



Communication

Organotellurium-catalyzed oxidative deoxygenation reactions using visible-light as the precise driving energy

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ABSTRACT

Irradiated by visible light, the recyclable (PhTe)₂-catalyzed oxidative deoxygenation reaction could occur under mild conditions. In comparison with the thermo reaction, the method employed reduced catalyst loading (1 mol% vs. 2.5 mol%), but afforded elevated product yields with expanded substrate scope. This work demonstrated that for the organotellurium-catalyzed reactions, visible light might be an even more precise driving energy than heating because it could break the Te—Te bond accurately to generate the active free radical catalytic intermediates without damaging the fragile substituents (e.g., heterocycles) of substrates. The use of O₂ instead of explosive H₂O₂ as oxidant affords safer reaction conditions from the large-scale application viewpoint.

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Visible light-driven reactions receive comprehensive attention in recent years not only for the mild reaction conditions, but also for the possibility of utilizing sustainable energy in chemical industry production instead of the traditional fossil energy to reduce the CO₂ emissions [1]. A plenty of protocols have been developed for the photocatalysis processes, but many of them are far from the practical applications for some technical defects. For example, the reactions require expensive metal or non-metal catalysts, some of which are high loading and not recyclable [2]. The use of stoichiometric/excess photo sensors or additives brings on the reaction waste generation [3]. In some reactions, environment-unfriendly solvents containing halogen, nitro, etc. are employed and unavoidable [4]. Developing new photocatalytic systems to avoid the above defects is the key for practical applications of related photocatalysis technology in the actual chemical production.

On the other hand, deoxygenation reaction is an important transformation with great industrial application potential [5]. Most oximes are stable crystals with constant melting points, making the oximation-deoxygenation processes able to be applied in the protection, purification and characterization of carbonyls. The related oximation-deoxygenation strategies have been widely applied in the total synthesis of natural products and medicines

(e.g., in the total synthesis of erythronolide A by Corey group) [6]. In fine chemical production, the deoxygenation reactions are used to synthesize ketones from non-carbonyl starting materials. For example, the industrial synthesis of high-value-added spice carvone from limonene involves a deoxygenation step [7]. However, the present deoxygenation techniques require explosive oxidants such as H₂O₂ [8], or use equivalent/excess additives leading to wastes [9], or use the environment-unfriendly solvents [10], or suffer the narrow substrate scope [11], or use the expensive noble metal catalysts [12], or employ the fragile enzyme catalysts that have to be used under dilute conditions restraining the production capacity [13]. Recently, people paid much attention to green deoxygenation technologies using novel catalytic materials [14]. In our cases, it was found that the organotellurium compounds are highly active [15] and could catalyze the thermal oxidative deoxygenation reactions via an unusual free radical mechanism [15a]. Herein, we wish to report an advanced low-loading (PhTe)₂-catalyzed deoxygenation reaction with O₂ using visible light as the precise driving energy.

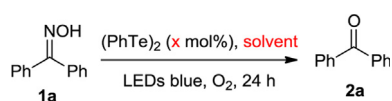
The benzophenone oxime (**1a**) substrate and 2.5 mol% of (PhTe)₂ catalyst were initially mixed together and the reaction was performed under solvent-free conditions. The mixture was irradiated by LEDs blue light and exposed in O₂ atmosphere. It was a gas-solid reaction and the reaction mixture gradually melted along with the process. The desired product benzophenone (**2a**) could be obtained in 91% yield after 24 h reaction (Table 1, entry 1). The catalyst loading could be further reduced and using 1 mol% of

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Table 1

Reaction condition optimization for the (PhTe)₂-catalyzed oxidative deoxygenation of benzophenone oxime (**1a**).^a



Entry	X (%) ^b	Solvent	2a yield (%) ^c
1	2.5	–	91
2	1.5	–	90
3	1.0	–	93
4	0.75	–	88
5	0.5	–	82
6	0.1	–	54
7	1.0	MeCN	95
8	1.0	EtOH	38
9	1.0	EtOAc	96
10	1.0	1,4-dioxane	97
11	1.0	Acetone	94

^a 0.5 mmol of **1a** and 1 ml of solvent (if used) were employed.

^b Molar ratio of (PhTe)₂ vs. **1a**.

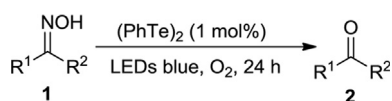
^c Isolated yields based on **1a**.

(PhTe)₂ was screened out to be the better conditions, affording **2a** in 93% yield (entries 3 vs. 1, 2, 4–6). The reactions with solvent were also tested and using MeCN, EtOAc, 1,4-dioxane, or acetone could lead to excellent product yields, while the protonic solvent EtOH was unfavorable (entries 8 vs. 7, 9–11).

A series of oximes were then employed as substrates to test the application scope of the reaction (Table 2). Different to the reaction of **1a**, the reaction of di-*p*-tolylmethanone oxime (**1b**) required EtOAc solvent, otherwise its speed was very slow and was not

Table 2

Photocatalytic oxidative deoxygenation reaction with (PhTe)₂ catalyst and without solvent.^a



Entry	1	R ¹	R ²	Yield of 2 (%) ^b
1	1a	Ph	Ph	2a : 93
2	1b	4-MeC ₆ H ₄	4-MeC ₆ H ₄	2b : 20(90), 96 ^c
3	1c	4-MeOC ₆ H ₄	4-MeOC ₆ H ₄	2c : 25(85), 95 ^c
4	1d	4-ClC ₆ H ₄	4-ClC ₆ H ₄	2d : NR, 96 ^c
5	1e	Ph	4-MeOC ₆ H ₄	2e : 18(87), 94 ^c
6	1f	4-FC ₆ H ₄	4-MeOC ₆ H ₄	2f : NR, 95 ^c
7	1g	Ph	Me	2g : NR, trace ^c , 82 ^d , 83 ^{d,e}
8	1h	4-MeC ₆ H ₄	Me	2h : 15(95), 28(75) ^c , 95 ^d
9	1i	3-MeC ₆ H ₄	Me	2i : trace, trace ^c , 95 ^d
10	1j	4-ClC ₆ H ₄	Me	2j : NR, trace ^c , 87 ^d
11	1k	3-ClC ₆ H ₄	Me	2k : NR, trace ^c , 83 ^d
12	1l	Ph	2-C ₁₀ H ₇	2l : trace, trace ^c , 93 ^d
13	1m	4-NO ₂ C ₆ H ₄	Me	2m : 75 ^d
14	1n	4-CNC ₆ H ₄	Me	2n : 81 ^d
15	1o	4-HOOC ₆ H ₄	Me	2o : trace ^d
16	1p	4-MeOOC ₆ H ₄	Me	2p : 86 ^d
17	1q	4-NH ₂ C ₆ H ₄	Me	2q : 0 ^d
18	1r	4-HSC ₆ H ₄	Me	2r : 0 ^d

NR = no reaction.

^a 0.5 mmol of **1** was employed.

^b Isolated yields based on **1** outside the parentheses; based on converted **1** inside the parentheses.

^c Reaction in 1 mL of EtOAc.

^d Reaction in 1 mL of MeCN.

^e With recycled catalyst in 100 mmol reaction.

completely converted within 24 h (entries 2 vs. 1). Similarly, the reactions of electron-enriched or deficient diaryl ketones **1c–f** occurred in EtOAc solvent, while the solvent-free reaction conditions were not preferable (entries 3–6). For (*E*)-1-phenylethan-1-one oxime substrate (**1g**), no reaction occurred without solvent, and only traces of the desired product **2g** was obtained in EtOAc solution. Fortunately, it could afford **2g** in 82% yield when using MeCN as the reaction solution (entry 7). The product and solvent could be separated *via* distillation in the 100 mmol reaction, while the residue could be used as the catalyst again and afforded the product without yield decreasing (entry 7). For methyl ketones **1h–k**, MeCN solvent was necessary to ensure the generation of related ketones in good yields (entries 8–11). Notably, the substrate **1l** bearing bulky substituent 2-C₁₀H₇ could be smoothly converted to give the desired ketone **2l** in 93% yield (entry 12). The reaction was tolerable for NO₂ and CN substituents in substrates **1m** and **1n**, affording the desired products **2m** and **2n** in 75% and 81% yields respectively (entries 13 and 14). Protogenic groups such as COOH disturbed the reaction, but the carboxylic COOMe was tolerable (entries 15 vs. 16). Since the reaction was performed under oxidative conditions, reductive groups in substrates, such as NH₂ and SH, were incompatible (entries 17 and 18). Deoxygenation of aldoximes suffered the poor reaction selectivity caused by the competitive side reactions such as the dehydration and deep oxidation of the products. For example, the reaction of benzaldoxime led to the mixtures of benzaldehyde, benzonitrile and benzoic acid in 16%, 23% and 46% yields respectively.

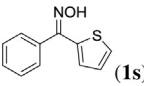
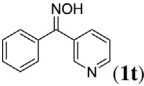
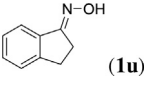
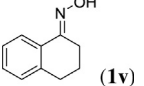
In comparison with the previously reported thermo reaction [15a], the photocatalytic reactions of heterocycle-containing oximes **1s** and **1t** afforded even higher product yields because the mild reaction conditions could significantly restrain the by-product generation, e.g., the break of the fragile heterocycles (Table 3, entries 1 and 2). For cyclic ketoximes **1u** and **1v**, the (PhTe)₂-catalyzed thermo reactions resulted in very poor product yields for the higher substrate steric hindrances of the carbocycles preventing the attack of the catalytic Te species from the back side of C=N [15a]. Interestingly, the same reactions could be significantly improved by using the photocatalytic protocol, affording the related cyclic ketones **2u** and **2v** in high yields over 80% (entries 3 and 4).

A series of control experiments were performed to disclose the possible reaction mechanism. They were all catalyzed by 1 mol% of (PhTe)₂ driven by the LEDs blue light. First, the reaction of **1a** under N₂ protection produced **2a** in only 8% yield, indicating that although deoxygenation process might occur *via* other methods (e.g., acid-promoted reaction), the oxidative deoxygenation reaction was the major process in the presence of (PhTe)₂ with visible light irradiation (Table 4, entry 1). The reaction, despite the solvent-free reaction or the reaction in EtOAc solvent, were both restrained by TEMPO (*i.e.*, 2,2,6,6-tetramethylpiperidine-1-oxyl), a common free radical scavenger (entries 2 and 3). Comparison of the results in Table 4, entries 4 vs. 5 showed that the free radical initiator AIBN (*i.e.*, azodiisobutyronitrile) could promote the reaction with 1 mol% of (PhTe)₂ under visible light irradiation under O₂. Therefore, it could be concluded that the visible light promoted oxidative deoxygenation reaction occurred *via* the free radical reaction mechanism. Moreover, without (PhTe)₂ or kept in dark, the deoxygenation could not occur, showing that both (PhTe)₂ and visible light irradiation were necessary for the transformation.

XPS (*i.e.*, X-ray photoelectron spectroscopy) analysis of the reaction mixture could provide additional information on the element valences. To prepare the test sample, silica was added into the reaction liquid as an adsorbent and the solvent was then removed by distillation with an evaporator. Spectrum of the residue indicated that Te was completely oxidized into Te⁴⁺ after

Table 3

Comparison of the photocatalytic reaction vs. thermo reaction of heterocyclic containing and cyclic ketoxime substrates.

1 $\xrightarrow[\text{thermo or photocatalytic reaction}]{(\text{PhTe})_2 \text{ (cat.)}}$ 2		2: Yield (%) ^a	
Entry	Structure (1)	Thermo ^b	Photo ^c
1	 (1s)	2s: 31 (100 °C) [15a]	2s: 78 ^d
2	 (1t)	2t: 40 (100 °C)	2t: 95
3	 (1u)	2u: trace (120 °C)	2u: 89
4	 (1v)	2v: NR (60 °C) [15a] 5 (100 °C) [15a] 26 (120 °C) [15a]	2v: 83

NR = no reaction.

^a Isolated yields based on 1.

^b Reaction performed under the thermo reaction conditions described in Ref. [15a]; Reaction temperature given in parentheses.

^c Reaction performed under the conditions described in Table 1, entry 9.

^d In MeCN solvent.

Table 4

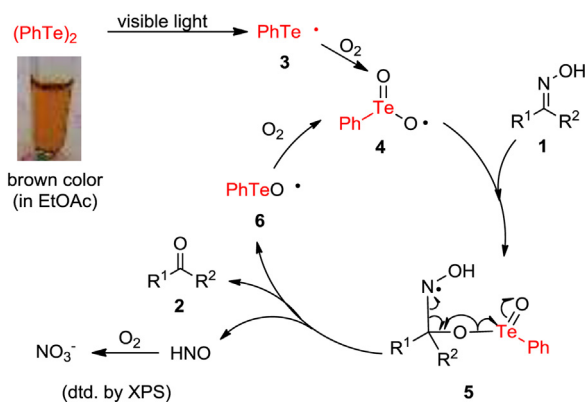
Control experiments.^a

1a $\xrightarrow[\text{conditions}]{(\text{PhTe})_2 \text{ (1 mol\%), LEDs blue}}$ 2a		2a yield (%) ^a
Entry	Conditions	2a yield (%) ^a
1	N ₂ , 24 h	8
2	TEMPO (100 mol%), O ₂ , 24 h	trace
3	TEMPO (100 mol%), EtOAc, O ₂ , 24 h	15
4	AIBN (100 mol%), EtOAc, O ₂ , 10 h	96
5	EtOAc, O ₂ , 10 h	37

^a Isolated yields based on 1a.

the reaction (Fig. S1a in Supporting information), while *ca.* 43% of nitrogen from the oxime group existed in the nitrate (NO₃⁻) form (Fig. S1b in Supporting information). Interestingly, the low-valent N–O species was also observed in the XPS spectrum, attesting the existences of the intermediate HNO species, which was difficult to capture for its high reducibility in the previous studies [16]. Owing to the mild oxidation condition of this reaction, partial of the active low-valent HNO species could be reserved. The mild reaction condition also led to the high product yields by restraining the by-product generation, especially for the substrates bearing the fragile heterocyclic substituents (Table 3, entries 1,2).

On the basis of the above experimental results as well as the literature reports [15a,17–19], a plausible mechanism of this



Scheme 1. Possible mechanism of the (PhTe)₂-catalyzed oxidative deoxygenation reaction driven by visible light.

photocatalytic oxidative deoxygenation reaction was supposed (Scheme 1). First, as a brown color chemical, (PhTe)₂ could well absorb the visible light to utilize its energy like (PhSe)₂ [17]. The process was even easier to occur than (PhSe)₂ for the weaker Te–Te bond [17c]. The visible light-driven homolytic cleavage of Te–Te bond in (PhTe)₂ produced the benzenetellururil radical 3 (Scheme 1), which was highly active and could be oxidized into the high valent benzenetellururil acid radical 4, as being reflected by the XPS analysis (Fig. S1a) [15a,18]. The addition of 4 to oxime 1 led to the intermediate 5 (Scheme 1). The process occurred via the free radical attack of 4 from the back side of C=N in oxime, which might be retarded when using cyclic oxime substrates bearing large steric hindrances such as 2o and 2p under thermo reaction conditions (Table 3, entries 3,4). The decomposition of 5 produced the product 2, the phenyltellururil radical 6 and the HNO species [19]. Oxidation of 6 led to the radical 4 and restarted the catalysis circle, while HNO might be oxidized into NO₃⁻ (Scheme 1).

In conclusion, we found that being irradiated by visible light, the (PhTe)₂-catalyzed oxidative deoxygenation reaction could occur under mild conditions. In comparison with the previously reported thermo reaction, this work not only provided a better method using reduced catalyst loading and affording elevated product yields with expanded substrate scope, but also demonstrated that for organotellurium-catalyzed reactions, visible light might be an even more precise driving energy than heating. Tellurium was the catalytic centre for the oxygen transfer reaction like selenium [20], but did not require metal additives to utilize molecular oxygen as oxidant [21], while the visible light irradiation could precisely break the Te–Te bond to generate the active free radical catalytic intermediates, and the fragile substituents, *e.g.*, heterocycles, in substrate could be well tolerated to reduce the side reactions. Further investigations on the applications of chalcogen-containing compounds/materials are ongoing in our laboratory [22].

Declaration of competing interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ccllet.2020.09.012>.

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