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"Ligand-Free" CuI-Catalyzed Highly Efficient Intramolecular S-Vinylation of Thiols with Vinyl Chlorides and Bromides

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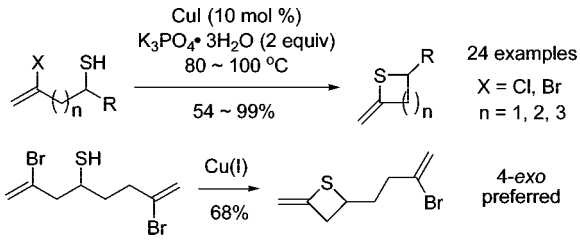

With CuI as the catalyst and $K_3PO_4 \cdot 3H_2O$ as the base, highly efficient intramolecular S-vinylation of thiols with vinyl chlorides or bromides was successfully implemented without the help of an additional ligand. Moreover, the competition experiments revealed that the 4-*exo* cyclization is fundamentally preferred over other modes (5-*exo*, 6-*exo*, and 6-*endo*) of cyclization.

Heterocyclic thioenol ethers are a group of sulfur heterocycles with important biological interest.[1] For example, the vinyl sulfide cyclized analogues of the octapeptide angiotension II show the agonist activity with K_i values less than 2 nM.[1c] Another typical example is Griseoviridin, which contains a nine-membered cyclic vinyl sulfide moiety and serves as a broad-spectrum antibiotic.[1d] In the meantime, heterocyclic thioenol ethers are also useful intermediates in organic synthesis.[1−5] Conjugated cyclic thioenol ethers have been used as precursors for the synthesis of substituted cyclopentenones via Ramberg−Bäcklund reactions.[2] They are also effective substitutes for unreactive *cis*-dienes in Diels−Alder reactions.[3] Vedejs et al. utilized the 1,4-addition of an amine to dihydrothiopyran-4-ones to construct the eight-membered ring intermediate for the synthesis of pyrrolizidine alkaloid octonecine.[4] More recently, Oh reported the synthesis of the biotin core from a simple cyclic vinyl sulfide.[5] Despite the significance of heterocyclic thioenol ethers in organic chemistry, methods for their synthesis are few and are dominated by the intramolecular nucleophilic substitution[6] or thio-Michael addition[7] reactions. Other methods include the iodocyclization of alkynyl sulfides,[8] the nickel-catalyzed electroreduction of unsaturated thioacetates and thiosulfonates,[9] as well as indirect methods that do not involve the formation of C−S bonds.[10] These strategies suffer from either low efficiency or limited scope of application. It is therefore highly desirable to develop efficient and general methods for the preparation of heterocyclic thioenol ethers. We report here that the copper-catalyzed intramolecular S-vinylation of thiols with vinyl chlorides or bromides provides a convenient and efficient entry to 2-alkylidene-substituted thietanes, tetrahydrothiophenes, and tetrahydro-2*H*-thiopyrans.

Metal-catalyzed C−S bond formations have played an important role in organosulfur chemistry.[11] With the renaissance of Ullmann coupling in the past few years,[12] the copper-catalyzed cross-coupling reactions of thiols and aryl halides have been demonstrated to be a powerful tool in the formation of aryl C−S bonds.[13] By the appropriate choice of copper source, ligand, and base, these coupling reactions have been developed to include a wide range of substrates under mild conditions.[13] The high stability and low cost of the copper catalysts, along with the easy availability of the ligands, make these transformations a superior choice in organic synthesis.[14] This method was then successfully extended to the intermolecular S-vinylation of thiols with vinyl iodides or bromides.[15] However, the

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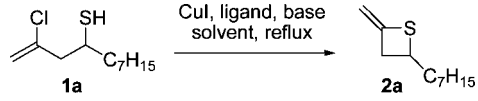
TABLE 1. Optimization of the Synthesis of 2a from 1a



1a **2a**

entry[a]	ligand[b]	base	solvent	yield (%)[c]
1	A	Cs_2CO_3	THF	0
2	A	Cs_2CO_3	CH_3CN	trace
3	A	Cs_2CO_3	dioxane	77
4	B	Cs_2CO_3	dioxane	66
5	C	Cs_2CO_3	dioxane	73
6	D	Cs_2CO_3	dioxane	78
7	E	Cs_2CO_3	dioxane	69
8	F	Cs_2CO_3	dioxane	78
9	F	K_2CO_3	dioxane	71
10	F	$K_3PO_4 \cdot 3H_2O$	dioxane	86
11	F	DABCO	dioxane	80
12	**none**	**$K_3PO_4 \cdot 3H_2O$**	**dioxane**	**86**
13	none	none	dioxane	0
14[d]	none	$K_3PO_4 \cdot 3H_2O$	dioxane	0

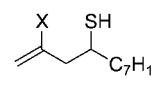
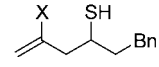
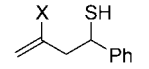
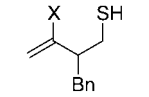
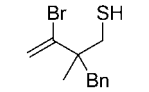
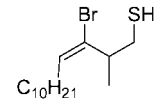
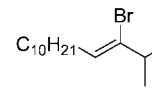
[a] Reaction conditions: **1a** (0.3 mmol), CuI (0.03 mmol), ligand (0.06 mmol), base (0.6 mmol), solvent (3 mL), reflux, 6 h. [b] A: 1,10-phenanthroline. B: *N*,*N*′-dimethylethylenediamine. C: 3,4,7,8-tetramethyl-1,10-phenanthroline. D: $Me_2NCH_2CO_2H \cdot HCl$. E: L-proline. F: triphenylphosphine. [c] Isolated yield based on **1a**. [d] No CuI was used.

corresponding intramolecular S-vinylation remains virtually unexplored. Owing to our interest in Cu(I)-catalyzed intramolecular vinylation reactions,[16] we set out to pursue this possibility.

Thus, 2-chloroundec-1-ene-4-thiol (**1a**), which was readily prepared from the corresponding homoallylic alcohol via conventional methods, was used as the model substrate for the optimization of reaction conditions. The results are summarized in Table 1. Substrate **1a** was first subjected to the following typical conditions for Ullmann coupling: 10 mol % of CuI, 20 mol % of 1,10-phenanthroline (**A**), 2 equiv of Cs_2CO_3, THF, reflux. No reaction occurred. Increasing the temperature to 80 °C (CH_3CN, reflux) did not help. However, when the reaction was carried out in refluxing dioxane for 6 h, the expected coupling product **2a** was achieved in 77% yield along with 22% of **1a** recovered. We then screened the ligands.[17] Surprisingly, all the ligands screened (**A**−**F**) gave similar results (entries 3−8, Table 1). We next examined the effects of different bases. Again, almost no difference could be observed (entries 8−11, Table 1). These results let us suspect that the ligands might not participate in the coupling reaction at all because dramatically different effects of ligands are usually observed in Ullmann coupling. Indeed, we were pleased to find that, in the absence of a ligand, the C−S coupling proceeded smoothly (entry 12, Table 1). On the other hand, without CuI or a base, no cyclization product could be obtained (entries 13 and 14, Table 1). The above data also suggested that the substrate thiol itself functions as the ligand. Since thiols bind to Cu(I) more strongly than many other ligands,[18] the presence of an additional ligand (**A**−**F**) did not make a difference.

The above optimized conditions (10 mol % of CuI, 2 equiv of $K_3PO_4 \cdot 3H_2O$, dioxane, reflux) were then applied to the reactions of a variety of homoallylic thiols **1b**−**1k**, and the results are summarized in Table 2. In all the cases tested, the expected 4-*exo* cyclization product thietanes **2** were achieved

TABLE 2. Synthesis of 2-Alkylidenethietanes 2

entry[a]	substrate		product (time, yield)[b]
1		**1a** (X = Cl)	**2a** (2.5 h, 90%)
2		**1b** (X = Br)	**2a** (0.5 h, 88%)
3		**1c** (X = Cl)	**2c** (2.5 h, 85%)
4		**1d** (X = Br)	**2c** (0.5 h, 80%)
5		**1e** (X = Cl)	**2e** (1.5 h, 93%)
6		**1f** (X = Br)	**2e** (0.5 h, 90%)
7		**1g** (X = Cl)	**2g** (2 h, 92%)
8		**1h** (X = Br)	**2g** (0.5 h, 90%)
9		**1i**	**2i** (0.5 h, 92%)
10		**1j**	**2j** (0.5 h, 99%)
11		**1k**	**2k** (0.5 h, 99%)

[a] Reaction conditions: **1** (0.3 mmol), CuI (0.03 mmol), $K_3PO_4 \cdot 3H_2O$ (0.6 mmol), solvent (3 mL), reflux. Dioxane was used as the solvent for the reactions of chlorides while acetonitrile was used as the solvent for the reactions of bromides. [b] Isolated yield based on **1**.

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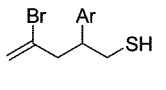
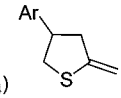
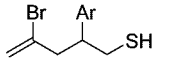
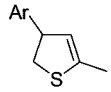
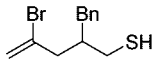
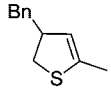
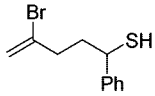
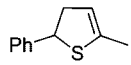
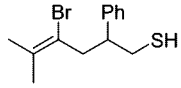
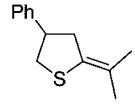
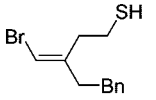
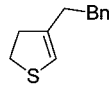
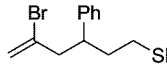
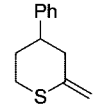
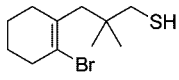
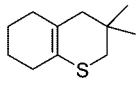
TABLE 3. Intramolecular S-Vinylation of Thiols 3

entry[a]	substrate	product (time, yield)[b]
1	 **3a** (Ar = Ph)	 **4a** (0.5 h, 88%)
2	**3b** (Ar = *p*-MeOC$_6$H$_4$)	**4b** (0.5 h, 86%)
3	 **3c** (Ar = *p*-CF$_3$C$_6$H$_4$)	 **4c** (0.5 h, 81%)
4	 **3d**	 **4d** (0.5 h, 70%)
5	 **3e**	 **4e** (0.5 h, 54%)
6	 **3f**	 **4f** (0.5 h, 81%)
7	 **3g**	 **4g** (1 h, 92%)
8	 **3h**	 **4h** (5 h, 70%)
9	 **3i**	 **4i** (24 h, 60%)

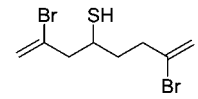
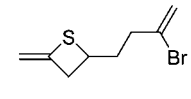
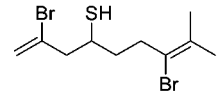
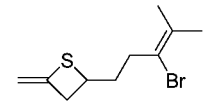
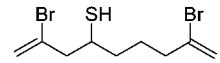
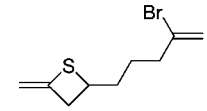
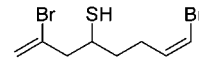
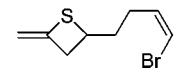
[a] Reaction conditions: **3** (0.3 mmol), CuI (0.03 mmol), $K_3PO_4 \cdot 3H_2O$ (0.6 mmol), CH_3CN (3 mL), reflux. [b] Isolated yield based on **3**.

in good to excellent yields. Vinyl bromides were more reactive than the corresponding chlorides, and their reactions proceeded at a lower temperature (CH_3CN, reflux) and were complete within a shorter period of time. The configuration of the C=C bond was nicely retained as evidenced by the reactions of **1j** and **1k** (entries 10 and 11, Table 2). Primary thiols had a performance similar to that of secondary thiols. Tertiary thiols were not screened because of their difficult preparations. It should be noted that the intermolecular C−S coupling reported in the literature[13,14] required the use of alkenyl iodides or bromides, and the reactions were typically performed at 80−110 °C. Thus, the successful S-vinylation with alkenyl chlorides shown above clearly demonstrated the ease of the S-vinylation via a 4-*exo* mode of cyclization.

The above strategy was then extended to the C−S bond formation via other modes of cyclization (Table 3). Thiols **3a** and **3b** underwent 5-*exo* cyclization in refluxing CH_3CN to afford the desired products **4a** and **4b** in high yields. The reactions of substrates **3c**−**3e** also proceeded smoothly, and the expected 2-methylenetetrahydrothiophenes, which could be observed by their crude NMR spectra, isomerized during flash chromatography on basic alumina to give products **4c**−**4e**, respectively. The *gem*-dimethyl substitution helped to stabilize the exocyclic double bond in **4f**, and no isomerization could be observed. Other than 5-*exo* cyclization, the 5-*endo* (**3g**), 6-*exo* (**3h**), and 6-*endo* (**3i**) ring closure were also successful under the optimized conditions.

The above results clearly demonstrated the efficiency of copper catalysis in the intramolecular S-vinylation of thiols.

TABLE 4. Preference of 4-*exo* Ring Closure

entry[a]	substrate	product	yield (%)[b]
1	 **5a**	 **6a**	68
2	 **5b**	 **6b**	85
3	 **5c**	 **6c**	82
4	 **5d**	 **6d**	83

[a] Reaction conditions: **5** (0.3 mmol), CuI (0.03 mmol), $K_3PO_4 \cdot 3H_2O$ (0.6 mmol), CH_3CN (3 mL), reflux, 0.5 h. [b] Isolated yield based on **5**.

Among various modes of cyclization investigated, the 5-*exo* cyclization seemed to have a rate comparable to that of the corresponding 4-*exo* cyclization, while a relatively longer reaction time was required for 6-*exo* or 6-*endo* cyclization. We recently reported that 4-*exo* ring closure is fundamentally preferred in the Cu(I)-catalyzed O- and N-vinylation.[15d,f] It is therefore interesting to see if this is also the case in the S-vinylation of thiols. Thus, dibromides **5a**−**5d**, each having two possible modes of cyclization, were prepared and subjected to the optimized conditions. We were delighted to find that, in all the cases, only the corresponding 4-*exo* cyclization products **6a**−**6d** were achieved, respectively (Table 4). These competition experiments clearly illustrated that the 4-*exo* cyclization is intrinsically favored over the 5-*exo* (**5a** and **5b**), 6-*exo* (**5c**) and 6-*endo* (**5d**) cyclization. The results in Table 4, along with our previous observations,[15d,f] strongly indicated that the preference of the uncommon 4-*exo* ring closure is a common phenomenon in Cu(I)-catalyzed vinylation reactions. Although the reason for such a preference remains unclear, it could be possible that the transition state for 4-*exo* cyclization as a Cu-containing five-membered ring is sterically more accessible. Theoretical analyses on this assumption are currently underway in our laboratory and will be reported in due course.

In conclusion, the Cu(I)-catalyzed intramolecular S-vinylation of thiols with vinyl halides has been investigated for the first time. Our efforts have revealed that these coupling processes are highly efficient under mild and "ligand-free" conditions, allowing the use of vinyl chlorides as the substrates. More importantly, the 4-*exo* ring closure is fundamentally preferred over other modes of cyclization, illustrating the unique property of Cu(I) catalysis. Furthermore, the assumption that the substrate thiols also act as the ligands should encourage the exploration of sulfur-based ligands for more effective Ullmann coupling, which is currently pursued in our laboratory.

Experimental Section

Typical Procedure for the Copper-Catalyzed S-Vinylation of Thiols with Vinyl Halides. The mixture of 2-chloroundec-1-ene-4-thiol (**1a**, 66 mg, 0.3 mmol), CuI (5.7 mg, 0.03 mmol), and $K_3PO_4 \cdot 3H_2O$ (160 mg, 0.6 mmol) in dioxane (3 mL) was refluxed for 6 h under nitrogen atmosphere. The resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated in

vacuo, and the crude product was purified by flash chromatography on basic alumina with hexane/Et_3N (100:1, v/v) as the eluent to give the pure product **2a** as a colorless oil: yield 48 mg (86%); IR (film) ν (cm^{-1}) 2956, 2926, 2855, 1632, 1466, 1131, 829, 722, 651; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, $J = 6.5$ Hz), 1.27 (10H, m), 1.76−1.83 (2H, m), 3.10−3.15 (1H, m), 3.56−3.67 (2H, m), 4.70 (1H, d, $J = 1.8$ Hz), 4.81 (1H, d, $J = 1.5$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.1, 22.6, 27.2, 29.1, 29.2, 31.8, 38.8, 43.8, 103.3, 141.3; EIMS *m*/*z* (rel intensity) 184 (M^+, 28), 141 (3), 127 (7), 113 (33), 99 (100), 85 (15), 81 (32). Anal. Calcd for $C_{11}H_{20}S$: C, 71.67; H, 10.94. Found: C, 71.48; H, 11.09.

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Supporting Information Available: Experimental procedures for S-vinylation and the characterizations of **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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