DOI: 10.1002/adsc.201300566

Copper-Catalyzed Synthesis of α-Thioaryl Carbonyl Compounds Through S–S and C–C Bond Cleavage

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Received: June 26, 2013; Revised: July 18, 2013; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300566.

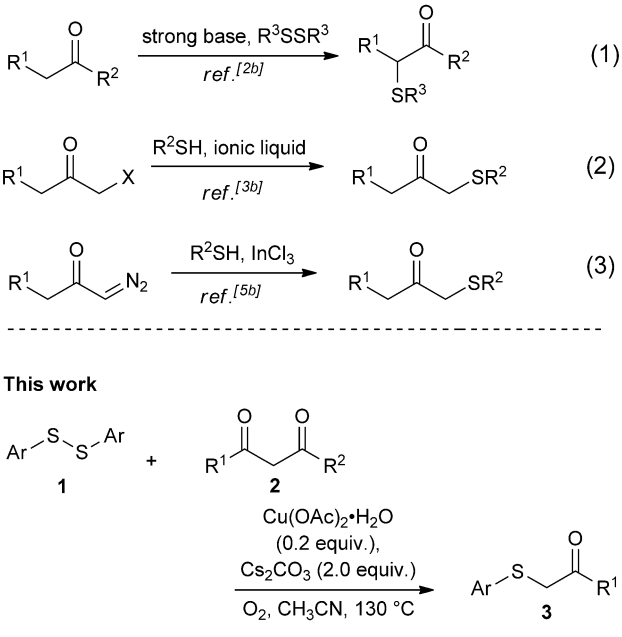
Abstract: A method to access α-thioaryl ketones and α-thioaryl esters employing copper acetate (hydrate) as catalyst and readily accessible diaryl disulfides and β-diketones (or β-keto esters) has been developed. Both alkyl- and aryl-substituted carbonyl compounds can be prepared.

Keywords: α-arylthio esters; α-arylthio ketones; C–C bond cleavage; copper catalysis; diaryl disulfides

α-Thioaryl carbonyl compounds are useful intermediates in organic synthesis.[1] Current methods employed for the preparation of such compounds include: (i) the sulfenylation of enolates with various sulfenylating agents, such as disulfides [Scheme 1, Eq. (1)],[2] (ii) the nucleophilic substitution of α-halogenated ketones with benzenethiols[3] or disulfides[4] [Scheme 1, Eq. (2)], or (iii) the metal-catalyzed intermolecular S–H insertion reaction of α-diazo ketones [Scheme 1, Eq. (3)].[5] In addition, a direct α-phenylthiolation of carbonyl compounds using diaryl disulfides in the presence of catalytic amounts of cesium carbonate and diphenyl diselenide was recently described by Nishiyama and co-workers.[6]

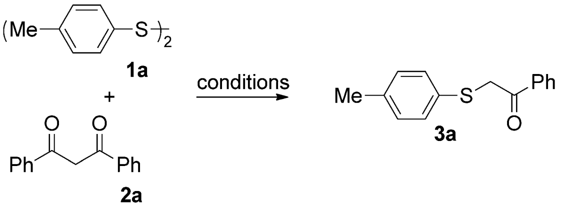
Transition metal-catalyzed reactions through selective C–C bond cleavage are of significant interest to chemists due to their broad application in organic synthesis.[7] Until recently, however, only a few examples regarding the catalytic activation of C–C bonds have been described in the literature, due in large part to the relative inertness of C–C bonds.[7c] Inspiringly, several transition metal-catalyzed carbon-carbon bond cleavage processes have been recently reported, in which complexes and salts of Rh, Ru, Cu, Fe, and Pd were utilized as efficient catalysts for these transformations.[8] To date, a variety of carbon-carbon bond forming processes have been reported utilizing the selective C–C bond cleavage of aliphatic alcohols,[9] diketones,[10] epoxides[11] and other functional groups.[12] To the best of our knowledge, however, the construction of C–S bonds through selective C–C cleavage of β-diketones has not been reported.

In the course of studying C–S bond formation,[13] we serendipitously discovered the copper-catalyzed selective C–C cleavage of β-diketones[14] and concomitant S–S cleavage of disulfides under an atmosphere of dioxygen. As such, we herein report a new approach to the synthesis of α-thiophenyl carbonyl compounds through a copper-catalyzed C–S bond forming reaction between diaryl disulfides and β-diketones or β-keto esters (Scheme 1, *bottom*).



Scheme 1. Representative procedures for the synthesis of α-thiophenyl carbonyl compounds.

Table 1. Screened reaction conditions.[a]



Entry	Catalyst	Base	Solvent	Yield [%][b]
1	$Cu(OAc)_2{\cdot}H_2O$	Cs_2CO_3	1,4-dioxane	trace
2	$Cu(OAc)_2{\cdot}H_2O$	Cs_2CO_3	DMF	trace
3	$Cu(OAc)_2{\cdot}H_2O$	Cs_2CO_3	DMSO	0
4	$Cu(OAc)_2{\cdot}H_2O$	Cs_2CO_3	CH_3NO_2	0
5	$Cu(OAc)_2{\cdot}H_2O$	Cs_2CO_3	toluene	0
6	$Cu(OAc)_2{\cdot}H_2O$	Cs_2CO_3	CH_3CN	85
7	CuBr	Cs_2CO_3	CH_3CN	43
8	$CuBr_2$	Cs_2CO_3	CH_3CN	57
9	$CuCl_2$	Cs_2CO_3	CH_3CN	48
10	–	Cs_2CO_3	CH_3CN	20
11[c]	$Cu(OAc)_2{\cdot}H_2O$	Cs_2CO_3	CH_3CN	9
12[d]	$Cu(OAc)_2{\cdot}H_2O$	Cs_2CO_3	CH_3CN	13
13[e]	$Cu(OAc)_2{\cdot}H_2O$	Cs_2CO_3	CH_3CN	35
14[f]	$Cu(OAc)_2{\cdot}H_2O$	Cs_2CO_3	CH_3CN	90 (87)
15[f]	CuI	Cs_2CO_3	CH_3CN	(57)
16[f]	$Cu(OTf)_2$	Cs_2CO_3	CH_3CN	(75)
17[f]	$Cu(OAc)_2$	Cs_2CO_3	CH_3CN	(77)

[a] *Reaction conditions:* di-*p*-tolyl disulfide (**1a**, 0.5 mmol), β-diketone (**2a**, 1.5 mmol), catalyst (0.1 mmol, 0.2 equiv.), base (1 mmol, 2.0 equiv.), solvent (1 mL), 130 °C, under an atmosphere of dioxygen, 24 h.

[b] GC yields, using tetradecane as an internal standard. Yields after column chromatography are given in parentheses.

[c] Under an atmosphere of argon.

[d] Under an atmosphere of air.

[e] Performed at 110 °C.

[f] Using 4.0 equiv. of **2a**.

The initial screening and optimization of the reaction conditions was conducted using di-*p*-tolyl disulfide (**1a**, 0.5 mmol scale) and dibenzoylmethane (**2a**) in a 1:3 ratio in the presence of 0.2 equivalents of $Cu(OAc)_2{\cdot}H_2O$ and 2.0 equivalents of Cs_2CO_3 under a dioxygen atmosphere (Table 1). At first, various solvents were screened for their influence on the reaction behaviour (Table 1, entries 1–6). The reaction in 1,4-dioxane or DMF afforded the desired product in only trace amounts. No product was observed when DMSO, CH_3NO_2 or toluene were used as solvent. To our delight, when acetonitrile was used as solvent, under an atmosphere of dioxygen, the α-arylthio ketone **3a** was obtained in 85% yield after 24 h at 130 °C (Table 1, entry 6). Alternative bases (Li_2CO_3, Na_2CO_3, K_3PO_4 and LiO-*t*-Bu) were then screened, however in these cases, only trace amounts of the product were identified, and Cs_2CO_3 was determined to be the ideal base for this transformation.

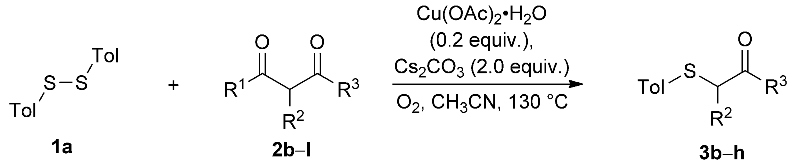
Next, alternative copper catalysts such as CuBr, $CuBr_2$ and $CuCl_2$ were screened, however these afforded **3a** in lower yields (Table 1, entries 7–9). In the absence of catalyst, α-arylthio ketone **3a** was obtained in 20% yield (Table 1, entry 10). Attempts to perform the reaction under an atmosphere of argon or air led to a drastic reduction in the yield of **3a** (Table 1, entries 11 and 12). Decreasing the reaction temperature to 110 °C also afforded **3a** in lower yield (Table 1, entry 13). Increasing the loading of **2a** to 4.0 equivalents led to the formation of α-arylthio ketone **3a** in 90% yield (Table 1, entry 14, 87% yield after column chromatography). Subsequently, with 4.0 equivalents of **2a**, CuI and $Cu(OTf)_2$ were probed as alternative copper sources, and product **3a** was isolated in 57% and 75% yields, respectively (Table 1, entries 15 and 16). Using anhydrous $Cu(OAc)_2$ as catalyst, **3a** was isolated in 77% yield (Table 1, entry 17).

With the optimized reaction conditions in hand (see footnote [a], Table 2), the scope of the reaction of β-diketones with di-*p*-tolyl disulfide (**1a**) was investigated. All the diaryl-substituted β-diketones employed in this study (**2b**, **2c** and **2g**) were readily synthesized from the corresponding acetophenones and methyl benzoates (see the Supporting Information), apart from dibenzoylmethane (**2a**), which was commercially available. Both aryl and alkyl β-diketones were compatible with this process (Table 2).

For β-diketones **2b** and **2c** the amount of solvent had to be increased (from 1 mL to 3 mL for a 0.5 mmol scale of **1a**) to obtain high yields of products **3b** and **3c** (87 % and 74 %, respectively, Table 2, entries 1 and 2). The reactions of alkyl-substituted β-diketones **2d** and **2e** as well as diethyl malonate (**2f**) with **1a** proceeded smoothly in accordance with the optimized reaction conditions using 1 mL solvent, affording products **3d–f** in excellent yields (Table 2, entries 3–5).

In order to determine which C–C bond was being cleaved preferentially, unsymmetrical β-diketone **2g**, bearing two aryl substituents with different stereoelectronic properties (*p*-CF_3- and *p*-MeO-), was applied and product **3c** was obtained in 75% yield (Table 2, entry 6). Substrate **2j** containing both a phenyl and a methyl substituent also reacted with **1a**, affording two products **3a** and **3d** in 30% and 61% yields, respectively (Table 2, entry 9). In the absence of acetonitrile, an excellent yield of α-thiophenyl carbonyl product **3f** (99%) was obtained using 10 mol% of catalyst and 10 equivalents of β-keto ester **2k** (Table 2, entry 10). Interestingly, for the substrate **2l**, bearing one methyl group in the α-position of the carbonyl, only trace amounts of product were obtained when the reaction was performed under an atmosphere of dioxygen. However, it was found that the C–C bond cleavage reaction proceeded to provide **3h** in

Table 2. Reactions of β-diketones with di-*p*-tolyl disulfide.[a]



Entry	R^1	R^2	R^3	Substrate	Product	Yield [%]
1	*p*-Tol	H	*p*-Tol	**2b**	**3b**	87[b]
2	*p*-MeO-C_6H_4	H	*p*-MeO-C_6H_4	**2c**	**3c**	74[b]
3	Me	H	Me	**2d**	**3d**	99[c]
4	Et	H	Et	**2e**	**3e**	95[c,d,e]
5	EtO	H	EtO	**2f**	**3f**	96[c]
6	*p*-CF_3-C_6H_4	H	*p*-MeO-C_6H_4	**2g**	**3c**	75[b]
7	CF_3	H	Me	**2h**	**3d**	85[c]
8	Me	H	NMe_2	**2i**	**3g**	88[c]
9	Me	H	Ph	**2j**	**3a/3d**	30/61
10	Me	H	EtO	**2k**	**3f**	99[c,d,e]
11	Me	Me	EtO	**2l**	**3h**	45[e,f]

[a] *Reaction conditions:* di-*p*-tolyl disulfide **1a** (0.5 mmol), β-dicarbonyl compound **2** (2.0 mmol, 4.0 equiv.), $Cu(OAc)_2{\cdot}H_2O$ (0.1 mmol, 0.2 equiv.), Cs_2CO_3 (1.0 mmol, 2.0 equiv), CH_3CN (1 mL), 130 °C, under an atmosphere of dioxygen, 24 h.

[b] Use of 3 mL of CH_3CN.

[c] Use of 10 equiv. of β-dicarbonyl compound, 16 h.

[d] Use of 0.1 equiv. of $Cu(OAc)_2{\cdot}H_2O$.

[e] Performed without acetonitrile.

[f] Performed on a 0.25 mmol scale with 10 equiv. of β-keto ester under an atmosphere of air.

45% yield, using an atmosphere of air in the absence of acetonitrile as solvent (Table 2, entry 11).

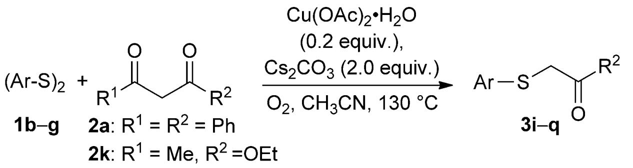
To further extend the substrate scope, the diaryl disulfide component **1** was varied to react with β-diketone **2a** and β-keto ester **2k** (Table 3). It was noteworthy that no solvent was needed for the reaction of **2k** with the corresponding disulfides. Furthermore, a lower catalyst loading (10 mol%) also promoted the process efficiently.

Accordingly, the coupling of **2a** and **2k** with diaryl-substituted disulfides (**1b–d**) provided **3i–n** in yields ranging from 75% to 99% (Table 3, entries 1–6). Substrate **1e** with an *o*-tolyl group also reacted well with **2k** to give **3o** in excellent yield, suggesting that steric factors on the arene group of the disulfide appear to play only a minor role in the success of the reaction process (Table 3, entry 7). As shown in previous examples, substrate **1f**, bearing an electron-withdrawing fluoro group in the 4-position, afforded **3p** in slightly lower, but still very satisfying yield (80%, Table 3, entry 8). The more bulky 2-naphthyl-substituted **1g** also provided the desired product **3q** in excellent yield (Table 3, entry 9).

Under the optimized reaction conditions, the reaction of dibenzyl disulfide (**1h**) with β-diketone **2a** was also examined. However, with this substrate combination, the expected C–C bond cleavage did not occur. Instead, the *in situ* reduction of one carbonyl group was observed, providing **3r** in 45% yield (Scheme 2).

To gain further understanding of this reaction process, additional investigations were performed (Scheme 3). Following analysis of the crude reaction

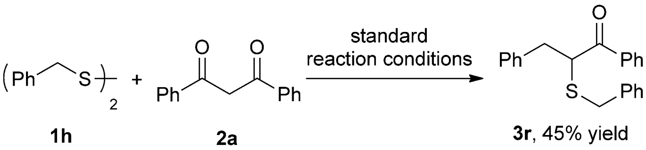
Table 3. The scope of thioarylation of β-diketones with diaryl disulfides.[a]



Entry	Ar=	Substrate	Product	Yield [%]
1	Ph (**1b**)	**2a**	**3i**	99
2	*p*-MeO-C_6H_4 (**1c**)	**2a**	**3j**	81
3	*p*-Cl-C_6H_4 (**1d**)	**2a**	**3k**	93
4	Ph (**1b**)	**2k**	**3l**	88[b]
5	*p*-MeO-C_6H_4 (**1c**)	**2k**	**3m**	85[b]
6	*P*-Cl-C_6H_4 (**1d**)	**2k**	**3n**	75[b]
7	*o*-Tol (**1e**)	**2k**	**3o**	98[b]
8	*p*-F-C_6H_4 (**1f**)	**2k**	**3p**	80[b]
9	2-naphthyl (**1g**)	**2k**	**3q**	92[b]

[a] *Reaction conditions:* diaryl disulfide **1** (0.5 mmol), β-dicarbonyl compound **2** (4.0 equiv.), $Cu(OAc)_2{\cdot}H_2O$ (0.2 equiv.), Cs_2CO_3 (2.0 equiv.), 130 °C, dioxygen atmosphere, 24 h.

[b] Use of 10 equiv. of **2k**, without acetonitrile as solvent, 0.1 equiv. of $Cu(OAc)_2{\cdot}H_2O$, 16 h.

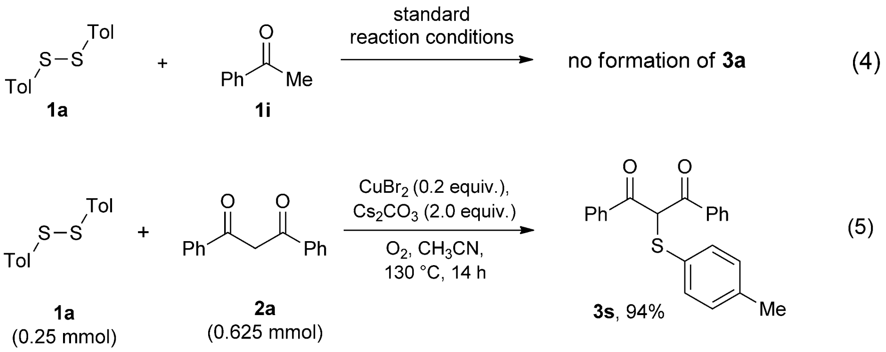


Scheme 2. Reaction of dibenzyl disulfide (**1h**) with β-diketone **2a**.

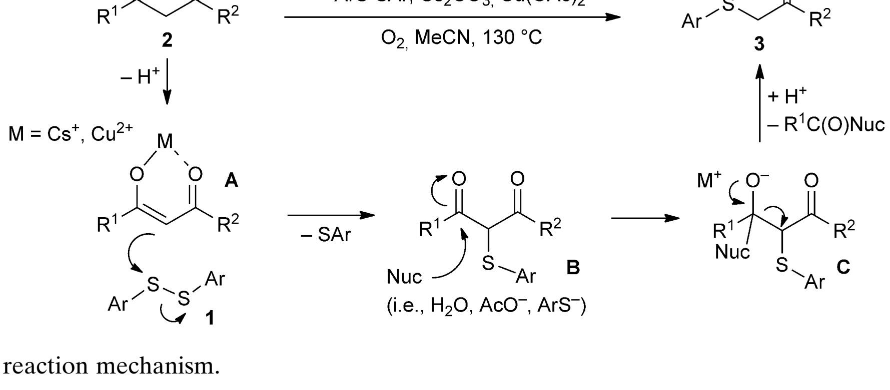
mixture by GC-MS the formation of acetophenone (**1i**) as a by-product in this reaction was observed.[15] The formation of **1i** was also detected when the reaction was carried out in the absence of diaryl disulfide (**1a**). However, the possibility of this reaction proceeding through an acetophenone intermediate (**1i**) was excluded using a control reaction [Scheme 3, Eq. (4)].[6] In another example, product **3s** was isolated in 94% yield using 2.5 equivalents of **2a** and 0.2 equivalents of CuBr with a reaction time of only 14 h [Scheme 3, Eq. (2)]. In this case, cleavage of the C–C bond did not take place.

For this process we postulate the reaction mechanism depicted in Scheme 4. A metal enolate species **A** is formed by deprotonation of **2** by the base. We assume that initially a cesium enolate is formed which can undergo transmetallation by reacting with copper(II) acetate (Scheme 4). Intermediate **A** then attacks the diaryl disulfide **1** cleaving the S–S bond to afford intermediate **B**. The C–C bond cleavage takes place following the attack of a nucleophilic species (of unknown nature) to the most electron deficient carbonyl group to form intermediate **C**, which then decomposes to afford the final product **3**. Both the copper catalyst and oxygen play a role, but their exact impact remains unclear at this stage. With regard to the nucleophile responsible for the initiation of the C–C bond cleavage process we hypothesize that residual water, acetate ions (from the catalyst or hydrolysis of acetonitrile at elevated temperatures) or a sulfur derivative are involved.[10a] That residual water is significant in the sequence is supported by the observation that the yield decreased slightly when anhydrous copper(II) acetate was employed as catalyst (Table 1, entry 15) and the yield increased significantly when acetonitrile that was not rigorously dried was used.[16]

In conclusion, we have developed a new approach to prepare a series of valuable α-arylthio ketones and α-arylthio esters starting from diaryl disulfides and β-diketones (or β-keto esters). In this process, the cleavage of both C-C and S–S bonds occurs efficiently in the presence of a copper catalyst and a dioxygen atmosphere. Both alkyl- and aryl-functionalized β-dike-



Scheme 3. Control reactions carried out.



Scheme 4. Proposed reaction mechanism.

tones/β-keto esters, as well as a variety of diaryl disulfides are well tolerated. From an economical and environmental perspective, this method provides an exciting alternative for the synthesis of α-arylthio carbonyl compounds, allowing the use of expensive and toxic halogenated carbonyl derivatives to be minimized.

Experimental Section

General Procedure for the Synthesis of Phenacyl *p*-Tolyl Sulfide (3a) starting from Di-*p*-tolyl Disulfide (1a) and Dibenzoylmethane (2a)

A 10-mL sealed tube equipped with a magnetic stirring bar was charged with **1a** (123 mg, 0.5 mmol), **2a** (448.5 mg, 2 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and $Cu(OAc)_2 \cdot H_2O$ (20.0 mg, 0.1 mmol). The aperture of the tube was then covered with a rubber septum, and purged using a dioxygen flow for 5 min. After the addition of acetonitrile (1 mL) by syringe, the septum was quickly replaced by a teflon-coated screw cap, and the reaction vessel was placed in a preheated oil bath at 130 °C and stirred for 24 h. It was cooled to room temperature and diluted with ethyl acetate. The resulting solution was directly filtered through a filter paper and concentrated under reduced pressure. Purification by flash chromatography (pentane/ethyl acetate = 20:1) gave **3a** as a yellow liquid; yield: 105.4 mg (0.435 mmol, 87%). A yellow solid was obtained following recrystallization from ethanol, mp 38–39 °C.

Acknowledgements

L.-H.Z. and J.M. thank the Chinese Scholarship Council (CSC) and the NRW Graduate School BrenaRo for predoctoral stipends, respectively. D.L.P. is grateful to the Alexander von Humboldt Foundation for a postdoctoral fellowship.

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[16] With HPLC grade acetonitrile instead of extra dry acetonitrile as solvent, the desired product **3a** was isolated in 98% yield. This implied that trace amounts of water might play an active role in the reaction.

Copper-Catalyzed Synthesis of α-Thioaryl Carbonyl Compounds Through S–S and C–C Bond Cleavage

Adv. Synth. Catal. **2013**, *355*, 1 – 7

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