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Copper-Induced Deselenative Coupling of Selenoamides Leading to 1,2-Enediamines

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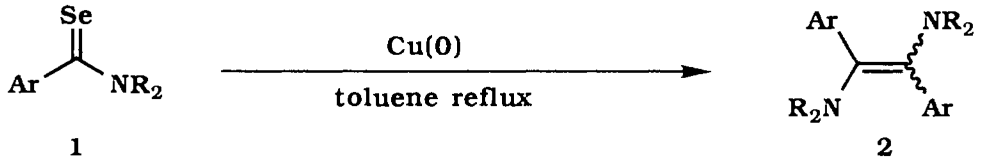
N,N-Disubstituted selenoamides were found to undergo deselenative coupling by the action of copper(0), providing 1,2-enediamines in good yields. The driving force of this reaction may be a high affinity of selenium for soft metals such as copper.

The deoxygenative coupling of aldehydes and ketones constitutes of an important method for olefin formation,$^{1)}$ and low valent titanium reagents, generated *in situ*, have been widely employed for this purpose.$^{2)}$ In sharp contrast, there is no example reported up to date, which attained an efficient coupling of amides leading to 1,2-enediamines.$^{3)}$ Herein we report that selenoamides, selenocarbonyl analogues of amides, undergo a novel deselenative coupling caused by copper(0), giving 1,2-enediamines in good yields.

The reaction of 1-selenobenzoylpiperidine (**1a**, 1 mmol) with copper powder (2 mmol) was carried out in refluxing toluene (0.5 mL) for 4 h with magnetic stirring. Filtration and concentration *in vacuo* provided an almost quantitative yield of 1,2-dipiperidinostilbene (**2a**), which was fairly pure as it stood (Eq. 1).$^{4)}$

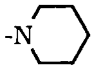
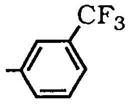
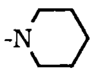
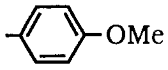
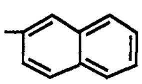


(1)

The assignment of the stereochemistry was confirmed unambiguously by the observed NOE enhancement (7%) of α-methylene protons of nitrogen upon irradiation of the aromatic protons in E-isomer. Similar conditions can be employed with several N,N-disubstituted selenoamides (**1b**-**1e**), and the corresponding 1,2-enediamines (**2b**-**2e**) were isolated in moderate to high yields (Table 1). When the coupling reaction of **1a** was carried out using equimolar amounts of copper powder, enediamine (**2a**) was formed in 48% yield with recovery of **1a** (52%). Among the metals examined, $W(CO)_6$ also caused the same coupling reaction, but the yield of 1,2-enediamine was not satisfactory (20%). Zinc powder exerted no effect on this reaction. In the cases of N-monosubstituted and N-unsubstituted selenoamides, the desired 1,2-enediamines were not formed under the same conditions: the former provided imine (Ar-CH=NR) in 86% yield, whereas the latter gave nitrile (ArCN) as a major product.

On the other hand, amides or thioamides did not undergo reductive coupling with Cu(0) under similar conditions. The difference of the reactivities between selenoamide and amide (or thioamide) is believed to be

Table 1. Copper-Induced Deselenative Coupling of Selenoamides[a]

Entry	Selenoamide		Product	Yield/%[b]	E/Z[c]
1	Ar = -Ph	NR_2 = 	**2a**	70 (100[d])	82/18
2	Ar = -Ph	NR_2 = NMe_2	**2b**	59 (76)	51/49
3	Ar = 	NR_2 = 	**2c**	89 (100[d])	83/17
4	Ar = 	NR_2 = 	**2d**	60 (97[d])	78/22
5	Ar = 	NR_2 = 	**2e**	52	80/20

a) Reaction conditions: selenoamide (1 mmol), Cu (2 mmol), toluene (0.5 mL), 111 °C, 4 h.
b) Isolated yields after purification by column chromatography on alumina. The yields in the parentheses are based on ^{1}H NMR. c) Determined by ^{1}H NMR. d) Fairly pure.

due to higher affinity of selenium for soft metals such as copper[5] and the instability of carbon-selenium double bond.[6]

Further extensions of this studies and elucidation of the precise mechanism are underway.

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References

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2) J. E. McMurry, *Chem. Rev.*, **89**, 1513 (1989); D. Lenoir, *Synthesis*, **1989**, 883.
3) 1,2-Bis(diethylamino)stilbene was obtained as a byproduct from the reaction of N,N-diethylbenzamide with triethylsilyllithium: D. A. Bravo-Zhivotovskii, S. D. Pigarev, I. D. Kalikhman, O. A. Vyazankina, and N. S. Vyazankin, *J. Organomet. Chem.*, **248**, 51 (1983); *Zh. Obshch. Khim.*, **53**, 1838 (1983).
4) Further purification by column chromatography on alumina using hexane as an eluent yielded 121 mg (0.35 mmol, 70%, E/Z = 82/18) of **2a**: mp 112.0-112.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) [E-isomer] δ 1.10-1.40 (brs, 12H), 2.12-2.42 (brs, 8H), 7.05-7.19 (m, 2H), 7.19-7.35 (brd, 8H); [Z-isomer] δ 1.40-1.60 (brs, 12H), 2.85-3.00 (brs, 8H), 6.83-6.97 (m, 6H), 6.97-7.05 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) [E-isomer] δ 24.43, 27.18, 52.91, 126.21, 127.64, 129.68, 136.52, 142.35; [Z-isomer] δ 24.79, 26.98, 51.90, 125.43, 127.06, 131.31, 137.71, 140.61; IR (NaCl) 3054, 3018, 2929, 2850, 2812, 1594, 1489, 1442, 1378, 1228, 1194, 1112, 755, 670 cm^{-1}; MS (EI, m/e) 346 (M^+, 100); Anal. Found: C, 82.99; H, 8.69; N, 8.02%. Calcd for $C_{24}H_{30}N_2$: C, 83.19; H, 8.73; N, 8.08%.
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6) F. S. Guziec, Jr., "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai, John Wiley & Sons, New York (1987), Vol. 2, Chap. 4.

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