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Visible-Light-Induced Oxidative Formylation of N-Alkyl-N-(prop-2yn-1-yl)anilines with Molecular Oxygen in the Absence of an **External Photosensitizer**

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A visible-light-induced oxidative formylation of N-alkyl-N-(prop-2yn-1-yl)anilines with molecular oxygen in the absence of an external photosensitizer was developed and afforded the corresponding formamides in good yields under mild conditions. Mechanism investigation disclosed that both the starting material and product act as photosensitizers, and ${}^{1}O_{2}$ and $O_{2}^{\bullet-}$ are generated through energy transfer and single electron transfer pathway and play important role in the reaction.

The ubiquitous and diverse of C-H bonds in organic molecules makes their activation and functionalizations via new C-C and C-heteroatom bond formations, providing a novel synthetic strategy for the constructions of organic compounds.¹ However, owing to their relatively inert property, the selective activation and functionalization of C-H bonds is still a challenge in organic synthesis. Besides C(sp2)-H activation,¹ which is mainly conducted through the use of transition-metal assisted transformations in the presence of an appropriate directing group,¹ activation of C(sp3)–H bonds is more difficult. The general method of C(sp3)-H bonds activation is via a free radical pathway.² However, their high bond energy makes them hard to be broken, and activating groups are required, such as phenyl, nitrogen and oxygen. The generated radical can be stabilized by the adjacent phenyl group or heteroatoms through conjugated $\boldsymbol{\pi}$ system or the lone pair electrons, and a variety of C(sp3)-H organic functionalizations were developed on the basis of this strategy.³ Especially, the oxidation of benzylic C(sp3)-H to ketones by molecular oxygen and further reactions to give amide or ester derivatives in the presence of transition-metal,⁴ or under transition-metal-free conditions were established.⁵ On the other hand, there is the oxidation of methylene C(sp3)-H bonds, which are activated by an aromatic amino group and an electron-withdrawing group in the presence of molecular oxygen, generating the corresponding ketones (Scheme 1a-c).⁶ Recently, Lei described a visible-light-induced oxidation of benzylic C(sp3)–H to ketones using O_2 in the presence of acridinium

salt as an photosensitizer,⁷ and Rueping reported the visible-light photoredox (Ir-catalyst)-catalyzed a radical reaction of N,Nwith oxygen,⁸ leading dimethyl-anilines to N-alkyl-Nphenylformamides as organic intermediates and formylation reagents in Vilsmeier-Haak reactions.⁹

A variety of visible-light induced organic transformations via single electron transfer, energy transfer, or hydrogen atom transfer process have recently received considerable attention.¹⁰ Several C-C and C-heteroatom formations in the presence of a photosensitizer under visible-light irradiation were reported.¹¹ In order to avoid the use of external photocatalysts, photo-induced organic reactions by using substrate, or in-situ generated electron donor-acceptor complex and possibly the formed product as light-absorbing species were developed.¹²

On the basis of this understanding, herein, we report a visiblelight-induced oxidative formylation of N-alkyl-N-(prop-2-yn-1yl)anilines with molecular oxygen in the absence of an external photosensitizer, affording the corresponding formamides in good yields under ambient conditions. The protocol provides an efficient transformation of activated methylene (CH₂) into aldehyde via air oxidation and selective cleavage of a C-C bond (Scheme 1d).

Previous works:



Scheme 1. The oxidation of activated methylenes.

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For the optimization of the reaction conditions, a model reaction of N,N-di(prop-2-yn-1-yl)aniline (1a) was chosen in 0.20 mmol scale. When the model reaction was carried out in CHCl₃ at room temperature under blue LED (420-425 nm, 1.5 W) irradiation for 18 h, the desired product **2a** was isolated in 29% yield (Table 1, entry 1). No reaction occurred when the model reaction was performed in DME, dioxane, DMSO, NMP or DMC instead of CHCl₃, and the starting material 1a was recovered quantitatively (Table 1, entries 2-6). Less than 10% yield of 2a was obtained when the reaction was conducted in CH₃OH, or toluene (Table 1, entries 7 and 8). To our delight, product 2a was generated in 76% yield using acetone as solvent (Table 1, entry 9). The light source also plays an important role in the reaction, and blue LED (420-425 nm) was the best one for the reaction. However, LED (365-370 nm), LED (380-385 nm), LED (390-395 nm) and blue LED (410-415 nm) were inferior owing to the formation of side product in small amount under shorter emission wavelengths, and blue LED (450-455 nm) and green LED (530-535 nm) exhibited no efficiency for initiating the reaction (Table 1, entries 11-16). In the absence of visible light, no product was detected, indicating that visible light is essential in the reaction (Table 1, entry 17). Further investigation indicated that the reaction did not occur under nitrogen atmosphere, and the corresponding product 2a was isolated in 71% yield under oxygen atmosphere (Table 1, entries 18 and 19). Thus, the optimal reaction conditions were found to be consisted of 1a (0.20 mmol) in acetone (2.0 mL) and air atmosphere under 1.5 W blue LED (420-425 nm) irradiation at room temperature for 18 h.

With the optimized conditions in hand, the tolerance of the reaction towards structural modification of the starting material was explored. First, a variety of N,N-di(prop-2-yn-1-yl)anilines (1) were examined, as in Scheme 2. The results indicate a broad tolerance of the reaction towards substituents on the aromatic rings. When N,N-di(prop-2-yn-1-yl)anilines with an electrondonating group, such as Me, Et, 'Pr, ^tBu or MeO at the *para*-position of the benzene rings underwent the oxidative formylation with molecular oxygen to generate the corresponding products (2b-2f) in 63-76% yields. Substrates 1 bearing 3-Me or 3,5-(Me)₂ on the aromatic rings afforded the desired products 2g and 2h in 70% and 74% yields, respectively. Furthermore, N,N-di(prop-2-yn-1yl)anilines that possessed an electron-withdrawing group, including F, Cl, Br, I, COCF₃, CO₂Et, CN or C₆H₅ at the *para*-position of the phenyl rings reacted with oxygen to provide the anticipated products (2i-2p) in 74-83% yields. Moreover, the oxidative formylation of substrates 1 substituted by 3-F, 3-Cl, 3-Br, or 3-(C=CH) on the benzene rings with molecular oxygen gave the corresponding products (2q-2t) in 75-78% yields. Interestingly, the reactions of 1 with 3,4-(Cl)₂, or 3,5-(Cl)₂ on the anilines afforded the products 2u and 2v in 73% and 75% yields, respectively. The oxidative carbonylation of N,N-di(prop-2-yn-1-yl)naphthalen-2amine with oxygen proceeded well and generated the product 2w in 71% yield. Also, N-mono(prop-2-yn-1-yl) derivatives such as Nmethyl-N-(prop-2-yn-1-yl)aniline, N-ethyl-N-(prop-2-yn-1-yl)aniline, N-butyl-N-(prop-2-yn-1-yl)aniline, N-phenyl-N-(prop-2-yn-1yl)aniline underwent the reaction smoothly to afford the desired products 2x-2aa in 70-76% yields. N-Methyl-N-(prop-2-yn-1-yl)-(3chlorophenyl)amine, N-methyl-N-(prop-2-yn-1-yl)-(3Table 1. Optimization of the reaction conditions.^a

	O ₂ in air (1.0 a visible-light irrad solvent, r.t., 18	tm) iation 3 h	H 2a
Entry	Light source	Solvent	Yield (%) ^b
1	420-425 nm (1.5 W)	CHCl₃	29
2	420-425 nm (1.5 W)	DME	0
3	420-425 nm (1.5 W)	Dioxane	0
4	420-425 nm (1.5 W)	DMSO	0
5	420-425 nm (1.5 W)	NMP	0
6	420-425 nm (1.5 W)	DMC	0
7	420-425 nm (1.5 W)	CH₃OH	<10
8	420-425 nm (1.5 W)	Toluene	<10
9	420-425 nm (1.5 W)	Acetone	76
10	420-425 nm (1.5 W)	DCM	trace
11	365-370 nm (1.5 W)	Acetone	58
12	380-385 nm (1.5 W)	Acetone	63
13	390–395 nm (1.5 W)	Acetone	64
14	410-415 nm (1.5 W)	Acetone	70
15	450-455 nm (1.5 W)	Acetone	trace
16	530–535 nm (1.5 W)	Acetone	0
17	-	Acetone	0 ^c
18	420-425 nm (1.5 W)	Acetone	trace ^d
19	420–425 nm (1.5 W)	Acetone	71 ^e

^{*a}Reaction conditions: N,N-*di(prop-2-yn-1-yl)aniline (1a, 0.20 mmol), solvent (2.0 mL) at room temperature under light irradiation in air for 18 h. ^{*b*}Isolated yield. ^{*c*}In dark. ^{*d*}N₂ atmosphere. ^{*c*}O₂ atmosphere.</sup>

bromophenyl)amine, N-methyl-N-(prop-2-yn-1-yl)-(4and bromophenyl)amine were further examined to react with oxygen, providing the corresponding products 2ab-2ad in 75-81% yields. However, no desired product (2ae) was detected when N-(tertbutyl)-N-(prop-2-yn-1-yl)-(3-bromophenyl)amine was used owing to the effect of steric hindrance. When N-benzyl derivative was selected as substrate, no oxidative formylation product (2af) was isolated owing to an alkyl radical near to aromatic ring would be formed firstly, then a further oxidation would undergo in other way. 4-Nitro-N,N-di(prop-2-yn-1-yl)aniline, 1-(prop-2-yn-1-yl)-1H-indole, and N-(prop-2-yn-1-yl)-N-(p-toluenesulfonyl)aniline failed to give the anticipated products (2ag-2ai) and in all cases only of the starting material was recovered. It maybe resulted from their strong electron withdrawing effect.

To expand the substrate scope, N,N-disubstituted anilines (3), such as N,N-diallylaniline, N,N-di(but-2-yn-1-yl)aniline, N,N-di(3phenylprop-2-yn-1-yl)aniline, N,N-di(3-(p-bromophenyl)prop-2-yn-1-vl)aniline. and 4-bromo-N,N-di(but-3-yn-1-yl)aniline were examined as substrates for the photosensitized reaction with oxygen, and the results are shown in Scheme 3. When methylene groups of substrates are activated by a carbon-carbon double bond or a carbon-carbon triple bond, their oxidative formylations with molecular oxygen proceeded smoothly to generate the corresponding products (4a-4d) in 60-74% yields. Meanwhile, a lower yield of product 4e was obtained starting from N,N-di(but-3yn-1-yl)aniline, in the structure of which the activated methylene group is separated by an additional carbon atom from the carboncarbon triple bond.

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Scheme 2. The scope of *N*-alkyl-*N*-(prop-2-yn-1-yl)anilines (1).

To gain mechanistic insights into this reaction, a radical scavenger, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added into the reaction of N,N-di(prop-2-yn-1-yl)(4-cyanophenyl)amine (10) under air atmosphere, the oxidative formylation was completely inhibited, along with the formation of its adduct 5 with TEMPO (Scheme 4a), which was detected by HRMS (high resolution mass spectroscopy) (Figure S1, ESI), demonstrating the formation of an aminomethyl radical during the reaction although it may be in a small amount. In addition, ¹⁸O₂ labeling experiments were performed, also shown in Scheme 4. When the irradiation of substrate 10 was performed under ¹⁸O₂ atmosphere, **20**-¹⁸O was isolated in 74% yield and was confirmed by HRMS (Figure S7, ESI) with no formation of unlabeled 20 (Scheme 4b). Moreover, when 10 was irradiated in the presence of air $({}^{16}O_2)$ and $H_2{}^{18}O$ (10 equiv), **20** was obtained in 73% yield and no 2a-¹⁸O was detected (Scheme 4c, Figure S8 of ESI). These results indicated that oxygen element in the products comes from molecular oxygen in air.

To determine the active species of oxygen in the reaction, capturing agents, 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were used to trap $O_2^{\bullet-}$ and ${}^{1}O_2$, respectively, and the recorded electron-spin resonance (ESR) spectra were presented in Figure S9 (ESI). There was no signal when DMPO was added into a solution of 4-bromo-*N*,*N*-di(prop-2-yn-1-yl)aniline (**1k**) in air-saturated acetone in the absence of light (Figure S9a). However, a strong characteristic signal of $O_2^{\bullet-}$ adduct with DMPO was obtained when the above solution was irradiated with LED (420–425 nm) (Figure S9b). The same characteristic signals of $O_2^{\bullet-}$ were observed upon prolonged irradiation, however with

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much higher intensity (Figure S9c and S9d). On the other hand, these signals of ¹O₂ adduct with TEMP was also recorded when the above solution was irradiated with LED (420-425 nm), but no signal was found without light irradiation (Figure S10). These results indicated that there are active species $O_2^{\bullet-}$ and 1O_2 formed in the reaction system. In addition, ultraviolet-visible absorption spectra of substrates and their corresponding products demonstrated that they absorb the light (420-425 nm) and act as photosensitizers (Figure S11–17), avoiding the need for any external photocatalyst. The formed products formamides absorb longer-wavelength light to activate molecular oxygen more efficiently, and the reaction rate is accelerated so that the entire oxidative formylation is selfsustaining in an autocatalytic fashion (Figure S18). When 2 mol% of rose bengal or 1 mol% of Ir(ppy)₃ was used as the sensitizer, the reaction of 1a could underwent smoothly and afforded the desired product 2a in 73% and 76% isolated yield, respectively.



On the basis of the above investigation, a possible reaction mechanism is proposed in Scheme 5. First, substrate 1 is excited by LED (420-425 nm) irradiation to generate the excited species 1*, which acts as a photosensitizer. The formed 1* then undergoes an energy transfer process with triplet oxygen $({}^{3}O_{2})$ in ground-state to generate highly reactive excited-state singlet oxygen $(^{1}O_{2})$ along with the regeneration of 1 in the ground state. The obtained singlet ${}^{1}O_{2}$ reacts with substrate **1** via a single electron transfer (SET) pathway to afford a free radical cation A and O2, , which further reacts with 1 to give A and O_2^{2-} . The formed A loses a proton to afford an aminomethyl radical B, which reacts with triplet oxygen ${}^{3}O_{2}$ to give a peroxide radical **C**. The **C** undergoes an intramolecular radical addition to form a four-membered peroxide D, which was trapped by TEMPO (Figure S2, ESI). The formed D further reacts with ${}^{3}O_{2}$ to give **E** via Path a, followed by an abstraction of HO[•] to intermediate F, which was detected by HRMS (Figure S3). Finally,

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two reverse [2+2] cycloadditions of **F** afford the desired product **2** along with the generation of CO_2 gas, which was determined by FT-IR (Figure S5), and 4-bromobenzonic acid in 20 % isolated yield. On the other hand, the obtained **D** reacts with HO[•] to afford **G** (it was confirmed by HRMS, as in Figure S4) through Path b, which further undergoes a reverse [2+2] cycloaddition to generate product **2**, and CO gas (detected by FT-IR, Figure S5), and 4-bromobenaldehyde, which was confirmed by GC-MS (Figure S6). Obviously, product **2** also acts as photosensitizer, thereby completing the catalytic cycle.

In summary, we have developed a visible-light-induced oxidative formylation of *N*,*N*-di(prop-2-yn-1-yl)anilines with molecular oxygen in the absence of any additional photosensitizer. Investigations support a mechanism whereby that both the starting material and product act as photosensitizers upon excitation using blue LED to photochemically promote ground-state oxygen ${}^{3}O_{2}$ to excited-state oxygen ${}^{1}O_{2}$ via an energy transfer process. EPR results demonstrated the formation of ${}^{1}O_{2}$ and $O_{2}^{\bullet-}$ via a single electron transfer (SET) process, which plays important role in the reaction. This protocol provides a simple and mild transformation of activated methylenes (C_{sp3} -H bonds) into aldehydes via air oxidation and the selective cleavage of carbon-carbon bonds. We tried to isolate intermediates **E** and **F**, but failed. A detailed investigation on the mechanism is underway in our laboratory.



Scheme 5. The possible reaction mechanism.

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