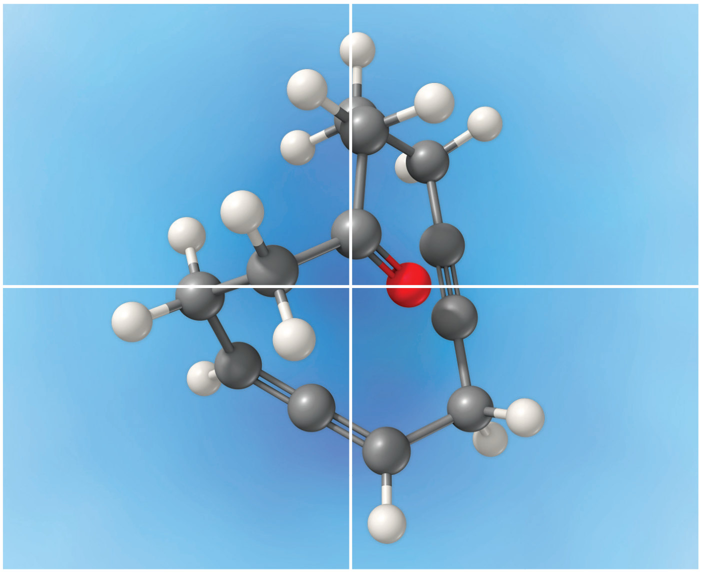

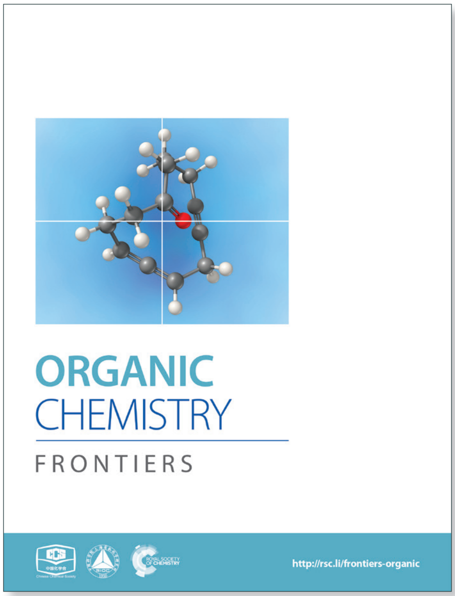
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Alkyl- and aryl-thioalkylation of olefins with organotrifluoroborates by photoredox catalysis

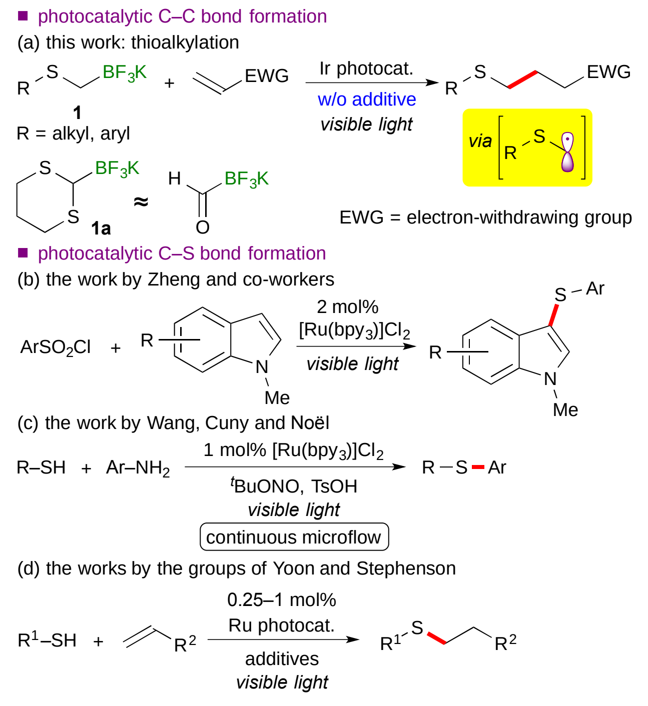
Yanjie Li, Kazuki Miyazawa, Takashi Koike* and Munetaka Akita*

A facile and environmentally benign protocol for alkyl- and aryl-thioalkylation of olefins has been developed. Photoredox catalysis with an Ir photocatalyst, $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ ($dF(CF_3)ppy$: 5-trifluoromethyl-2-(2,4-difluorophenyl)pyridine, bpy: 2,2'-bipyridine), induces efficient oxidation of a variety of alkyl- and aryl-thioalkyltrifluoroborates under visible light irradiation at room temperature, leading to generation of α-thioalkyl radicals *via* deboronation. Generated α-thioalkyl radicals smoothly react with electron-deficient olefins to afford addition products in good yields. The present photocatalytic method provides us with simple and new access to a range of alkylsulphides under mild reaction conditions.

Introduction

Recently, visible-light-induced single electron transfer (SET) processes mediated by well-defined ruthenium(II) polypyridine complexes and the relevant cyclometalated iridium(III) derivatives have been recognized as an useful redox protocol from the viewpoint of radical chemistry and green chemistry.[1] In particular, oxidatively generated α-aminoalkyl radicals from various nitrogen-containing compounds by photoredox catalysis has become a powerful method for synthesis of useful nitrogen-containing building blocks.[2,9d] The nucleophilic α-aminoalkyl radicals can react with electron-deficient moieties such as unsaturated bonds and arenes to enable functionalization of a carbon atom adjacent to the nitrogen atom. Further expansion into functionalization of ether derivatives advances steadily.[3,9b] In contrast, reaction of α-sulfur atom substituted alkyl radicals, *i.e.* α-thioalkyl radicals,[4] by photoredox catalysis has not been reported yet, though it can become a new strategy for synthesis of organic sulphides. Additionally, sulphides are known as important functional groups in the field of medicinal chemistry and material chemistry.[5]

Herein we describe the first example of photoredox-catalyzed thioalkylation of olefins through generation of α-thioalkyl radicals *via* oxidation of alkyl- and aryl-thioalkyltrifluoroborates (Scheme 1(a)). So far, a few examples of synthesis of sulphides by photoredox catalysis have been reported.[6] In 1978 and 1979, Kellog et al. presented pioneering works about reductively formation of sulphides from reaction of organosulfonium salts with Hantzsch ester in the presence of $[Ru(bpy)_3]Cl_2$ (bpy = 2,2'-bipyridine).[6a,b] In 2012, Zheng and co-workers showed coupling reaction of *N*-methylindoles and arylsulfonyl chlorides *via* reduction of sulfonyl chlorides (Scheme 1(b)).[6c] In 2013, Wang, Cuny and Noël described one-pot Stadler-Ziegler type reaction by photoredox catalysis in continuous microflow system (Scheme 1(c)).[6d] Furthermore, radical thiol-ene reactions involved in $[Ru(bpz)_3]^{2+}$ (bpz = 2,2'-bipyrazine) and $[Ru(bpy)_3]^{2+}$ were reported by the groups of Yoon and Stephenson, respectively (Scheme 1(d)).[6e,f,g] Their proposed reactive intermediates are different from α-thioalkyl radicals.

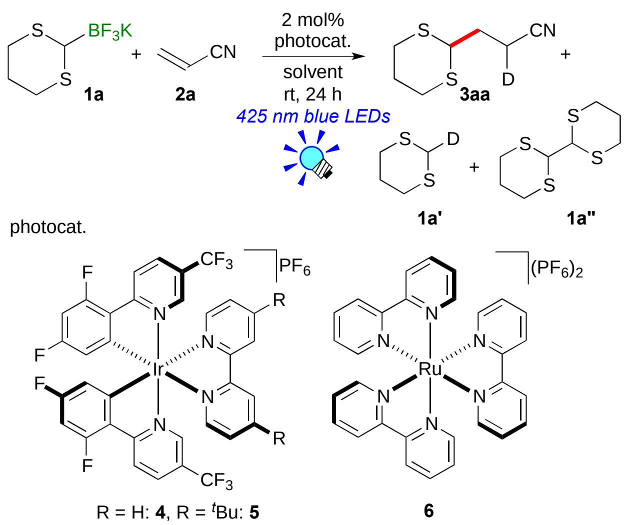


Scheme 1 Synthesis of sulphides by photoredox catalysis.

Organoborates are widely used in synthetic chemistry because of their easy-to-handle properties and compatibility with a variety of functional groups including sulphide.[7] In addition, generation of organic radicals by oxidation of organoborates have been well-documented so far.[8] Recently, our group and the groups of Chen and Molander reported on photocatalytic reactions using organoborates.[9,10] In particular, we have extensively developed redox-neutral α-heteroatom methylation such as radical aminomethylation[9d] and radical alkoxymethylation[9b] of olefins using the corresponding organotrifluoroborates by photoredox catalysis. Although radical thioalkylation is the continuous subject of the present article, the reaction of potassium 1,3-dithian-2-yltrifluoroborate (**1a**) can be regarded as a synthetic equivalent of formylation (Scheme 1(a)). Because 1,3-dithianes represent protected acyl groups for useful transformations.[11] Nucleophilic 1,3-dithian-2-yl radicals can be utilized as acyl anion equivalents. Thus, radical dithianylation can be connected to nucleophilic acylation. [4d,f,g]

Results and discussion

Table 1 Optimization of photocatalytic radical reaction of **1a** with **2a**[a]

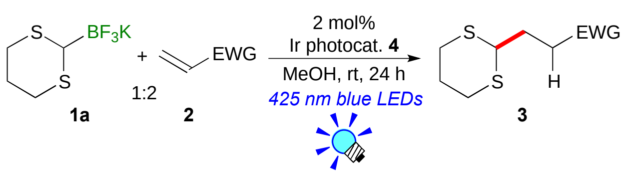


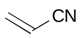
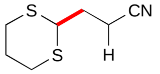
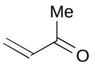
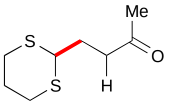
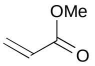
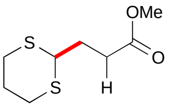
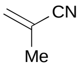
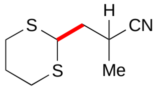
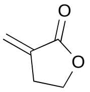
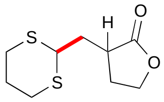
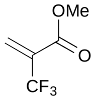
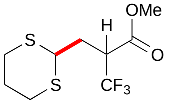
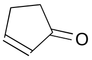
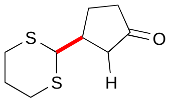
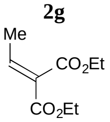
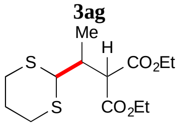
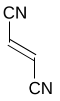
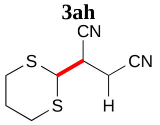
Entry	1a:2a	Photocat.	Solvent	NMR yield of /%		
				3aa	1a’	1a’’
1	1:1	4	Acetone-d_6/CD_3OD (1/1)	56	33	10
2	1:2	4	Acetone-d_6/CD_3OD (1/1)	90	6	3
3	1:2	5	Acetone-d_6/CD_3OD (1/1)	73	17	2
4	1:2	6	Acetone-d_6/CD_3OD (1/1)	79	15	1
5	1:2	4	CD_3OD	93	5	1
6	1:2	4	Acetone-d_6	10	12	1
7	1:2	4	CD_3CN	17	11	0
8	1:2	4	DMSO-d_6	10	10	5
9[b]	1:2	4	CD_3OD	0	0	0
10	1:2	None	CD_3OD	0	0	0

[a] Reaction conditions: A reaction mixture of **1a** (0.05 mmol), **2a** (0.05 mmol or 0.10 mmol), photocatalyst (1.0 μmol), $SiEt_4$ (an internal standard) and solvent (0.40 mL) was irradiated by 3 W blue LEDs (λ = 425 ± 15 nm) at room temperature for 24 h. [b] The reaction was conducted in the dark.

We initially examined the visible-light reaction of potassium 1,3-dithian-2-yltrifluoroborate (**1a**) with 1 equivalent of acrylonitrile (**2a**) in the mixed solvent system, acetone-d_6 and CD_3OD (1/1) in the presence of the Ir photocatalyst **4**, $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ ($dF(CF_3)ppy$: 5-(trifluoromethyl)-2-(2,4-difluorophenyl)pyridine), which can serve as a strong oxidant ($E_{1/2}$ = +0.91 V *vs.* Cp_2Fe) when photochemically excited.[12]

Table 2 The scope of the present photocatalytic hydrodithianylation[a]



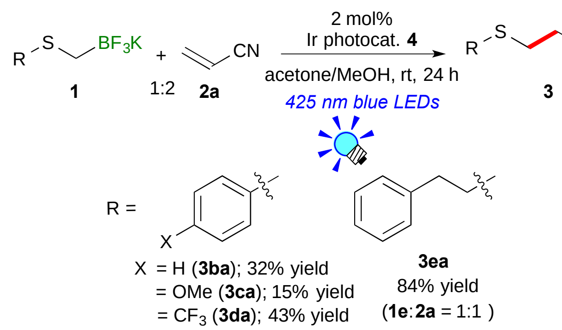
Entry	Olefin 2	Product 3	Isolated yield/%
1	 **2a**	 **3aa**	80
2	 **2b**	 **3ab**	78
3	 **2c**	 **3ac**	71
4	 **2d**	 **3ad**	64
5	 **2e**	 **3ae**	78
6	 **2f**	 **3af**	80
7	 **2g**	 **3ag**	–
8	 **2h**	 **3ah**	–
9	 **2i**	 **3ai**	86

[a] Reaction conditions: A reaction mixture of **1a** (0.25 mmol), olefin **2** (0.50 mmol), Ir photocatalyst **4** (5.0 μmol), degassed MeOH (2.0 mL) was irradiated by 3 W blue LEDs (λ = 425 ± 15 nm) at room temperature for 24 h.

As a result, hydrodithianylated product **3aa** was obtained in a 56% NMR yield together with formation of 2-deuterated-1,3-

dithiacyclohexane **1a'** (33%) and 1,3-dithianyl dimer **1a"** (10%) (entry 1 in Table 1). The formation of these by-products suggests that 1,3-dithian-2-yl radical is involved in the present photocatalytic reaction. Next, the use of 2 equivalents of acrylonitrile (**2a**) dramatically increased the yield of **3aa** (90% NMR yield) and suppressed the side reactions (entry 2). Other photocatalysts, $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ (**5**) (dtbbpy: 4,4'-di-*tert*-butyl-2,2'-bipyridine) and $[Ru(bpy)_3](PF_6)_2$ (**6**),[13] resulted in lower yields (entries 3 and 4). CD_3OD and the mixed solvent system, acetone-d_6 and CD_3OD, turned out to be appropriate solvent system (entries 5–8). Furthermore, the present reaction required both of visible-light irradiation and the photocatalyst (entries 9 and 10).

With the optimal reaction conditions in hand, the preparative scale hydrodithianylation of olefins was performed (Table 2). The reactions of typical electron-deficient alkenes, acrylonitrile (**2a**), 3-buten-2-one (**2b**) and methyl acrylate (**2c**), proceeded smoothly to give the corresponding products (**3aa**–**3ac**) in good yields (71–80%) (entries 1–3). 1,1-Disubstituted olefins such as methacrylonitrile (**2d**), α-methylene-γ-butyrolactone (**2e**) and methyl 2-(trifluoromethyl)acrylate (**2f**) could also be applied to the present reaction (**3ad**–**3af**: 65–80% yields) (entries 4–6). However, olefins with a substituent at the reaction site, 2-cyclopenten-1-one (**2g**) and diethyl ethylidenemalonate (**2h**), resulted in low conversions of the olefins and significant formation of deborohydrogenated by-product **1a'** (entries 7 and 8). By contrast, the reaction of fumaronitrile (**2i**) afforded the hydrodithianylated product (**3ai**) in an 85% yield (entry 9). These results suggest that the present photocatalytic dithianylation is effective for terminal olefins bearing electron-withdrawing groups and highly electron-deficient internal olefins.

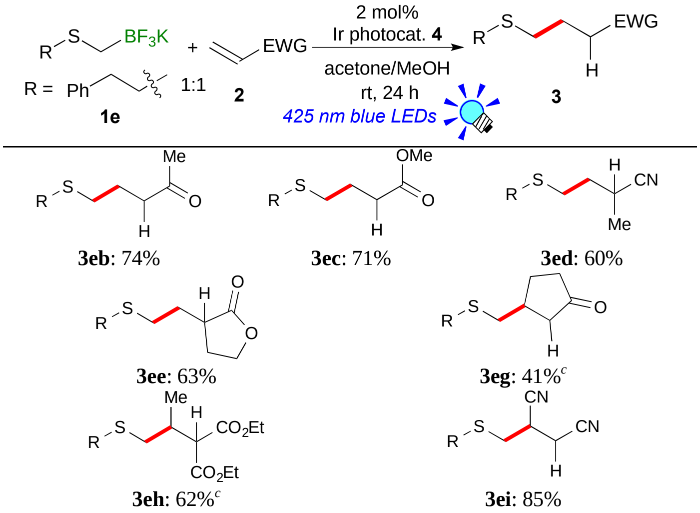


Scheme 2 Examination of substituents on the sulphur atom in thiomethyltrifluoroborates.

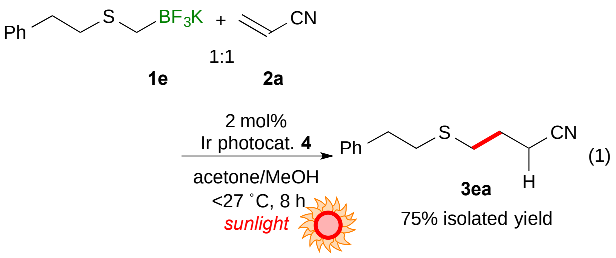
Next, the scope of aryl- and alkyl-thiomethyltrifluoroborates was examined (Scheme 2). The reactions of potassium phenylthiomethyltrifluoroborate (**1b**), potassium 4-methoxyphenylthiomethyltrifluoroborate (**1c**), and potassium 4-trifluoromethylphenylthiomethyltrifluoroborate (**1d**) with acrylonitrile (**2a**) afforded the corresponding arylthiomethylated products (**3ba**–**da**) in moderate yields (15–43%) due to formation of a considerable amount of arylthiomethanes **1'** as a by-product. Notably, the electron-withdrawing CF_3 group hinders formation of the byproduct. These results suggest that electron-withdrawing group stabilizes the generated arylthiomethyl radical under these reaction conditions. In contrast, potassium phenethylthiomethyltrifluroborate (**1e**) gave the alkylthiomethylated product **3ea** in an excellent yield (84 % yield). In addition, the reaction of **1e** did not require an excess amount of olefin.

In the light of high reactivity and selectivity of potassium phenethylthiomethyltrifluroborate (**1e**), the scope of olefins was investigated (Table 3). Electron-deficient olefins (**2b–e**, **2i**) were also applicable to the present reaction. It should be noted that the reaction with **1e** enabled alkylthiomethylation of olefins with a substituent at the reaction site, 2-cyclopenten-1-one (**2g**) and diethyl ethylidenemalonate (**2h**), which could not be applied to the reaction with **1a** *vide supra*. The alkylthiomethylated products were obtained in 42% (**3eg**) and 63% yields (**3eh**) with the use of an excess amount of borate and 5 mol% of Ir catalyst **4**. These results suggest that the phenethylthiomethyl radical serves as a species more nucleophilic than 1,3-dithian-2-yl radical and arylthiomethyl radicals presumably due to steric and electronic reason.

Table 3 The scope of the present photocatalytic phenethylthiomethylation[a,b]

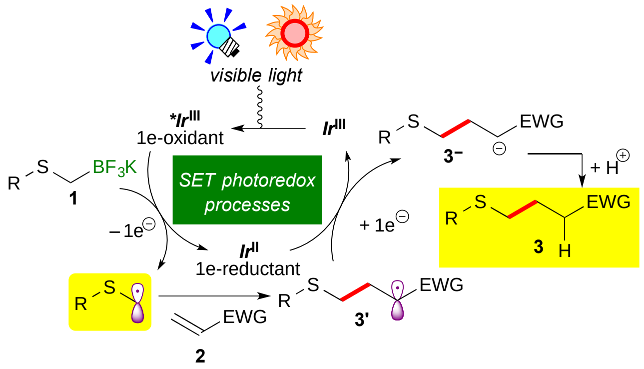


[a]Reaction conditions: A reaction mixture of **1a** (0.25 mmol), olefin **2** (0.25 mmol), Ir photocatalyst **4** (5.0 μmol), degassed acetone (1.0 mL) and MeOH (1.0 mL) was irradiated by 3 W blue LEDs (λ = 425 ± 15 nm) at room temperature for 24 h. [b]Isolated yields. [c]**1e**:**2** = 2:1, 5 mol% of Ir catalyst **4** was used.



Utilization of sunlight as a light source for photoreaction is promising in terms of green and sustainable chemistry. Thus, sunlight-driven photocatalytic alkyltiomethylation of **2a** with **1e** was performed. As a result, the reaction proceeded more efficiently (8 h) than the reaction irradiated by blue LEDs (eqn. 1).

To gain an insight into reaction mechanism, electrochemical analysis for organoborates and luminescence quenching experiments were carried out (See the Supporting Information). Oxidation potentials for all above-mentioned α-thioalkylborates (**1a**–**1e**) were less than +0.72 V *vs*. Cp_2Fe, indicating that they can be easily oxidized by the photoactivated Ir photocatalyst **4** ($E_{1/2}$ = +0.91 V *vs*. Cp_2Fe). In addition, potassium phenethylthiomethyltrifluroborate (**1e**) strongly quenched luminescence from the triplet excited state of **4**, supporting that the first SET event occurs between the excited Ir species and **1**.



Scheme 3 A plausible reaction mechanism.

A plausible reaction mechanism is illustrated in Scheme 3. Visible light irradiation induces excitation of the Ir photocatalyst (***Ir***^{III}) into the photoactivated state (****Ir***^{III}), which serves as a strong oxidant. One-electron oxidation of alkyl- or aryl-thioalkylborate **1** by ****Ir***^{III} generates α-thioalkyl radical *via* deboronation accompanying formation of the highly reduced Ir species, ***Ir***^{II}. Subsequent addition of α-thioalkyl radical to electron-deficient olefins **2** affords the radical intermediate **3'**, which undergoes second SET event from ***Ir***^{II} to be converted into carboanionic intermediate **3**$^{-}$. Finally, protonation by the solvent produces alkyl- or aryl-thioalkylated product **3**. A control experiment in CD_3OH revealed the H atom in the product **3** does not result from hydrogen abstraction from the CD_3 group but from protonation with the OH group (see the Supporting Information). At the present moment, we cannot rule out radical propagation mechanism at all. But the present reaction required continuous irradiation of visible light to proceed steadily (See the Supporting Information). Therefore, radical propagation process is not the major reaction pathway if any.

Conclusions

We have developed alkyl- and aryl-thioalkylation of olefins using the corresponding organotrifluoroborates by visible-light-induced photoredox catalysis. The present photocatalytic protocol enables facile generation of α-thioalkyl radical and access to a new range of alkysulphides without any additives under mild reaction conditions: room temperature and visible light irradiation including natural sunlight. Now our effort is directed to synthesis of new useful compounds through photoredox processes.

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Notes and references

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. E-mail: koike.t.ad@m.titech.ac.jp, makita@res.titech.ac.jp; Fax: +81-45-924-5230; Tel: +81-45-924-5230

† Electronic Supplementary Information (ESI) available: Experimental details and spectral data. See DOI: 10.1039/b000000x/

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