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CONVENIENT SYNTHESIS OF PRIMARY SELENOAMIDES FROM ARYL NITRILES, SELENIUM AND SODIUM BOROHYDRIDE

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ABSTRACT: *Aryl nitriles react smoothly with sodium hydrogen selenide, itself prepared in situ from selenium and sodium borohydride, in ethanol to give the corresponding primary selenoamides in moderate to good yield.*

Primary selenoamides are important intermediates for preparations of several types of nitrogen- and selenium containing heterocyclic compounds.[1-4] However, only a few methods have been developed for the synthesis of selenoamides, and all these methods suffer limitations, especially when the starting materials and/or reagents which are not generally available or the highly toxic reagent such as hydrogen selenide are used, and severe reaction conditions are needed.[5] The earliest procedures involved direct addition of gaseous hydrogen selenide to nitriles.[6-7] Nitriles and aluminum selenide in a mixture of aqueous pyridine and triethylamine afford primary selenoamides.[8] Reaction of nitriles with a mixture of selenium, water and triethylamine under 5 atm of carbon monoxide leads to the formation of primary selenoamides.[9] A recent report described the preparation of primary selenoamides from nitriles by the treatment of bis(trimethylsilyl) selenide and

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BF_3·OEt_2.[10] Secondary and tertiary selenoamides can be prepared in moderate yield by aminolysis of the corresponding selenoesters,[11] via acetylenic selenol-selenoketene intermediates analogous to the preparation of selenoester,[12] or by reactions of sodium hydrogen selenide with chlorimidates,[13] S-alkylated thioamides[14] and iminium salts.[15]

We now wish to describe a new convenient method for the synthesis of primary selenoamides from the corresponding nitriles by treatment with selenium powder and sodium borohydride, in which the active reagent is sodium hydrogen selenide. Sodium hydrogen selenide, readily prepared *in situ* from selenium and sodium borohydride in ethanol under nitrogen atmosphere, has been widely used in organic synthesis.[16] We now found that treatment of aromatic nitriles **1** with NaSeH ethanol solution gave rise to the corresponding N-unsubstituted selenoamides **2** as shown in Scheme 1. The yields of selenocarboxamides were moderate to good (57-70%) except for **2d** (Table 1). In every case no by-products but the starting nitriles were found, thus the purification was simple.

The primary selenoamides prepared were readily assigned by the spectra, elemental analysis (for **2f**) and by the previously reported works.[7-8] The IR and NMR spectra are listed in Table 2. In most cases two broad singlets were observed in a lower field ^1H NMR spectra, due to the resonance structure of -C(SeH)=NH.[8]

This method possesses the advantages of simple procedure, mild conditions and easy availability of starting materials and reagents.

Scheme 1

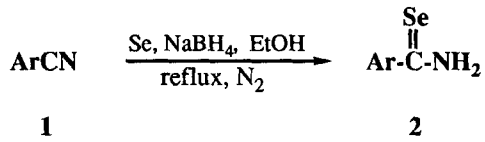

Table 1. Preparations of Aryl Selenoamides 2

No.	Ar	reaction time (h)	Yield (%)	m.p. (°C)	lit. mp. (°C)	Ref.
2a	C_6H_5	6	62	119-120	125	8
2b	m-$CH_3C_6H_4$	7	70	84-85	74	8
2c	p-$CH_3C_6H_4$	7	57	165 (dec.)	161	7
2d	p-$CH_3OC_6H_4$	9	27	157-159	157	8
2e	p-ClC_6H_4	8	63	126-127	129	8
2f	o-ClC_6H_4	8	58	66-67 [a]		

a. Calcd. for C_7H_6ClNSe: C, 45.47; H, 3.63; N, 7.40. Found: C, 45.65; H, 3.80; N, 7.61.

Table 2. IR and ^1H NMR spectra of selenoamides 2

No.	IR (ν cm^{-1})	^1H NMR ($CDCl_3$, δ)
2a	3345, 3290, 1630	7.15-7.52 (m, 3H), 7.68-7.85 (m, 2H) 8.15 (br, H), 9.00 (br, 1H)
2b	3275, 1650	2.33 (s, 3H), 7.02-7.60 (m, 4H), 7.97 (br, 1H) 8.91 (br, 1H)
2c	3380, 3285, 1630	2.34 (s, 3H), 7.02-7.17 (d, 2H), 7.67-7.82 (d, 2H) 8.10-8.72 (br, 2H)
2d	3380, 3285, 1610	3.34 (s, 3H), 6.81-6.95 (d, 2H), 7.93 (d, 2H) 9.92 (br, 1H), 10.35 (br, 1H)
2e	3345, 3300, 1640	7.23 (d, 2H), 7.73 (d, 2H), 8.21 (br, 2H) 8.92 (br, 1H)
2f	3360, 1640	7.15-7.26 (m, 4H), 8.70 (br, 1H), 9.19 (br, 1H)

Experimental

Melting points were measured on an electrothermal melting point apparatus and uncorrected. ^1H NMR spectra were obtained with an Ac-80 (80 MHz) spectrometer using TMS as internal standard. IR spectra (KBr) were recorded on a Perkin Elmer 683 instrument. The Elemental analysis was conducted on a Carlo-Erba 1106 elemental analyser.

Selenobenzamide. Typical Procedure:

Anhydrous ethanol (20 ml) was added slowly to a mixture of selenium powder (0.79 g, 10 mmol) and sodium borohydride (0.46 g, 12 mmol) under N_2 at 0-5 °C. After a few minutes, the ice-bath was removed and the mixture was allowed to warm up to room temperature. To this sodium hydrogen selenide solution was added benzonitrile (1.03 g, 10 mmol) and the mixture was refluxed for 6 hr. After cooling to room temperature, hydrochloric acid (6N, 2 ml) was added and the solution was stirred for about an hour. Water (20 ml) was then added and the solution was filtered off, extracted with methylene chloride (3 x 20 ml) and dried over $MgSO_4$. Evaporation of solvent gave the crude product which was recrystallized from cyclohexane to yield selenobenzamide as orange needles (1.15 g, 62%).

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