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Facile Synthesis of Selenocarboxamides from Nitriles Using Se/CO/H_2O under Atmospheric Pressure

Yahong Chen,[1,2] Fengshou Tian,[2] Maoping Song,[2] and Shiwei Lu[3]

[1]*Department of Chemistry, Zhoukou Normal University, Zhoukou, Henan 466000, People's Republic of China*

[2]*Department of Chemistry, Zhengzhou University, Zhengzhou, Henan 450052, People's Republic of China*

[3]*Dalian Institute of Chemical Physics, Dalian, Liaoning 116023, People's Republic of China*

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ABSTRACT: *Aromatic and aliphatic nitriles can be conveniently converted into the corresponding selenocarboxamides with Se/CO/H_2O under atmospheric pressure without use of a base.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:211–214, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20398

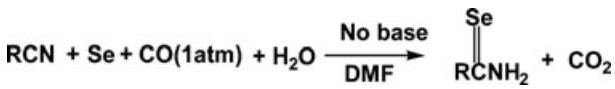
INTRODUCTION

Selenocarboxamides have received considerable attention because of their importance as useful precursors for the synthesis of various selenium-containing heterocycles [1]. Therefore, some attempts for the synthesis of primary selenocarboxamides have been described. In general, selenocarboxamides have been prepared by the addition of hydrogen selenide to the corresponding nitriles [2]. In earlier investigations, hydrogen selenide was directly bubbled into the reaction solution; however, the yields were very low. In recent investigations, hydrogen selenide formed in a reaction vessel from its precursors such as Al_2Se_3 [3] and H_2O. NaSeH was used to react with aromatic nitriles, and better results were obtained [4]. In addition, selenating reagents, such as bis(trimethylsily)selenide [5], 4-methylselenobenzoate [6], or monoselenophosphate [7], are also used in these preparations. Reaction of nitriles with a mixture of selenium, water, and triethylamine under 5 atm of carbon monoxide leads to the formation of primary selenocarboxamides [8].

Recently, we reported the synthesis of symmetrical diselenides from aldehydes by means of a modified Se/CO/H_2O system [9]. Herein, we report a new and facile method for the synthesis of primary selenocarboxamides using nitriles as substrates with Se/CO/H_2O/DMF under atmospheric pressure without use of a base (see Scheme 1).

RESULTS AND DISCUSSION

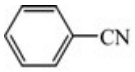
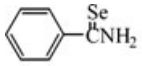
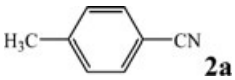
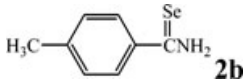
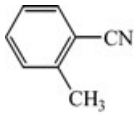
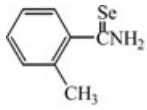
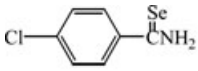
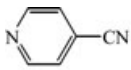
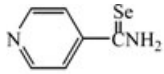
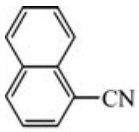
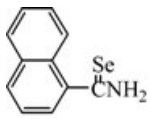
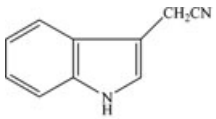
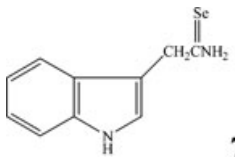
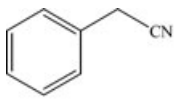
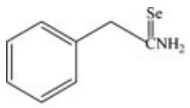
Our initial attempts to prepare phenyl selenocarboxamide are by the reaction of benzonitrile with Se/CO/H_2O under a variety of conditions (variations of the stoichiometry, temperature, solvent such as $PhCH_3$, EtOH, DMSO, THF). We have eventually found that phenyl selenocarboxamide can be prepared in 80% yields by the reaction of



SCHEME 1

Correspondence to: Fengshou Tian; e-mail: fengshoutian@163.com.

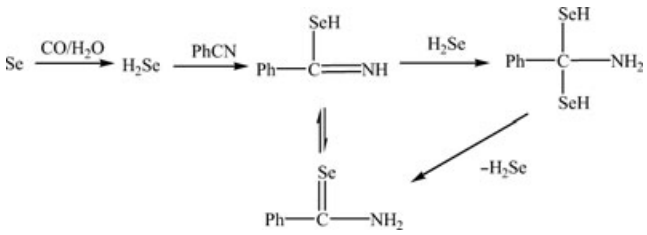
TABLE 1 Synthesis of Selenocarboxamides

Entry	*Substrate*	*Product*	*Melting Point (°)*	*Yield (%)*[a]
1	 **1a**	 **1b**	Yellow solid 125–126 (126–126.5) [8]	80
2	 **2a**	 **2b**	164–165 (165–167) [8]	96
3	 **3a**	 **3b**	Yellow solid 102–104 (104–106) [8]	34
4	 **4a**	 **4b**	Yellow solid 127–128 (126–127) [8]	92
5	 **5a**	 **5b**	Yellow solid >148 (>154 Dec.) [8]	85
6	 **6a**	 **6b**	Yellow solid 131–133 (131–132) [8]	80
7	 **7a**	 **7b**	Yellow solid 122–124	40
8	 **8a**	 **8b**	Yellow solid 88–90 (92–93) [6]	45
9	n-BuCN **9a**	 **9b**	Yellow liquid	30
10	$NCCH_2COOCH_2CH_3$ **10a**	 **10b**	Yellow liquid	42

[a]Isolated yield.

benzonitrile with $Se/CO/H_2O/DMF$ at 90°C for 5 h under atmospheric pressure without use of a base.

To study the preparative scope of our method, aromatic and heterocyclic and aliphatic selenocarboxamides were successfully synthesized from the corresponding nitriles as shown in Table 1. From the Table 1, we can see that the yields of aromatic selenocarboxamides were high except for some cases



SCHEME 2

of sterically hindered selenocarboxamides such as **3b** (entries 1–6). The aromatic selenocarboxamides are obtained as yellow solid and are stable enough under nitrogen at ordinary temperature. However, when aliphatic nitriles were used as the reaction substrates, poor yields (30%–45%) of the corresponding products were obtained (entries 7–10). The reasons are that these selenocarboxamides isolated were thermally unstable under nitrogen and highly sensitive to air. Aliphatic selenocarboxamides are assumed to be less stable because of the lack of conjugation between the aromatic ring and the selenocarbonyl group observed in aromatic ones.

In analogy with the mechanism proposed for the reaction of aromatic aldehydes with Se/CO/H_2O/DMF, the possible mechanism for the reaction of nitriles with Se/CO/H_2O/DMF is shown in Scheme 2.

In summary, a facile method for the synthesis of selenocarboxamides from nitriles using Se/CO/H_2O/DMF under atmospheric pressure has been found. The present method for the synthesis of selenocarboxamides described obtained high-yield aromatic and heterocyclic selenocarboxamides with simple and facile operations and made it possible to prepare unstable aliphatic selenocarboxamides.

EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF SELENOCARBOXAMIDES

In a 100-mL three-necked flask, nitrile (2.5 mmol), selenium (2.5 mmol), water (2 mL), DMF (20 mL), and a magnetic stirring bar were placed. Carbon monoxide was introduced and bubbled into the reaction mixture with vigorous stirring at 90°C for 5 h. After the reaction was complete, 20 mL water was added and the reaction mixture was extracted with diethyl ether (3 × 40 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and evaporated the solvent under reduced pressure to afford a yellow oil. Further purification by column chromatography on silica gel or TLC gave the pure product. All the products were identified by NMR and/or comparison with the authentic samples.

Data of Products

1b: ^{1}H NMR (Me_2SO-d_6, 400 MHz), δ 7.38–7.89 (m, 5H), 10.21 (1H), 10.80 (1H). ^{13}C NMR (Me_2SO-d_6, 400 MHz), δ 127.40, 127.90, 131.25, 142.17, 203.89 (C=Se).

2b: ^{1}H NMR (Me_2SO-d_6, 400 MHz), δ: 7.09–7.98 (m, 5H), 9.76 (1H), 10.57 (1H), 2.52 (s, 3H).

3b: ^{1}H NMR (Me_2SO-d_6, 400 MHz), δ 2.31 (s, 3H), 7.75–7.78 (4H), 10.05 (1H), 10.77 (1H). ^{13}C NMR (Me_2SO-d_6, 400 MHz), δ 20.07, 127.38, 127.55, 1301.12, 1312.14, 146.02, 204.77 (C=Se).

4b: ^{1}H NMR (Me_2SO-d_6, 400 MHz), δ 7.58 (2H), 7.99 (2H), 10.38 (1H), 10.99 (1H). ^{13}C NMR (Me_2SO-d_6, 400 MHz), δ 127.97, 129.18, 136.17, 140.82, 202.22 (C=Se).

5b: ^{1}H NMR (Me_2SO-d_6, 400 MHz), δ 7.70 (2H), 8.66 (2H), 10.54 (1H), 11.21 (1H). ^{13}C NMR (Me_2SO-d_6, 400 MHz), δ 120.66, 149.17, 149.82, 202.08 (C=Se).

6b: ^{1}H NMR (Me_2SO-d_6, 400 MHz), δ 7.40–8.19 (m, 7H), 10.60 (1H), 11.28 (1H).

7b: ^{1}H NMR (Me_2SO-d_6, 400 MHz), δ 4.14 (2H), 7.08–7.76 (5H), 9.94 (NH), 10.53 (1H), 11.06 (1H). ^{13}C NMR (Me_2SO-d_6, 400 MHz), δ 45.82, 109.20, 111.80, 118.50, 118.91, 121.72, 124.30, 126.96, 136.13, 209.65 (C=Se). Anal. Calcd for $C_{10}H_{10}SeN_2$: C 50.64, H 23.70, N 11.81; found: C 50.52, H 23.68, N 11.97.

8b: ^{1}H NMR (Me_2SO-d_6, 400 MHz), δ 4.02 (2H), 7.13–7.43 (5H), 7.87 (1H), 10.17 (1H). ^{13}C NMR (Me_2SO-d_6, 400 MHz), δ 56.12, 128.20, 128.43, 129.52, 129.84, 135.47, 211.46 (C=Se).

9b: ^{1}H NMR (Me_2SO-d_6, 400 MHz), δ 0.92 (3H), 1.73 (2H), 2.65 (2H), 9.91 (1H), 10.15 (1H).

10b: ^{1}H NMR (Me_2SO-d_6, 400 MHz), δ 1.27–1.32 (5H), 4.19 (2H), 10.28 (1H), 10.73 (1H). ^{13}C NMR (Me_2SO-d_6, 400 MHz), δ 14.04, 24.59, 60.77, 166.65, 200.74 (C=Se). Anal. Calcd for $C_5H_9SeO_2N$: C 30.93, H 0.46, N 11.86; found: C 31.08, H 0.42, N 12.06.

ACKNOWLEDGMENT

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