

Selenophilicity of Copper in Selenium-Carbon Bond Formation from Selenous Acid Using Cu(II)/Sn(II) Reagent

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A selenium transfer reaction from selenous acid to benzyl and alkyl halides is initiated in the presence of stannous chloride and a catalytic amount of cupric chloride resulting in the formation of the corresponding diorganoselenides and/or diorganodiselenides as the major products as indicated by ¹H, ¹³C, ⁷⁷Se NMR, and MS. The reaction is characterized by a dual-metal effect at the selenium activation and transfer step. Thus, initial reaction of stannous chloride, cupric chloride, and selenous acid gives rise to α -Cu₂Se. Selenium transfer from the latter to the organic halide takes place with additional assistance of stannous chloride.

 ${\bf Keywords}~{\rm Bimetallic}~{\rm catalysis;}~{\rm Cu(II)}/{\rm Sn(II)};$ diorganoselenides; selenium transfer; selenous acid

INTRODUCTION

By virtue of their electronic and opto-electronic properties, inorganic selenides are key targets for a large number of investigations in materials science and in nano-chemistry.¹ At the same time, their merit as synthons or reactive intermediates in organic synthesis remains unabated. Metal organoselenolates RSeM are of interest in areas such as ligand-assisted cluster design, molecular precursors for new materials, and as selenium transfer reagents.^{2–4}

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Diorgano(poly)selenides (RSe_nR, RSe_nR') are an important class of compounds in organic chemistry and are widely used as precursors for various organic transformations. Major selenium transfer routes to diorganoselenides include the reaction of organic halides, esters or synthons thereof with (a) metal selenides/polyselenides,⁵ (b) metal organoselenolates (RSeM),⁶ and (c) mixed metal selenium hydrides.⁷ Other conceptually different strategies involve (a) the reaction of an organometallic reagent with metallic selenium (elemental grey selenium) or a diorganodiselenide;⁸ (b) selenium transfer from *N*-seleno derivatives;⁹ and (c) organoselenium transfer using novel selenotungstate and molybdenum-sulfur reagent.¹⁰

The use of selenous acid (H₂SeO₃) and selenium dioxide (SeO₂) in organic synthesis is so far limited to oxidation reactions alone. Examples include oxidation of ketones, aldehydes, quinolines and allylic hydroxylations of alkenes.^{11,12} Herein, we present a selenium transfer reaction directly from selenous acid to benzyl and activated alkyl halides as organic electrophiles supported by Cu(II)/Sn(II) reagent resulting in the formation of diorganoselenides/diselenides as the major product. Mechanistic studies indicate the distinct role of copper, and the initial formation of a copper(I) selenide, namely α -Cu₂Se. Selenium transfer from the latter to the organic halide takes place with additional assistance of stannous chloride.

RESULTS AND DISCUSSION

Organic Reactivity

Treatment of selenous acid (1 mmol) with stannous chloride dihydrate (3.2 mmol), 4-methylbenzyl iodide **1a** (1 mmol) and a catalytic amount of cupric chloride dihydrate (0.3 mmol, 30 mol% with respect to selenous acid) in THF-DMSO (1:2, 3 mL) under argon at ambient temperature initially resulted in a brown colored suspension. The suspension turned into a clear yellow solution within 15 h. Aqueous work up afforded the corresponding ditolyl diselenide **2d** as the major product (85% according to ¹H NMR). The minor products are ditolylselenide **2m** and the triselenide **2t** (Scheme 1, Table I). With respect to reaction time and yields, THF-DMSO resulted as the best solvent as compared to DCM, THF, MeCN, DMSO, DCM-DMSO, and MeCN-DMSO.

Similar reactions of selenous acid with benzyl bromide, 4chlorobenzyl iodide, and 4-nitrobenzyl bromide 1b-1d give the corresponding diorganoselenides 3m-5m and diselenides 3d-5d in varying ratios (Scheme 1, Table I). Minute traces of RSe₃R (3t-5t) could be detected in the ¹H NMR spectrum of the product mixture in certain



cases (Scheme 1, Table I). Interestingly, the reaction of 2-nitrobenzyl bromide **1e** led to the formation of the corresponding diorganodiselenide **6d** and triselenide **6t** in a 85:15 ratio (Scheme 2, Table I). Similarly, 2-carbomethoxybenzyl bromide **1f** gave the corresponding di- and triselenide **7d** and **7t** in a 86:14 ratio. The coordinating ability of -NO₂ and -CO₂Me groups might be influencing the stabilization of triselenide linkage.¹³Intramolecular selenium coupling reaction takes place with α, α' -dibromo-o-xylene **1g** yielding 1,4-dihydro-2,3-diselena-naphthalene **8d** (Scheme 2, Table I).

TABLE I Formation of Diorgano Selenides R-(Se)_n-R (n = 1, 2, 3) from the Reaction of Selenous Acid and an Organic Halide (RX) (Schemes 1 and 2)^{*a*}

R	Products	Product $Ratio^b$	Total Se Conversion (%) ^c		
4-Me-C ₆ H ₄ CH ₂ -	2m:2d:2t	10:85:5	37		
$C_6H_5CH_2$ -	3m:3d:3t	50:45:5	52		
4-Cl-C ₆ H ₄ CH ₂ -	4m:4d:4t	62:34:4	57		
$4-NO_2-C_6H_4CH_2-$	5m:5d:5t	20:75:5	41		
2-NO ₂ -C ₆ H ₄ CH ₂ -	6d:6t	85:15	30		
$2-MeOC(O)-C_6H_4CH_2-$	7d:7t	86:14	43		
1,2-[-CH ₂ -C ₆ H ₄ -CH ₂ -]	8d	100	38		

^aReaction conditions: RX (1 mmol), H_2SeO_3 (1 mmol), $SnCl_2 \cdot 2 H_2O$ (3.2 mmol), CuCl_2 \cdot 2 H_2O (0.3 mmol), THF-DMSO (1:2, 3 mL), ambient temp., 15 h.^b The ratio is based on ¹H NMR of the product mixture.^cBased on isolated yield of the product/product mixture from two reactions (accuracy \pm 5%).



Spectroscopic Characterization

¹H (200 MHz), ¹³C (50 MHz), and ⁷⁷Se NMR (52.7 MHz) spectra of the organoselenides were recorded in CDCl₃ as solvent (Table II). Along with the chemical shifts in ⁷⁷Se NMR, the number of signals i.e. for monoselenide and diselenide: one signal, and for triselenide: two signals with a ratio of 1:2, is used as a clear diagnostic tool. The ⁷⁷Se chemical shifts of RSe_nR (n = 1, 2, 3) range between 200 and 650 ppm, and shift to lower field with increasing n-value. The signals for the α -hydrogen and α -carbon atoms are observed at 3.0–4.5 and at

R	$\delta^1 H$ of Se-CH ₂ -		$\delta^{13} \mathrm{C}$ of Se-C			$\delta^{77} \mathbf{Se}^a$			
	Se	Se_2	Se ₃	Se	Se_2	Se_3	Se	Se_2	Se_3
4-Me-C ₆ H ₄ CH ₂ -	3.60	3.77	4.17	27.2	32.4	34.5	329	397	_
$C_6H_5CH_2$ -	3.74	3.85	4.27	27.5	32.5	34.6	330	400	_
4-Cl-C ₆ H ₄ CH ₂ -	3.67	3.81	4.21	26.7	31.7	33.5	335	406	_
4-NO ₂ -C ₆ H ₄ CH ₂ -	3.73	3.83	4.27	26.9	31.2	32.7	341	494	_
$2-NO_2-C_6H_4CH_2-$	_	4.14	4.44		30.8	31.6	_	528	558, 622
2-MeOC(O)-C ₆ H ₄ CH ₂ -	_	4.21	4.54	_	32.7	34.2	—	563	593, 663
1,2-[-CH ₂ -C ₆ H ₄ -CH ₂ -]	—	4.23	—	—	29.8	—	—	443	_

TABLE II Selected ¹H, ¹³C, and ⁷⁷Se NMR chemical shifts (ppm) of R-(Se)_n-R (n = 1, 2, 3)

 $^{a}\delta^{77}$ Se values agree well with those reported in the literature^{5g,5h}



SCHEME 3

23.5–39.0 ppm, respectively. Qualitatively $\Delta \delta$ is markedly higher between di- and triselenide than between mono- and diselenide. All of the above results fit well with those of previous studies.^{5c,5g–5h}

Mass spectrometric studies of organoselenium compounds are of continuing interest.¹⁴ From the mass spectra (EI, 70 eV) of the organoselenides, molecular ion and daughter ion peaks could be diagnosed easily from the characteristic selenium isotope pattern. The spectra of dibenzyldiselenides **2d–5d** show a uniform skeletal rearrangement pattern (Scheme 3). The principal fragmentation involves cleavage of the Se-Se bond (*path-A*), H-migration to selenium (*path-B*), and loss of SeH radical (*path-C*). The ease of H-migration over Se-Se cleavage is strongly pronounced in the case 1,4-dihydro-2,3-diselenanaphthalene **8d**, which results in the formation of ion **A**. Loss of SeH radical produces the benzocyclobutane ion **B**.

Mechanistic Studies

The following results provided further insight into the reactivity of the Cu(II)/Sn(II) bimetallic reagent system in the present selenium transfer reactions.

- 1. No reaction takes place either in the absence of the copper salt or in presence of nickel and palladium salts or complexes such as NiCl₂, NiCl₂(PPh₃)₂, Pd(OAc)₂, Pd₂(dba)₃, and PdCl₂(PPh₃)₂ as catalysts. This emphasizes the special role of copper in the reaction.
- 2. Neither allyltributyltin nor allyltrichlorostannane reacts with selenous acid in the presence or absence of copper(II) halides. *The possibility of an organotin intermediate is thereby ruled out.*
- 3. Selenous acid does not form any complex with copper salts (UV monitoring). *Hence a copper-selenolate intermediate is most unlikely*.
- 4. The mixture which is prepared from selenous acid and stannous chloride (1:3) does not react with any organic halide in the absence of a copper halide. The formation of any organoselenyltin species (RSe-Sn) is thereby ruled out.
- 5. As noted earlier, the selenium transfer proceeded through a brownblack suspension, which turned into a clear yellow solution as the reaction was progressed. The suspension was quickly filtered, washed with THF and an XRD was recorded (Sample A; Figure 1). In an independent experiment, the reaction of stannous chloride dihydrate (24 mmol), cupric chloride dihvdrate (16 mmol) and selenous acid (4 mmol) in THF resulted in a brown-black precipitate, which was washed with THF and dried (Sample B, XRD shown in Figure 1). Qualitative analysis of the precipitate indicated the presence of chloride. The precipitate was washed with aqueous ammonia till a constant weight was reached (Sample C, Figure 1). Analysis of the XRD spectra clearly allowed us to identify the species in the three samples. Thus, while sample C corresponds to pure α -Cu₂Se, samples **A** and **B** are mixtures of α -Cu₂Se and CuCl.¹⁵ ICP-AAS analysis of sample **C** further supports the composition to be Cu₂Se (Anal. calcd. for Cu₂Se: Cu, 61.68; Se, 38.32%. Found Cu, 61.83%). It may be pointed out that Xie *et al.* have recently described the synthesis of nanocrystalline copper selenides from the reaction of sodium selenosulfate and cuprous iodide under sonochemical irradiation.¹⁶
- 6. Curiously, when a mixture of sample C (α -Cu₂Se) and an organic halide (1 equiv.) was stirred in THF-DMSO, there was no indication of product formation. Addition of stannous chloride (1 equiv. with respect to the organic halide) caused spontaneous reaction leading to the formation of the corresponding diorganoselenides. *This further augments the bimetallic reactivity of the Cu(II)/Sn(II) reagent.*



FIGURE 1 XRD pattern of Samples **A**, **B**, **C** and of α -Cu₂Se and CuCl.¹⁵ d-Values (%) for Sample **C**: 3.42 (76), 2.06 (100), 1.75 (28), 1.45 (15); for α -Cu₂Se: 3.37 (70), 2.06 (100), 1.76 (31), 1.46 (7).

7. In an earlier study,¹⁷we have demonstrated that the reaction of the Cu(II)/Sn(II) reagent with PhSeSePh results in the formation of Cu_2 SePh. The latter reacts with an organic halide in the presence of a tin(II) halide via an intermediate having a Cu-Se-Sn core unit (Scheme 4).

All of the above experimental results, the known chemistry of stannylcuprates and the established selenophilicity of copper guide us to indicate the major bond-forming steps (Scheme 5). These include: (a) formation of α -Cu₂Se from CuCl₂, SnCl₂ and H₂SeO₃, (b) activation



SCHEME 4

of Cu_2Se by $SnCl_2$, (c) activation of the organic halide at the copper site and concomitant selenium transfer to generate "R-Se-Cu", and (d) elimination of the diorganoselenide. A complete elaboration of the above steps must require model studies, which are presently underway in our laboratory.

In summary, we have demonstrated a novel 'copper-directed reactivity' and dual-metal effect for selenium transfer from selenous acid to organic electrophiles. The selenophilicity of copper is well known in literature, especially in ligand-assisted chemistry. In light of these insights, efforts are underway to critically look into the selenium transfer steps in detail.

EXPERIMENTAL

All reactions were performed under an inert atmosphere of argon. All the starting materials were > 98% pure according to ¹H NMR. ¹H and ¹³C NMR spectra were recorded in CDCl₃ using a Brucker-200 spectrometer. ⁷⁷Se NMR spectra were obtained in CDCl₃ with a Brucker-300 spectrometer using diphenyl diselenide ($\delta = 460$ ppm) as external standard. EIMS (70 eV) spectra were recorded using



a VG MicroMass 7070H and a VG Autospec M mass spectrometer. FAB/MS spectra were recorded with a JEOL SX 102/DA-6000 mass spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. X-ray powder diffraction data were obtained with a Phillips PW-1840 instrument using a Cu-K α target at 40 kV. ICP-AAS analyses were carried out at Central Glass & Ceramics Research Institute, Kolkata.

Reaction of 4-Methylbenzyl lodide with Selenous Acid

A mixture of selenous acid (129 mg, 1 mmol) and stannous chloride dihydrate (722 mg, 3.2 mmol) was stirred in THF-DMSO (1:2, 3 mL) under argon at ambient temperature, yielding a pale yellow solution within 30 min. A solution of 4-methylbenzyl iodide **1a** (232 mg, 1 mmol) and a catalytic amount of cupric chloride dihydrate (51 mg, 0.3 mmol, 30 mol% with respect to selenous acid) in THF-DMSO (1:2, 3 mL) was added drop wise to the above solution. A brown colored suspension was observed, which turned into a clear yellow solution within 15 h. An aqueous solution of ammonium fluoride (15%, 10 mL) was added to the reaction mixture, the organic layer was extracted with diethyl ether (3 × 20 mL), washed with water (2 × 10 mL), brine (2 × 10 mL), and dried over magnesium sulfate. Removal of the solvent followed by short column chromatography (silica gel 60–120 mesh, SRL, eluent *n*hexane) afforded 69 mg of a product mixture containing **2m:2d:2t** in a 10:85:5 ratio (according to ¹H NMR).

2d: ¹H NMR (CDCl₃): $\delta = 2.25$ (s, 6H), 3.77 (s, 4H), 6.99–7.11 (m, 8H); ¹³C NMR (CDCl₃): $\delta = 21.1$, 32.4, 128.8, 129.1, 136.1, 136.9; ⁷⁷Se NMR (CDCl₃): $\delta = 397$.

2m: ¹H NMR (CDCl₃): $\delta = 2.25$ (s, 6H), 3.60 (s, 4H), 6.99–7.11 (m, 8H); ¹³C NMR (CDCl₃): $\delta = 21.0$, 27.2, 128.8, 129.1, 136.1, 136.6; ⁷⁷Se NMR (CDCl₃): $\delta = 329$; EIMS m/z (rel. intensity): 370 (24), 290 (12), 209 (29), 185 (22), 105 (100), 77 (59).

Reaction of Benzyl Bromide with Selenous Acid

The procedure described for **1a** was identically followed using **1b** (171 mg, 1 mmol) to afford 102 mg of a product mixture containing **3m:3d:3t** in a 50:45:5 ratio (according to ¹H NMR).

3d: ¹H NMR (CDCl₃): δ = 3.85 (s, 4H), 7.22–7.37 (m, 10H); ¹³C NMR (CDCl₃): δ = 32.6, 127.2, 128.4, 129.0, 139.0; ⁷⁷Se NMR (CDCl₃): δ = 400; FABMS *m*/*z* (rel. intensity): 342 (51), 181 (49), 154 (81).

3m: ¹H NMR (CDCl₃): δ = 3.74 (s, 4H), 7.22–7.37 (m, 10H); ¹³C NMR (CDCl₃): δ = 27.5, 127.0, 128.4, 129.0, 139.1; ⁷⁷Se NMR (CDCl₃): δ = 330; FABMS *m*/*z* (rel. intensity): 262 (43), 181 (11), 154 (100).

Reaction of 4-Chlorobenzyl lodide with Selenous Acid

The procedure described for **1a** was identically followed using **1c** (253 mg, 1 mmol) to afford 146 mg of a product mixture containing **4m:4d:4t** in a 62:34:4 ratio (according to ¹H NMR). Compounds **4m** and **4d** were separated by column chromatography.

4d: ¹H NMR (CDCl₃): δ = 3.81 (s, 4H), 7.11–7.37 (m, 8H); ¹³C NMR (CDCl₃): δ = 31.6, 128.6, 130.3, 132.9, 137.4; ⁷⁷Se NMR (CDCl₃): δ = 406; FABMS *m*/*z* (rel. intensity): 410 (12), 125 (30).

4m: ¹H NMR (CDCl₃): $\delta = 3.67$ (s, 4H), 7.11–7.37 (m, 8H); ¹³C NMR (CDCl₃): $\delta = 26.7$, 128.5, 130.2, 132.4, 137.4; ⁷⁷Se NMR (CDCl₃): $\delta = 335$.

Reaction of 4-Nitrobenzyl Bromide with Selenous Acid

The procedure described for **1a** was identically followed using **1d** (216 mg, 1 mmol) to afford 93 mg of a product mixture containing **5m:5d:5t** in a 20:75:5 ratio (according to ¹H NMR).

5d: ¹H NMR (CDCl₃): δ = 3.83 (s, 4H), 7.19–7.29 (m, 4H), 8.08–8.13 (m, 4H); ¹³C NMR (CDCl₃): δ = 31.2, 123.9, 129.7, 146.5, 146.9; ⁷⁷Se NMR (CDCl₃): δ = 494.

5m: ¹H NMR (CDCl₃): δ = 3.73 (s, 4H), 7.19–7.29 (m, 4H), 8.08-8.13 (m, 4H); ¹³C NMR (CDCl₃): δ = 26.9, 123.7, 129.6, 146.3, 146.9; ⁷⁷Se NMR (CDCl₃): δ = 341; EIMS *m*/*z* (rel. intensity): 432 (8), 352 (21), 272 (35), 216 (3), 136 (100), 90 (61), 78 (69).

Reaction of 2-Nitrobenzyl Bromide with Selenous Acid

The procedure described for 1a was identically followed using 1e (216 mg, 1 mmol) to afford 62 mg of a product mixture containing bis(2-nitrobenzyl)diselenide **6d** and bis(2-nitrobenzyl)triselenide **6t** in a 85:15 ratio (according to ¹H NMR).

6d: ¹H NMR (CDCl₃): δ = 4.14 (s, 4H), 7.16–7.21 (m, 2H), 7.29–7.52 (m, 4H), 7.96–8.01 (m, 2H); ¹³C NMR (CDCl₃): δ = 30.8, 125.6, 128.3, 132.1, 133.4, 135.3, 147.3; ⁷⁷Se NMR (CDCl₃): δ = 528.

6t: ¹H NMR (CDCl₃): δ = 4.44 (s, 4H), 7.16–7.21 (m, 2H), 7.29–7.52 (m, 4H), 7.96–8.01 (m, 2H); ¹³C NMR (CDCl₃): δ = 31.6, 125.8, 128.4, 132.3, 133.4, 135.3, 147.3; ⁷⁷Se NMR (CDCl₃): δ = 558, 622.

Reaction of 2-Carbomethoxybenzyl Bromide with Selenous Acid

The procedure described for 1a was identically followed using 1f (229 mg, 1 mmol) to afford 99 mg of a product mixture containing bis(2-carbomethoxybenzyl)diselenide 7d and bis(2-carbomethoxybenzyl)triselenide 7t in a 86:14 ratio (according to ¹H NMR).

7d: ¹H NMR (CDCl₃): δ = 3.82 (s, 6H), 4.21 (s, 4H), 7.05–7.36 (m, 6H), 7.85–7.89 (m, 2H); ¹³C NMR (CDCl₃): δ = 32.7, 52.0, 127.0, 127.9, 130.9, 131.2, 132.0, 142.0, 167.4; ⁷⁷Se NMR (CDCl₃): δ = 563.

7t: ¹H NMR (CDCl₃): $\delta = 3.81$ (s, 6H), 4.54 (s, 4H), 7.05–7.36 (m, 6H), 7.85–7.89 (m, 2H); ¹³C NMR (CDCl₃): $\delta = 34.2$, 52.7, 127.2, 128.4, 130.3, 132.1, 132.3, 142.0, 167.4; ⁷⁷Se NMR (CDCl₃): $\delta = 593$, 663; FABMS m/z (rel. intensity): 535 (<2), 458 (24), 229 (10), 149 (52).

Reaction of α, α' -Dibromo-o-xylene with Selenous Acid

The procedure described for **1a** was identically followed using **1g** (264 mg, 1 mmol) to give 1,4-dihydro-2,3-diselena-naphthalene **8d**. Isolated yield: 50 mg (19%). ¹H NMR (CDCl₃): $\delta = 4.23$ (s, 4H), 7.03–7.17 (m, 8H); ¹³C NMR (CDCl₃): $\delta = 29.8$, 125.9, 126.4, 141.7; ⁷⁷Se NMR (CDCl₃): $\delta = 443$; EIMS m/z (rel. intensity): 262 (2), 183 (68), 103 (22), 83 (100).

Preparation of Sample B and Sample C

Stannous chloride dihydrate (1.81 g, 8 mmol) was added in portions to a solution of selenous acid (0.516 g, 4 mmol) in THF (25 mL) with stirring at ambient temperature and under argon atmosphere. A red colored precipitate was formed. To the above was added a mixture of stannous chloride dihydrate (3.61 g, 16 mmol) and cupric chloride dihydrate (2.73 g, 16 mmol) in THF (30 mL). The resulting brown-black precipitate was further stirred for 1 h, the solid was filtered under argon, washed with THF (10 × 10 mL) and diethylether (5 × 10 mL) and finally dried under vacuum (**Sample B**; yield 1.71 g).

Sample B (1.5 g) was further washed with 25% aqueous ammonia solution (10×7 mL), followed by distilled water (5×10 mL), and ethanol (5×10 mL) and dried under vacuum until a constant weight was reached (**Sample C**; yield 0.310 g).

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