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Copper(II)/Tin(II) Reagent for Allylation, Propargylation, Alkylation, and Benzylation of Disulfides and Elemental Sulfur: New Insight into the "Copper Effect"†

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Organic bromides and iodides react with diorganodisulfides in the presence of stannous chloride and catalytic cupric halide, giving rise to corresponding unsymmetrical sulfides. Similar reactions but with elemental sulfur provide trisulfides and tetrasulfides. The reactions proceed by copper thiolate as principal reactive intermediate.

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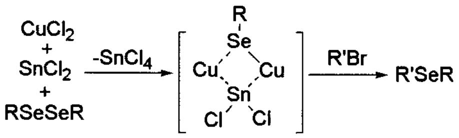
Introduction

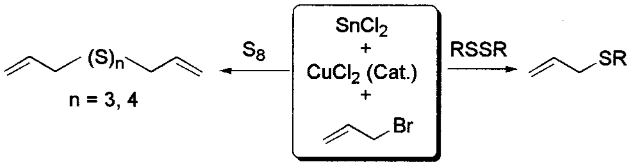
Contemporary chemistry is characterized by the number and variety of topics, which cut across traditional divides. The interest in combining transition and main group elements to generate new structural motifs, often a cluster, provides distinct opportunities[1] in the fields of "catalysis" and "molecular precursors to new materials". In this direction ligand-assisted cluster designing is a well-adapted approach. A similar exercise, but in a ligand-free environment, poses significant diagnostic difficulties. Our recent success[2] in introducing a Cu(II)/Sn(II) reagent for carbonyl allylation and propargylation prompted us to study the reactivity of the same toward the cleavage of the diselenide bond. The investigation suggested a bimetallic reactivity toward the formation of unsymmetrical diorganoselenides under extremely mild conditions (Scheme 1).

In this note, we present a novel finding pertaining to the reactivity of Cu(II)/Sn(II) toward the activation of diorganodisulfides and elemental sulfur leading to the facile formation of sulfides, trisulfides, and tetrasulfides (Scheme 2).[3] A distinct "copper effect" underlines the observed reactivity and is believed to mediate via new copper thiolate intermediates.

Scheme 1



Scheme 2



Results and Discussion

Activation of Disulfide. The reaction of stannous chloride dihydrate with allyl bromide and diphenyl disulfide in the presence of catalytic cupric chloride in THF under reflux gives rise to allylphenylsulfide **1** in 84% isolated yield (Table 1, entry 1).

The reaction proceeds as well with catalytic cupric bromide. On the other hand, reaction in the absence of copper halide shows less than 5% conversion. THF is judged as the best solvent when compared with DCM, DCM−H_2O (1:1 v/v), and THF−H_2O (1:1 v/v). γ-Substituted allyl halides give predominantly the linear unsymmetrical sulfides. Thus, reaction of 1-bromo-3-methyl-2-butene with diphenyl disulfide in THF gave 85% of 3-methyl-2-butenyl(phenyl)sulfide **3** and 8% of the branched isomer (entry 4). The same reaction in THF−H_2O (1:1 v/v) gives 65% of **3** and 5% of the branched isomer along with unreacted diphenyl disulfide (entry 5). The reaction is further extended to

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(1) (a) Fenske, D. In *Clusters and Colloids-From Theory to Applications*; Schmid, G., Ed.; VCH: Weinheim, Germany, 1994. (b) Wang, W.; Geng, Y.; Yan, P.; Liu, F.; Xie, Y.; Qian, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4062.

(2) (a) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics* **1997**, *16*, 4796. (b) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics* **1999**, *18*, 2782. (c) Kundu, A.; Roy, S. *Organometallics* **2000**, *19*, 105.

(3) For reviews on −S−S− cleavage, please see: (a) Procter, D. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 835−871 (b) Clennan, E. L.; Stensaas, K. L. *Org. Prep. Proc. Int.* **1998**, *30*, 551−600. (c) Rayner, C. M.; *Contemp. Org. Synth.* **1995**, *2*, 409−440. (d) Solladie, G. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 6, pp 133−170.

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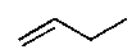
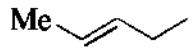
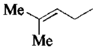
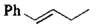
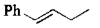
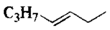
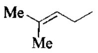
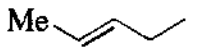
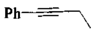
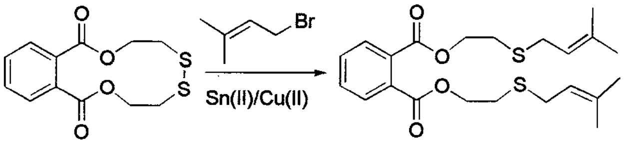
Table 1. Formation[a] of Unsymmetrical Sulfides RSR′ from the Reaction of RSSR and R′Br

$$\underset{(0.5\ \text{mmol})}{\text{RSSR}} + \underset{(1.5\ \text{mmol})}{\text{R'Br}} \xrightarrow[\substack{\text{CuCl}_2.2\text{H}_2\text{O}\ (0.1\ \text{mmol})\\ \text{THF}}]{\text{SnCl}_2.2\text{H}_2\text{O}\ (1.2\ \text{mmol})} \text{R'SR}$$

#	R	R'	Time (h)	Catalyst[b]	Product No.	Yield[c] (%)
1	Ph		10	A	**1**	84
2			4	A	**2**	88[d]
3			4	NIL	**2**	<5
4			3	B	**3**	93[d]
5			12	B	**3**	70[d, e]
6			12	A	**4**	48
7	PhCH$_2$		14	A	**5**	65
8			14	B	**6**	71
9	n-C$_4$H$_9$		10	B	**7**	75
10	Cyclohexyl		14	B	**8**	68
11	Ph		20	B	**9**	40
12			30	B	**10**	25

[a] All reactions were carried out in refluxing THF. [b] A = CuCl$_2$·2H$_2$O, B = CuBr$_2$. [c] Isolated yields after chromatography based on disulfides. [d] Ratio of linear and branched isomer 9:1. [e] Reaction carried out in refluxing THF−H$_2$O.

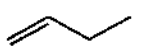
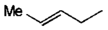
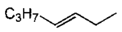
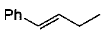
Scheme 3



11 **12**

Table 2. Formation of Diorganotri- and Tetrasulfides R$_2$S$_3$ and R$_2$S$_4$ from the Reaction of Elemental Sulfur S$_8$ and Organic Halides RX

$$\underset{(1.5\ \text{mmol})}{\text{RX}} + \underset{(2\ \text{g-atom})}{\text{S}_8} \xrightarrow[\substack{\text{CuCl}_2.2\text{H}_2\text{O}\ (10\ \text{mol\%})\\ \text{THF-DMSO}\ (2:1\ \text{v/v})}]{\text{SnCl}_2.2\text{H}_2\text{O}\ (1.05\text{mmol})} \text{R}_2\text{S}_3 + \text{R}_2\text{S}_4$$

#	RX	Temp (°C)	Time (h)	Product No. n = 3	Product No. n = 4	Conversion (%)[a]	NMR Ratio n = 3	NMR Ratio n = 4
1		70	1.5	**13a**	**13b**	78	60	40
2		30	10	**13a**	**13b**	42	72	28
3		70	1	**14a**	**14b**	72	42	58
4		70	4	**15a**	**15b**	30	49	51[b]
5		50	9	**16a**	**16b**	42	48	52[b]
6	CH$_3$CH$_2$CO$_2$CH$_2$	70	2	**17a**	**17b**	73	62	38
7		30	12	**17a**	**17b**	68	62	38
8	MeI	50	1	**18a**	**18b**	48	71	29
9		30	12	**18a**	**18b**	28	64	36
10	PhCH$_2$	30	12	**19a**	**19b**	48	46	54[b]
11	4-NO$_2$C$_6$H$_4$CH$_2$	30	12	**20a**	**20b**	26	67	33[c]

[a] With respect to halide. [b] 10−15% of disulfide isolated. [c] 25% of halide isolated.

various diorganodisulfides RSSR (R = 1°, 2° alkyl, benzyl). The latter were prepared from the corresponding halides and (benzyltriethylammonium) tetrathiomolybdate.[4] Reactions of substituted allyl bromides with dibenzyl disulfide, di(*n*-butyl)disulfide, and dicyclohexyl disulfide give the corresponding allylic sulfides **5**−**8** in good to excellent yields (entries 7−10). Activation of propargyl bromide is also achieved in the reaction with diphenyl disulfide, giving rise to corresponding sulfides **9**−**10** (entries 11, 12). We are delighted to find that the present protocol is equally effective for the cleavage of cyclic disulfide (Scheme 3). Thus, disulfide **11**, prepared from phthalic anhydride in two steps, reacts with 1-bromo-3-methyl-2-butene to give the corresponding bis-allylated product **12** in 61% isolated yield. Compound **12** is an attractive precursor for ring-closing metathesis reaction toward the synthesis of redox-switched crown ethers.[5]

Activation of Elemental Sulfur. The distinct reactivity of Cu(II)/Sn(II) to cleave the −S−S− bond in disulfides, as illustrated above, prompted us to determine whether the reagent can cleave the −S−S− bond in elemental sulfur. Addition of elemental sulfur (α-rhombic, 2 g-atom) to a mixture of stannous chloride dihydrate (1.05 mmol) and catalytic cupric chloride dihydrate (0.1 mmol) in THF−DMSO (2:1 v/v) leads to the immediate formation of a brown precipitate. Addition of allyl bromide (1.5 mmol) to this mixture at 70 °C results in a clear yellow solution after 1.5 h. Workup afforded a mixture of diallyltrisulfide **13a** and diallyltetrasulfide **13b** (3:2 vide NMR) with an overall yield of 78% with respect to halide (Table 2, entry 1). The reaction proceeds equally well with cupric bromide or cuprous chloride as catalyst. *The "pronounced copper effect" in the transformation can be judged from the fact that no reaction occurs either in the absence of copper salts or in the presence of nickel chloride, bis(triphenylphosphine)nickel dichloride, palladium acetate, and tetrakis(triphenylphosphine)palladium as catalysts.* Negligible product is formed with Cu(II)/Sn(II) in solvents such as DCM, MeCN, THF, DCM−DMSO (2:1 v/v), and MeCN−DMSO (2:1 v/v).

The sulfur-activation reaction is extended to various allyl (entries 3−5), 1°-alkyl (entry 6−9) and benzyl (entry 10−11) halides, giving rise to the corresponding diorganotrisulfides **14a**−**20a** and diorganotetrasulfides **14b**−**20b** in moderate yields. However the reaction fails in the case of aryl halides. We have noticed further that reactions conducted at room temperature do not alter the product ratio significantly (entries 2, 7, 9). This indicates the inherent reactivity of the reagent in promoting trisulfide and tetrasulfide formation. Attempts are underway to vary reaction conditions to enhance the selectivity of the reactions.

The Nature of Intermediates. The "*copper effect*", indicated earlier, prompted us to carry out a series of control experiments, as detailed below.

1. Neither allyltributylstannane nor allyltrichlorostannane reacts with diphenyl disulfide and elemental sulfur

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(4) Ramesha, A. R.; Chandrasekaran, S. *Synth. Commun.* **1992**, *22*, 3277.

(5) (a) Delgado, M.; Martin, J. D. *J. Org. Chem.* **1999**, *64*, 4798. (b) Ramesha, A. R.; Chandrasekaran, S. *J. Org. Chem.* **1994**, *59*, 1354.

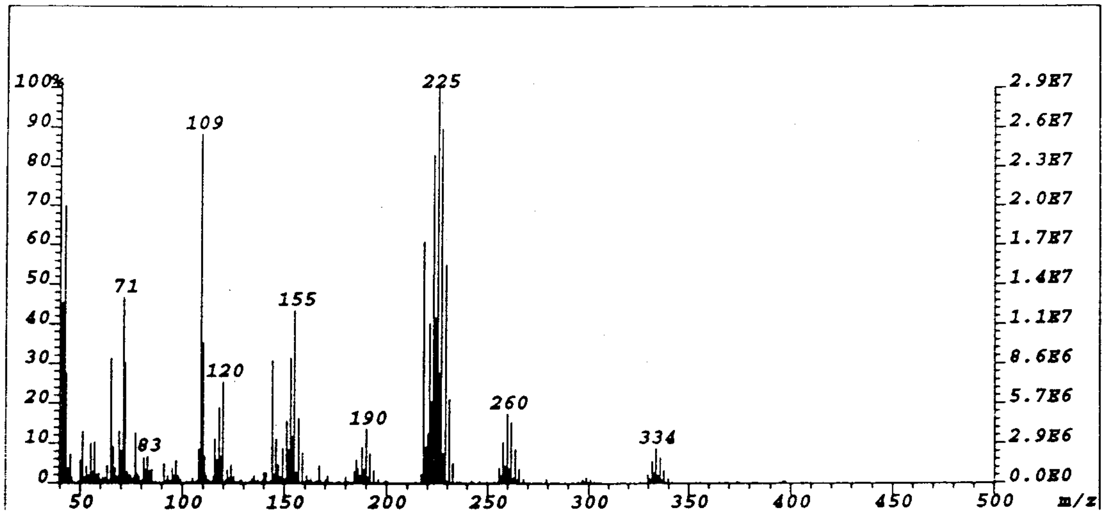

Figure 1. EIMS spectra of the filtrate from the reaction of $CuCl_2{\cdot}2H_2O-SnCl_2{\cdot}2H_2O-PhSSPh$ = 2:2.1:1. (m/z) 334 = $[PhSSnCl_3]^+$; 260 = $[SnCl_4]^+$; 225 = $[SnCl_3]^+$; 218 = $[PhSSPh]^+$; 190 = $[SnCl_2]^+$; 155 = $[SnCl]^+$; 120 = $[Sn]^+$; 109 = $[PhS]^+$.

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even in the presence of cuprous or cupric halides. This rules out the possibility of similar organotin intermediates.[6]

2. Diphenyl disulfide and sulfur alone does not form any complex with CuCl, $CuCl_2$, or $SnCl_2$ (UV and TLC monitoring) and is quantitatively isolated back after 24 h.[7]

3. The nature of the intermediate in the reaction of Cu(II)/Sn(II) with disulfide is investigated by EIMS. A solution of stannous chloride dihydrate (2.1 mmol), cupric chloride dihydrate (2 mmol), and diphenyl disulfide (1 mmol) in THF (5 mL) is refluxed for 6 h and filtered. The filtrate, upon direct injection into the mass spectrometer probe, shows major peaks (m/z) due to $PhSSnCl_3$ (334), $SnCl_4$ (260), and unreacted PhSSPh (218) (Figure 1). These and all the fragmentation peaks have been confirmed by comparison with simulated spectra We assume that (thiophenyl)trichlorostannate, $RSSnCl_3$, is an important intermediate during the cleavage reaction of disulfide.

4. As mentioned earlier, in the reaction of Cu(II)/Sn(II) with sulfur, a brown precipitate appears in the beginning of reaction, which slowly dissolves upon addition of organic halide. The brown precipitate **21** is independently prepared from the reaction of stannous chloride dihydrate, cupric chloride dihydrate, and sulfur (2:2:1 and 4:4:1) in THF. The IR spectrum of **21** is very similar to those of cupric sulfide and cuprous sulfide. Elemental analysis for copper in **21** affords a value of 41.21 ± 0.02 and corresponds to an empirical formula of $CuS_{2.83}$. Sulfur-rich copper species of the formula $CuS_{2.5}$ and $CuS_{2.67}$ have been reported earlier.[8] The X-ray powder pattern of compound **21** (Figure 2) is compared to known copper sulfide species (Table 3).[9]

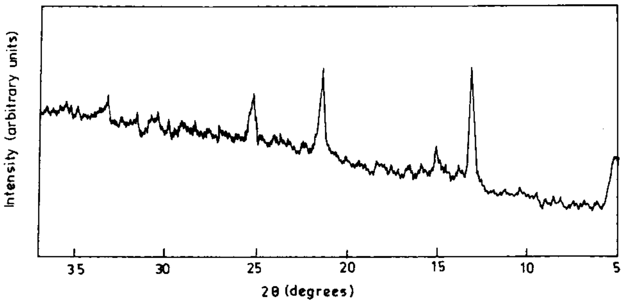

Figure 2. XRD spectra of brown compound **21**. d-values = 3.093, 2.688, 1.915, 1.629.

Table 3. Comparison of XRD Peaks (d-values) of 21 with Known Copper Sulfide Species

compound	XRD data (d-values)	reference
21	3.09, 2.69, 1.92, 1.63	this work
CuS	3.048, 2.813, 1.893	*a*
$Cu_{1-x}S$	3.58, 2.22	*b*
$Cu_{1+x}S$	3.65, 2.25	*b*
Cu_2S	3.43, 3.04, 1.99, 1.86, 1.70, 1.65	*c*
$Cu_{2-x}S$	3.78, 2.30	*b*

[a] JCPDS card no. 6-0464; only major peaks noted. [b] Engelken, R. D.; McCloud, H. E. *J. Electrochem. Soc.* **1985**, *132*, 567. [c] Das, S. R.; Vankar, V. D.; Nath, P.; Chopra, K. L. *Thin Solid Films* **1978**, *51*, 257.

The results indicate similarities with Cu(II) sulfide species.[10] The EPR spectrum of **21** (Figure 3) shows the presence of axially compressed Cu(II) species.[11] It is further noteworthy that compound **21** remains inactive toward allyl bromide, but spontaneously reacts in the presence of stannous chloride to give trisulfide as the major product.

The thiophilic nature of copper is well documented and is further relevant to the chemistry[12] of metallothioneins and cytochrome-c oxidase and application[13] in

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(6) For the reaction of organometallics of main group elements with disulfides and sulfur, please see: (a) Wardell, J. L. In *The Chemistry of the Thiol Group, Part I*; Patai, S., Ed.; Wiley: New York, 1974. (b) Harrison, P. G. *Chemistry of Tin*; Blackie: London, 1989.

(7) (a) Very weak interaction of CuCl with diethyl disulfide is reported: Branden, C.-I. *Acta Chem. Scand.* **1967**, *21*, 1000. (b) Interaction of diphenyl disulfide with In(0) and Sn(0) results in oxidative −S−S− cleavage: Kumar, R.; Mabrouk, H. E.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1988**, 1045.

(8) (a) Buckley, A. N.; Woods, R. *Aust. J. Chem.* **1984**, *37*, 2403. (b) Bieger, T.; Horne, M. D. Electrochemical Society Spring Meeting; Cincinnati, 1984; Abstract No. 16.

(9) (a) JCPDS card no. 6-0464; only major peaks noted. (b) Das, S. R.; Vankar, V. D.; Nath, P.; Chopra, K. L. *Thin Solid Films* **1978**, *51*, 257. (c) Engelken, R. D.; McCloud, H. E. *J. Electrochem. Soc.* **1985**, *132*, 567.

(10) The room-temperature magnetic moment of **21** (μ_{eff}, BM) is 0.561, suggesting significant metal−metal interaction. Efforts are underway to obtain an XPS analysis of **21**.

(11) Hathway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1987; Vol. 5, pp 662−673.

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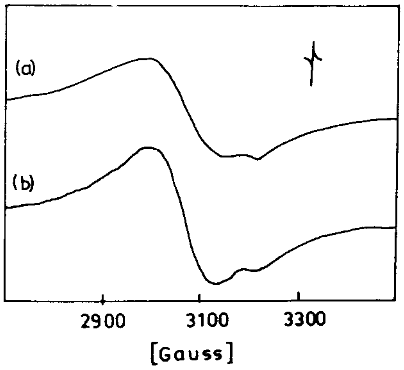
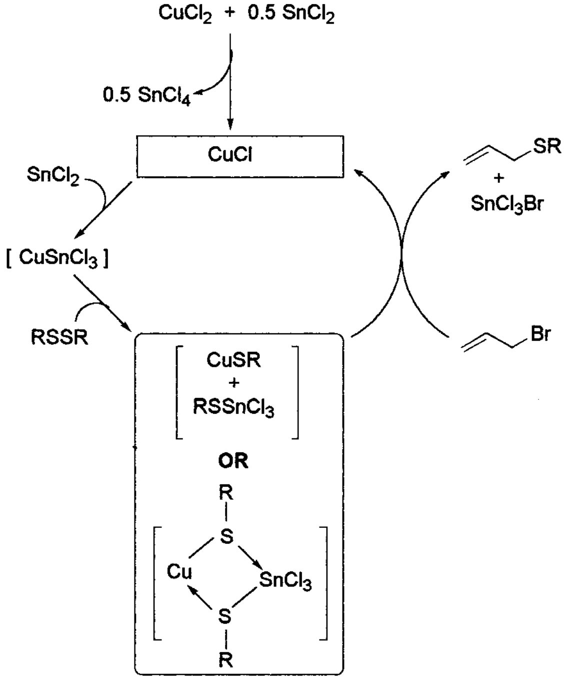


Figure 3. EPR spectra of brown compound **21**. (a) At room temp, $g_{\|} = 2.072$; $g_{\perp} = 2.169$ (b) At liquid nitrogen temp, $g_{\|} = 2.075$; $g_{\perp} = 2.17$.

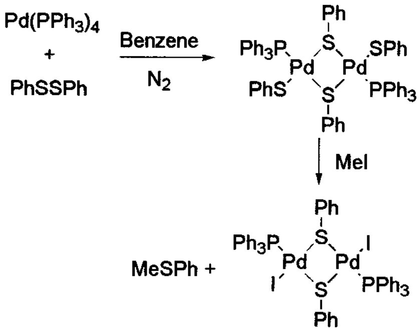
the field of materials science. A number of structurally diverse copper thiolate complexes are synthesized by the ligand-assisted approach.[14] In the case of ligand-free systems, earlier reports confirm the complexity in the stoichiometry and structure of copper–sulfur species.[9,15] Formation of nonstoichiometric sulfides of copper(I) in the electroreduction of copper salts in the presence of elemental chalcogen is reported.[16] Geochemical studies[17,18] on the formation of copper sulfide minerals clearly show that the Cu(I) oxidation state is preferred at low oxygen fugacity, high sulfur fugacity, and high temperature. However the Cu(II) oxidation state is preferred in minerals near earth's surface under the conditions of low temperature, aqueous environment, and pH 6–8.

Plausible Reaction Pathway. In the present study the acquired evidence, presented above, is yet insufficient to postulate the true course of –S–S– cleavage reactions. The experimental evidence, however, suggests that bimetallic participation is mandatory during the cleavage and subsequent carbon–sulfur bond formation. Any mechanism is, therefore, required to be consistent with this view. A suggestion, pertaining to this hypothesis, for the activation of disulfide is shown in Scheme 4, involving the prior formation of intermediate $CuSnCl_3$ from the reaction of copper(I) chloride and stannous chloride.[19] Formation of $PhSSnCl_3$ (vide EIMS) from the reaction of $CuCl_2$, $SnCl_2$, and PhSSPh is discrete proof of the bimetallic reactivity.[20] Pd(0)-promoted cleavage of disulfide follows a nearly similar path (Scheme 5).[21] However, in the present case, the major question to be addressed is, "between $PhSSnCl_3$ and CuSPh, which is the principle reactive intermediate?"[22] Toward this, the following model studies have been carried out starting from readily available $PhSSn^nBu_3$ **22** (Scheme 6).[23]

Scheme 4



Scheme 5



1. Reaction of **22** with stoichiometric allyl bromide under reflux and after 8 h affords allylphenylsulfide **1** in 18% isolated yield along with unreacted starting material.

2. The above reaction, but in the presence of CuCl (0.2 equiv) and after 8 h, affords **1** in 34% isolated yield along with $^nBu_3SnCl$.

3. Reaction of authentic CuSPh **23** and stoichiometric allyl bromide *proceeds smoothly under ambient conditions* and after 8 h affords **1** in 60% isolated yield.

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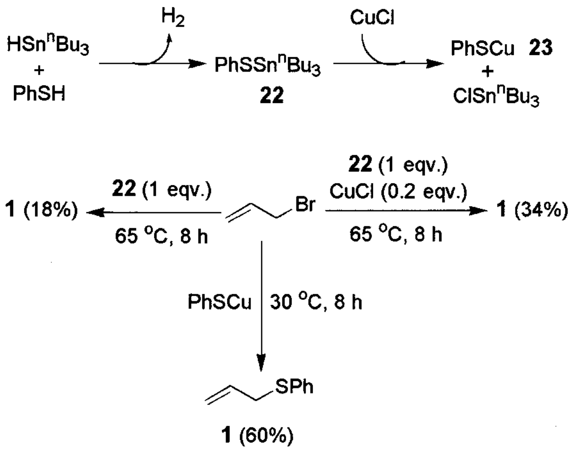
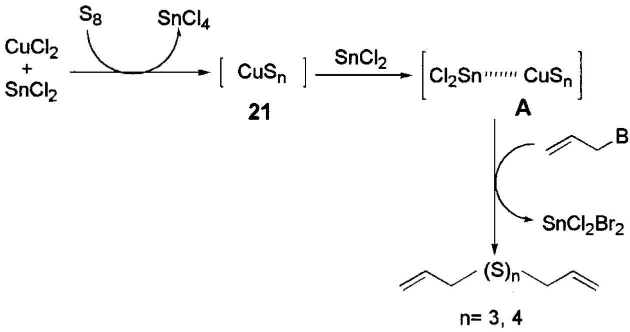
Scheme 6



Scheme 7



The above model study clearly establishes "the catalytic role of copper" and demonstrates that the sulfur transfer reaction is proceeding majorly via in-situ-generated copper thiolate.

The mechanism of activation of sulfur appears to be more complex. Whether a species such as **A** (Scheme 7) is involved is worthy of further investigation. In the case of ligand-assisted syntheses, formation of CuS_3 and CuS_4 cores is well known.[3b,24] Even more recently Cu_4SnS_6 and Cu_2SiS_3 have been identified.[25]

Synthetic Perspective. The allylation of disulfides using Cu(II)/Sn(II) offers a mild route to unsymmetrical sulfides. The methodology argues well for the recently reported reagents[26] such as Zn/$CoCl_2$, In(0), Sn(0), Sm(0)/$BiCl_3$, and CuI(stoichiometric)/HMPA. The formation of diorganotrisulfides and tetrasulfides as major products in the reaction of elemental sulfur appears to be attractive, more so since there are only a few reports available in this area to date.[27]

Experimental Section

General Methods. All reactions were performed under an inert atmosphere of argon. Substituted allyl bromides and propargyl bromides were prepared from the corresponding alcohols (Lancaster) using standard protocol. The disulfides were prepared rather easily according to literature procedure.[6] All the starting materials were >98% pure vide NMR. Stannous chloride dihydrate (Ranbaxy), cupric chloride dihydrate (S.D. Fine Chemicals), and cupric bromide (Lancaster) were used as received. Sulfur powder AR (S.D. Fine Chemicals) was recrystallized from carbon disulfide.

^1H NMR spectra were taken in $CDCl_3$ or DMSO-d_6 on Varian INOVA-500, Brucker-300, and Gemini-200 spectrometers. EIMS (70 eV) spectra were recorded using VG Micro-Mass 7070H and VG Autospec M mass spectrometers. IR spectra were recorded on a Perkin-Elmer 883 instrument. X-ray powder diffraction data were obtained using a Phillips PW-1840 instrument using a Mo Kα target at 40 kV. Copper estimations of compounds **21** and **23** were done by standard iodometric titration using reported digestion methods.[28]

Typical Procedure for the Synthesis of Unsymmetrical Sulfides. A mixture of cyclic disulfide **11** (142 mg, 0.5 mmol) and 1-bromo-3-methyl-2-butene (447 mg, 3 mmol) in THF (4 mL) was slowly added to a stirred solution containing stannous chloride dihydrate (271 mg, 1.2 mmol) and cupric chloride dihydrate (17 mg, 0.1 mmol) in THF (4 mL) and under argon. The solution was refluxed for 6 h. Solvent removal followed by column chromatography (silica gel 60–120 mesh, SRL; eluent *n*-hexane–ethyl acetate 9:1) afforded sulfide **12** as a viscous oil (128 mg, 61% with respect to disulfide). ^1H NMR ($CDCl_3$): δ 1.66 (s, 6H), 1.75 (s, 6H), 2.75 (t, 4H, $J = 5.7$ Hz), 3.17 (d, 4H, $J = 5.3$ Hz), 4.39 (t, 4H, $J = 6.2$ Hz), 5.20 (t, 2H, $J = 5.3$ Hz), 7.48 (m, 2H), 7.76 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 17.68, 25.62, 29.38, 29.73, 64.59, 120.26, 128.92, 131.05, 131.97, 135.81, 167.11. EIMS *m*/*z* (rel abundance): 353 [$(M - C_5H_9)^+$, 3], 293 (3), 193 (7), 149 (42), 129 (75), 100 (54), 69 (99), 41 (100). HRMS: calcd for $C_{17}H_{21}O_4S_2$ 353.088128, found 353.086415.

Typical Procedure for the Synthesis of Trisulfides and Tetrasulfides. Sulfur (64 mg, 2 g-atom) was added to a stirred solution containing stannous chloride dihydrate (237 mg, 1.05 mmol) and cupric chloride dihydrate (17 mg, 0.1 mmol) in THF–DMSO (2:1 v/v). A brown precipitate was formed immediately. 1-Bromo-2-butene (0.15 mL, 1.5 mmol) was added dropwise to the reaction mixture kept under argon. The solution was refluxed at 70 °C for 1 h (TLC monitoring on silica gel, eluent: hexane). An aqueous solution of ammonium fluoride (15%, 10 mL) was added to the reaction mixture, and the organic layer was extracted with diethyl ether (3 × 20 mL), washed with water (2 × 10 mL) and brine (2 × 10 mL), and dried over magnesium sulfate. Solvent removal followed by column chromatography (silica gel 100–200 mesh, SRL; eluent *n*-hexane) afforded a viscous oil (72% wt halide) containing the corresponding trisulfide **14a** and tetrasulfide **14b** (42:58 vide NMR). All products were fully characterized by ^1H NMR (500 MHz), MS, and comparison with authentic samples wherever possible.

Preparation of Compound 21. A mixture of stannous chloride dihydrate (1.805 g, 8 mmol) and cupric chloride dihydrate (1.364 g, 8 mmol) was stirred under argon. To the resulting mixture was added sulfur (64 mg, 2 mmol), and a brown compound was formed immediately. After additional stirring for 5 min, the solid was filtered, washed with THF (3 × 20 mL), and dried under vacuum at 100 °C for 2 h. Yield: 0.830 g. Anal. Found for Cu: 41.21 ± 0.02. The compound is stable under vacuum for 2 days; however in air the brown color slowly changes to green.

Reaction of PhSSn^{n}Bu$_3$[23] and Allyl Bromide in the Presence of CuCl. Allyl bromide (0.8 mL, 1 mmol) was added

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to a stirred solution of $PhSSn^nBu_3$ **22** (400 mg, 1 mmol) and CuCl (20 mg, 0.2 mmol) in THF (3 mL) under argon, and the mixture was refluxed for 8 h (TLC monitoring silica gel/hexane). Solvent removal under reduced pressure, followed by column chromatography (silica gel 60−120 mesh, SRL; eluent *n*-hexane), afforded allylphenylsulfide **1** (51 mg, 34%).

Reaction of $PhSSn^nBu_3$ and Allyl Bromide in the Absence of CuCl. Similar reaction as above but in absence of CuCl afforded allylphenyl sulfide **1** (27 mg, 18%).

Preparation of Phenylthiocopper(I). A mixture of $PhSSn^nBu_3$ (160 mg, 0.4 mmol) and CuCl (40 mg, 0.4 mmol) in THF (6 mL) and under argon was stirred at room temperature for 7 h. The canary yellow precipitate of CuSPh **23** was centrifuged under argon, washed with THF (3 × 1 mL), and finally dried under vacuum (55 mg, 82%). Anal. Calcd for CuSPh: Cu, 36.81. Found: Cu, 34.48. CuSPh was also prepared by literature methods from the reaction of lithium thiophenoxide and copper(I) iodide.[29] Between the two, the former route offers operational simplicity.

Reaction of CuSPh and Allyl Bromide. CuSPh **23** (34 mg, 0.2 mmol) and allyl bromide (0.6 mL, 0.8 mmol) was stirred in THF (2 mL) under argon, and stirring was continued for 8 h at room temperature (TLC monitoring on silica gel eluent hexane), solvent removal under reduced pressure, followed by column chromatography (silica gel 60−120 mesh, SRL; eluent *n*-hexane) afforded allylphenyl sulfide **1** (18 mg, 60% wt CuSPh).

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Supporting Information Available: Listings of spectral data and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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