


Cite this: *RSC Adv.*, 2020, **10**, 12599

Visible light-mediated photocatalytic oxidative cleavage of activated alkynes *via* hydroamination: a direct approach to oxamates†

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Received 15th December 2019
Accepted 26th February 2020

DOI: 10.1039/c9ra10555g
rsc.li/rsc-advances

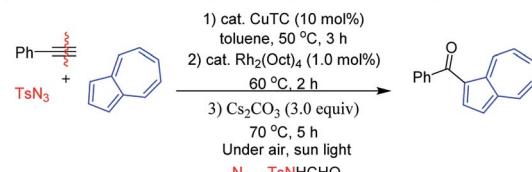
The direct oxidative cleavage of activated alkynes *via* hydroamination has been described using organic photocatalyst under visible-light irradiation at room temperature. In this reaction, the single electron oxidation of an *in situ* formed enamine followed by radical coupling with an oxidant finally delivers the oxamate. The key features of this photocatalytic reaction are the mild reaction conditions, metal-free organic dye as a photocatalyst, and TBHP playing a dual role as "O" source and for the regeneration of the photocatalyst.

Introduction

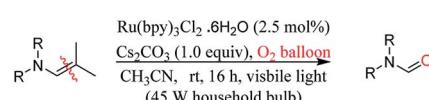
C–C bond cleavage reactions have been paid considerable attention to, owing to the potential utility of resulting functionalized intermediates in organic transformations and medicinal chemistry.¹ Other than organic synthesis, one also finds C–C bond cleavage applications in photocatalytic degradation leading to environment remediation and further in generation of fine chemicals from biomass based organic materials. In the past decades, various strategies for C–C single, double and triple bond breakage have been developed.² Among C–C bond cleavage reactions, although the cleavage of the C–C triple bond has been extensively studied, still it remains a challenging issue in contemporary organic synthesis due to its large bond dissociation energy.³ In recent years, several proficient transition-metal-catalysed reactions have been demonstrated for C–C triple bond cleavages.⁴ To circumvent the use of precious transition-metal catalysts, recently metal-free approaches have become more attractive and provide potential building blocks such as amides, nitriles, acids, and esters from C–C triple bond cleavage.⁵ Despite the progress made, metal-free methods with economic and readily available reagents are still highly desirable and remain a challenge. In this context, recently, visible-light induced photocatalysis has emanated as an enabling platform to access new chemical transformations under mild conditions.⁶ However, the complete C–C triple bond cleavages under photocatalysis are

scarce. Recently, Lee research group has developed the C–C triple bond cleavage strategy to synthesize azulen-1-yl ketones *via* *N*-sulfonyl enamides under photocatalysis (Scheme 1a).⁷ Enamines have gained significant attention in oxidative C–C bond cleavages.⁸ In this regard, Wang and co-workers have presented the oxidative cleavage of electron rich enamines to amides under Ru catalyzed visible-light irradiation (Scheme 1b).⁹ To the best of our knowledge, visible light induced organic photocatalyzed oxidative cleavage of C–C triple bond *via* hydroamination leading to oxamates has not been reported (Scheme 1c).

a) Photoredox oxidative cleavage of C–C triple bond *via* *N*-sulfonyl enamides

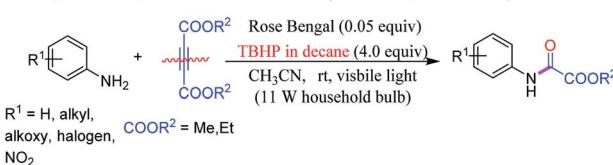


b) Photoredox oxidative cleavage of C–C double bond of electron rich enamines



This work:

c) Metal-free photoredox oxidative cleavage of C–C triple bond *via* hydroamination



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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ra10555g

Scheme 1 Selected examples for photocatalysis oxidative cleavage of C–C double and triple bonds.



In recent years, alkynes as appealing substrates have pinched great attention in the synthesis of heterocycles and building blocks as well.^{8c,d,10} With our continuing interests in developing sustainable methods leading to potential intermediates and heterocycles of bio relevance under metal-free catalysis^{8c,d,11} from the amines and electron deficient alkynes as key starting materials, herein we report visible-light induced Rose Bengal photocatalyzed C–C triple bond oxidative cleavage.

Organic molecules containing amide (peptide bond) α to ester functionality are important in the synthesis of bioactive molecules.¹² In this context, oxamates are well known as versatile building blocks for the synthesis of functionalized organic molecules, biologically active molecules and natural products.¹³ Consequently, few methods have been developed for the construction of oxamates and their analogues using metal or metal-free catalysts.¹⁴ Traditional methods involved the coupling of amines with precursors such as monoesters of oxalyl chloride or diester of oxalic acid in generating oxamates.¹⁴ However, the monoesters of oxalyl chlorides are thermally

unstable and require in stoichiometric amounts, and moreover, the preparation methods are laborious and involve the distillation process of the reaction mixture. Although alternative methods documented in the literature,¹⁴ the use of a dehydrating agent, the high pressure of CO/O₂, expensive metal catalyst, limited substrate scope, and difficulty in separation of catalyst from product and its reuse are significant drawbacks. Very recently, oxamates could also be successfully synthesized *via* C–C and C=C bonds of acetoacetamides and enamines by employing metal catalyst and harsh reaction conditions respectively.¹⁵ However, the development of sustainable methods toward the synthesis of oxamates is highly desirable.

Results and discussion

In this sense, we investigated visible-light-mediated C–C triple bond cleavage by using aniline **1a** and diethyl acetylenedicarboxylate **2a** as model substrates in the presence of 4 equiv. of aqueous tertiary butyl hydrogen peroxide (aq. TBHP) as the

Table 1 Optimization of reaction conditions for the synthesis of **3aa**^a

Entry	Photocatalyst (equiv.)	Oxidant (equiv.)	Solvent	Yield ^b (%)
1	Rose Bengal (0.05)	aq. TBHP (4.0)	DMF	22
2	Rose Bengal (0.05)	aq. TBHP (4.0)	CH ₃ CN	58
3	Rose Bengal (0.05)	O ₂ balloon	CH ₃ CN	40 ^c
4	Rose Bengal (0.05)	TBHP in decane (4.0)	CH ₃ CN	55 ^d
5	Rose Bengal (0.05)	TBHP in decane (4.0)	CH ₃ CN	82
6	Rose Bengal (0.05)	DTBP (4.0)	CH ₃ CN	39
7	Rose Bengal (0.05)	TBP (4.0)	CH ₃ CN	16
8	Eosin Y (0.05)	TBHP in decane (4.0)	CH ₃ CN	68
9	Riboflavin (0.05)	TBHP in decane (4.0)	CH ₃ CN	62
10	Rhodamine B (0.05)	TBHP in decane (4.0)	CH ₃ CN	45
11	Ru(bpy) ₃ Cl ₂ (0.05)	TBHP in decane (4.0)	CH ₃ CN	83
12	Ru(bpy) ₃ Cl ₂ ·6H ₂ O (0.05)	TBHP in decane (4.0)	CH ₃ CN	80
13	Ru(bpy) ₃ Cl ₂ ·6H ₂ O (0.05)	O ₂ balloon	CH ₃ CN	43
14	Rose Bengal (0.05)	TBHP in decane (4.0)	CH₃CN	81, 80^e
15	Rose Bengal (0.025)	TBHP in decane (4.0)	CH ₃ CN	75
16	Rose Bengal (0.15)	TBHP in decane (4.0)	CH ₃ CN	82
17	—	TBHP in decane (4.0)	CH ₃ CN	Nd
18	Rose Bengal (0.05)	TBHP in decane (4.0)	CH ₃ CN	Trace ^f
19	Rose Bengal (0.05)	TBHP in decane (4.0)	CH ₃ CN	21 ^g
20	Rose Bengal (0.05)	TBHP in decane (4.0)	CH ₃ CN	71 ^h
21	Rose Bengal (0.05)	TBHP in decane (4.0)	CH ₃ CN	78 ⁱ
22	Rose Bengal (0.05)	TBHP in decane (4.0)	CH ₃ CN	82 ^j
23	Rose Bengal (0.05)	TBHP in decane (4.0)	CH ₃ CN	82 ^k
24	Rose Bengal (0.05)	TBHP in decane (4.0)	DCE	71
25	Rose Bengal (0.05)	TBHP in decane (4.0)	DMSO	14
26	Rose Bengal (0.05)	TBHP in decane (4.0)	DCM	56
27	Rose Bengal (0.05)	TBHP in decane (4.0)	DMA	43

^a Reaction conditions: **1a** (0.53 mmol), **2a** (0.53 mmol), solvent (1.5 mL), rt (27 °C), 11 W CFL household bulb, for 48 h. ^b Isolated yields after silica-gel column chromatography. ^c Reaction mixture was degassed before providing O₂ atmosphere (balloon). ^d Reaction mixture was degassed before providing N₂ atmosphere. ^e Reaction is performed on presynthesized enamine. ^f Reaction carried out in dark. ^g Reaction performed under sunlight. ^h 5 W household bulb used. ⁱ 15 W household bulb used. ^j DIPEA (di isopropyl ethylamine) (1.0 equiv.) used. ^k Cs₂CO₃ (1.0 equiv.) used. TBHP (5.0–6.0 M) in decane. DTBP = di-*tert*-butyl peroxide, TBP = *tert*-butyl peroxybenzoate.



oxidizing agent, 5 mol% Rose Bengal in DMF at room temperature under irradiation with 11 W CFL household bulb, pleasantly which afforded the desired product ethyl 2-oxo-2-(phenylamino)acetate **3aa** with 22% yield after 48 h (Table 1, entry 1). Change of solvent from DMF to CH_3CN improved the yield to 58% (Table 1, entry 2). Inspired by this result, we screened other oxidants (Table 1, entries 3–7) and TBHP in decane was found to be most effective (82%, Table 1, entry 5). To further improve the yield, we then investigated the reaction with various photocatalysts such as eosin Y, riboflavin, rhodamine B, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot \text{H}_2\text{O}$. Although the two Ru based photocatalysts and Rose Bengal were found to be sufficient for C–C triple bond cleavage (Table 1, entries 11–13 and 5), The low cost, easy accessible and metal-free nature of Rose Bengal¹⁶ inspired us to further optimize the reaction conditions with this organophotocatalyst. Next, we have screened the reaction by varying the equiv. of Rose Bengal photocatalyst, and 0.05 equiv. was found to be optimum (Table 1, entries 14–16). We were pleased to find oxamate **3aa** in 81% yield with 0.05 equiv. of Rose Bengal, 4 equiv. of TBHP (in decane) and 11 W CFL bulb as a light source in CH_3CN solvent (Table 1, entry 14). The reaction did not proceed either in the absence of photocatalyst or visible light, indicating that both components are crucial for C–C triple bond cleavage (entries 17 and 18). Endeavors to use sunlight instead of 11 W CFL bulb gave a very poor yield of **3aa** (entry 19). Other CFL bulbs such as 5 W and 15 W did not improve the yield (entries 20 and 21). The use of bases such as DIPEA and Cs_2CO_3 were not successful (entries 22 and 23). Among solvents examined (entries 24–27), CH_3CN showed that it is the most suitable solvent for the present transformation (entry 14).

After optimization of the reaction conditions, we next tested the broad range of anilines **1**. Anilines **1** containing electron-neutral and electron-rich functional groups were well participated in oxidative C–C triple bond cleavage to afford the corresponding oxamates (**3aa**, **3ab**, **3ba**, **3bb** & **3da**, Table 2) with very good yields. Weak electron withdrawing groups like halogens substituted anilines reacted well, providing the corresponding products (**3ea**, **3eb**, **3fa**, **3fb**, **3ga**, **3ha**, **3ia**, **3ja** & **3ka**) with good yields. Slightly lower yields were observed for electron-withdrawing nitro-substituted anilines, this may be due to less formation of enamine or hydroamination product (**3la** & **3lb**). We sought to further explore this oxidative C–C triple bond cleavage reaction with aliphatic amines. The low yields of (**3ma** & **3nb**) in case of aliphatic amines, could be due to the less stabilization of radical cation (**II**) and imminium ion (**III**) when compared to other aromatic amines. Furthermore, other diverse *in situ* generated enamines failed to participate in oxidative C–C cleavage, due to failure in the formation of radical cation intermediate (**II**) and imminium ion (**III**) in case of (**3ac** & **3ad**) wherein we have $-\text{CH}_3$ and $-\text{Ph}$ in the ' α ' position of enamine, which might not facilitate oxidation and $t\text{-BuO-O}^\bullet$ radical addition, thus indicating CO_2Et group is crucial in the ' α ' position of enamine. Alternatively, more EWG like CF_3 might also not favor the oxidation of enamine to intermediate (**II**) in the presence of Rose Bengal catalyst.

Based on our observations and literature reports^{7,9} a plausible mechanism for the visible light Rose Bengal photocatalyzed C–C

Table 2 Substrates scope with respect to aniline and alkynes^{a,b}

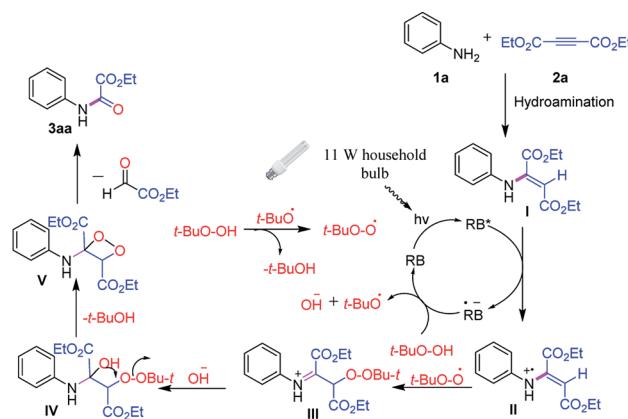
		Rose Bengal (0.05 equiv) TBHP in decane (4.0 equiv) CH_3CN , rt, visible light, 48 h (11 W household bulb)	

^a Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), Rose Bengal (5 mol%), TBHP in decane (4.0 equiv.), 11 W CFL bulb, CH_3CN (1.5 mL), rt, for 48 h.

^b Isolated yields after silica-gel column chromatography.

triple bond oxidative cleavage is illustrated in Scheme 2. The visible-light-excited Rose Bengal (RB^*) would undergo oxidative quenching by hydroamination product **I** to afford Rose Bengal radical anion ($\text{RB}^{\bullet-}$) and radical cation **II**.

Rose Bengal radical anion upon transfer of an electron to $t\text{-BuO-OH}$ would provide the tertiary butoxide radical, hydroxide anion and complete the photocatalysis cycle by the generation of Rose Bengal. On the other hand, radical cation **II** would undergo addition reaction simultaneously by tertiary butyl peroxide



Scheme 2 Plausible reaction mechanism.



radical and hydroxide anion to form intermediate **IV**. Upon intramolecular cyclization by giving up a *t*-BuOH, 1,2 dioxetane **V** would be formed which further undergoes fragmentation to give the desired product **3aa**.

Conclusion

We have developed a visible light driven Rose Bengal photocatalysis oxidative cleavage of C–C triple bond through hydroamination for the direct synthesis of oxamates from amines and electron deficient alkynes as a key starting material. The key features of this transformation are the mild conditions, metal-free organic dye as a photocatalyst, TBHP playing a dual role as “O” source and for the regeneration of photocatalyst, and a tandem hydroamination-oxidative C–C triple bond cleavage, thus enabling the preparation of oxamate derivatives. Notably, the present method offers a wide range of oxamate derivatives as of potential building blocks which are difficult to synthesize using previously developed methods.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge the Council of Scientific and Industrial Research (02(0297)/17/EMR-II) and the Department of science and Technology-science and Engineering Research Board (DST-SERB- EMR/ 2016/ 000952) New Delhi, India, and Indian Institute of Technology Hyderabad (IITH) for financial support. NRK and MO thanks DST-SERB, AVM thanks UGC, SA thanks CSIR, New Delhi, India for the award of research fellowship.

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