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Visible-Light-Promoted Redox-Neutral Cyclopropanation Reactions of α-Substituted Vinylphosphonates and Other Michael Acceptors with Chloromethyl Silicate as Methylene Transfer Reagent

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Abstract: The alkene cyclopropanation with chloromethyl silicate as a methylene transfer reagent has been accomplished via visible-light-mediated redox-neutral catalysis. This method features broad functional group tolerance and mild conditions. In addition to α-substituted vinylphosphonates, a range of Michael acceptors including *α,β*-unsaturated acrylate, ketone, amide and sulfone are suitable substrates for this photocatalytic cyclopropanation. An application of this protocol to the cyclopropanation of estrone derivative is also presented.

Keywords: Photoredox catalysis; Cyclopropanation; Radical; Michael acceptor; 1-Arylcyclopropylphosphonate

The cyclopropane derivatives are important cyclic structural motif and found in many useful biologically active natural products or pharmacologically interesting compounds.[1] They are also useful synthetic intermediates due to their unique structural and electronic characteristics.[2] Among the numerous available methods,[3] alkene cyclopropanation with a methylene transfer reagent represents a conceptual and convenient methodology. As for the preparation of cyclopropane ring with unsubstituted carbon atoms, significant progress has been achieved via CH_2 group transfer reactions of olefins employing (iodomethyl)zinc carbenoids,[4] diazomethane,[5] and ylide[6] as the methylene resource.[7] Among available synthetic approaches toward accessing cyclopropanes from alkenes using photocatalysis,[8] the parent CH_2 transfer reaction of alkenes by means of visible-light photoredox catalysis was still rarely explored.[9] Recently, Suero and co-workers uncovered a new photocatalytic cyclopropanation reaction of styrenes[10a] and Michael acceptors[10b] employing diiodomethane as the methylene source.

The cyclopropylphosphonates and cyclopropylphosphonic acids are important cyclic structural motif and found in many useful biologically active natural products or pharmacologically interesting compounds.[11] 1-Arylcyclopropylphosphonates are conformationally constrained analogs of 1-arylethylphosphonic acids which are phosphorus analogs of 2-arylpropionic acids (a well-known class of nonsteroidal antiinflammatory and analgesic drugs such as naproxen and ibuprofen). However, among the many available methods for the preparation of cyclopropylphosphonates,[12] the access to 1-arylcyclopropylphosphonate is still limited. According to the Beletskaya method,[13] 1-arylcyclopropylphosphonates could be accessed via two steps involving treatment of 1-arylethenylphosphonic acids or their esters with diazomethane followed by thermolysis of 3-aryl-4,5-dihydro-3*H*-pyrazol-3-ylphosphonates. Intrigued with our photoredox-catalyzed Giese-type reactions[14] of *α*-aryl vinylphosphonates,[15] we envisioned that the interesting 1-arylcyclopropylphosphonates would be accessible via photocatalytic cascade $ClCH_2$· addition/cyclopropanation reactions. Herein, we report a general and efficient protocol for the cyclopropanation of alkenes with chloromethyl silicate[16,17] as the methylene source by means of visible-light photoredox catalysis.

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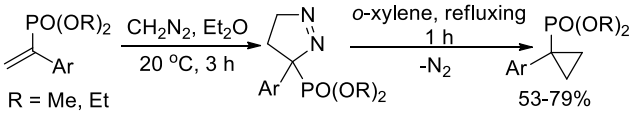
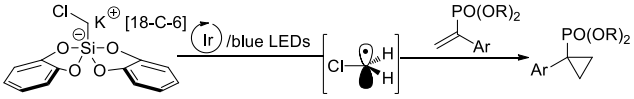
(a) [3+2] cycloaddition followed by thermolysis reactions (*Beletskaya et al.*)



(b) cyclopropanation of alkenes via photocatalytic CH_2 transfer reaction (*this work*)



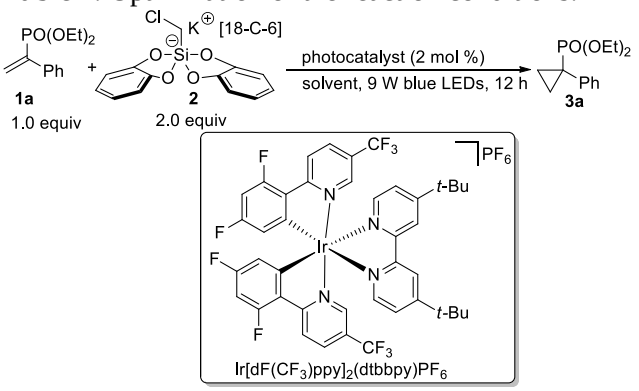
[18-C-6] = 18-crown-6 ether

Scheme 1. Synthetic approaches toward accessing 1-arylcyclopropylphosphonates.

To test the feasibility of this cyclopropanation reaction, we initially selected *α*-phenyl vinyphosphonate **1a** as the model substrate and chloromethyl silicate **2** as the methylene source. Fortunately, the desired 1-phenyl cyclopropylphosphonate **3a** was isolated in 42% yield when a solution of **1a** with 2.0 equiv of **2** in the presence of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol %) in THF (0.02 M) was illuminated with blue LEDs (9 W) at room temperature for 12 h (entry 1). Among the solvents tested, the optimal yield was observed employing DMSO as the solvent (entries 2-5). In light of the photocatalysts (entries 5-8), the organic dye 1,2,3,5-tetrakis(carbazolyl)-4,6-dicyanobenzene (4CzIPN)[18] gave a similar result under the examined condition (entry 6). We also performed some control experiments, which showed that the process was completely inhibited in the absence of photocatalyst (entry 9) or light (entry 10). Also the presence of TEMPO resulted in no product formation (entry 11), which suggests that radical plays a vital part in this reaction.

With the optimized reaction condition in hand (Table 1, entry 5), we assessed the scope with vinylphosphonates, and the desired cyclopropylphosphonates were accessed in good to high yields (Table 2). Generally, *α*-substituted vinylphosphonates containing electron-donating group such methyl or methoxyl on the phenyl ring could be easily cyclopropanated to afford the expected 1-aryl cyclopropylphosphonates **3b**-**g** in high yields. The presence of halogens was well tolerated, providing opportunities for further elaboration of the produced cyclopropanes. It is worth noting that the electronics of the aromatic moiety have a great impact on the outcome of the cyclopropanation reactions. In the case of cyclopropanation of the vinylphosphonate bearing 3,4-dichloro phenyl ring, a mixture of

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



entry	solvent	photocatalyst	yield (**3a**, %)[b]
1	THF	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	42
2	CH_3CN	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	43
3	DMF	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	49
4	DMA	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	59
5	DMSO	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	91
6	DMSO	4CzIPN	87
7	DMSO	*fac*-$Ir(ppy)_3$	trace
8	DMSO	$[Ru(bpy)_3](PF_6)_2$	20
9	DMSO	no	0
10[c]	DMSO	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	0
11[d]	DMSO	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	0

[a] Reaction conditions: a reaction mixture of **1a** (0.2 mmol), **2** (0.4 mmol), photocatalyst (2 mol %), and solvent (6 mL) was irradiated by 9 W blue LEDs at room temperature for 12 h.
[b] Yield of the isolated product **3a**.
[c] The reaction was run in the dark.
[d] TEMPO (1 mmol) was added.

cyclopropylphosphonate **3k** and Michael adduct was obtained. Fortunately, the conjugate adduct could be easily transformed into cyclopropylphosphonate via intramolecular S_N2 reaction with *t*-BuOK as the base at room temperature[19] (see Supporting Information (SI)). Also, appreciable formation of the Michael adduct from an incomplete ring-closure event was observed in the case of the aromatic rings bearing strong electron-withdrawing groups (CO_2Me, COMe, CN, and NO_2). Nicely, 48-88% isolated yields of cyclopropylphosphonates **3l**-**o** could be achieved after 12 h irradiation followed by treatment of *t*-BuOK. Additionally, alkenylphosphonates possessing naphthyl and biphenyl groups also worked uneventfully to afford **3p** and **3q** in 86% and 96% yields, respectively. Notably, heterocyclic furan-containing vinylphosphonate also proved to be competent for this transformation, albeit in somewhat lower yield (**3r**, 50%). Moreover, the cyclopropanation smoothly afforded the corresponding *n*-butyl substituted

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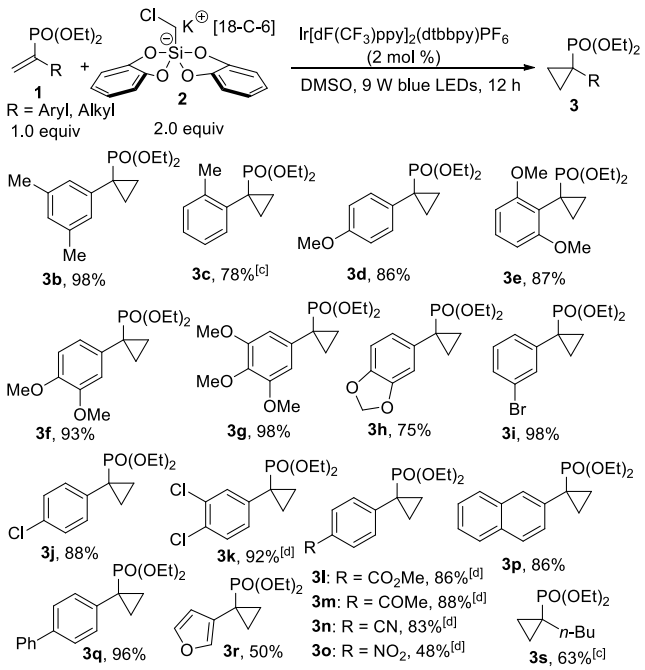
Table 2. Scope of *α*-substituted vinylphosphonates.[a,b]

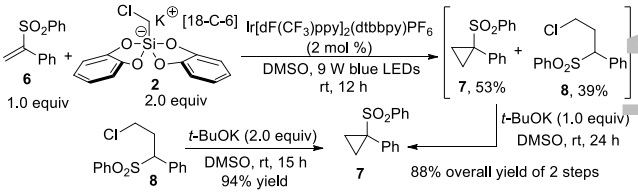


[a] Reaction conditions: a reaction mixture of **1** (0.2 mmol), **2** (0.4 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2 mol %), and DMSO (6 mL) was irradiated by 9 W blue LEDs at room temperature for 12 h.
[b] Yield of the isolated product **3**.
[c] Reaction time is 24 h.
[d] Overall yield of two steps via 12 h irradiation followed by treatment with *t*-BuOK in DMSO at room temperature for 15-18 h (see SI).

cyclopropylphosphonate **3s** in 63% yield. This result clearly shows that the presence of an aromatic ring at *α*-carbon of vinylphosphonate is not essential for the successful cyclopropanation reaction. However, the cyclopropanation of diethylvinylphosphonate was fruitless and a complex mixture was obtained.

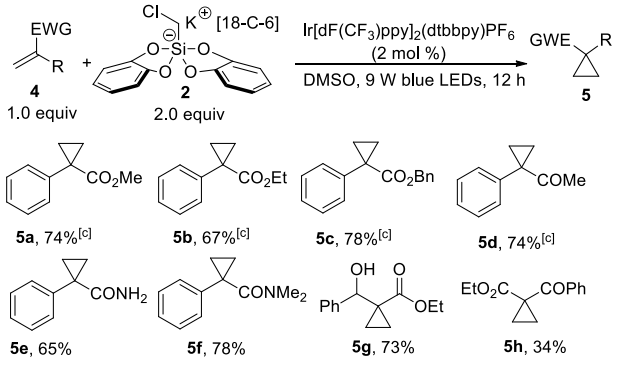
Encouraged by the results obtained with the vinylphosphonates, we next turned our attention to the cyclopropanation of different Michael acceptors **4**. With *α*,*β*-unsaturated acrylate and *α*,*β*-unsaturatedketone as the radical acceptor, a mixture comprising cyclopropane and radical adduct was observed. After treatment of the mixture with *t*-BuOK, the cyclopropane products **5a-d**[20] were isolated in 67-78% yields. Of note, no expected product **5b** was observed with triethylammonium bis(catecholato)chloromethylsilicate as the methylene transfer reagent.[21] Interestingly, *α*,*β*-unsaturated amides could be cyclopropanated nicely to afford the corresponding products **5e-f**. Moreover, Morita-Baylis-Hillman derived alcohol was also suitable substrate for this photo-catalytic cyclopropanation reaction, giving **5g** in 73% yield. Moderate yield of the cycopropane product **5h** was obtained, plagued notably by the formation of polymer/oligomer.[22]

With respect to the reaction of *α*,*β*-unsaturated sulfone **6**, a mixture consisting of phenyl 1-phenylcyclopropyl sulfone **7** and radical adduct **8** was obtained, affording **7** and **8** in 53% and 39% yields, respectively. Indeed, direcet treatment of the reaction mixture after irradiation with *t*-BuOK provided the cyclopropane **7** in 88% overall yield of two steps. Moreover, the cyclopropanation reaction took place efficiently with treatmeant of *t*-BuOK of pure radical adduct **8**, producing **7** in 94% yield.



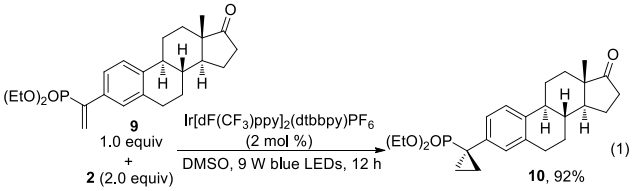
Scheme 2. Photocatalytic cyclopropanation of vinylsulfone.

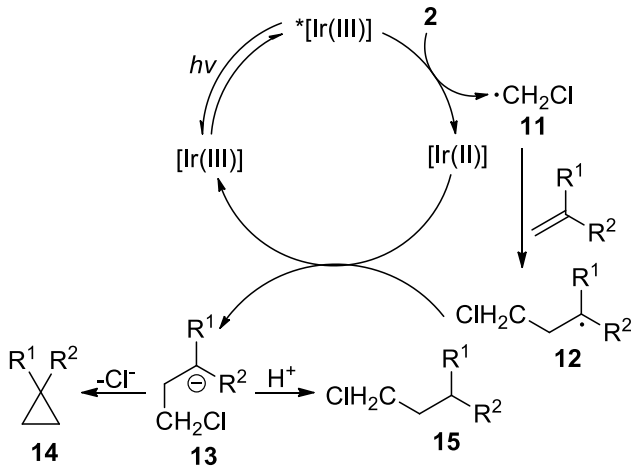
Table 3. Michael acceptor scope.[a,b]



[a] Reaction conditions: a reaction mixture of **4** (0.2 mmol), **2** (0.4 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2 mol %), and DMSO (6 mL) was irradiated by 9 W blue LEDs at room temperature for 12 h.
[b] Yield of the isolated product **5**.
[c] Overall yield of two steps via irradiation and treatment of the mixture with *t*-BuOK (see SI).

To demonstrate the application of this method in pharmaceutical research, vinylphosphonate **9** derived from estrone was selected as a representative substrate for photocatalytic redox-neutral cyclopropanation reaction. Under standard catalytic conditions, we are able to isolate the cyclopropylphosphonate derivative **10** in 92% yield (eq 1), which highlights the good functional group tolerance and potential applicability of this visible-light-promoted cyclopropanation reaction protocol in complex settings.





Scheme 3. Possible pathway for photocatalytic cyclopropanation of alkenes.

On the basis of our study as well as literature precedent, one plausible pathway through a redox-neutral process is depicted in Scheme 3. The photoexcited *Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ ($E_{1/2}$ [*Ir^{III}/Ir^{II}] = +1.21 V vs SCE in CH$_3$CN)[23] acts as a strong oxidant and undergoes a single electron transfer (SET) with chloromethyl silicate **2** (E_{ox} = +0.87 V vs SCE in DMF)[16] to generate ClCH$_2$· **11**. The resulting radical reacts with alkene to give the new radical **12** ($E_{1/2}^{red}$ = -0.60 V vs SCE for α-acyl raidcal)[24] which can receive an electron from the photochemically reduced iridium complex ($E_{1/2}^{red}$ [Ir^{III}/Ir^{II}] = -1.37 V vs SCE in CH$_3$CN).[23] The resulting anion **13** would undergo intramolecular substitution to provide the desired cyclopropane **14**. At this stage, the carbanionic intermediate **13** could be also protonated, affording the undesired linear side adduct **15**.

In conclusion, we have developed a general and efficient protocol for the cyclopropanation reaction of alkenes with chloromethyl silicate as methylene source by means of photoredox-neutral catalysis. The reactions are operationally simple and tolerate a variety of functional groups. Moreover, a great deal of Michael acceptors involving α,β-unsaturated phosphonate, acrylate, ketone, amide, and sulfone, are suitable substrates under this photocatalytic redox neutral conditons. New applications of chloromethyl silicate as C1 feedstock in photocatalysis will be reported in due course.

Experimental Section

To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)-chloromethylsilicate (**2**) (238.9 mg, 0.4 mmol, 2 equiv), the corresponding alkene (0.2 mmol, 1 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times, and was charged with degassed DMSO (6 mL, 0.033 M). The tube was irradiated with 9 W blue LEDs light strip spiraled within a bowel for 12 h or 24 h. After complete consumption of the starting alkene monitored by TLC, the reaction was quenched by saturated Na_2CO_3 aqueous solution (10 mL), extracted with EtOAc (4 x 10 mL), and dried over $MgSO_4$. After concentration of the crude product *in vacuo*, flash chromatography over silica gel afforded the product.

Acknowledgements

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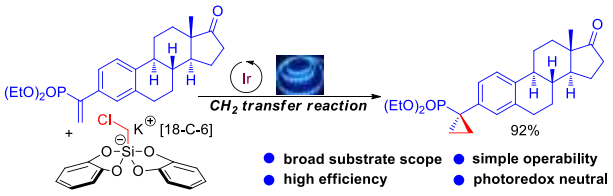

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