphonation–Annulation: An Efficient Strategy to Synthesize β-Phosphonopyrrolidines and β-Phosphonolactones



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A new type of phosphine radical precursor for C-P bond formation has been developed and successfully used in visible-light-catalyzed phosphonation-annulation of unsaturated sulfonamides and carboxylic acids. The catalytic process is simple and green accessible, and no additional oxidant or base is needed. Mechanistic studies suggest that the reaction proceeds via a single electron transfer pathway.