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Visible-light-enabled oxyazidation of alkenes leading to α-azidoketones in air†

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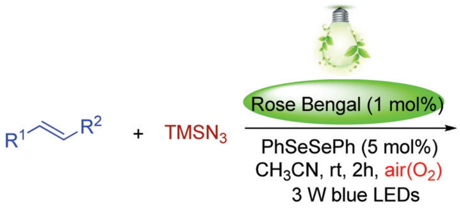
A new and facile visible-light-enabled method for the synthesis of α-azidoketones has been developed *via* oxyazidation of alkenes with $TMSN_3$ in air at room temperature. A series of α-azidoketones could be easily and efficiently obtained in moderate to excellent yields *via* cascade C–N and C=O bond formation by simply using low-toxic and inexpensive Rose Bengal (1 mol%) and PhSeSePh (5 mol%) as co-catalysts.

Organic azides have attracted a great deal of interest owing to their wide applications in synthetic chemistry[1] and materials science.[2] In particular, α-azidoketones are very important building blocks in the synthesis of diverse triazoles,[3] aziridines,[4] and other heterocyclic compounds,[5] which exhibit a variety of biological activities such as anti-allergic, anti-microbial, and anti-HIV properties.[6] Furthermore, α-azidoketones can also serve as useful intermediates for the synthesis of vicinal amino alcohols, which are key parts of some important compounds such as sphingosines, daunosamine and hydroxy amino acids.[7] In light of their widespread utilities, considerable efforts have been devoted towards α-azidoketones.

Traditionally, α-azidoketones are prepared by direct nucleophilic substitution of α-halo ketones[8] and α-tosyloxy ketones with azide ions.[9] Alternative methods such as the direct azidation of arylketones with NaN_3 in the presence of a hypervalent iodine reagent,[10] the azidation of silyl enol ethers using a benziodoxole-derived azide,[11] and the conversion of olefins to α-azidoketones in the presence of a stoichiometric amount of chromium trioxide (CrO_3), cerium(IV) ammonium nitrate (CAN), *cis*-1,4-bis(triphenylphosphonium)-2-buteneperoxodisulfate (BTPBPD) or *in situ*-generated modified IBX[12] have also been developed. Very recently, Szpilman also reported the α-azidation of the preformed enolonium species leading to α-azidoketones in the presence of Koser's hypervalent iodine reagents at low temperature.[13] Nevertheless, most of these methods still involve the use of a large excess of expensive and hazardous oxidants, toxic metal reagents, or multi-step synthetic sequences, which would lead to increased cost and environmental concerns and limit their practical utility. Therefore, the development of a facile, efficient, economic and eco-friendly method to construct α-azidoketones is still highly desirable.

From green and sustainable points of view, the direct utilization of O_2 as an oxidant and oxygen source is one of the most ideal methodologies for the construction of oxygen-containing compounds. In particular, air demonstrates more advantages over pure dioxygen in terms of safety, accessibility, and low cost. It is still an appealing but challenging task to develop mild and selective aerobic oxidation reaction systems to access important and structurally diverse oxygenated compounds.[14] In recent years, visible-light photocatalysis has offered a technically attractive and energy-saving platform for promoting various aerobic chemical transformations under mild conditions.[15] On the other hand, organoselenium compounds as an attractive alternative to transition-metal-catalysts are increasingly utilized in organic synthesis owing to their easy availability, cheap and less toxic characteristics.[16] Although some achievements have been made in this field, the study of organoselenium catalysis is still in its infancy and new reaction systems remain to be further explored.



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In continuation of our interest in the development of new aerobic oxidation reactions,[17] here, we wish to report a mild

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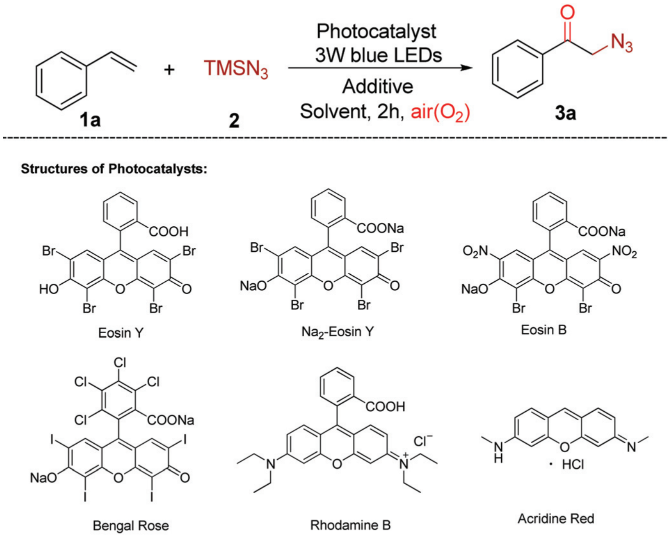
and facile visible-light-induced method for the construction of α-azidoketones *via* Rose Bengal (1 mol%) and PhSeSePh (5 mol%) co-catalyzed oxyazidation of alkenes with $TMSN_3$ and dioxygen (air) (eqn (1)). The present protocol offers an efficient and green route to a series of α-azidoketones with good functional-group tolerance, in which the C–N and C=O bonds are formed in a single operation under mild and metal-free conditions. To the best of our knowledge, this is the first example of a metal-free photocatalytic approach to access α-azidoketones.[18]

Initially, styrene **1a** and $TMSN_3$ were selected as the model substrates to optimize conditions such as photocatalysts, additives, solvents, and amounts of reactants under irradiation with 3 W blue LED lamps. Fortunately, when the model reaction was carried out in the presence of Eosin Y (2 mol%) and PhSeSePh (5 mol%) in MeCN in air, the desired α-azidoketone **3a** was obtained in 66% yield (Table 1, entry 1). The replacement of Eosin Y with other commercially available photocatalysts found that Rose Bengal was the best one to give the product **3a** in 74% yield (Table 1, entry 6), while others such as Na_2-Eosin Y, Eosin B, Rhodamine B, and Acridine Red were deleterious to the product yield (Table 1, entries 2–5). The screening of the loading of the photocatalyst found that 1 mol% Rose Bengal gave the best yield (92%) of the desired product **3a** (Table 1, entry 8). No transformation was observed in the absence of the photocatalyst (Table 1, entry 9). Solvent was also crucial for this oxyazidation reaction. A notable decrease of yield was observed when other solvents such as THF, 1,4-dioxane, DME, DCE, toluene, DMF, EtOH, or acetone were employed as the reaction media to replace MeCN (Table 1, entries 10–17). Increasing or decreasing the loading of PhSeSePh failed to improve the reaction efficiency (Table 1, entries 18 and 19). Only 5% product was obtained in the absence of PhSeSePh (Table 1, entry 20). The replacement of PhSeSePh with PhSSPh did not improve the reaction efficiency (Table 1, entry 21). In addition, when the reaction was conducted under irradiation with 3 W white or green LED lamps, the desired product was only obtained in 71% and 52% yields, respectively (Table 1, entries 22 and 23). In contrast, the oxyazidation of alkenes did not occur in the dark or replacing $TMSN_3$ with NaN_3 (Table 1, entries 24 and 25).

Table 1 Optimization of the reaction conditions[a]

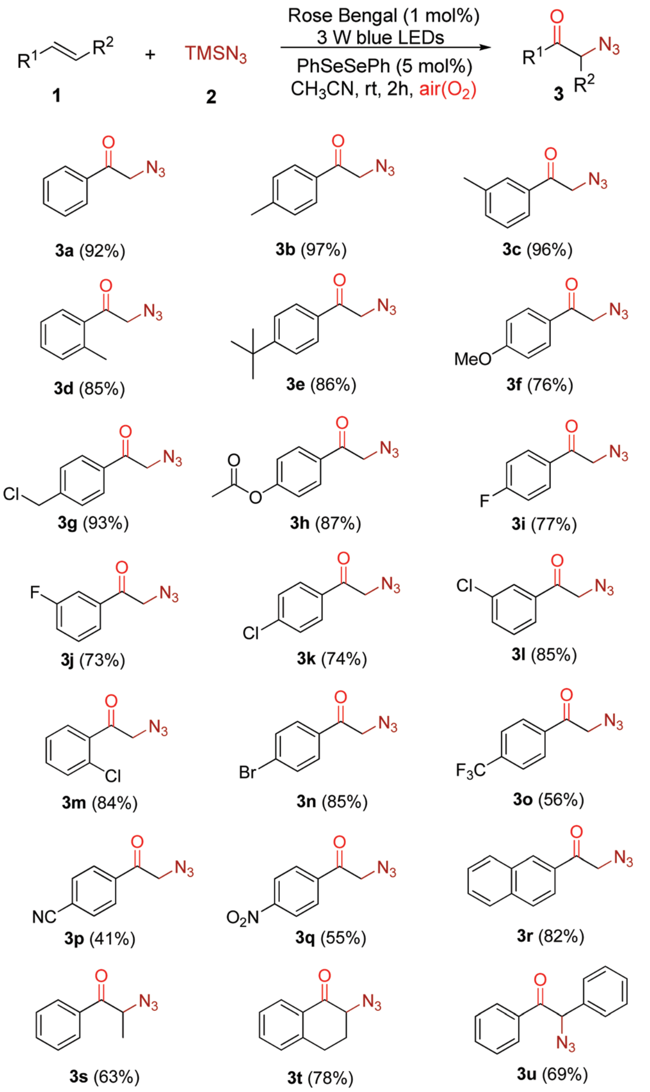


Entry	Photocatalyst (mol%)	Additive (mol%)	Solvent	Yield[b] (%)
1	Eosin Y (2)	PhSePh(5)	CH_3CN	66
2	Na_2-Eosin Y (2)	PhSeSePh(5)	CH_3CN	25
3	Eosin B (2)	PhSeSePh(5)	CH_3CN	Trace
4	Rhodamine B (2)	PhSeSePh(5)	CH_3CN	33
5	Acridine Red (2)	PhSeSePh(5)	CH_3CN	20
6	Rose Bengal (2)	PhSeSePh(5)	CH_3CN	74
7	Rose Bengal (5)	PhSeSePh(5)	CH_3CN	48
8	**Rose Bengal (1)**	**PhSeSePh(5)**	**CH_3CN**	**92**
9	—	PhSeSePh(5)	CH_3CN	0
10	Rose Bengal (1)	PhSeSePh(5)	THF	Trace
11	Rose Bengal (1)	PhSeSePh(5)	1,4-Dioxane	10
12	Rose Bengal (1)	PhSeSePh(5)	DME	30
13	Rose Bengal (1)	PhSeSePh(5)	DCE	27
14	Rose Bengal (1)	PhSeSePh(5)	Toluene	12
15	Rose Bengal (1)	PhSeSePh(5)	DMF	23
16	Rose Bengal (1)	PhSeSePh(5)	EtOH	15
17	Rose Bengal (1)	PhSeSePh(5)	Acetone	77
18	Rose Bengal (1)	PhSeSePh(1)	CH_3CN	76
19	Rose Bengal (1)	PhSeSePh(10)	CH_3CN	68
20	Rose Bengal (1)	—	CH_3CN	5
21	Rose Bengal (1)	PhSSPh(5)	CH_3CN	Trace
22	Rose Bengal (1)	PhSeSePh(5)	CH_3CN	71[c]
23	Rose Bengal (1)	PhSeSePh(5)	CH_3CN	52[d]
24	Rose Bengal (1)	PhSeSePh(5)	CH_3CN	0[e]
25	Rose Bengal (1)	PhSeSePh(5)	CH_3CN	0[f]

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), photocatalyst (1–5 mol%), additive (1–10 mol%), solvent (analytical reagent) 1 mL, 3 W blue LED lamps, rt, air (O_2), 2 h. [b] Isolated yields based on **1a**. [c] 3 W white LED lamps. [d] 3 W green LED lamps. [e] In the dark. [f] NaN_3 was used instead of $TMSN_3$.

With optimized visible-light photoredox conditions in hand, the substrate scope for oxyazidation of alkenes with $TMSN_3$ was surveyed. As shown in Table 2, aromatic alkenes containing electron-rich or electron-poor groups on the aryl rings were suitable for this process to provide the corresponding products in moderate to good yields. The electronic nature of the substrates has great influence on the reaction efficiency, and bearing electron-donating group substituted aromatic alkenes (**3a–3h**) showed better activity in comparison with those containing strong electron-withdrawing groups (**3o–3q**). The reaction efficiency was not obviously affected by the steric effect, and substrates bearing a methyl or chloro group in the *para*-, *meta*-, or *ortho*-position of the aryl ring were all suitable for this reaction (**3b–3d**, **3k–3m**). Also, functional groups such as chloromethyl, acetoxy, halogen, cyano and nitro groups survived well in this reaction leading to the corresponding products **3g–3q**, which can be applied in further modifications. In addition, 2-vinylnaphthalene could smoothly convert to the expected product **3r** in 82% yield. Notably, internal aromatic alkenes such as β-methyl styrene, 1,2-dihydronaphthalene and 1,2-diphenylethene could also work smoothly under the current conditions, affording the desired products **3s–3u** in good yields. Nevertheless, when ali-

Table 2 Results for visible-light-induced oxyazidation of alkenes leading to α-azidoketones[a,b]



[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), Rose Bengal (1 mol%), PhSeSePh(5 mol%), CH_3CN (analytical reagent, 1 mL), 3 W blue LED lamps, rt, air (O_2), 2 h. [b] Isolated yields based on **1**.

phatic alkenes such as hex-1-ene and cyclopentene were used as the substrates, none of the desired products were detected.

It is noteworthy that α-azidoketones as useful building blocks could be transformed into a series of valuable compounds.[19] For example, as shown in Fig. 1, β-azido alcohol **4a** and 2-nitroacetophenone **4b** can be easily obtained from product **3a** through the simple reduction and oxidation reaction, respectively.[19a,b] 3-Acylisoquinoline **4c** was obtained from the reaction of phenacyl azide **3a** with *o*-phthalaldehyde and triphenylphosphine.[19c] Five membered rings such as imidazole **4d** and pyrazole **4e** were efficiently synthesized by the condensation of phenacyl azide **3a**.[19d,e] Undoubtedly, a click reaction was employed to yield β-carbonyl triazole **4f**.[19f]

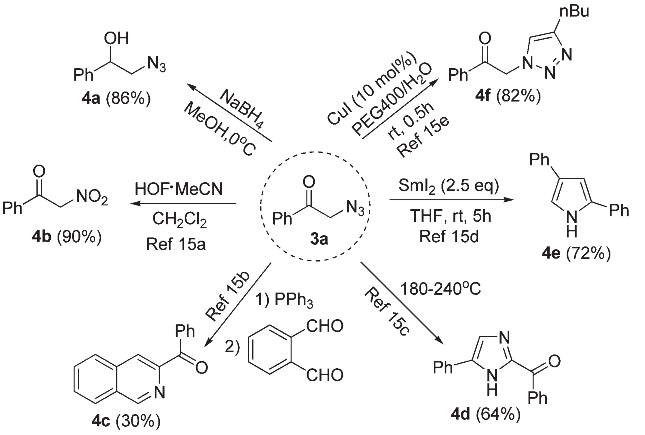
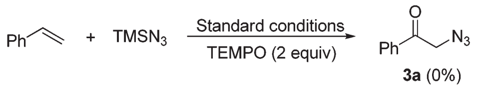


Fig. 1 Synthetic application of α-azidoketones.

Subsequently, we turned our attention to explore the possible reaction mechanism. As presented in eqn (2), the model reaction was completely inhibited when 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added under standard conditions, suggesting that the present transformation might involve a radical process. Only a trace amount of the desired product was detected when the model reaction was carried out under a nitrogen atmosphere (eqn (3)). Furthermore, when the reaction of styrene **1a** and $TMSN_3$ was carried out in the presence of H_2O^{18} in dry CH_3CN in air, the corresponding product **3a** was obtained in 81% yield and none of O^{18}-**3a** was detected by LC-MS (eqn (4)). These results suggested that dioxygen should be the key oxidant and oxygen source in the present reaction system. Moreover, in addition to the desired product **3a**, β-hydroperoxy azide **5a** was isolated in 74% yield when the model reaction was performed in the absence of PhSeSePh (eqn (5)). Furthermore, when the preformed β-hydroperoxy azide **5a** was treated with PhSeSePh (5 mol%) in CH_3CN at room temperature, the desired product **3a** was isolated in 94% yield (eqn (6)). These results suggested that β-hydroperoxy azide **5a** should be the key intermediate in this reaction and PhSeSePh could promote the elimination of water from **5a**.



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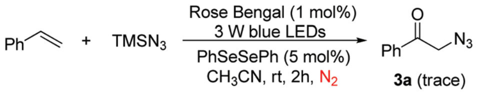
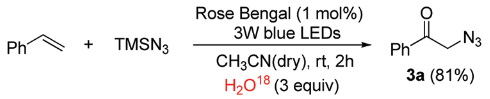


(3)



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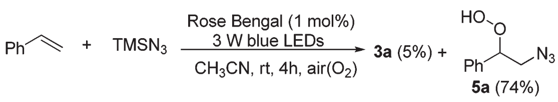

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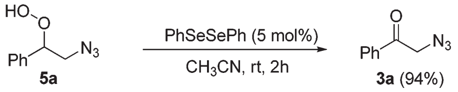


(6)

Next, on/off visible-light irradiation experiments were performed to prove the effect of photo-irradiation, and the result demonstrated that continuous irradiation of visible-light is necessary for this oxyazidation reaction (Fig. 2). Finally, fluorescence quenching (Stern–Volmer) experiments were also carried out to certify an energy transfer process between Rose Bengal and $TMSN_3$ under visible-light irradiation. As shown in Fig. 3 and 4, the emission intensity of excited Rose Bengal gradually decreased with the increasing of the concentration of $TMSN_3$. In contrast, such an effect was not found when Rose Bengal was separately mixed with styrene **1a** and PhSeSePh (see the ESI†). These results indicated that the single-electron transfer (SET) process actually occurred between Rose Bengal and $TMSN_3$ under visible-light irradiation.

Based the above results and previous reports,[15–17,20–22] a possible reaction pathway is demonstrated in Scheme 1. Firstly, the excited RB* was generated from Rose Bengal under visible-light irradiation. Subsequently, a single electron transfer (SET) process occurred between $TMSN_3$ **2** and RB* to give azido radical **6** and $RB^{\bullet-}$ radical anions. Furthermore, the ground state Rose Bengal and $O_2^{\bullet-}$ would be formed through the oxidation of $RB^{\bullet-}$ by molecular oxygen (air). Then, the addition of azido radical **6** to alkene **1** produced alkyl radical **7**. Next, the interaction of radical **7** with $O_2^{\bullet-}$ and H_2O afforded hydroperoxide intermediate **5**. The oxidation of $(PhSe)_2$ by hydroperoxide **5** yielded the corresponding reactive organoselenium species **8** and PhSeOH.[22] Finally, the interaction of PhSeOH with reactive intermediate **8** produced the desired product **3** and regenerated $(PhSe)_2$ along with the elimination of water.

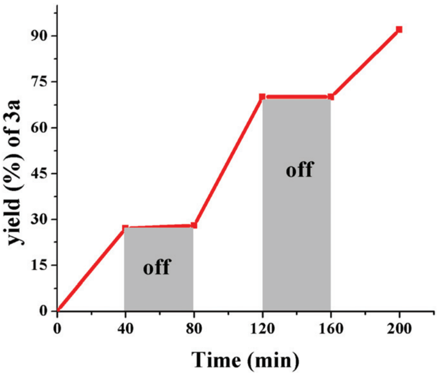


Fig. 2 On/off experiments.

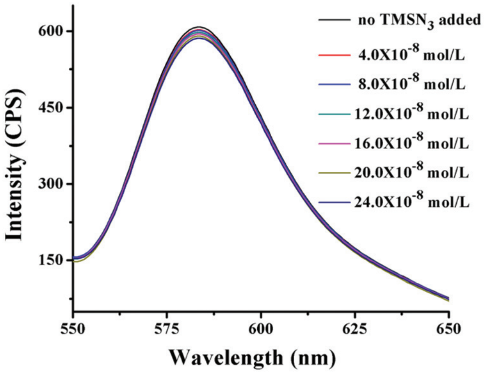


Fig. 3 Quenching of Rose Bengal fluorescence emission in the presence of $TMSN_3$.

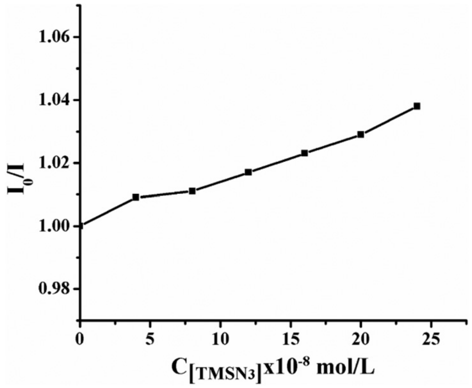
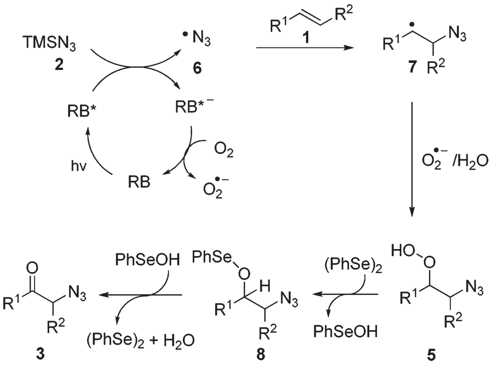


Fig. 4 Stern–Volmer plots.



Scheme 1 Possible reaction pathway.

In conclusion, we have presented a facile visible-light-enabled method for the construction of α-azidoketones *via* metal-free Rose Bengal and $(PhSe)_2$ co-catalyzed oxyazidation of alkenes. Considering the desirable features, such as the cheap and non-toxic catalyst, clean oxidant, eco-friendly energy source, mild reaction conditions and simplicity of operation, this reaction offers an efficient and green route to produce a series of α-azidoketones. Further studies on the detailed reaction mechanism and the synthetic application are currently ongoing in our lab.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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