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# *Notes*

## Copper(II)/Tin(II) Reagent for Allylation, Propargylation, Alkynylation, and Benzylation of Diselenides: A Novel Bimetallic Reactivity[#]

Abhijit Kundu[†] and Sujit Roy*[,†,‡]

*Metallo-Organic Laboratory, Inorganic Division, Indian Institute of Chemical Technology, Hyderabad 500007, India, and Organometallics & Catalysis Laboratory, Chemistry Department, Indian Institute of Technology, Kharagpur 721302, India*

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*Summary: Reactions of allyl, propargyl, benzyl, and alkynyl bromides with diorganodiselenides in the presence of stannous chloride and catalytic cupric halide result in the formation of corresponding unsymmetrical selenides in good to excellent yields via a novel dicopper(selenophenyl) intermediate.*

### Introduction

Organoselenium compounds have emerged as versatile synthons in organic synthesis.[1] Metal-assisted cleavage of the −Se−Se− bond in diorganodiselenides is of potential interest to organometallic and organic chemists alike.[2] The selenium−metal bond thus formed can offer rich organic reactivity akin to higher order hetereometalates. We were drawn into this area by (a) recent reports[3] of allylic activation of diorganodiselenides by In(0), Sm(0), and Sm(II), (b) our recent success[4] in introducing a Cu(II)/Sn(II) reagent for Barbier-like carbonyl allylation and propargylation, and (c) the achievement of Chandrasekaran et al.[5] in devising a facile and mild route to functionalized diselenides.

In this note, we wish to report an extremely facile route to unsymmetrical selenides from activated organic bromides and diorganodiselenides using stannous chloride and catalytic cupric halide (Scheme 1). While probing into the “copper effect”, we were delighted to find a distinct bimetallic reactivity suggesting the interplay of a complex mechanism.

**Scheme 1**

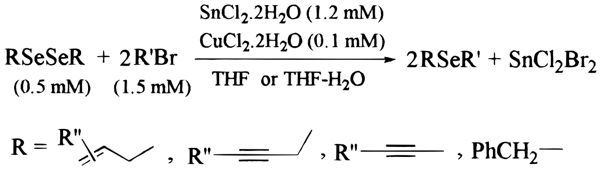
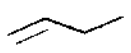
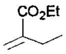
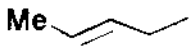
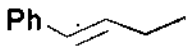
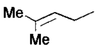
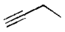


**Table 1. Formation of Unsymmetrical Selenides RSeR′ from the Reaction of RSeSeR and R′Br**

| # | R | R′ | time(h) | catalyst[a] | yield(%)[b] |
|---|---|---|---|---|---|
| 1 | Ph |  | 8 | A | 85 |
| 2 | | | 10 | A | 80[c] |
| 3 | | | 12 | Nil | <10 |
| 4 | |  | 15 | B | 88 |
| 5 | n-$C_6H_{13}$- |  | 10 | B | 82 |
| 6 | | | 12 | B | 80[c] |
| 7 | -$CH_2CO_2Et$ |  | 10 | A | 90 |
| 8 | $PhCH_2$- |  | 6 | A | 82 |
| 9 | | | 8 | A | 80[c] |
| 10 | Ph |  | 8 | A | 70[d] |
| 11 | -$CH_2CO_2Et$ |  | 16 | B | 65[d] |
| 12 | Ph |  | 3 | A | 85 |
| 13 | n-$C_6H_{13}$- | | 10 | B | 52[d] |
| 14 | Ph | $PhCH_2$- | 4 | A | 71[d] |
| 15 | $PhCH_2$- | | 15 | B | 60[d] |

[a] A = $CuCl_2{\cdot}2H_2O$, B = $CuBr_2$. [b] Isolated yields after chromatography based on diselenides. [c] Reaction in THF/$H_2O$. [d] Under reflux.

### Results and Discussion

The reaction of stannous chloride dihydrate with allyl bromide and diphenyldiselenide in the presence of catalytic cupric chloride dihydrate in THF at ambient

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* Corresponding author at Indian Institute of Technology.

[†] Indian Institute of Chemical Technology.

[‡] Indian Institute of Technology.

(1) For general reviews please see: (a) Kataoka, T.; Yoshimatsu, M. In *Comprehensive Organic Transformations*; Ley, S. V., Ed.; Pergamon: Oxford, 1995; Vol. 2, pp 277−295. (b) Krief, A. In *Comprehensive Organic Synthesis*; Schreiber, S., Ed.; Pergamon: Oxford, 1993; Vol. 1, pp 629−728. (c) Krief, A. In *Comprehensive Organometallic Chemistry II*; Mckillop, A., Ed.; Pergamon: Oxford, 1995; Vol. 11, pp 515−569. (d) Liotta, D.; Monahan, R. *Science* **1986**, *231*, 356. (e) *Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1986; Vol. 1.

(2) (a) Kumar, R.; Mabrouk, H. E.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1988**, 1045. (b) Zingaro, R. A. In ref 1e, pp 343−368 (c) Gysling, H. J. In ref 1e, pp 679−855. (d) Mathur, P. *Adv. Organomet. Chem.* **1997**, *41*, 243.

(3) (a) Fukuzawa, S.; Fujinami, T.; Sakai, S. *Chem. Lett.* **1990**, 927. (b) Yu, M.; Zhang, Y.; Bao, W. *Synth. Commun.* **1997**, *27*, 609. (c) Bao, W.; Zheng, Y.; Zhang, Y.; Zhou, J. *Tetrahedron Lett.* **1997**, *52*, 9333.

(4) (a) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics* **1997**, *16*, 4796. Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics* **1999**, *18*, 2782.

(5) Prabhu, K. R.; Chandrasekaran, S. *J. Chem. Soc. Chem. Commun.* **1997**, 1021.

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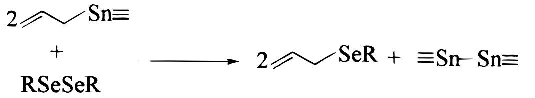
**Scheme 2**



temperature for 8 h gives rise to the allylphenyl selenide in 85% isolated yield (Table 1, entry 1). When substituted allyl bromides are used, exclusive α-regioselectivity is observed in all the cases (entries 5, 7, 8). The reaction proceeds well with catalytic cuprous halide also. *On the other hand, reaction in the absence of copper halide (entry 3) shows <10% conversion*. The allylation reaction is further extended to alkyl (entries 5, 6) and benzyl (entries 8, 9) diselenides, affording good to excellent yields of corresponding allyl selenides. Ester groups can also be tolerated (entry 7). We are delighted in finding yet another practical feature of the present route whereby reactions can be carried out even in aqueous organic medium without any significant loss in product yield (entries 2, 6, 9).

The Cu(II)/Sn(II) reagent combination is equally effective in activating propargyl, alkynyl, and benzyl bromides (entries 10–15). In all cases, the unsymmetrical selenides are isolated in good to excellent yield. However, alkyl, aryl, and vinyl bromides remain unreactive. Efforts are underway to tune the reaction condition in this direction.

We initially assumed that, like the reactivity of allylindium and allylsamarium reagents toward diorganodiselenides,[3] the present allylation reaction proceeds via the intermediacy of allylstannane (Scheme 2).

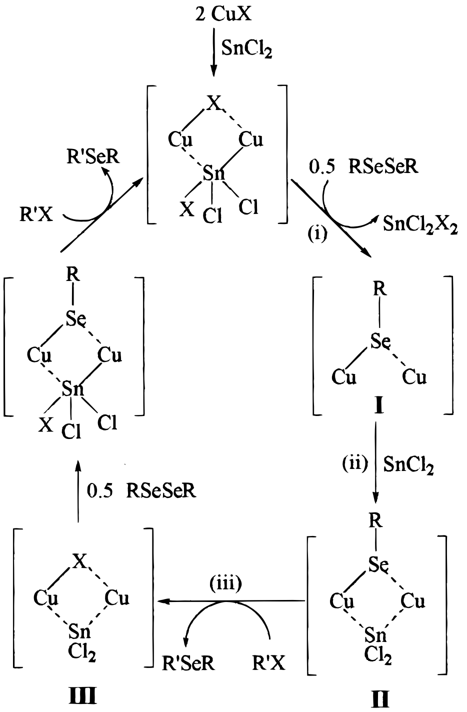
*To our surprise, neither allyltributylstannane nor allyltrichlorostannane reacts with diphenyldiselenide, even in the presence of cuprous or cupric halides.* This prompted us to carry out a series of control experiments, as detailed below.

1. The reaction proceeds with ease in the presence of catalytic $[CuCl(PPh_3)]_4$ but is extremely sluggish with $[CuCl(PPh_3)_3]$, thereby suggesting *the requirement of coordinative unsaturation at the "copper site"*.

2. A brown-colored precipitate appears upon addition of diphenyldiselenide (0.5 mM) to a solution of cupric chloride (0.1 mM) and stannous chloride (1.2 mM). Addition of allyl bromide (1.5 mM) causes slow disappearance of the color, and at the end of the reaction, a white precipitate remains.

3. Reaction of cupric chloride, stannous chloride, and diphenyldiselenide in 4:4.2:1 molar ratio results in the formation of an air-sensitive orange-brown colored precipitate **I**.[6] Compound **I** is insoluble in all common organic solvents and also shows a negative test for halide. Several attempts by us to grow crystals of **I** failed. Elemental analysis is consistent with an empirical formula $Cu_2SePh$ (Anal. Calcd for $Cu_2SeC_6H_5$: C, 25.43; H, 1.779. Found: C, 25.35; H, 1.97). ICP analysis further confirms the absence of Sn and the presence of Cu and Se in a ratio of 2:1 (observed 1.904:1). The IR spectrum of **I** is similar but not identical to an authentic sample of CuSePh.[7]

**Scheme 3**



4. Diphenyldiselenide alone does not form any complex with either CuCl, $CuCl_2$, or $SnCl_2$ (UV and TLC monitoring) and is quantitatively isolated back after 24 h.

5. *Neither authentic CuSePh nor **I** is reactive to allyl bromide, but addition of $SnCl_2$ causes spontaneous reaction leading to the formation of allylphenylselenide.*

From the above experiments we conclude that the present reaction involves a complex catalytic cycle, a tentative outline of which is shown in Scheme 3. While we are not clear about the identity of various intermediates, the following features appear to be salient.

1. The complex with empirical formula $[Cu_2SePh]$ is the initial species formed during the catalytic cycle (step i). The selenophilic nature of copper is well documented, and recent literature testifies formation of unusual clusters and nanoparticles bearing copper and selenium.[8]

2. Activation of **I** by stannous halide is mandatory toward further reaction of organic halides (steps ii and iii). This is partly reminiscent of the reactivity of stannylcuprates.[9]

3. The nature of activation of halide (step iii) is an important feature for further probing, in particular for allylic halides. $\sigma$- and/or $\pi$-allyllic intermediates are possible candidates in such activation steps.

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(6) The filtrate from the above reaction, upon direct injection into the EIMS probe, shows major peaks arising from $SnCl_4$ along with a very weak signal due to $PhSeSnCl_3$. However, under deficient copper conditions ($CuCl_2/SnCl_2/PhSeSePh$ = 2:3:1 or $CuCl/SnCl_2/PhSeSePh$ = 2:2:1) the solution, after filtration of **I**, shows major peaks due to $PhSeSnCl_3$ and unreacted PhSeSePh (please see Supporting Information). Addition of allyl bromide to the filtrate shows no reaction (vide TLC). We believe that $PhSeSnCl_3$ is a probable intermediate toward the formation of **I**.

(7) Authentic CuSePh was synthesized following the procedure in: Back, T. G.; Collins, S.; Krishna, M. V.; Law, K.-W. *J. Org. Chem.* **1987**, *52*, 4258.

(8) (a) Liu, C. W.; Chen, H.-C.; Wang, J.-C.; Keng, T.-C. *J. Chem. Soc., Chem. Commun.* **1998**, 1831. (b) Fenske, D.; Krautscheid, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1452. (c) Wang, W.; Geng, Y.; Yan, P. Liu, F.; Xie, Y.; Qian, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4062.

(9) (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987. (b) Fleming, I. In *Organocopper Reagents: A Practical Approach*; Taylor, R. J. K., Ed.; Oxford University Press: New York, 1994; pp 257–292, and references therein.

4. The structures of intermediates **I**, **II**, and **III** are subject to isolation and confirmation by crystallographic studies. While we invoked a direct Cu−Sn bond formation in the above intermediates, halo-bridged geometries are worthy of further consideration.

Toward a complete elaboration of the catalytic cycle, we are undertaking model studies to understand (a) the structure of intermediates **I**, **II**, and **III** and the true course of their formation and (b) the metal site (Cu or Sn) responsible for activation of organic halides.

In conclusion, we have presented a mild and efficient protocol for the synthesis of unsymmetrical selenides using readily available reagents and hope that the same will find general acceptance in the organic and organometallic chemists' workbook. Furthermore, a novel bimetallic reactivity has been shown suggesting interesting mechanistic feature.

## Experimental Section

**General Methods.** General information regarding instruments and techniques is the same as mentioned in our earlier papers.[4] Substituted allyl bromides and propargyl bromides were prepared from the corresponding alcohols (Lancaster) using standard protocol. The diselenides 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. The solution for ICP experiment was prepared following literature procedure.[10]

**Typical Procedure for the Synthesis of Unsymmetrical Selenides.** A mixture of diphenyldiselenide (157 mg, 0.5 mmol) and allyl bromide (182 mg, 1.5 mmol) in tetrahydrofuran (3 mL) was slowly added to a stirred solution containing $SnCl_2 \cdot 2H_2O$ (271 mg, 1.2 mmol) and $CuCl_2 \cdot 2H_2O$ (17 mg, 0.1 mmol) in THF (3 mL) and under nitrogen. The solution was stirred at ambient temperature until completion (TLC monitoring on silica gel, eluent 5:95 ethyl acetate/hexane). Solvent removal followed by column chromatography (silica gel 60−120 mesh, Acme-India; eluent *n*-hexane) afforded pure allylphenylselenide as a light yellow oil (168 mg, 85% with respect to diselenide).

Reactions in aqueous organic media were carried out exactly as above but using THF/water (1:1 v/v). Following completion, 15% aqueous $NH_4F$ solution (10 mL) was added to the solution, which 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 afforded pure compound. All products were fully characterized by $^1H$ NMR (200 MHz), HRMS, and comparison with authentic samples wherever possible.

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

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(10) Reamer, D. C.; Veillon, C. *Anal. Chem.* **1981**, *53*, 1192.