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Photocatalyst-Free Visible-Light-Promoted C(sp²)-S Coupling: A Strategy for the Preparation of S-Aryl Dithiocarbamates

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S Supporting Information

ABSTRACT: We have successfully developed a green and efficient multicomponent reaction protocol to synthesize Saryl dithiocarbamates under visible light. Most appealingly, the reaction can proceed smoothly without adding any transitionmetal catalysts, ligands, or photocatalysts while minimizing chemical wastes and metal residues in the end products. The advantages of this method meet the requirements of sustainable and green synthetic chemistry, and it provides a straightforward way to create valuable S-aryl dithiocarbamates.

arbon-sulfur bonds are well-known in natural products, pharmacologically active molecules, and organic materials.¹ The development of novel and efficient approaches for the construction of C-S bonds has always been an ongoing curiosity in organic chemistry.² The traditional methods for the construction of C-S bonds include the transition-metalcatalyzed cross-couplings of thiols or disulfides with aryl halides, arylboronic acids, or pseudo halides.³ Despite having great benefits, these reactions could possess some limitations such as requirement of high temperature, specially designed ligands, high catalyst loading, and toxic metal salt catalysts which could not meet the requirements of sustainable and green chemistry. Thus, it remains a thought-provoking and attractive task to develop simpler, more efficient, and environmentally benign strategies for the construction of C-S bonds.

As important sulfur-containing compounds, organic dithiocarbamates are ubiquitous in a variety of biologically active compounds (Figure 1).⁴ For example, they are commonly used in medicinal chemistry and have found application in the treatment of cancer.⁵ Importantly, their biological properties and critical roles in agriculture have led to the development of synthetic methods for these compounds. Moreover, they also function as useful synthetic intermediates, linkers in solid phase organic synthesis,⁶ and protecting groups in peptide synthesis.⁷ As a result, development of efficient and novel methods for the synthesis of this kind of significant sulfurcontaining compounds will be of great value for the screening of biologically active molecules. Traditionally, one-pot procedures by reaction of amines with carbon disulfide and alkyl halides have been demonstrated to be convenient methods for the synthesis of alkyl dithiocarbamates.⁸ However,





Figure 1. Representative organic dithiocarbamates with pharmaceutical activity.

approaches for the formation of aryl dithiocarbamates are quite limited and the available methods involved the Wittig reaction of aldehydes with phosphonium ylides⁹ and the reaction of the sodium salt of dithiocarbamic acid with hypervalent iodine compounds.¹⁰ Recently, transition-metal-catalyzed approaches for the formation of aryl dithiocarbamates have been developed.^{5e,11} For example, very recently, Dong and Bolm developed an efficient route utilizing copper-catalyzed coupling reactions for the synthesis of aryl dithiocarbamates using inexpensive thiuram disulfide reagents (Scheme 1a).¹¹ Although some achievements have been made, these reactions could come across certain limitations, including harsh reaction conditions, toxic metal salt catalysts, and unavailability of the precursors.

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Scheme 1. Strategies for the Synthesis of S-Aryl Dithiocarbamates



As a greener substitute to the transition-metal-catalyzed strategies in organic synthesis chemistry, photochemical reactions have the advantage of avoiding the excessive use of expensive and toxic metal catalysts, ultimately avoiding the metal residues in target products.¹² Recently, diverse and efficient light-induced organic transformations have been widely used to construct C-C and C-heteroatom bonds. Recenlty, many studies on the light-promoted C-S bond forming reactions have been reported.¹³ In 2016, Oderinde, Johannes and co-workers developed an efficient photoinduced Ni-catalyzed method for the cross-coupling of thiols with aryl and heteroaryl iodides.^{13d} In 2017, Miyake et al. developed an efficient visible-light-induced protocol for the C-S crosscoupling of thiols and aryl halides in the absence of photoredox catalysts.^{13f} In the same year, Fu and co-workers developed an elegant visible-light photoredox arylation of thiols with aryl halides at room temperature.^{13g} As an important organic synthesis means, multicomponent reactions (MCRs) have attracted extensive attention since complex and diverse structures are generated in a single operation which improves the atom economy of the reaction procedure and reduces the pollution to the greatest extent possible.¹⁴ However, studies on the construction of C-S bonds based on light-induced MCRs strategies are rare. As a part of our continuing studies on the photochemical reactions¹⁵ and synthesis of sulfur-containing molecules,¹⁶ herein, we report an efficient, innovative, and simple visible-light-promoted method for the construction of S-aryl dithiocarbamates through MCRs of aryl halides, carbon disulfide, and amines at room temperature without using transition metals or other photocatalysts (Scheme 1b).

Initially, we selected 1-(4-iodophenyl) ethan-1-one (1a), carbon disulfide (2), and N-methylaniline (3a) as the model substrates to explore the optimal reaction conditions, including the bases, photocatalysts, and solvents under an atmosphere of nitrogen and an irradiation of visible light with a 23 W compact fluorescent light (CFL). As shown in Table 1, four photoredox catalysts were screened in DMSO with the use of 2.0 equiv of Cs_2CO_3 (relative to amount of 1a) as the base, and Rose Bengal provided the maximum yield (79%) (entries 1-6, Table 1). Notably, the yield also reached 78% without a photocatalyst (entry 5, Table 1). Encouraged by this result, we next screened the solvents such as DMF, DMSO, THF, CH₃CN, and 1,4-dioxane in order to improve the transformation efficiency, and the results showed that DMSO was the ideal solvent for this procedure (comparing the entry 5 with entries 6-9). Other bases tested (entries 10-18) were found to be inferior to Cs₂CO₃. No reaction occurred without the irradiation of visible light (entry 19). Highly pure Cs_2CO_3 (99.995% purity, trace metals <55.0 ppm) was used to avoid

	1			
Me	⟨ + 1a	$\begin{array}{ccc} \mathbf{CS}_2 & + & \mathbf{N}_2 \\ 2 & \mathbf{H} \\ 3 \\ 3 \end{array} & \begin{array}{c} \mathbf{base,} \\ \mathbf{base,} \\$	23 W CFL Me	Me S S 4a
Structures of Photocatalysts:				
	CI CI COONa COONa I e Bengal		[fac-Ir(ppy)3]	
	A	В	c	D
entry	base	photoredox catalyst	solvent	yield (%) ^b
1	Cs_2CO_3	А	DMSO	79
2	Cs_2CO_3	В	DMSO	45
3	Cs_2CO_3	С	DMSO	51
4	Cs_2CO_3	D	DMSO	23
5	Cs ₂ CO ₃	None	DMSO	78
6	Cs_2CO_3	None	DMF	24
7	Cs_2CO_3	None	CH ₃ CN	Trace
8	Cs_2CO_3	None	THF	12
9	Cs_2CO_3	None	1,4-Dioxane	Trace
10	КОН	None	DMSO	Trace
11	NaOH	None	DMSO	Trace
12	K_2CO_3	None	DMSO	54
13	DBU	None	DMSO	45
14	DBN	None	DMSO	49
15	Pyridine	None	DMSO	Trace
16	DABCO	None	DMSO	7
17	t-BuOK	None	DMSO	5
18	Et_3N	None	DMSO	6
19	Cs_2CO_3	None	DMSO	NR ^c
20	Cs_2CO_3	None	DMSO	78 ^d

Table 1. Optimization of the Reaction Conditions^a

^{*a*}Reaction conditions: 1-(4-iodophenyl)ethan-1-one 1a (0.3 mmol), carbon disulfide 2 (0.8 mmol), *N*-methylaniline 3a (0.4 mmol), base (0.6 mmol), solvent (1.5 mL), temperature (rt, ~25 °C), time (24 h). ^{*b*}Isolated yield. ^{*c*}No light. ^{*d*}Use of highly pure Cs₂CO₃ from Sigma-Aldrich Company (99.995% purity). NR = No reaction. CFL = compact fluorescent light.

the involvement of other transition metals in the present transformation, and the reaction gave a 78% yield (entry 20), which was the same when the analytically pure Cs_2CO_3 (99%) was used.

Using the optimized conditions, we next began to explore the generality and scope of the visible-light-promoted $C(sp^2)$ -S coupling process, and the results are summarized in Scheme 2. To our delight, a variety of aryl halides reacted smoothly with CS₂ and amines, affording the analogous S-aryl dithiocarbamates in moderate to good yields. Various aryl halides including aryl iodides and bromides were successfully coupled with CS₂ and amines. Undoubtedly, the reactivity followed in the order of aryl iodides > aryl bromides, while aryl chlorides did not work in the present transformation. For aryl iodides, the electronic effects of substituents exerted obvious influence on the reaction. Although aryl iodides bearing the electron-withdrawing groups displayed high reactivity, those bearing electron-donating ones were found to be poor substrates (see the Supporting Information (SI) for details). Further exploration on the scopes and limits of the synthetic application are in progress. It is worth noting that aromatic amines showed good reactivity compared to alkyl amines.

4c (70%)

NC





4z' (92%)

4s (67%) 4v (61%) 4w (64%) 4y (65%) 4x (60%) 4z (0%) 23 W CFL Cs₂CO₃ DMSO, rt , H H

^aReaction conditions: aryl halides 1 (0.3 mmol), CS₂ 2 (0.8 mmol), amines 3 (0.4 mmol), Cs₂CO₃ (0.6 mmol), DMSO (1.5 mL), reaction time (24 h). ^bIsolated yield. Unless otherwise noted, all products were obtained from aryl iodides.

Finally, a primary amine was also investigated under the standard conditions. Interestingly, when p-toluidine (31) was used, no dithiocarbamate (4z) was observed, and the thiourea

(4z') was obtained in 92% yield. This result indicates the secondary amines are crucial for the present transformation. The visible-light-promoted domino multicomponent reactions could tolerate quite a few functional groups such as ketone, aldehyde, methyl group, ester, nitro group, and cyano group, leaving ample room for further modification.

To further demonstrate the synthetic application of this method, a gram-scale synthesis of 4a using 1-(4-iodophenyl)ethan-1-one (1a), CS₂ (2), and N-methylaniline (3a) was performed. Under the irradiation of two 23 W CFLs, the desired product (4a) could be formed with a yield of 72% (5.0 mmol scale) (Scheme 3a). This transformation can be also

Scheme 3. Synthetic Applications



applied to the late-stage functionalization of a pharmaceutically relevant molecule (Scheme 3b). A L-menthol derivative with a iodine motif could be readily converted to the corresponding dithiocarbamate product (4aa) in moderate yields (63%).

In order to explore the probable mechanism of this visiblelight-promoted $C(sp^2)-S$ coupling, several control experiments were conducted (Figure 2 and Figure 3). We initially performed UV-vis spectroscopic measurements on various combinations of 1a, 2, 3a, and Cs₂CO₃ in DMSO for each species. As shown in Figure 2a, when 1a, 2, and 3a were mixed in DMSO, the color of the solution transformed from pale yellow to brown, and its optical absorption spectrum showed a bathochromic shift in the visible region, demonstrating the formation of an electron donor-receptor EDA complex.¹⁷ Subsequently, a Job plot using UV/vis absorption experiments was drawn to evaluate the stoichiometry of the EDA complex between 1a and 7, where 7 was formed through reaction of 2 and 3a. The maximal absorption obtained at 50% molar fraction of [2 + 3a] suggested a 1:1 ratio of 1a and 7 (Figure 3). In addition, reactivity was also suppressed in the presence of TEMPO (2 equiv) and under an aerobic atmosphere (see the SI for details).

Additionally, in order to investigate the effect of photoirradiation on the system, an on/off visible light irradiation experiment was performed. The graph preliminarily points toward the requirement of continuous visible-light irradiation for the onset as well as continuity of the reaction (Figure 4).

On the basis of the preliminary results reported above and in combination with the previous reports,^{13,17} a plausible



Figure 2. UV-vis spectroscopic measurements on various combinations of 1a, 2, 3a, and Cs_2CO_3 in DMSO.



Figure 3. Job's plot for ratio between 1a and 7.

mechanism is herein presented (Scheme 4). Initially, CS_2 (2) would react with amines (3) in the presence of Cs_2CO_3 to give the corresponding thiolate (A). Then, an aryl halide and a thiolate anion first associate, forming an EDA complex. This EDA complex is subsequently activated by visible-light irradiation to induce a SET (single electron transfer) from the thiolate anion, and an aryl radical (B). Finally, the aryl radical coupled with the thiyl radical, forming the coupling product (4).

In conclusion, a green and efficient MCR protocol has been developed for the synthesis of S-aryl dithiocarbamates under visible light conditions. A series of S-aryl dithiocarbamates could be conveniently obtained with good functional group



Figure 4. "Light/dark" experiments over the time.

Scheme 4. Possible Reaction Pathway



tolerance. Through this protocol, one new C–N bond and one C–S bond are constructed simultaneously in a single step. This method provides a sustainable and straightforward way to construct valuable S-aryl dithiocarbamates. Further investigation of the detailed mechanism and further exploration regarding the scopes and limits of the synthetic application are ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b02921.

Experimental details and compound characterization (PDF)

Accession Codes

CCDC 1943687–1943689 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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