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A New Synthetic Method for N-Substituted Selenoamides

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Abstract: Benzotriazole, aldehydes and primary selenoamides react together with elimination of water to form 1:1:1 adducts which are reduced smoothly by $NaBH_4$ to give the N-substituted selenoamides in good yield.

Keywords: Selenoamides, benzotriazole, aldehydes, synthesis.

Selenoamides are versatile precursors for preparation of selenium-nitrogen hetercycles[1,2]. However the synthetic application of selenoamides has been greatly restricted due to the difficulty in preparation. There are only a few known methods for the synthesis of N-substituted selenoamides[3-6] such as the reaction of phosphorous pentaselenides with amines, the addition of secondary amines to alkyneselenols. However, those methods are not general and covenient. Perhaps the best known method for N-substituted selenoamides is the exchange reaction of the resulting primary selenoamide with primary or secondary amines[7].

We have reported that the primary selenoamides could be synthesized by the reaction of aryl nitries with sodium hydrogen selenide in ethanol conveniently[8]. We now report a new synthesis for N-substituted selenoamides from the primary selenoamides **(Scheme 1)**. A variety aldehydes reacted with the primary selenoanides, in the presence of benzotriazole to yield adducts **5** readily by loss of water. The 1:1:1 adducts were reduced by $NaBH_4$ in refluxed THF to give the expected N-substituted selenoamides **6**. The structure of compounds **5a-f** and **6a-e** were confirmed by IR and ^{1}H NMR and elemental analysis.

General procedure

Under nitrogen, the mixture of benzotriazole **1** (3 mmol), benzoaldehyde **2** (3 mmol) and selenobenzamide **4** (3 mmol) in dry toluene (30 mL) was refluxed for 4-30 h. Then toluene was removed *in vacuo* and the residue was dissolved in dichloromethane. The solution was washed with water (40 mL×3) and 10% Na_2CO_3 (20 mL), dried over $MgSO_4$ and concentrated. The residue was chromatographed with a silica gel plate

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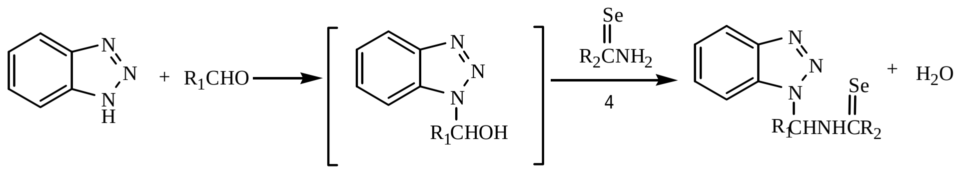
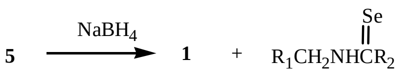
(cyclohexane-ethyl ether as an eluent) and to give pure adduct **5a~f** in 30-70% yield.

Scheme 1



1 2 3 5a~f



6a~e

	R_1	R_2
5a	n-C_3H_7	m-$CH_3C_6H_4$
5b	n-C_8H_{17}	C_6H_5
5c	n-C_8H_{17}	m-$CH_3C_6H_4$
5d	n-C_8H_{17}	p-$CH_3C_6H_4$
5e	n-C_9H_{19}	m-CH_3C6H_4
5f	n-C_9H_{19}	p-$CH_3C_6H_4$
6a	n-C_3H_7	C_6H_4
6b	n-C_8H_{17}	C_6H_5
6c	n-C_8H_{17}	m-$CH_3C_6H_4$
6d	n-C_9H_{17}	C_6H_4
6e	n-C_9H_{19}	m-CH_3C6H_4

Adduct **5** (1 mmol) was dissolved in dry THF (30 mL). Solid sodium borohydride (1.2 mmol) was added in one portion to the stirred solution. The solution was refluxed for 2 h under N_2. Then the reaction mixture was washed with 10% Na_2CO_3 (20 mL) and water (20 mL × 2), dried over $MgSO_4$ and concentrated. The residue was separated with a silica gel plate (cyclohexane-ethyl ether as an eluent) to give pure solid product **6a~e** in 96-98% yield.

The spectral data and physical chemical consistants of compounds **5e-f** and **6a-e** are as follows.

5a: mp 91-93°C. orange solid, yield 30%. IR (KBr): 3195, 1500 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.87-1.07 (t, 3H, J=6Hz, CH_3), 1.22-1.74 (m, 2H, CH_2), 2.26 (s, 3H, m-CH_3), 2.36-2.62 (q, 2H, J=7Hz, CH_2), 7.00-7.88 (m, 9H, ArH, CH), 9.14 (d, 1H, J=9Hz, NH). $C_{18}H_{20}N_4Se$ (Calcd: C, 58.23; H, 5.43; N, 15.09; Found: C, 58.48; H, 5.54; N, 14.99).
5b: mp 124-126°C. orange solid, yield 60%. IR (KBr): 3195, 1530 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.82-1.67 (m, 15H, $CH_3(CH_2)_6$), 2.45-2.84 (m, 2H, CH_2), 7.17-8.03 (m, 10H, ArH, CH), 9.26 (d, 1H, J=9Hz, NH). $C_{22}H_{28}N_4Se$ (Calcd: C, 61.83; H, 6.60; N, 13.11; Found: C, 62.04; H, 6.67; N, 12.97).
5c: mp 99-101°C. orange solid, yield 60%. IR (KBr): 3192, 1548 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.82-1.89 (m, 15H, $CH_3(CH_2)_6$), 2.26 (s, 3H, m-CH_3), 2.48-2.64 (m, 2H, CH_2), 7.00-7.92 (m, 9H, ArH, CH), 9.39 (d, 1H, J=9Hz, NH). $C_{23}H_{30}N_4Se$ (Calcd: C, 62.58; H, 6.85; N, 12.69; Found: C, 62.80; H, 7.02; N, 12.53).
5d: mp 132-134°C. orange solid, yield 70%. IR (KBr): 3190, 1510 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.82-1.73 (m, 15H, $CH_3(CH_2)_6$), 2.31 (s, 3H, p-CH_3), 2.49-2.67 (m, 2H, CH_2), 7.08-7.98 (m, 9H, ArH, CH), 9.24 (d, 1H, J=9Hz, NH). $C_{23}H_{30}N_4Se$ (Calcd: C,

62.58; H, 6.85; N, 12.69; Found: C, 62.81; H, 6.97; N, 12.57).

5e: mp 132-133°C. orange solid, yield 50%. IR (KBr): 3197, 1546 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.73-1.68 (m, 17H, $CH_3(CH_2)_7$), 2.12 (s, 3H, *m*-CH_3), 2.44-2.59 (m, 2H, CH_2), 6.97-7.85 (m, 9H, ArH, CH), 9.14 (d, 1H, *J*=8.5Hz, NH). $C_{24}H_{32}N_4Se$ (Calcd: C, 63.29; H, 7.08; N, 12.30; Found: C, 63.38; H, 7.21; N, 12.12).

5f: mp 126-127°C. orange solid, yield 65%. IR (KBr): 3193, 1510 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.89-1.84 (m, 17H, $CH_3(CH_2)_7$), 2.31 (s, 3H, *p*-CH_3), 2.50-2.77 (m, 2H, CH_2), 7.02-8.01 (m, 9H, ArH, CH), 9.78 (d, 1H, *J*=9Hz, NH). $C_{24}H_{32}N_4Se$ (Calcd: C, 63.29; H, 7.08; N, 12.30; Found: C, 63.46; H, 7.23; N, 12.48).

6a: orange oil (lit.,[4] oil), yield 98%. IR (KBr): 3180, 1530 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.84 (t, 3H, *J*=6Hz, CH_3), 1.20-1.90 (m, 4H, $(CH_2)_2$), 3.53 (q, 2H, *J*=7Hz, CH_2), 6.70-7.70 (m, 5H, ArH), 8.40 (br, 1H, NH). $C_{11}H_{15}NSe$ (Calcd: C, 55.00; H, 6.29; N, 5.83; Found: C, 55.08; H, 6.35; N, 5.90).

6b: orange oil, yield 96%. IR (KBr): 3210, 1540 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.80-1.92 (m, 17H, $CH_3(CH_2)_7$), 3.63-3.94 (q, 2H, *J*=7Hz, CH_2), 7.29-7.79 (m, 5H, ArH), 8.15 (br, 1H, NH). $C_{16}H_{25}NSe$ (Calcd: C, 69.92; H, 8.12; N, 4.51; Found: C, 69.99; H, 8.23; N, 4.32).

6c: mp 43-44°C. orange solid, yield 98%. IR (KBr): 3215, 1535 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.74-2.17 (m, 17H, $CH_3(CH_2)_7$), 2.26 (s, 3H, *m*-CH_3), 3.40-3.76 (q, 2H, *J*=7Hz, CH_2), 7.01-7.43 (m, 4H, ArH), 8.30 (br, 1H, NH). $C_{17}H_{27}NSe$ (Calcd: C, 62.95; H, 8.39; N, 4.32; Found: C, 63.11; H, 8.46; N, 4.23).

6d: mp 33-34°C. orange solid, yield 97%. IR (KBr): 3210, 1540 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.79-1.73 (m, 19H, $CH_3(CH_2)_8$), 3.63-3.98 (q, 2H, *J*=7Hz, CH_2), 7.23-7.80 (m, 5H, ArH), 8.10 (br, 1H, NH). $C_{17}H_{27}NSe$ (Calcd: C, 62.95; H, 8.39; N, 4.32; Found: C, 63.13; H, 8.50; N, 4.25).

6e: mp 40-41°C. orange solid, yield 98%. IR (KBr): 3210, 1540 cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.66-2.27 (m, 19H, $CH_3(CH_2)_8$), 2.32 (s, 3H, *m*-CH_3), 3.36-3.66 (q, 2H, *J*=6Hz, CH_2), 6.90-7.33 (m, 5H, ArH), 8.01 (br, 1H, NH). $C_{18}H_{29}NSe$ (Calcd: C, 63.89; H, 8.64; N, 4.14; Found: C, 64.02; H, 8.78; N, 4.06).

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