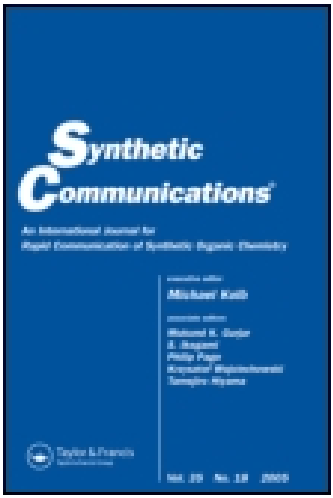

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A New Synthetic Method for N-Mono- and N,N-Disubstituted Selenoamides

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A NEW SYNTHETIC METHOD FOR *N*-MONO- AND *N,N*-DISUBSTITUTED SELENOAMIDES

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Abstract: *N*-Mono and *N,N*-disubstituted selenoamides are synthesized in a one-pot procedure from nitriles, selenium metal and $NaBH_4$ followed by the amine group exchange of the intermediate primary selenoamide with an amine.

Although selenoamides have been known for more than one hundred years, they are still little-studied compounds.[1] Selenoamides are versatile precursors for preparations of selenium-nitrogen heterocycles, such as selenazoles,[2,3] 1,2,4-selenadiazoles,[4,5] 1,2,4-diaelenazoline,[6] 1,3,5-oxaselenazines,[7] and diselenazolium.[8] Various selenium-containing fused heterocycles have been synthesized from primary selenoamides.[9,10] Besides, selenoamides are also useful in preparations of selenoethers[11] and dialkyl diselenides.[12] However, the synthetic application of selenoamides has been greatly restricted due to the difficulty in

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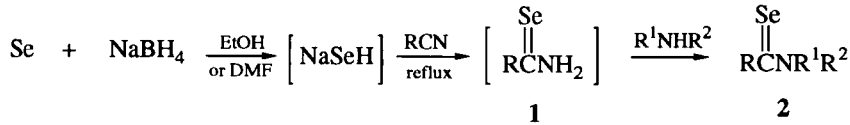
preparing selenoamides and to their far less stability compared with the corresponding thioamides. Primary selenoamides have been prepared from hydrogen selenide and nitriles,[13] or an improved method by using nitriles and aluminum selenide in boiling water,[14] and from nitriles, carbon monoxide and water under pressure.[15] Recently aryl selenoamides have been synthesized by the reaction of nitriles with sodium hydrogen selenide.[16,17] There are only a few known methods for the synthesis of *N*-substituted selenoamides: the reaction of phosphorous pentaselenide with amines;[18] the reaction of selenoesters with alkylamide magnesium bromides or secondary amines;[19] and the addition of secondary amines to alkyneselenols.[20] However, none of these previous methods are general and convenient for the preparation of *N*-mono- and *N,N*-disubstituted selenoamides. Perhaps the best known method for *N*-substituted selenoamides is the one-pot reaction from nitriles, metallic selenium, carbon monoxide, water and amines.[21] But this method needs an autoclave reaction under high pressure. We now wish to report a new convenient method for the synthesis of *N*-mono and *N,N*-disubstituted selenoamides from nitriles, metallic selenium and sodium borohydride followed by the amine exchange reaction of the resulting primary selenoamide with primary or secondary amines.

We have previously reported that sodium hydrogen selenide reacted with aryl nitriles to give the *N*-unsubstituted aryl selenoamides.[17] In the present work, sodium hydrogen selenide, prepared by reduction of selenium powder with sodium borohydride in DMF or ethanol, was treated with either aryl or alkyl nitriles under nitrogen for 3-5 hours yielding the intermediates *N*-unsubstituted aryl and alkyl selenoamides **1**, respectively. The *N*-unsubstituted selenoamide intermediates **1** were then treated with a primary or secondary amine in refluxing ethanol or in dry DMF at 100 °C to give the corresponding *N*-substituted selenoamides via the amino

Scheme 1



2	R	R^1	R^2	2	R	R^1	R^2	2	R	R^1	R^2
a	Ph	$PhCH_2$	H	**e**	Ph	$n\text{-}C_6H_{13}$	$n\text{-}C_6H_{13}$	**i**	Ph	$-CH_2CH_2CH_2CH_2CH_2-$	
b	Ph	$n\text{-}C_8H_{17}$	H	**f**	Ph	i-Pr	i-Pr	**j**	n-Pr	$n\text{-}C_5H_{11}$	H
c	Ph	$n\text{-}C_{11}H_{23}$	H	**g**	Ph	$n\text{-}C_5H_{11}$	H	**k**	n-Pr	$-CH_2CH_2CH_2CH_2CH_2-$	
d	Ph	$n\text{-}C_{12}H_{25}$	H	**h**	Ph	$n\text{-}C_4H_9$	H	**l**	n-Pr	$PhCH_2$	H

group exchange reaction (Scheme 1). Practically, DMF is preferable for the amino group exchange because the reaction can be carried out at higher temperature.

The results listed in Table 1 show that both aromatic and aliphatic, and both *N*-mono- and *N,N*-disubstituted selenoamides were readily prepared from a nitrile and an amine. Alternatively, aromatic substituted selenoamides can also be prepared from the reaction of primary aryl selenoamides and an amine in toluene because aryl selenoamides are stable and ease to make in large scale.[17] The yield of *N*-monosubstituted selenoamides ranges from good to excellent, especially for aromatic selenoamides. *N,N*-Disubstituted selenoamides are given in moderate yield. However, the amino exchange by using diisopropylamine only gives 7% of the desired selenoamides (**2g**), presumably due to steric hindrance.

The *N*-substituted selenoamides, including some new compounds, were characterized by IR and NMR spectra and by elemental analyses (Tables 1-2).

Experimental

^1H NMR spectra were recorded on an AC-80 (80 MHz) instrument. IR spectra

Table 1. Preparations of *N*-Substituted Selenoamides

No.	yield (%)	m.p. (°C)	Lit. m.p.[21] (°C)	Calcd.			Found		
				C	H	N	C	H	N
2a	92	76-78	76-78						
2b	86	oil	oil						
2c	82	oil		63.89	8.64	4.14	64.13	8.64	3.97
2d	82	41-42		64.75	8.87	3.97	64.73	8.94	3.73
2e	43	170 (dec.)		64.75	8.87	3.97	64.73	8.47	3.78
2f	7	140 (dec.)		58.21	7.14	5.22	58.30	7.09	5.23
2g	87	oil		56.71	6.71	5.50	56.61	6.66	5.45
2h	89	oil	oil						
2i	58	88-89	89-89.5						
2j	52	oil		49.09	8.70	6.36	49.15	8.62	6.51
2k	59	62-63		49.54	7.85	6.42	49.60	7.69	6.30
2l	73	53-54	53.5-54						

were taken on a Perkin Elmer 683 spectrophotometer. Elemental analyses were performed on a Carlo Erba 1160 analyzer. Melting points were measured on an electrothermal melting point apparatus and uncorrected. Nitriles, amines, ethanol, toluene and DMF were dried over molecular silver and redistilled before use.

***N*-Benzyl selenobutyramide, general procedure:** Dry DMF or ethanol (10 ml) was added to a mixture of selenium powder (0.40 g, 5 mmol) and sodium borohydride (0.23 g, 6 mmol) under nitrogen at room temperature. After heated at 80-90 °C (refluxing when ethanol was used as the solvent) for 10 min., butyronitrile (0.36 g, 5 mmol) was added to this sodium hydrogen selenide solution. The mixture was heated at the same temperature for 5 hr. Benzylamine

Table 2. IR and ^{1}H-NMR Spectral Data of N-Substituted Selenoamides

Comps.	IR		^{1}H NMR (δ, TMS, CCl_4)
	ν NH	ν C=Se	
2a	3155	1520	4.84 (d, 2H), 7.00-7.80 (m, 10H), 8.20 (brs, 1H)
2b	3180	1530	0.88 (t, 3H), 1.30 (m, 12H), 3.57 (m, 2H), 6.80-7.70 (m, 5H), 8.56 (br, 1H)
2c	3240	1540	0.87 (t, 3H), 1.25 (m, 18H), 3.57 (m, 2H), 6.90-7.70 (m, 5H), 8.90 (br, 1H)
2d	3230	1540	0.87 (t, 3H), 1.25 (m, 20H), 3.57 (m, 2H), 7.30-7.90 (m, 5H), 8.90 (br, 1H)
2e		1500	0.97 (t, 6H), 1.33 (m, 16H), 3.13 (m, 4H), 7.30-7.85 (m, 5H)
2f		1500	1.36 (d, 12H), 4.84 (m, 2H), 7.17 (m, 5H)
2g	3180	1530	0.86 (t, 3H), 1.35-1.80 (m, 6H), 3.80 (m, 2H), 6.90-7.90 (m, 5H), 8.40 (br, 1H)
2h	3180	1530	0.84 (t, 3H), 1.20-1.90 (m, 4H), 3.53 (m, 2H), 6.70-7.70 (m, 5H), 8.40 (br, 1H)
2i		1500	1.74 (m, 6H), 3.46 (m, 2H), 4.38 (m, 2H), 7.18 (m, 5H)
2j	3200	1540	0.90 (t, 3H), 1.15 (t, 3H), 1.25-2.09 (m, 8H), 2.66 (t, 2H), 3.62 (q, 2H), 8.70 (br, 1H)
2k		1550	1.14 (t, 3H), 1.50-1.90 (m, 8H), 2.93 (m, 2H), 3.67 (m, 2H), 4.32 (m, 2H)
2l	3125	1530	1.03 (t, 3H), 1.80 (m, 2H), 2.62 (t, 2H), 4.75 (d, 2H), 7.26 (s, 5H), 8.10 (br, 1H)

(1.1 g, 10 mmol) was added. The reaction was continued at 100 °C for 5 hr. Diluted HCl acid was added and the solution was extracted with CH_2Cl_2 (3 x 5 ml) and dried over $MgSO_4$. Evaporation of solvent gave the crude product which was purified by column chromatography (silica gel, cyclohexane/ethyl acetate 4:1). Other *N*-substituted selenoamides are similarly prepared (see Table 1).

Preparation of *N*-benzyl selenobenzamide from selenobenzamide and benzylamine: The mixtrue of selenobenzamide[17] (0.85 g, 5 mmol) and benzylamine (1.07 g, 10 mmol) in toluene (20 ml) was stirred at 100 °C for 4 hrs. Toluene was removed under reduced pressure and the residue was purified similarly as described above.

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