Organic LETTERS

Letter

Cite This: Org. Lett. XXXX, XXX, XXX-XXX

pubs.acs.org/OrgLett

Visible-Light-Driven α-Allenylic C−O Bond Cleavage and Alkenyl C−S Formation: Metal-Free and Oxidant-Free Thiolation of Allenyl Phosphine Oxides

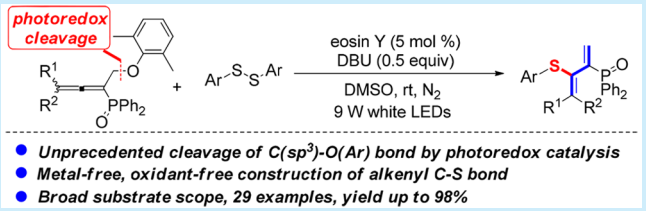
Ling Zhang,[†] Jie Zhu,[†] Jing Ma,[†] Lei Wu,*[,†,‡] and Wei-Hua Zhang*[,†]

[†]Jiangsu Key Laboratory of Pesticide Science and Department of Chemistry, College of Sciences, Nanjing Agricultural University, Nanjing 210095, P. R. China

[‡]Beijing National Laboratory for Molecular Sciences and Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

Supporting Information

ABSTRACT: A visible-light photoredox cleavage of α-allenylic C−O bond and alkenyl C−S formation is disclosed for the first time. The thiolation of allenyl phosphine oxides with diaryl disulfides occurs smoothly in metal-free and mild conditions, affording novel S,P-bifunctionalized butadienes with moderate to excellent yields. Mechanistic studies explain the cleavage of a C(sp^3)−O(Ar) bond in initiating a key alkenyl radical intermediate.



Alkenyl sulfides are fundamental building blocks in synthetic intermediates, naturally occurring molecules, and drugs.[1] Not surprisingly, considerable effort has been focused toward the synthesis of alkenyl sulfides, which undoubtedly represents an active research area in recent decades.[1b,h] Typically, the most powerful methods for constructing alkenyl sulfides rely on the thiolation of alkynes[2] and transition-metal-catalyzed cross-coupling of vinyl precursors with sulfur sources, where palladium, copper, nickel, iron, and other metals have been successfully employed as catalysts.[1b,3] Given the increasing demands in green and sustainable chemistry, contributions have also been extended to oxidative cross-couplings between C(sp^2)−H and RS−H/RSSR nucleophiles,[4] most often with molecular iodine and/or synthetic oxidants. Although many achievements have been made, the necessity of expensive ligand, a narrow substrate scope, harsh reaction conditions, and stoichiometric oxidants often limits its application.

Alternatively, visible-light-driven reactions have emerged as wonderful strategies for C(sp^2)−S formations, exhibiting great superiority for both reaction conditions and substrate tolerance.[5] For recent elegant studies, Lei and co-workers reported an intramolecular aromatic C−H thiolation by dual cobalt and visible-light photoredox catalysis under oxidant-free conditions (Scheme 1a).[5c] Lately, Fu et al. developed an efficient visible-light photoredox system for arylation of thiols with aryl halides, including less reactive aryl chlorides.[5g] However, alkenyl C−S formation by visible light photocatalysis has been under-developed. This process has been dominantly confined within the synthesis of benzothiophene derivatives to date.[5k−m] In 2012, König revealed the first example of alkenyl C(sp^2)−S formation with organic dyes, in which the radical cyclization was initiated by the decomposition of diazonium salt upon irradiation by green light (Scheme 1b).[5k] Inherently, these achievements mainly relied on the visible-light-generated sulfur radicals in the early stage, or single-electron oxidation of *in situ* generated sulfur radical species.

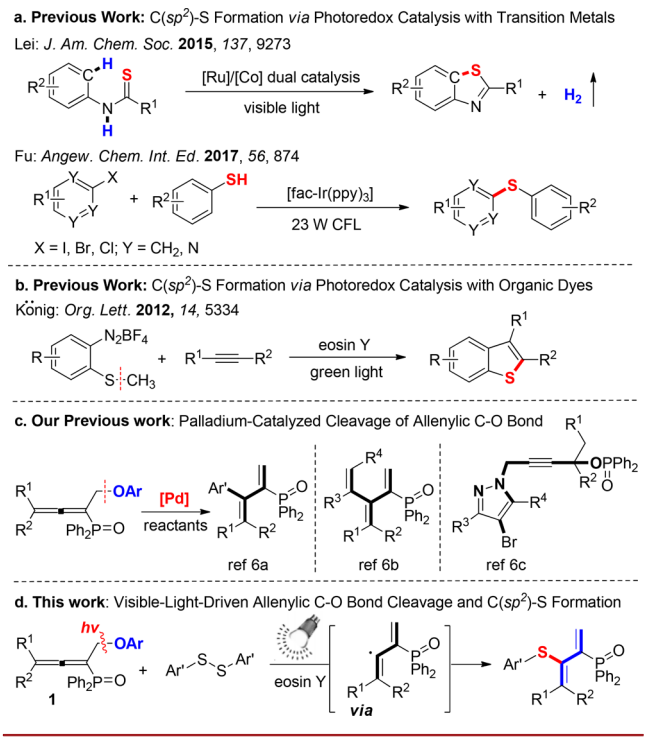
Our group has advanced a series of studies on the reaction of allenylphosphine oxides (**1**) via palladium-catalyzed cleavage of an α-allenylic C−O bond (Scheme 1c).[6] Later, acetic acid mediated sulfonylation of the allenylphosphine oxide offered divergent sulfonylated allenes and butadienes, exhibiting the special reactivity of the α-allenylic C−O bond with acid activation.[7] Inspired by recent work on photocatalytic cleavage of C−C and C−X bonds,[8] we envisioned that an alkenyl radical species might form via a photocatalytic C−OAr cleavage,[9] rendering new chemistry for alkenyl C−S formation (Scheme 1d). From our continuing explorations on photoredox catalysis and radical chemistry,[10] we herein disclose an unprecedented organic-dye-sensitized photocatalytic α-allenylic C−OAr bond cleavage and alkenyl C−S formation.

Taking into account that sulfur radicals, generated from thiol or dialkyl disulfide in the early stage, would alter the proposed reaction pathway from allenylphosphine oxide (**1**), diaryl disulfide was selected as the sulfur source. This choice was based on the recent reports that diaryl disulfides exhibited difficulty during photolysis under visible light from the LEDs, but were good as radical acceptors.[11] We initially performed the visible-light photoredox thiolation of allenylphosphine oxide (**1a**)[12] with diphenyl disulfide (**2a**) as a model reaction to optimize the conditions, including photocatalyst, base, solvent, atmosphere, and reaction time. No conversion could be observed when the reactions were conducted in the dark or without a

Received: September 29, 2017

DOI: 10.1021/acs.orglett.7b03052
Org. Lett. XXXX, XXX, XXX−XXX

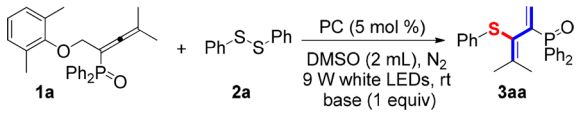
Scheme 1. (a and b) Representative Studies on C(sp^2)−S Formation *via* Photoredox Catalysis; (c) Our Previous Work; (d) This Work



photocatalyst (Table 1, entries 1−2). By employing a photosensitizer under weak alkaline conditions, the desired product S,P-bifunctionalized 1,3-butadiene (**3aa**) was obtained smoothly, with no other additives. Screening different solvents revealed that aprotic polar solvents afford higher yields and DMSO is the best solvent for this process with a yield of 95% (see the Supporting Information (SI) for details, Table S1). Afterward, several commercial organic dyes as photocatalysts (PCs) were tested (entries 4−7), among which eosin Y outperformed the others leading to the highest yield. In the absence of a base, only <5% yield of **3aa** was observed by ^{31}PNMR (entry 8). When the reaction was conducted in the presence of stronger bases, such as DBU, DABCO, Cs_2CO_3, and *t*-BuOK, the yields of **3aa** increased substantially compared to case of $NaHCO_3$ (entry 9). DBU enabled the reaction with an excellent yield of 98% (entries 11). Notably, the yield remained high even when using 0.5 equiv of DBU, giving the target product **3aa** in the same yield (entry 13). As a comparison, lower loadings of the inorganic base led to a substantial yield decrease to 39% (entry 14), suggesting a distinct reaction mechanism depending on the base type. A dramatic decrease in yield was observed when the reaction was carried out under air, with only a trace amount of product detected (entry 15). These results indicate that light, eosin Y, a base, and a nitrogen atmosphere are all essential to achieve the reaction with high efficiency.

Encouraged by the preliminary results, various allenylphosphine oxides (**1b−1q**) were evaluated using the optimal conditions, with the results summarized in Scheme 2. In general,

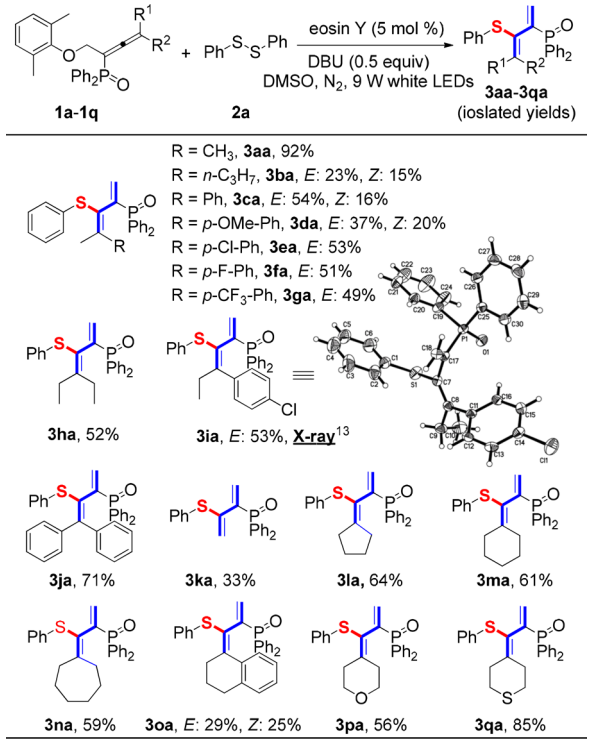
Table 1. Optimization of the Reaction Conditions[a]



entry	photocatalyst (PC)	base	yield (%)[b]
1	–	PivONa	N.R.
2[c]	eosin Y	PivONa	N.R.
3	eosin Y	PivONa	93(86)
4	fluorecein	PivONa	63
5	rhodamine B	PivONa	67
6	eosin B	PivONa	83
7	alizarin Red S	PivONa	91
8	eosin Y	–	<5
9	eosin Y	$NaHCO_3$	50
10	eosin Y	Cs_2CO_3	97
11	eosin Y	DBU	98
12	eosin Y	*t*-BuOK	97
13[d]	**eosin Y**	**DBU**	**98(92)**
14[d]	eosin Y	PivONa	43(39)
15[e]	eosin Y	DBU	trace

[a]Reaction conditions: allenylphosphine oxide (**1a**, 0.2 mmol), diphenyl disulfides (**2a**, 0.2 mmol), photocatalyst (PC, 5 mol %), base (1 equiv), N_2, 8 h. [b]Yields based on ^{31}PNMR, N.R. = no reaction, isolated yields in bracket. [c]Under dark. [d]0.5 equiv of base. [e]Under air.

Scheme 2. Substrates Scope on Allenylphosphine Oxides



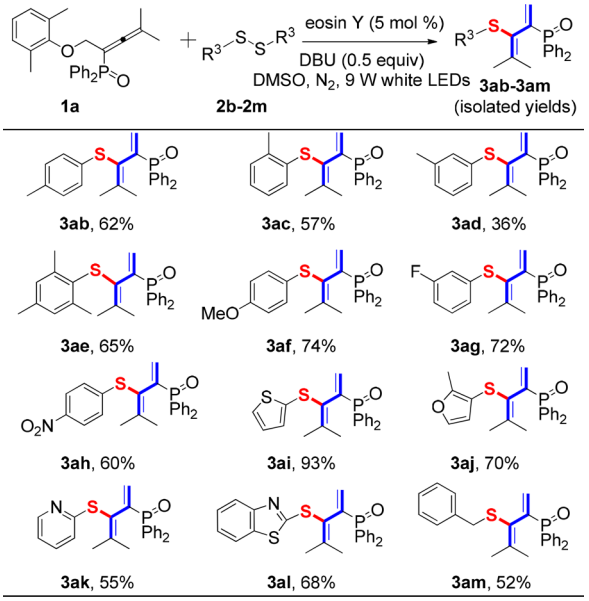
allenylphosphine oxides with terminal alkyl, cyclic, aromatic, or heterocyclic substitutions afforded the corresponding thioether products with moderate to good yields. With aromatic substitutions, both electron-rich groups (such as *p*-MeO) and electron-deficient groups (such as *p*-Cl, *p*-F, and *p*-CF_3) on the phenyl moiety proceeded smoothly in the system, without a distinct electronic effect on the reactivity being observed. For alkyl, alicyclic substituted allenes or endmost aromatics with electron-neutral and -rich substituents, however, two isomers could be isolated with slight preferences of *E*-selectivity in ratios of 1.2:1−3.4:1 (**3ba**, **3ca**, **3da**, and **3oa**). It is worthy to mention that, owing to a combined effect of the stabilization of electron-

DOI: 10.1021/acs.orglett.7b03052
Org. Lett. XXXX, XXX, XXX−XXX

deficient groups to radical intermediates and $\pi-\pi$ stacking between the aromatic substitutions and $P(O)Ph_2$ moiety, *E*-isomers of **3ea**, **3fa**, **3ga**, **3ia** were obtained exclusively. The stereoselectivity was elucidated by the X-ray structure of **3ia** (CCDC 1573645). Allene without terminal substitution (**1k**) produced a lower yield, which might be rationalized by relative differences in the stability and reactivity of radical intermediates when there were substitution groups on allenes. Cyclopentyl-, cyclohexyl-, and cycloheptyl-derived allenes were also effective in furnishing the corresponding products (**3la**–**3na**), giving similar yields ranging from 59% to 64%. In addition, *O*- and *S*-heterocyclic terminated allenes (**1p**, **1q**) were applicable with yields of 56% and 85%, respectively.

Next, the nature of diaryl disulfides was examined to verify the generality of this photoinduced approach. As shown in Scheme 3,

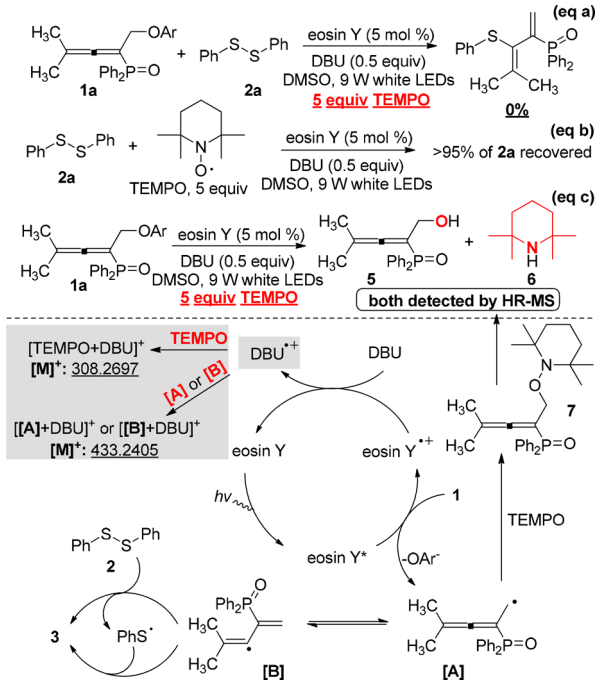
Scheme 3. Substrates Scope on Disulfides



high compatibility was exhibited with functional groups such as methyl, methoxy, halo, and nitro substituents. *Ortho*-, *meta*-, and *para*-substituted diaryl disulfides were all well tolerated, but *meta*-substituted methyl impaired the reactivity somehow, giving a lower yield compared with the others. Notably, heteroaromatic disulfides, including thienyl, furyl, pyridinyl, and benzothiazolyl disulfides, performed well, providing the corresponding thiolated product in medium to excellent yields, which offered further functionalization of the products. Furthermore, benzyl disulfide underwent the reaction successfully to give product **3am** in a 52% yield.

To gain some insight into the reaction mechanism, several control experiments were conducted, as described in Scheme 4. On one hand, in the presence of 5 equiv of TEMPO, the coupling reaction of **1a** and **2a** was entirely inhibited (Scheme 4, eq a), indicating a radical pathway. On the other hand, as shown in eq b, an attempt to capture the radical species generated from diphenyl disulfides failed under current conditions, which was in line with the previous reports.[11a] Intriguingly, from monitoring the high-resolution mass spectrum (HR-MS), allenic alcohol (**5**) and 2,2,6,6-tetra-methylpiperidine (**6**) were detected in the reaction of allene **1a** with 5 equiv of TEMPO. These two compounds were probably produced from the decomposition of a radical trapping product (**7**). Fortuitously, a coupling product of

Scheme 4. Mechanism Studies



proposed $[DBU]^{+\cdot}$ and radical intermediates [**A**] or [**B**] could be detected, as well as the DBU cation radical and TEMPO (see HR-MS details in the SI). The mechanistic studies clearly support the photoredox cleavage of an α-allenylic C–O bond to initiate radical intermediates instead of a sulfur radical.

On the basis of the experimental facts, quenching experiments (in SI), and previous reports,[11,13] a plausible reaction mechanism is presented in Scheme 4. Initially, eosin Y changes to its excited state (eosin Y*) under visible light irradiation, which donates a single electron to allenylphosphine oxide (**1**) to form the ArO anion as well as an α-allenylic radical species ([**A**]) and turned into the eosin Y radical cation itself. Subsequently, [**A**] tautomerizes to an alkenyl radical [**B**], which reacts with diphenyl disulfides to deliver the S,P-bifunctionalized 1,3-butadiene (**3**) and a sulfur radial PhS·. In addition, the PhS· could be trapped by another alkenyl radical to furnish **3**. There was evidence that DBU played a role in the transference of an electron to eosin Y radical cation to regenerate eosin Y.

In summary, we revealed a practical and efficient method for alkenyl C–S bond construction through photocatalytic thiolation of allenyl phosphine oxides with diaryl disulfides. Under visible light irradiation, successive cleavage of an α-allenylic C–O bond and alkenyl C–S formation were involved, delivering a series of novel S,P-bifunctionalized butadienes with moderate to excellent yields. The reactions exhibited many advantages including mild conditions, eco-benign procedures, and good functional group compatibility. We expect this new and operationally simple protocol to provide novel scaffolds for building potential bioactive compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03052.

Experimental procedures; spectral data for all new compounds (PDF)

DOI: 10.1021/acs.orglett.7b03052
Org. Lett. XXXX, XXX, XXX–XXX

Accession Codes

CCDC 1573645 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: rickywu@njau.edu.cn.
*E-mail: zhwh@njau.edu.cn.

ORCID

Lei Wu: 0000-0001-9130-6619

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project is supported by the Fundamental Research Funds for the Central Universities (NJAU, Grant No. KYTZ201604).

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Org. Lett. XXXX, XXX, XXX−XXX