



Cite this: *Chem. Commun.*, 2019, 55, 2214

Received 15th January 2019,  
Accepted 25th January 2019

DOI: 10.1039/c9cc00347a

rsc.li/chemcomm

# Photoredox-catalyzed sulfonylation of alkyl iodides, sulfur dioxide, and electron-deficient alkenes†

Shengqing Ye,<sup>‡a</sup> Danqing Zheng,<sup>‡b</sup> Jie Wu<sup>‡\*ab</sup> and Guanyinsheng Qiu<sup>\*bc</sup>

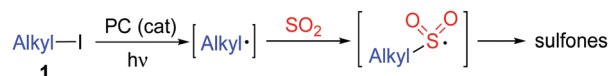
**A photoredox-catalyzed sulfonylation of alkyl iodides, sulfur dioxide, and electron-deficient alkenes under mild conditions is achieved. This reaction proceeds through alkyl radicals formed *in situ* from alkyl iodides under visible light irradiation in the presence of a photoredox catalyst. The alkyl radical intermediates would react with sulfur dioxide leading to alkylsulfonyl radicals, which would be trapped by electron-deficient alkenes giving rise to alkyl sulfones. Various functional groups including nitro, halo, acetyl, sulfonyl, and pyridinyl are all tolerated under the photoredox conditions.**

Transition metal-catalyzed coupling reactions of aryl/alkyl halides have been utilized broadly, due to aryl/alkyl halides being easily available and cheap.<sup>1</sup> Recently, reactions of aryl/alkyl halides under photoredox catalysis have attracted much attention. It is well recognized that the photoinduced C–X bond dissociation of aryl/alkyl halides would produce the corresponding carbon radicals *via* electron transfer.<sup>2</sup> Therefore, the possibility of the β-H elimination of alkyl halides under transition metal catalysis may be avoided under photoinduced conditions. So far, progress of photoinduced C–X bond dissociation has been witnessed. For example, Peters and Fu reported photoinduced Ullmann C–N coupling by using a stoichiometric or catalytic amount of copper salt under visible light irradiation at room temperature.<sup>2a</sup>

In the past decade, synthesis of sulfonyl compounds through the insertion of sulfur dioxide has developed rapidly,<sup>3</sup> which avoids the utilization of pre-installed sulfonyl precursors.<sup>4</sup> Currently, the sulfur dioxide surrogates including

DABCO·(SO<sub>2</sub>)<sub>2</sub> (1,4-diazabicyclo[2.2.2]octane-sulfur dioxide)<sup>5–7</sup> and inorganic sulfites<sup>8</sup> have been used broadly in the sulfonylation process. As part of a program for the generation of sulfonyl compounds, we are interested in the radical process with the insertion of sulfur dioxide.<sup>7</sup> So far, various radical precursors have been employed in the sulfonylation reaction including aryldiazonium tetrafluoroborates,<sup>7</sup> aryl/alkyl halides,<sup>9</sup> diaryliodonium salts,<sup>10</sup> and potassium alkyltrifluoroborates.<sup>11</sup> Among these precursors, aryl/alkyl halides are especially attractive, as they are easily available and cheap. For instance, aryl/alkyl halides could react with sulfur dioxide and hydrazines under ultraviolet irradiation.<sup>8a</sup> Although this transformation was efficient, the reaction could not be extended to other partners due to the ultraviolet irradiation. Thus, method development for the sulfonylation of aryl/alkyl halides with the insertion of sulfur dioxide under mild conditions, especially in the presence of visible light, would be highly desirable. Herein, we report a photoredox-catalyzed sulfonylation of alkyl iodides, sulfur dioxide, and electron-deficient alkenes under mild conditions. This reaction proceeds through alkyl radicals formed *in situ* from alkyl iodides under visible light irradiation in the presence of a photoredox catalyst, leading to diverse sulfones. Various functional groups including nitro, halo, acetyl, sulfonyl, and pyridinyl are all tolerated under the photoredox conditions (Scheme 1).

At the outset, a model reaction of cyclohexyl iodide **1a**, DABCO·(SO<sub>2</sub>)<sub>2</sub>, and (*E*)-chalcone **2a** in the presence of TTMS and photocatalyst (5 mol%) was explored. The results are summarized in Table 1. Initially, the reaction was catalyzed by [Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> in 1,2-dichloroethane irradiated by a 15 W blue LED (Table 1, entry 1). To our delight, the corresponding sulfone **3a** was obtained in 31% yield. Inferior results



**Scheme 1** Generation of sulfones under photoredox catalysis with the insertion of sulfur dioxide.

<sup>a</sup> Institute for Advanced Studies, Taizhou University, 1139 Shifu Avenue, Taizhou 318000, China. E-mail: jie\_wu@fudan.edu.cn

<sup>b</sup> Department of Chemistry, Fudan University, 2005 Songhu Road, Shanghai 200438, China

<sup>c</sup> College of Biological, Chemical Science and Engineering, Jiaying University, 118 Jiahang Road, Jiaying 514001, China. E-mail: qiuguanyinsheng@mail.zjxu.edu.cn

† Electronic supplementary information (ESI) available: Experimental details and spectral data, and copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra. See DOI: 10.1039/c9cc00347a

‡ S. Ye and D. Zheng contributed equally.





Scheme 3 Control experiments.

acceptor systems holding a  $\beta$ -alkyl substituent were used as substrates.

As mentioned above, we proposed that under photoredox catalysis, alkyl radical intermediates would be produced to initiate the reaction. Therefore, several control experiments were performed, as presented in Scheme 3. As expected, no reaction occurred with the addition of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in the mixture of cyclohexyl iodide **1a**, DABCO·(SO<sub>2</sub>)<sub>2</sub>, and (*E*)-chalcone **2a** under the standard conditions, and compound **4** was detected by HRMS (Scheme 3, eqn (a)). Additionally, (iodomethyl)cyclopropane was employed in the reaction of DABCO·(SO<sub>2</sub>)<sub>2</sub> with (*E*)-chalcone **2a**, resulting in the formation of compound **3x** in 56% yield (Scheme 3, eqn (b)). This result demonstrated that a cyclopropylmethyl radical might be generated during the reaction process. These results indicated that a radical process might be involved, as proposed in Scheme 4.

On the basis of the above results and previous reports,<sup>11</sup> we postulated that under visible light irradiation, the excited state of the photocatalyst would assist the formation of a trimethylsilylsilyl radical (Scheme 4). Thus, the trimethylsilylsilyl radical would react with alkyl iodide **1** leading to an alkyl radical intermediate, which would be captured by sulfur dioxide to provide an alkylsulfonyl radical. Then, the alkylsulfonyl radical would attack the double bond of electron-deficient alkene **2**, giving rise to radical intermediate **A**. Subsequently, two possible pathways might occur. In path a, radical intermediate **A** would undergo a reductive single electron transfer (SET) to produce anion intermediate **B**. Further protonation would afford the corresponding sulfone **3**. Alternatively, radical **A** would go through



Scheme 4 Plausible mechanism.

proton abstraction from TTMS, giving rise to the desired product **3** (path b).

In summary, we have described a photoredox-catalyzed sulfonylation of alkyl iodides, sulfur dioxide, and electron-deficient alkenes under mild conditions. This reaction proceeds through alkyl radicals formed *in situ* from alkyl iodides under visible light irradiation in the presence of a photoredox catalyst. The alkyl radical intermediates would react with sulfur dioxide leading to alkylsulfonyl radicals, which would be trapped by electron-deficient alkenes giving rise to alkyl sulfones. Various functional groups including nitro, halo, acetyl, sulfonyl, and pyridinyl are all tolerated under the photoredox conditions.

Financial support from the National Natural Science Foundation of China (No. 21672037 and 21532001) is gratefully acknowledged.

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- For selected examples, see: (a) *Transition Metal Reagents and Catalysts*, ed. J. Tsuji, John Wiley & Sons, Ltd, 2000; (b) K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem., Int. Ed.*, 2005, **44**, 4442; (c) K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem., Int. Ed.*, 2005, **44**, 4490.
- For selected examples, see: (a) S. E. Creutz, K. J. Lotito, G. C. Fu and J. C. Peters, *Science*, 2012, **338**, 647; (b) D. T. Ziegler, J. Choi, J. M. Muñoz-Molina, A. C. Bissember, J. C. Peters and G. C. Fu, *J. Am. Chem. Soc.*, 2013, **135**, 13107; (c) L. Li, W. Liu, H. Zeng, X. Mu, G. Cosa, Z. Mi and C.-J. Li, *J. Am. Chem. Soc.*, 2015, **137**, 8328; (d) Y. C. Tan, J. M. Muñoz-Molina, G. C. Fu and J. C. Peters, *Chem. Sci.*, 2014, **5**, 2831; (e) J. A. Terrett, J. D. Cuthbertson, V. W. Shurtleff and D. W. C. MacMillan, *Nature*, 2015, **524**, 330; (f) Z. Zuo, D. T. Ahneman, L. Chu, J. A. Terrett, A. G. Doyle and D. W. C. MacMillan, *Science*, 2013, **339**, 1593; (g) Z. Zuo, D. T. Ahneman, L. Chu, J. A. Terrett, A. G. Doyle and D. W. C. MacMillan, *Science*, 2014, **345**, 437; (h) Z. Zuo, H. Cong, W. Li, J. Choi, G. C. Fu and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2016, **138**, 1832; (i) L. Chu, J. M. Lipshultz and D. W. C. MacMillan, *Angew. Chem., Int. Ed.*, 2015, **54**, 7929.
- For reviews: (a) D. Zheng and J. Wu, *Sulfur Dioxide Insertion Reactions for Organic Synthesis*, Nature Springer, Berlin, 2017; (b) G. Qiu, K. Zhou, L. Gao and J. Wu, *Org. Chem. Front.*, 2018, **5**, 691; (c) G. Liu, C. Fan and J. Wu, *Org. Biomol. Chem.*, 2015, **13**, 1592; (d) P. Bissert and N. Blanchard, *Org. Biomol. Chem.*, 2013, **11**, 5393; (e) A. S. Deeming, E. J. Emmett, C. S. Richards-Taylor and M. C. Willis, *Synthesis*, 2014, 2701; (f) E. J. Emmett and M. C. Willis, *Asian J. Org. Chem.*, 2015, **4**, 602; (g) K. Hofman, N.-W. Liu and G. Manolikakes, *Chem. – Eur. J.*, 2018, **24**, 11852; (h) G. Qiu, L. Lai, J. Cheng and J. Wu, *Chem. Commun.*, 2018, **54**, 10405; (i) G. Qiu, K. Zhou and J. Wu, *Chem. Commun.*, 2018, **54**, 12561; (j) S. Ye, G. Qiu and J. Wu, *Chem. Commun.*, 2019, **55**, 1013; (k) J. Zhu, W.-C. Yang, X.-D. Wang and L. Wu, *Adv. Synth. Catal.*, 2018, **360**, 386.
- For selected examples, see: (a) L.-Y. Xie, S. Peng, F. Liu, G.-R. Chen, W. Xia, X. Yu, W.-F. Li, Z. Cao and W.-M. He, *Org. Chem. Front.*, 2018, **5**, 2604; (b) W. Li, G. Yin, L. Huang, Y. Xiao, Z. Fu, X. Xin, F. Liu, Z. Li and W.-M. He, *Green Chem.*, 2016, **18**, 4879; (c) L.-Y. Xie, S. Peng, L.-L. Jiang, X. Peng, W. Xia, X. Yu, X.-X. Wang, Z. Cao and W.-M. He, *Org. Chem. Front.*, 2019, **2**, 167; (d) L.-Y. Xie, S. Peng, J.-X. Tan, R.-X. Sun, X. Yu, N.-N. Dai, Z.-L. Tang, X. Xu and W.-M. He, *ACS Sustainable Chem. Eng.*, 2018, **6**, 16976; (e) Y. Su, X. Zhou, C. He, W. Zhang, X. Ling and X. Xiao, *J. Org. Chem.*, 2016, **81**, 4981; (f) L.-Y. Xie, Y.-J. Li, J. Qu, Y. Duan, J. Hu, K.-J. Liu, Z. Cao and W.-M. He, *Green Chem.*, 2017, **19**, 5642.
- P. S. Santos and M. T. S. Mello, *J. Mol. Struct.*, 1988, **178**, 121.
- For selected examples, see: (a) B. Nguyen, E. J. Emmet and M. C. Willis, *J. Am. Chem. Soc.*, 2010, **132**, 16372; (b) F. Liu, J.-Y. Wang,

- P. Zhou, G. Li, W.-J. Hao, S.-J. Tu and B. Jiang, *Angew. Chem., Int. Ed.*, 2017, **56**, 15570; (c) Y. Wang, L. Deng, Y. Deng and J. Han, *J. Org. Chem.*, 2018, **83**, 4674; (d) J. Sheng, Y. Li and G. Qiu, *Org. Chem. Front.*, 2017, **4**, 95; (e) A. Shavnya, S. B. Coffey, A. C. Smith and V. Mascitti, *Org. Lett.*, 2013, **15**, 6226; (f) D. Yang, P. Sun, W. Wei, F. Liu, H. Zhang and H. Wang, *Chem. – Eur. J.*, 2018, **24**, 4423; (g) M. W. Johnson, S. W. Bagley, N. P. Mankad, R. G. Bergman, V. Mascitti and F. D. Toste, *Angew. Chem., Int. Ed.*, 2014, **53**, 4404; (h) Z.-J. Shen, Y.-N. Wu, C.-L. He, L. He, W.-J. Hao, A.-F. Wang, S.-J. Tu and B. Jiang, *Chem. Commun.*, 2018, **54**, 445; (i) D. Sun, K. Yin and R. Zhang, *Chem. Commun.*, 2018, **54**, 1335; (j) X. Wang, L. Xue and Z. Wang, *Org. Lett.*, 2014, **16**, 4056; (k) V. Vedovato, E. P. A. Talbot and M. C. Willis, *Org. Lett.*, 2018, **20**, 5493; (l) Y. Wang, L. Deng, J. Zhou, X. Wang, H. Mei, J. Han and Y. Pan, *Adv. Synth. Catal.*, 2018, **360**, 1060; (m) H. Wang, B. Wang, S. Sun and J. Cheng, *Org. Chem. Front.*, 2018, **5**, 2547; (n) T. Wang, F. Wang, J. Shen, T. Pang, Y. Ren, B. Wu and X. Zhang, *Tetrahedron Lett.*, 2018, **59**, 1183; (o) A. S. Deeming, C. J. Russell and M. C. Willis, *Angew. Chem., Int. Ed.*, 2015, **54**, 1168; (p) N. Wolff, J. Char, X. Frogneux and T. Cantat, *Angew. Chem., Int. Ed.*, 2017, **56**, 5616; (q) C. C. Chen and J. Waser, *Org. Lett.*, 2015, **17**, 736; (r) Y. Luo, X. Pan, C. Chen, L. Yao and J. Wu, *Chem. Commun.*, 2015, **51**, 180; (s) A. S. Deeming, C. J. Russell and M. C. Willis, *Angew. Chem., Int. Ed.*, 2016, **55**, 747; (t) A. S. Tsai, J. M. Curto, B. N. Roche, A. R. Dechert-Schmitt, G. K. Ingle and V. Mascitti, *Org. Lett.*, 2016, **18**, 508; (u) A. L. Tribby, I. Rodriguez, S. Shariffudin and N. D. Ball, *J. Org. Chem.*, 2017, **82**, 2294; (v) J. Zhang, Y. An and J. Wu, *Chem. – Eur. J.*, 2017, **23**, 9477; (w) Y. Chen, P. R. D. Murray, A. T. Davies and M. C. Willis, *J. Am. Chem. Soc.*, 2018, **140**, 8781.
- 7 For selected examples, see: (a) D. Zheng, Y. An, Z. Li and J. Wu, *Angew. Chem., Int. Ed.*, 2014, **53**, 2451; (b) D. Zheng, J. Yu and J. Wu, *Angew. Chem., Int. Ed.*, 2016, **55**, 11925; (c) R. Mao, Z. Yuan, R. Zhang, Y. Ding, X. Fan and J. Wu, *Org. Chem. Front.*, 2016, **3**, 1498; (d) Y. An and J. Wu, *Org. Lett.*, 2017, **19**, 6028; (e) T. Liu, W. Zhou and J. Wu, *Org. Lett.*, 2017, **19**, 6638; (f) H. Xia, Y. An, X. Zeng and J. Wu, *Chem. Commun.*, 2017, **53**, 12548; (g) Y. Xiang, Y. Kuang and J. Wu, *Chem. – Eur. J.*, 2017, **23**, 699; (h) T. Liu, D. Zheng and J. Wu, *Org. Chem. Front.*, 2017, **4**, 1079; (i) J. Zhang, F. Zhang, L. Lai, J. Cheng, J. Sun and J. Wu, *Chem. Commun.*, 2018, **54**, 3891; (j) K. Zhou, J. Zhang, L. Lai, J. Cheng, J. Sun and J. Wu, *Chem. Commun.*, 2018, **54**, 7459; (k) H. Xia, Y. An, X. Zeng and J. Wu, *Org. Chem. Front.*, 2018, **5**, 366; (l) K. Zhou, M. Chen, L. Yao and J. Wu, *Org. Chem. Front.*, 2018, **5**, 371; (m) X. Wang, Y. Li, G. Qiu and J. Wu, *Org. Chem. Front.*, 2018, **5**, 2555; (n) J. Zhang, K. Zhou and J. Wu, *Org. Chem. Front.*, 2018, **5**, 813; (o) F.-S. He, X. Cen, S. Yang, J. Zhang, H. Xia and J. Wu, *Org. Chem. Front.*, 2018, **5**, 2437; (p) F.-S. He, Y. Wu, J. Zhang, H. Xia and J. Wu, *Org. Chem. Front.*, 2018, **5**, 2940.
- 8 For selected examples by using inorganic sulfites as the source of sulfur dioxide, see: (a) S. Ye and J. Wu, *Chem. Commun.*, 2012, **48**, 10037; (b) M. Wang, S. Chen and X. Jiang, *Org. Lett.*, 2017, **19**, 4916; (c) M. W. Johnson, S. W. Bagley, N. P. Mankad, R. G. Bergman, V. Mascitti and F. D. Toste, *Angew. Chem., Int. Ed.*, 2014, **53**, 4404; (d) Y. Wang, B. Du, W. Sha, J. Han and Y. Pan, *Org. Chem. Front.*, 2017, **4**, 1313; (e) J. Zhang, Y. An and J. Wu, *Chem. – Eur. J.*, 2017, **23**, 9477; (f) A. Shavnya, S. B. Coffey, A. C. Smith and V. Mascitti, *Org. Lett.*, 2013, **15**, 6226; (g) A. Shavnya, K. D. Hesp, V. Mascitti and A. C. Smith, *Angew. Chem., Int. Ed.*, 2015, **54**, 13571; (h) H. Konishi, H. Tanaka and K. Manabe, *Org. Lett.*, 2017, **19**, 1578; (i) X. Gong, J. Chen, L. Lai, J. Cheng, J. Sun and J. Wu, *Chem. Commun.*, 2018, **54**, 11172; (j) N.-W. Liu, S. Liang and G. Manolikakes, *Adv. Synth. Catal.*, 2017, **359**, 1308; (k) H. Zhu, Y. Shen, Q. Deng, J. Chen and T. Tu, *Chem. Commun.*, 2017, **53**, 12473; (l) K. Zhou, J. Zhang, G. Qiu and J. Wu, *Org. Lett.*, 2019, **21**, 278; (m) J. Zhang, K. Zhou, G. Qiu and J. Wu, *Org. Chem. Front.*, 2019, **6**, 36; (n) H. Liao, A. Chatupheeraphat, C. C. Hsiao, I. Atodiresei and M. Rueping, *Angew. Chem., Int. Ed.*, 2015, **54**, 15540; (o) M. Wang, Q. Fan and X. Jiang, *Green Chem.*, 2018, **20**, 5469.
- 9 (a) Y. Li, D. Zheng, Z. Li and J. Wu, *Org. Chem. Front.*, 2016, **3**, 574; (b) K. Zhou, H. Xia and J. Wu, *Org. Chem. Front.*, 2016, **3**, 865; (c) X. Gong, Y. Ding, X. Fan and J. Wu, *Adv. Synth. Catal.*, 2017, **359**, 2999; (d) J. Zhang, K. Zhou, G. Qiu and J. Wu, *Org. Chem. Front.*, 2019, **6**, 36.
- 10 (a) X. Gong, J. Chen, J. Liu and J. Wu, *Org. Chem. Front.*, 2017, **4**, 2221; (b) N.-W. Liu, S. Liang and G. Manolikakes, *Adv. Synth. Catal.*, 2017, **359**, 1308; (c) M. Wang, S. Chen and X. Jiang, *Org. Lett.*, 2017, **19**, 4916; (d) Z. Chen, N.-W. Liu, M. Bolte, H. Ren and G. Manolikakes, *Green Chem.*, 2018, **20**, 3059.
- 11 (a) T. Liu, Y. Li, L. Lai, J. Cheng, J. Sun and J. Wu, *Org. Lett.*, 2018, **20**, 3605; (b) T. Liu, Y. Ding, X. Fan and J. Wu, *Org. Chem. Front.*, 2018, **5**, 3153.