Organic Letters
Letter
pubs.acs.org/OrgLett

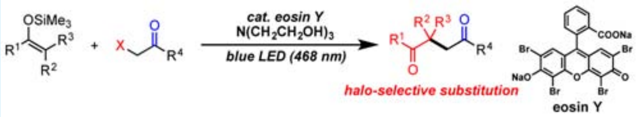
Synthesis of 1,4-Dicarbonyl Compounds from Silyl Enol Ethers and Bromocarbonyls, Catalyzed by an Organic Dye under Visible-Light Irradiation with Perfect Selectivity for the Halide Moiety over the Carbonyl Group

Naoto Esumi,[†] Kensuke Suzuki,[†] Yoshihiro Nishimoto,*[,‡] and Makoto Yasuda*[,†]

[†]Department of Applied Chemistry and [‡]Frontier Research Base for Global Young Researchers Center for Open Innovation Research and Education (COiRE), Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

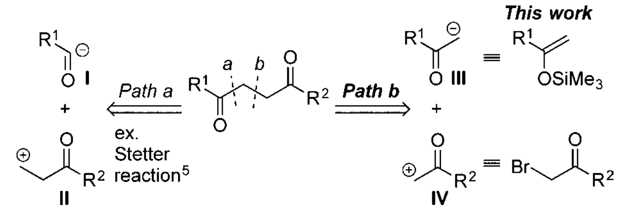
Supporting Information

ABSTRACT: We report the visible-light-induced radical coupling reaction of silyl enol ethers with α-bromocarbonyl compounds to give 1,4-dicarbonyls. The reaction was effectively accelerated using an inexpensive organic dye (eosin Y) as a photoredox catalyst. 1,4-Dicarbonyl compounds alone were afforded, without the generation of carbonyl adducts of the α-halocarbonyls, which are usually generated in the presence of fluoride anions or Lewis acids. A variety of silyl enol ethers, α-bromoketones, α-bromoesters, and α-bromoamides were applied to this system to produce the coupling compounds.



1,4-Dicarbonyl compounds are an important class of compounds as building blocks for biological molecules[1] and precursors for the Paal−Knorr synthesis, which gives five-membered heteroarenes.[2] Several synthetic methods have been developed to afford the broadly useful 1,4-dicarbonyl compounds.[3] For a retrosynthesis of the 1,4-dicarbonyl compounds, two strategies were designed, as illustrated in Scheme 1: the reaction of an acyl anion equivalent **I** with a carbonylethyl cation **II** (path a) or the reaction of a carbonylmethyl anion **III** with a cation **IV** (path b). Path a indicates that the generation of the acyl anion **I** was limited due to difficulties associated with controlling its reactivity.[4] Consequently, a reaction involving the Breslow intermediates as acyl anion equivalents, which are generated by an in situ reaction between the aldehydes and carbenes, and unsaturated carbonyl compounds was developed (Stetter reaction).[5] Path b corresponds to the reaction of enolates with α-halocarbonyls.[6] This reaction system intrinsically suffers from chemoselectivity problems because the α-halocarbonyls include two electrophilic moieties: carbonyl and halide groups. Previously, our group reported the synthesis of 1,4-dicarbonyls using highly coordinated tin enolates and α-halocarbonyls via a halo-substitution reaction.[6a] The carbonyl addition reaction of the tin enolates, which possess high nucleophilicity, was avoided by controlling the reactivity of the tin enolates using ligands that formed higher-order tin enolates with a low reactivity toward carbonyl groups.[7] The selectivity was not perfect, however, and some amount of carbonyl adducts accompanied the 1,4-dicarbonyls.[6a]

Scheme 1. Retrosynthesis of 1,4-Dicarbonyls

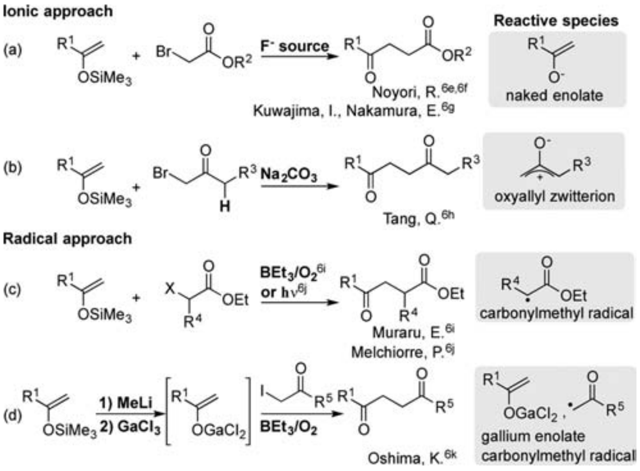


The use of moderately nucleophilic silyl enol ethers shows promise for providing a high chemoselectivity; however, these compounds are inert to halocarbonyls under thermal conditions in the absence of additives.[8] To the best of our knowledge, only four processes using silyl enol ethers and halocarbonyls have been identified for the synthesis of 1,4-dicarbonyls.[6e−k] Fluoride-anion-activated silyl enol ethers may be applied to the reaction with haloesters in ionic approaches (Scheme 2a).[6e−g] The naked enolate species generated by fluoride anions in situ has a high nucleophilicity; therefore, the reaction of the haloester, with a carbonyl group that is less electrophilic than that of the haloketones, was established. Recently, Tang's group reported the reaction of silyl enol ethers with haloketones in the presence of weak bases to give 1,4-dicarbonyls (Scheme 2b).[6h] Although haloketones were applied to this system, the substrate scope was intrinsically limited to aliphatic substrates bearing an α'-hydrogen due to the generation of a key oxyallyl zwitterion intermediate. In radical approaches, a radical initiator or photosensitizer promotes the coupling reaction to generate the reactive carbonylmethyl radical; however, only haloesters were used (Scheme 2c).[6i,j] A alternative approach involves a reaction using gallium enolate generated by the treatment of silyl enol ethers and gallium chloride under basic conditions (Scheme 2d).[6k] This reaction was applied to the haloketone, although the yield was low. As described above, the generality of the halocarbonyls has been quite limited.

Received: September 29, 2016
Published: October 25, 2016

DOI: 10.1021/acs.orglett.6b02869
Org. Lett. 2016, 18, 5704−5707

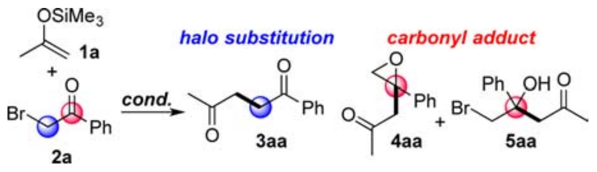
Scheme 2. Reported Syntheses of 1,4-Dicarbonyls by Reactions of Silyl Enol Ethers with Halocarbonyls



Recently, photoredox processes were developed using ruthenium or iridium complexes or organic dyes as photocatalysts.[9] Our group reported α-allylation of halocarbonyls using allyltrifluoroborate salts promoted by fluoride salts and organic dye eosin Y as a photoredox catalyst.[10] On the basis of our previous work, we started the investigation of the reaction of halocarbonyls with silyl enol ethers. Herein, a new strategy for synthesizing 1,4-dicarbonyl compounds from silyl enol ethers and halocarbonyls by triethanolamine and eosin Y catalysis is reported.[11]

First, we explored reported reaction systems for reactions of silyl enol ether **1a** with α-bromoketone **2a** (Table 1). In F⁻-accelerated reactions, the epoxide **4aa** was mainly produced via carbonyl addition of **1a** to **2a**, although the targeted 1,4-dicarbonyl compound **3aa** was obtained (Table 1, entry 1).[6g] In entry 2 involving Na_2CO_3,[6h] the reaction did not occur at all. Under radical conditions using Et_3B (Table 1, entry 3),[6i] the selective formation of **3aa** was confirmed, but the yield was low. The photochemical reaction catalyzed by *p*-anisaldehyde gave no coupling products (Table 1, entry 4).[6j] A Mukaiyama-type reaction system catalyzed by $TiCl_4$[12] provided the halohydrin **5aa** via the addition of a carbonyl group (Table 1, entry 5). In contrast with these reactions, our developed photoredox reaction system produced **3aa** in a high yield and with perfect chemoselectivity (Table 1, entry 6).

Table 1. Selectivity in the Reactions of Silyl Enol Ether 1a with Bromoketone 2a[a]

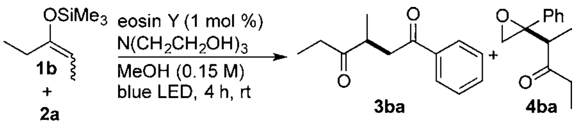


entry	conditions	yield (%) 3aa	4aa	5aa
1	Bu_4NF, -78 °C to rt	6	32	0
2	Na_2CO_3, rt	0	0	0
3	Et_3B/O_2, rt	16	0	0
4	*p*-$MeOC_6H_4CHO$, CFL	0	0	0
5	$TiCl_4$, -78 °C to rt	0	0	30
6	**eosinY, $N(CH_2CH_2OH)_3$ blue LED (468 nm)**	**80**	**0**	**0**

[a] A detailed list of the reaction conditions is provided in the Supporting Information.

Investigations of the reaction conditions involving silyl enol ether **1b** and bromoketone **2a** are summarized in Table 2.

Table 2. Optimization of the Reaction Conditions[a]



entry	modification of conditions	yield (%)[b] 3ba	4ba
1	none	76(70)[c]	0
2[d]	CsF instead of $N(CH_2CH_2OH)_3$	27	18
3	without $N(CH_2CH_2OH)_3$	3	0
4	$N(CH_2CH_2OH)_3$ (0.5 equiv)	54	0
5	NEt_3 instead of $N(CH_2CH_2OH)_3$	45	0
6	$Ru(bpy)_3Cl_2$ instead of eosin Y	41	0
7	$Ir(ppy)_3$ instead of eosin Y	76	0
8	erythrosine B instead of eosin Y	75	0
9	without eosin Y or in the dark	0	0

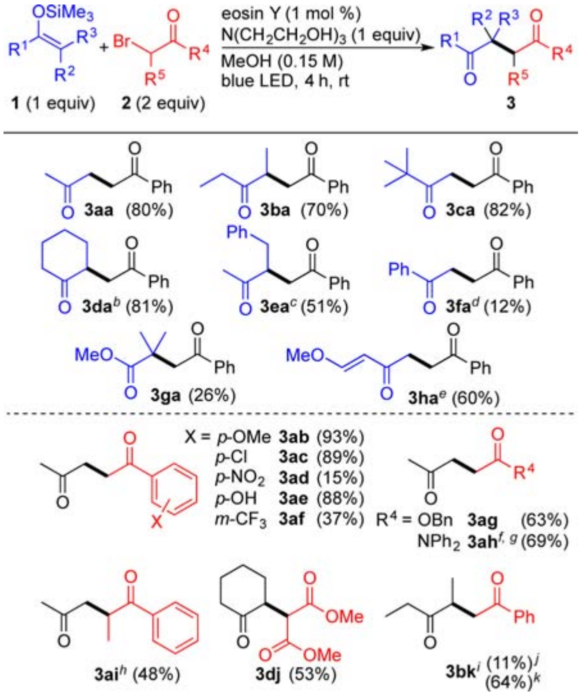
[a] Conditions: **1b** (0.3 mmol), **2a** (0.6 mmol), eosin Y (0.003 mmol), $N(CH_2CH_2OH)_3$ (0.3 mmol), MeOH (2 mL), room temperature, and 3 W blue LED (468 nm). [b] ^1H NMR yield with 1,1,1,2-tetrachloroethane as an internal standard. [c] Isolated yield. [d] DMF was used instead of MeOH as a solvent.

Effective reaction conditions were identified employing 1 mol % of eosin Y as a photocatalyst and 1 equiv of triethanolamine as a reductive quencher under blue LED (468 nm) irradiation (Table 2, entry 1). Although **3ba** was obtained using our reported allylation conditions,[10] carbonyl adduct **4ba** was also obtained because the reactivity of the silyl enol ether activated by the fluoride anion was too high (Table 2, entry 2). A low yield of **3ba** was observed in the presence of smaller amounts of triethanolamine (Table 2, entries 3 and 4). Triethylamine was less effective as a reductive quencher than triethanolamine ($E_{ox}(TEOA^{\bullet+}/TEOA) = +0.82$ V; $E_{ox}(NEt_3^{\bullet+}/NEt_3) = +0.99$ V vs SCE)[13a,b] (Table 2, entry 5). The transition metal photoredox catalyst $Ru(bpy)_3Cl_2$ gave **3ba** in a moderate yield (Table 2, entry 6). In the case of $Ir(ppy)_3$, the coupling product **3ba** was obtained in a high yield comparable to that obtained using the eosin Y catalyst (Table 2, entry 7). Erythrosine B also provided a catalytic activity comparable to that of eosin Y (Table 2, entry 8). Control experiments revealed that both the organic dye and visible-light irradiation were essential for the formation of **3ba** (Table 2, entry 9).

We explored the reaction of the silyl enol ethers **1** with bromocarbonyls **2**, which is summarized in Scheme 3. First, we investigated the scope of the silyl enol ethers **1**. The 1,4-diketones were given by using the silyl enol ethers derived from dialkyl ketones, without producing carbonyl adducts **3aa**, **3ba**, **3ca**, **3da**, and **3ea**. Although the yield of **3fa** was low, the reaction of a silyl enol ether derived from aromatic ketones proceeded. The reaction tolerates silyl ketene acetal **1g** and Danishefsky diene **1h** to yield the coupling product **3ga** and **3ha**, respectively. Next, the scope of bromocarbonyls was investigated. In addition to various types of bromoketones **3ab**, **3ac**, **3ad**, **3ae**, and **3af**, bromoester **2g** and bromoamide **2h** were also used in this reaction to yield the coupling products **3ag** and **3ah**. Secondary bromoketone **2i** afforded the desired product **3ai** in a moderate

DOI: 10.1021/acs.orglett.6b02869
Org. Lett. 2016, 18, 5704–5707

Scheme 3. Substrate Scope of the Reaction of Silyl Enol Ether 1 with α-Bromocarbonyl 2[a]

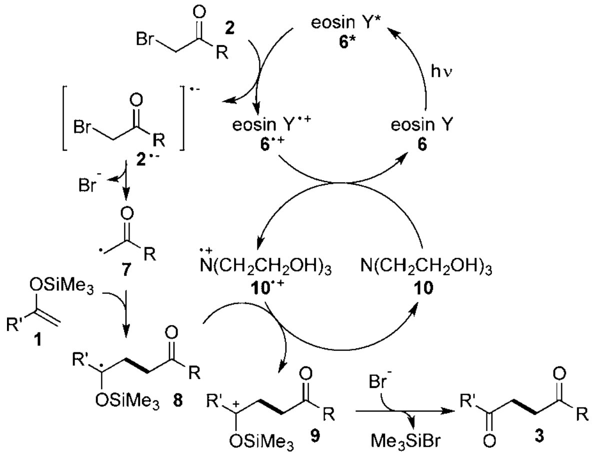


[a] Conditions: silyl enol ether **1** (0.3 mmol), bromocarbonyl **2** (0.6 mmol), eosin Y (0.003 mmol), $N(CH_2CH_2OH)_3$ (0.3 mmol), MeOH (2 mL), room temperature, and 3 W blue LED (468 nm). Yield of isolated product. [b] **1d** (2 equiv), **2a** (1 equiv). [c] **1e** (1 equiv), **2a** (3 equiv). [d] **1f** (1 equiv), **2a** (2 equiv). [e] **1h** (3 equiv), **2a** (1 equiv). [f] Solvent (MeOH/MeCN = 1:1). [g] **2h** (3 equiv). [h] **2i** (3 equiv). [i] 2-Chloroacetophenone was used. [j] ^{1}H NMR yield with 1,1,1,2-tetrachloroethane as an internal standard. [k] NaI (2 equiv) was added as an additive.

yield due to steric hindrance. Bromomalonate **2j** gave tricarbonyl compound **3dj** in moderate yield. The addition of NaI accelerated the coupling reaction between **1b** and chloroketone **2k** via in situ halogen exchange to produce product **3bk**.

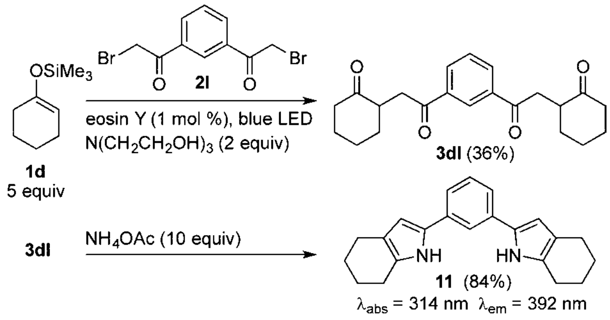
A plausible reaction mechanism is shown in Scheme 4. Blue LED irradiation generates the photoexcited eosin Y (**6***). Then, it reduces the bromocarbonyl **2** via single-electron transfer to give the eosin Y radical cation ($\mathbf{6}^{\bullet+}$) and the bromocarbonyl radical anion $\mathbf{2}^{\bullet-}$. The first process is supported by the luminescence quenching studies (see Supporting Information). The reduction of the eosin Y radical cation ($\mathbf{6}^{\bullet+}$) by triethanolamine (**10**) regenerates eosin Y (**6**) and produces a triethanolamine radical cation ($\mathbf{10}^{\bullet+}$). The photocatalyst is effectively quenched using excess amounts of triethanolamine.[14] Elimination of Br^- from bromocarbonyl radical anion $\mathbf{2}^{\bullet-}$ affords carbonylmethyl radical **7**. Radical **7** adds to silyl enol ether **1** to give siloxy-substituted carbon radical **8**. Radical **8** is oxidized by a triethanolamine radical cation ($\mathbf{10}^{\bullet+}$) to afford cation **9** and triethanolamine **10**.[15] Finally, elimination of the trimethylsilyl group from carbocation **9** produces 1,4-dicarbonyl **3**.

Scheme 4. Plausible Reaction Mechanism for the Eosin Y Catalyzed Radical Coupling of Silyl Enol Ether 1 and α-Bromocarbonyl 2



The utility of this protocol was demonstrated by synthesizing bis(pyrrolyl)arene, a useful fluorescent compound,[16a] through a combination of the present reaction system and the Paal–Knorr method (Scheme 5). The tetracarbonyl compound **3dl** was successfully synthesized by the reaction of **2l**, possessing two bromocarbonyl moieties, with silyl enol ether **1d**. Treatment of **3dl** by the Paal–Knorr method afforded bis(pyrrolyl)arene **11**. Generally, the synthesis of these types of 1,3-bis(pyrrolyl)arenes requires a multistep process involving expensive transition metal catalysts[16] or the use of highly toxic phosgene;[17] however, the sequential process developed here is safer and less expensive. UV–vis absorption and emission spectra of bispyrrole **11** (λ_{abs} and λ_{em} = 314 and 392 nm in CH_2Cl_2) are provided in the Supporting Information.

Scheme 5. Synthesis of Bis(pyrrol-2-yl)benzene Derivatives



In conclusion, we developed a practical synthetic method for preparing 1,4-dicarbonyl compounds via a reaction between α-halocarbonyls and silyl enol ethers, accelerated by the inexpensive eosin Y as a photoredox catalyst under visible-light irradiation. The halo-substitution reaction proceeded with perfect chemoselectivity. Triethanolamine was found to function as an appropriate reductant to regenerate eosin Y. Various types of silyl enol ethers and α-bromocarbonyl compounds were applicable to this reaction. Finally, we demonstrated the utility of the present synthetic method for the preparation of dipyrrolarenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02869.

Experimental details and characterization data (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: nishimoto@chem.eng.osaka-u.ac.jp.
*E-mail: yasuda@chem.eng.osaka-u.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the JSPS KAKENHI Grant Nos. JP15H05848 (in Middle Molecular Strategy) and JP16K05719. Y.N. thanks the Frontier Research Base for Global Young Researchers at Osaka University, a program of MEXT.

REFERENCES

(1) (a) Li, S.-H.; Wang, J.; Niu, X.-M.; Shen, Y.-H.; Zhang, H.-J.; Sun, H.- D.; Li, M.-L.; Tian, Q.-E.; Lu, Y.; Cao, P.; Zheng, Q.-T. *Org. Lett.* **2004**, *6*, 4327–4330. (b) Lu, P.; Mailyan, A.; Gu, Z.; Guptill, D. M.; Wang, H.; Davies, H. M. L.; Zakarian, A. *J. Am. Chem. Soc.* **2014**, *136*, 17738–17749. (c) Zheng, C.; Dubovyk, I.; Lazarski, K. E.; Thomson, R. J. *J. Am. Chem. Soc.* **2014**, *136*, 17750–17756. (d) Lu, P.; Gu, Z.; Zakarian, A. *J. Am. Chem. Soc.* **2013**, *135*, 14552–14555. (e) Peng, F.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2012**, *134*, 18860–18867. (f) Furusaki, A.; Matsumoto, T.; Ogura, H.; Takayanagi, H.; Hirano, A.; Omura, S. *J. Chem. Soc., Chem. Commun.* **1980**, 698. (g) Enomoto, Y.; Shiomi, K.; Hayashi, M.; Masuma, R.; Kawakubo, T.; Tomosawa, K.; Iwai, Y.; Omura, S. *J. Antibiot.* **1996**, *49*, 50–53. (h) Kosuge, T.; Tsuji, K.; Hirai, K.; Yamaguchi, K.; Okamoto, T.; Iitaka, Y. *Tetrahedron Lett.* **1981**, *22*, 3417–3420.

(2) (a) Paal, C. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 2756–2767. (b) Knorr, L. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 2863–2870. (c) Trost, B. M.; Doherty, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 3801–3810. (d) Amarnath, V.; Anthony, D. C.; Amarnath, K.; Valentine, W. M.; Wetterau, L. A.; Graham, D. G. *J. Org. Chem.* **1991**, *56*, 6924–6931. (e) Amarnath, V.; Amarnath, K. *J. Org. Chem.* **1995**, *60*, 301–307. (f) Kaleta, Z.; Makowski, B. T.; Soos, T.; Dembinski, R. *Org. Lett.* **2006**, *8*, 1625–1628.

(3) See refs 5 and 6.

(4) (a) Obora, Y.; Ogawa, Y.; Imai, Y.; Kawamura, T.; Tsuji, Y. *J. Am. Chem. Soc.* **2001**, *123*, 10489–10493. (b) Obora, Y.; Nakanishi, M.; Tokunaga, M.; Tsuji, J. *J. Org. Chem.* **2002**, *67*, 5835–5837. (c) Hanzawa, Y.; Tabuchi, N.; Taguchi, T. *Tetrahedron Lett.* **1998**, *39*, 6249–6252. (d) Sakurai, H.; Tanabe, K.; Narasaka, K. *Chem. Lett.* **1999**, *28*, 309. (e) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77–84. (f) Lever, O. W., Jr. *Tetrahedron* **1976**, *32*, 1943–1971. (g) Seyferth, D.; Hui, R. C.; Wang, W.-L. *J. Org. Chem.* **1993**, *58*, 5843–5845. (h) Hiiro, T.; Morita, Y.; Inoue, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 455–457. (i) Seyferth, D.; Weinstein, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 5534–5535.

(5) (a) Stetter, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 639–712. (b) Yetra, S. R.; Patra, A.; Biju, A. T. *Synthesis* **2015**, *47*, 1357–1378. (c) Bugaut, X.; Glorius, F. *Chem. Soc. Rev.* **2012**, *41*, 3511–3522. (d) Biju, A. T.; Kuhl, N.; Glorius, F. *Acc. Chem. Res.* **2011**, *44*, 1182–1195. (e) Esposti, S.; Dondi, D.; Fagnoni, M.; Albini, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 2531–2534.

(6) (a) Yasuda, M.; Oh-hata, T.; Shibata, I.; Baba, A.; Matsuda, H. *J. Chem. Soc., Perkin Trans. 1* **1993**, 859–865. (b) Yasuda, M.; Katoh, Y.; Shibata, I.; Baba, A.; Matsuda, H.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 4386–4392. (c) Yasuda, M.; Tsuji, S.; Shigeyoshi, Y.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 7440–7447. (d) Liu, C.; Deng, Y.; Wang, J.; Yang, Y.; Tang, S.; Lei, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 7337–7341. (e) Noyori, R.; Nishida, I.; Sakata, J. *Tetrahedron Lett.* **1980**, *21*, 2085–2088. (f) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598–1608. (g) Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1982**, *104*, 1025–1030. (h) Luo, J.; Jiang, Q.; Chen, H.; Tang, Q. *RSC Adv.* **2015**, *5*, 67901. (i) Baciocchi, E.; Muraglia, E. *Tetrahedron Lett.* **1994**, *35*, 2763–2766. (j) Arceo, E.; Montroni, E.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2014**, *53*, 12064–12068. (k) Usugi, S.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2049–2052.

(7) Yasuda, M.; Chiba, K.; Baba, A. *J. Am. Chem. Soc.* **2000**, *122*, 7549–7555.

(8) The reaction of silyl enol ether **1b** with bromoketone **2a** in MeOH or MeCN solutions did not proceed at all under reflux conditions, although the reaction of tin enolate with bromoketone gave the carbonyl adduct. See ref 6a.

(9) For recent reviews of photoredox catalysts, see: (a) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322–5363. (b) Reckenthäler, M.; Griesbeck, A. G. *Adv. Synth. Catal.* **2013**, *355*, 2727–2744. (c) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102–113. (d) Teplý, M. *Collect. Czech. Chem. Commun.* **2011**, *76*, 859–917. (e) Hopkinson, M. N.; Sahoo, B.; Li, J.-L.; Glorius, F. *Chem. - Eur. J.* **2014**, *20*, 3874–3886. (f) Koike, T.; Akita, M. *Inorg. Chem. Front.* **2014**, *1*, 562–576. (g) Hari, D. P.; König, B. *Chem. Commun.* **2014**, *50*, 6688–6699. (h) Ravelli, D.; Protti, S.; Fagnoni, M. *Chem. Rev.* **2016**, *116*, 9850–9913. (i) Skubi, K. L.; Blum, T. R.; Yoon, T. P. *Chem. Rev.* **2016**, *116*, 10035–10074. (j) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075–10166.

(10) Suzuki, I.; Esumi, N.; Yasuda, M. *Asian J. Org. Chem.* **2016**, *5*, 179–182.

(11) For important work of the synthesis of 1,4-dicarbonyls from enamines or silyl enol ethers, including the single-electron transfer mechanism, see: (a) Jang, H.-Y.; Hong, J. B.; MacMillan, D. W. C *J. Am. Chem. Soc.* **2007**, *129*, 7004–7005. (b) Nicewicz, D. A.; MacMillan, D. W. C *Science* **2008**, *322*, 77–80. (c) Yasu, Y.; Koike, T.; Akita, M. *Chem. Commun.* **2012**, *48*, 5355–5357. (d) Zhu, Y.; Zhang, L.; Luo, S. *J. Am. Chem. Soc.* **2014**, *136*, 14642–14645.

(12) (a) Mukaiyama, T.; Narasaka, K.; Banno, K. *Chem. Lett.* **1973**, *2*, 1011–1014. (b) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503–7509.

(13) (a) Zhang, J.; Wang, L.; Liu, Q.; Yang, Z.; Huang, Y. *Chem. Commun.* **2013**, *49*, 11662–11664. (b) Hari, D. P.; König, B. *Org. Lett.* **2011**, *13*, 3852–3855.

(14) Excess amounts of a tertiary amine were used to effectively quench the photocatalyst. (a) Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 5426–5434. (b) Amador, A. G.; Sherbrook, E. M.; Yoon, T. P. *J. Am. Chem. Soc.* **2016**, *138*, 4722–4725.

(15) A mechanism was proposed in which the tertiary amine radical cation works as a reductant of the alkyl radical species. See ref 14.

(16) (a) Saroukou, M. S. M.; Skalski, T.; Skene, W. G.; Lubell, W. D. *Tetrahedron* **2014**, *70*, 450–458. (b) Setsune, J.-I.; Toda, M.; Watanabe, K.; Panda, P. K.; Yoshida, T. *Tetrahedron Lett.* **2006**, *47*, 7541–7544. (c) Eerdun, C.; Hisanaga, S.; Setsune, J.-I. *Chem. - Eur. J.* **2015**, *21*, 239–246.

(17) (a) Sessler, J. L.; An, D.; Cho, W.-S.; Lynch, V.; Marquez, M. *Chem. - Eur. J.* **2005**, *11*, 2001–2011. (b) Turac, E.; Ak, M.; Sahmetlioglu, E.; Sener, M. K.; Kaya, M. A. *Russ. J. Gen. Chem.* **2011**, *81*, 2510–2516.

DOI: 10.1021/acs.orglett.6b02869