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Copper-Catalyzed Aerobic Formation of Unstable Sulfinyl Radicals for the Synthesis of Sulfinates and Thiosulfonates

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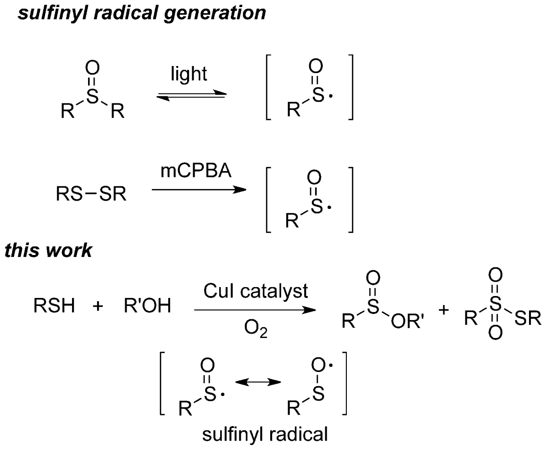
Abstract: Copper-catalyzed aerobic coupling of thiols and alcohols affords sulfinates and thiosulfonates. These products are assumed to form *via* sulfinyl radicals which are not commonly found in oxidative coupling reactions of thiols. A reaction mechanism involving sulfinyl radicals is proposed, and mass and electron paramagnetic resonance (EPR) experimental results are provided.

Keywords: aerobic oxidation; copper; sulfinates; sulfinyl radicals; thiosulfonates

The oxidation of sulfur compounds is one of the most important reactions in synthetic chemistry, biological processes, and environmental and material industries.[1] Sulfinyl radicals are proposed to form during the aerobic oxidation of biologically abundant thiols (e.g., cysteine and glutathione) *in vivo*, which is associated with the malfunction of oxidized biomolecules.[2] Other than these biological reactions, synthetic methods for the generation of sulfinyl radicals have not been intensively studied. During photo-cleavage of sulfoxides, thermolysis of sulfinimines, and oxidation of disulfides, vicinal disulfoxides and thiosulfonates are formed, which is considered to be evidence of the presence of sulfinyl radical intermediates (Scheme 1).[3]

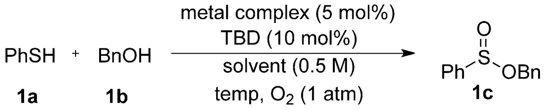
Copper-catalyzed aerobic oxidation has been applied to the modification of thiols, due to the environmentally friendly nature of this catalytic system.[4] Disulfide formation and C–S/P–S/N–S/S–S bond formation are frequently reported examples.[5] Despite intensive research on copper-catalyzed aerobic coupling of thiols, the formation of sulfinyl radicals by currently known methods has not been reported, which encouraged us to attempt the direct oxidation of thiols to sulfinyl radicals.

Sulfinates are widely utilized as versatile sulfinylating agents in the synthesis of a diverse range of organosulfur compounds including sulfoxides and sulfinamides,[6,7,8] which justifies the development of various synthetic protocols for sulfinates. Generally, sulfinates are synthesized by alkylation of sulfinic acid (or sodium sulfinate), substitution of sulfinyl chloride with alcohols, or oxidative coupling of disulfides with alcohols using stoichiometric amounts of oxidants, e.g., *N*-bromosuccinimide (NBS), phenyliodine bis(trifluoroacetate) (PIB), or $Pb(OAc)_4$.[9] Since the pioneering synthesis of sulfinates *via* sulfinyl chloride was reported by Douglass in 1965,[9a] catalytic reaction conditions for the direct synthesis of sulfinates from thiols have not been reported. Herein, a copper-catalyzed aerobic coupling of thiols and alcohols to afford sulfinates is presented, in which the direct oxidation of thiols to sulfinyl radicals occurs, followed by S–O bond formation.[10] In the absence of alcohols, the catalytic system using copper salts induces the formation of thiosulfonates *via* sulfinyl radicals (Scheme 1).



Scheme 1. Generation of sulfinyl radical intermediates.

Table 1. Optimization of the conversion of **1a** to **1b**.

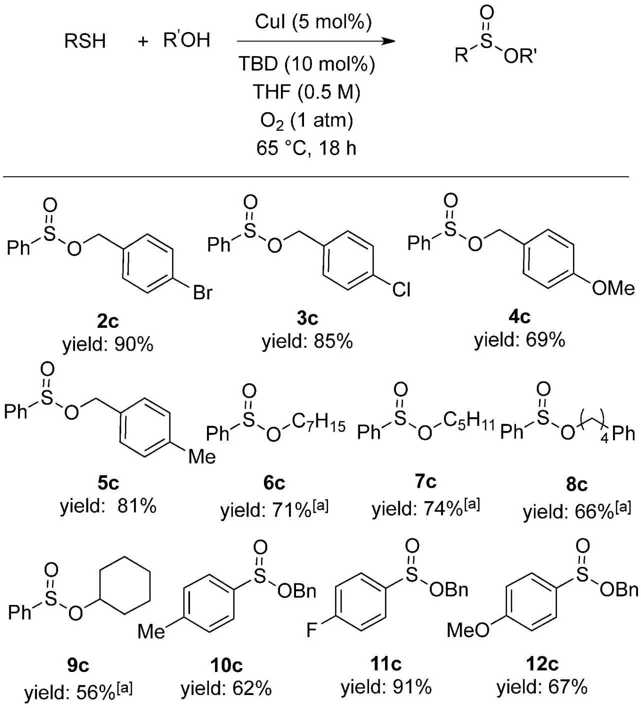


Entry	Metal Complex	Solvent (Temp. [°C])	Yield
1	CuI	toluene (100)	74% (0%)[a]
2	CuI	toluene (100)	0%[b]
3	CuI-TEMPO	toluene (100)	67%
4	CuI-2,2′-bipy	toluene (100)	60%
5	CuI-1,10-phen	toluene (100)	57%
6	CuBr	toluene (100)	48%
7	CuSPh	toluene (100)	41%
8	$CuBr_2$	toluene (100)	35%
9	CuI	dioxane (100)	77%
10	CuI	THF (65)	83%
11	CuI	CH_3CN (80)	60%
12	CuI	DMF (100)	33%
13	CuI	DMSO (100)	0%
14	–	THF (65)	0%

[a] The reaction was run under nitrogen atmosphere

[b] No TBD.

Based on our previous work on copper-catalyzed reactions of benzyl thiols and alcohols,[10] optimization was performed on the reaction of thiophenol **1a** and benzyl alcohol **1b** in the presence of CuI (5 mol%) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 10 mol%) at 100 °C under 1 atm of oxygen (see Table 1). A reaction mixture of **1a** and **1b** was subjected to the above conditions to provide **1c** in 74% yield (Table 1, entry 1). In the absence of oxygen, the desired coupling did not occur (Table 1, entry 1). When the reaction is conducted without TBD, **1c** is not obtained (Table 1, entry 2). Other than TBD, the strong organic bases 1,8-diazabicycloundec-7-ene, 1,1,3,3-tetramethylguanidine, and 1,3-diphenylguanidine, afford **1c** in 13%, 3%, and 1% yield, respectively. The inorganic base KO-*t*-Bu does not promote this transformation. To modulate the oxidation activity of copper salts, catalytic amounts (5 mol%) of 2,2,6,6-tetramethylpiperidinyl 1-oxy (TEMPO), 2,2′-bipyridine (2,2′-bipyr), and 1,10-phenanthroline (1,10-phen) were used, but the yield of **1c** did not increase (Table 1, entries 3–5). Next, copper salts were checked; CuBr, CuSPh, and $CuBr_2$ catalyzed the reaction to provide **1c** in 48%, 41%, and 35% yield, respectively (Table 1, entries 6–8). The effect of solvents was also investigated. Dioxane, THF, CH_3CN, DMF, and DMSO were employed in this reaction (Table 1, entries 9–13). The reaction in THF shows the highest yield even at a lower reaction temperature (Table 1, entry 10). In the absence of copper salts, the formation of **1c** does not occur (Table 1, entry 14).

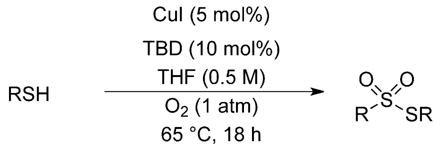


[a] 1 equiv. of TBD was used.

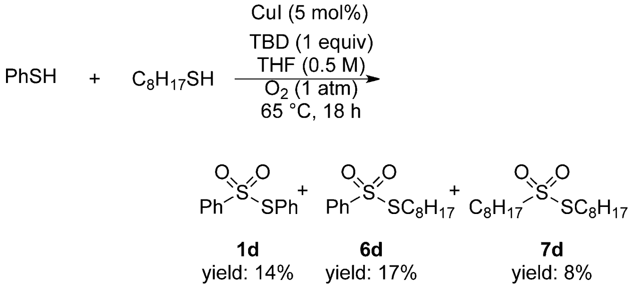
Figure 1. The substrate scope for sulfinate formation.

The substrate scope of the reaction was also explored (see Figure 1). Halogen-substituted benzyl alcohols react with thiophenols to afford the desired sulfinates **2c** and **3c** in 90% and 85% yield, respectively. The reaction using electron-rich methoxy-substituted benzyl alcohol shows a decreased yield, compared to halogen- and methyl-substituted alcohols. In the case of aliphatic alcohols, the amount of TBD was increased to 1 equivalent. Heptanol and pentanol are efficiently transformed to **6c** and **7c** in 71% and 74% yield, respectively. An aliphatic alcohol possessing a phenyl group affords **8c** in 66% yield. The use of sterically hindered cyclohexanol results in a decreased yield (56%). In addition to thiophenol, methyl-, fluoro-, and methoxy-substituted thiophenols also reacted with benzyl alcohols to form the desired products **10c**, **11c**, and **12c** in 62%, 91%, and 67% yield, respectively. The reactions of aliphatic thiols with benzyl alcohols were conducted. As reported by us,[10] benzyl mercaptan undergoes the oxidation to form thioaldehydes, which react with benzyl alcohols to afford benzyl benzoates *via* oxidative esterification followed by S-O exchange. A less reactive aliphatic thiol, octyl thiol was subjected to the optimized conditions to form only dioctyl disulfide. Heteroaromatic thiols (2-mercaptobenzimidazole, 2-mercaptopyrimidine, and 4-mercaptopyridine) were exposed to the optimized conditions. 2-Mercaptobenzimidazole did not participate in the reaction, to recover starting materials. 2-Mercaptopyrimidine and 4-mercaptopyridine form thioethers in low yields (see the Supporting Information).

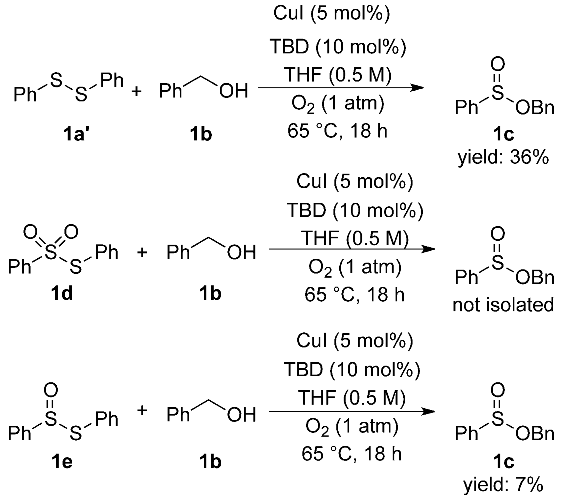
Table 2. Examples of the thiosulfonates.



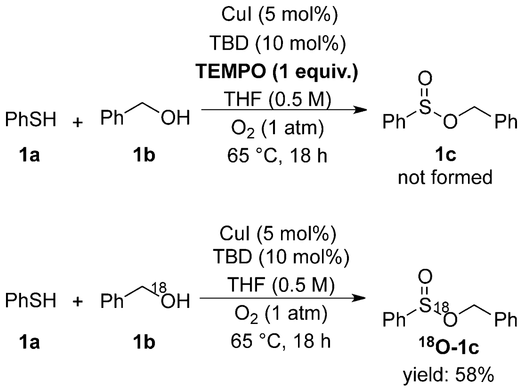
Entry	R	Yield
1	C_6H_5	85% (**1d**)
2	*p*-ClC_6H_4	81% (**2d**)
3	*p*-FC_6H_4	89% (**3d**)
4	*p*-$CH_3C_6H_4$	76% (**4d**)
5	*p*-$CH_3OC_6H_4$	86% (**5d**)



Scheme 2. Reactions of thiophenol and octyl thiol.



Scheme 3. Reactions of disulfide, thiosulfonate, and thiosulfinate with benzyl alcohol.



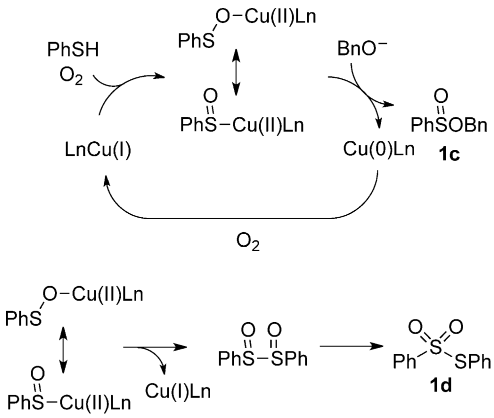
Scheme 4. Control experiments.

During the reaction of thiols and alcohols, we observed thiosulfonates as minor products, which become the major products in the absence of alcohols. As shown in Table 2, various aromatic thiols undergo oxidative dimerization to form thiosulfonates (**1d**–**5d**) in good yields. In addition to dimerization of thiols, a cross-coupling reaction using thiophenol (1 equiv.) and octylthiol (1 equiv.) was conducted (Scheme 2). Three different thiosulfonates are formed by homo-dimerization and cross-coupling reaction under the indicated conditions. The homo-dimerization of octyl thiols to form thiosulfonates in the absence of thiophenols was attempted, but dioctyl disulfides were observed.

Because the CuI-catalyzed reaction of thiols provides sulfinates in the presence of alcohols, and thiosulfonates in the absence of alcohols, it is proposed that sulfinates might be formed by the reaction of oxidized thiol intermediates with alcohols (Scheme 3). First, diphenyl disulfide **1a′** was employed under the optimized reaction conditions to form **1c** in 36% yield. Thiosulfonate **1d**, which was isolated from the reaction in the absence of alcohols, was also subjected to the catalytic reaction and found to show no sulfinate formation. Finally, thiosulfinate **1e**, which was synthesized independently, reacts with benzyl alcohol **1b** to form **1c** in 7% yield.[11] According to these experiments, sulfinate **1c** is not formed from either thiosulfonates or thiosulfinates. Disulfide **1a′** might participate in the reaction with alcohols after being dissociated into the corresponding thiophenol by copper catalysts.[12]

To explore the reaction mechanism further, 2,2,6,6-tetramethylpiperidinyl 1-oxyl (TEMPO) as a radical scavenger was added to the reaction mixture (Scheme 4). Instead of forming **1c**, diphenyl disulfides were formed.[13] ^{18}O-Labelled benzyl alcohol was used to probe the source of oxygen incorporated into the S=O bonds, to confirm that oxygen from O_2 is incorporated into the S=O bond.

In accordance with the control experimental results, a reaction mechanism is proposed in Scheme 5. The reaction begins with the copper-catalyzed oxidation of thiophenol to a sulfinyl radical.[2,5m] The sulfinyl radical may form a sulfinyl-Cu(II) complex. The sulfinyl-Cu(II) complex undergoes S−O bond formation with alcohols to form **1c**. The sulfinyl radical dissociated from the Cu(II) complexes undergoes dimerization to afford 1,2-disulfoxides. The unstable 1,2-disulfoxide isomerizes to **1d**. The formation of **1d** along with **1c**



Scheme 5. Reaction mechanisms to form **1c** and **1d**.

implies the existence of sulfinyl radicals in this aerobic coupling reaction.[3] The mass spectrum of the reaction mixture using **1a** also shows the fragments of sulfinyl species (see the Supporting Information). The electron paramagnetic resonance (EPR) spectra shown in Figure 2 provide evidence of copper(II) species possessing a sulfinyl ligand. For the EPR measurements, the copper-catalyzed reaction of **1a** and **1b** was quenched after 6 and 10 h, respectively, by cooling the reaction cell in liquid nitrogen. Both EPR spectra shown in Figure 2 are very similar, except with respect to the absolute intensity, suggesting a change in the population of the Cu(II) species only. The detailed spectral features clearly indicate the presence of a paramagnetic species with $S=\frac{1}{2}$, localized to a Cu(II) ion with $I=3/2$. The appearance of a series of peaks at 315, 296 and 278 mT originates from a high axial nuclear hyperfine constant (A_z) of the nucleus, as well as a large g_z value. The A_z and g_z values determined from the simulated EPR spectrum are 585 MHz and 2.254, respectively. The large A_z value is due to the characteristically large hyperfine coupling along g_z of the Cu(II) ion. In addition, a value of g_z larger than g_x (or g_y) is largely associated with a stabilization of the d_{z^2} orbital, possibly through a lengthening of the bond along the z axis,[14] as is known for $Cu(H_2O)_6^{2+}$ ($g_z=2.4$).[15] The g_z value is strongly dependent on the local bonding environment. Sulfur coordination has been reported to lower the g_z value to 2.16.[5g] The measured g_z value of 2.254 in our case, is quite close to that of sulfur coordinated Cu(II) complexes, but is definitely higher than the case of sulfur alone. Thus, it is inferred that the measured g_z value is due to the binding of the Cu(II) ion to a sulfinyl radical, which is represented as two resonance forms (Scheme 5).

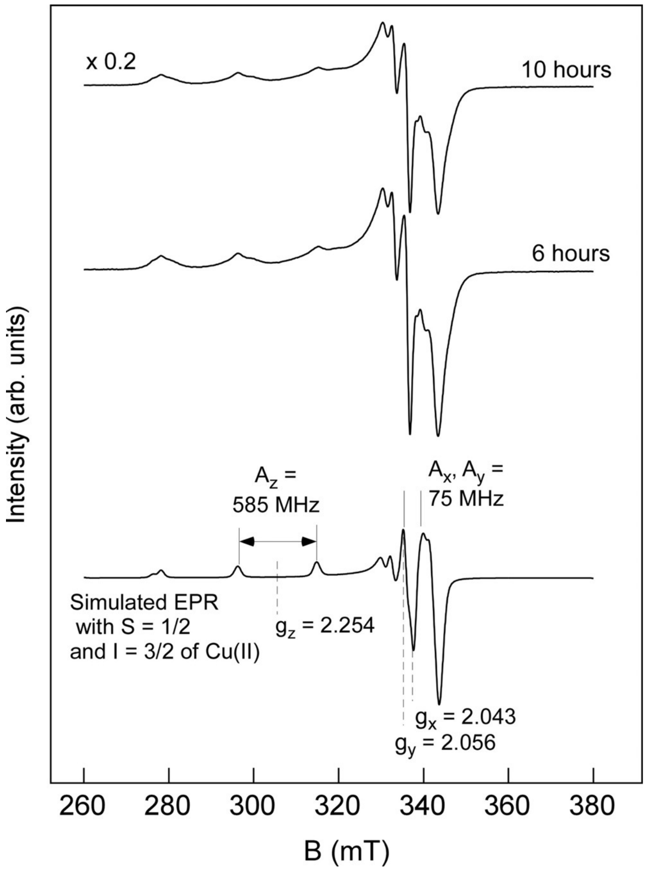


Figure 2. EPR spectra taken from the reaction mixture after quenching at 6 and 10 h, respectively. Also shown is the simulated EPR spectrum with $S=1/2$ and $I=3/2$ for Cu(II) species using *EasySpin*.[16]

In conclusion, the direct copper-catalyzed aerobic oxidation of thiolphenols to generate sulfinyl radicals was investigated. Compared to thiyl radicals ($RS^{\bullet}$), sulfinyl radicals ($RSO^{\bullet}$) are not often observed during catalytic oxidative reactions. In this study, the judicious choice of copper catalysts and TBD additives allowed the trapping of sulfinyl radicals to afford sulfinates and thiosulfonates in modest to good yields. The presence of sulfinyl radicals was supported by mass spectral and EPR analysis. The involvement of the sulfinyl-Cu(II) complex during the reaction was supported by EPR analysis.

Experimental Section

Representative Procedure for the Synthesis of 1c

A mixture of thiophenol (159 μL, 1.5 mmol), benzyl alcohol (52 μL, 0.50 mmol), CuI (4.8 mg, 0.025 mmol) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (7.1 mg, 0.05 mmol) in THF (1 mL) was stirred at 65 °C for 18 h under 1 atmosphere of oxygen. The solvent was removed with a rotary evaporator, and the residue was purified by column chromatography on a silica gel eluting with hexane and ethyl acetate (hexane: ethyl acetate = 98:2) to afforded **1c**; yield: 96.5 mg (83%). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=7.76$–7.73 (2H, m), 7.55–7.51 (3H, m), 7.34–7.24 (5H, m), 5.05 (1H, d, $J=11.6$ Hz), 4.58 (1H, d, $J=11.6$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=144.5, 135.3, 132.2, 129.0, 128.5, 128.4, 125.3, 66.0; HR-MS (EI): m/z=232.0557 ([M]$^+$), calcd. for $C_{13}H_{12}O_2S$: 232.0558; FT-IR (neat): ν=3062, 2945, 1598, 1476, 1132 cm^{-1}.

Supporting Information

Detailed experimental procedures and spectra of products are provided in the Supporting Information.

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