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Received October 2, 1997

(*Z*)-3-Methylideneselenophthalides **5A** and (*Z*)-3-methylidenetellurophthalides **5B** were easily prepared by the regioselective and stereoselective reaction of 2-ethynylbenzoyl chlorides **3** with sodium hydroselenide and sodium hydrotelluride in good yields, respectively.

J. Heterocyclic Chem., **35**, 165 (1998).

It is known that organotellurium and organoselenium compounds [2] display certain characteristic peculiarities of structure and reactivity in comparison with those of the sulfur analogs. Thus, recently considerable attention has been focused on synthetic studies of various selenium-containing or tellurium-containing heterocycles [3]. However, there are only a few reports [4] on the preparation of lactone-type compounds containing selenium or tellurium.

We have already reported the synthesis of new seven-membered ring systems, 3-benzotellurepines [5], 1-benzotellurepines and 1-benzoselenepines [6], and a practical synthetic method for the preparation of a chalcogen-containing five-membered heterocycles [7]. Our synthetic strategy [5,6,7] for the preparation of these compounds is based on the intramolecular addition of the selenol and tellurol moieties to an acetylenic group. In this regard, we would like to report the synthesis of the title compounds from *o*-bromoethynylbenzenes **1**.

Compounds **1** [7] were lithiated with *tert*-butyllithium in anhydrous tetrahydrofuran at -80° under an argon atmosphere, and then successively treated with excess dry ice to afford the corresponding *o*-ethynylbenzoic acids **2** in *ca.* 70-75% yields. The acid chlorides **3** were generated by treatment of **2** with thionyl chloride in the usual manner, and used for the next reaction without

purification. The reaction of **3** with sodium hydroselenide, easily available from selenium powder and sodium borohydride, in two phases (water-toluene) in the presence of tetrabutylammonium hydrogen sulfate as a phase transfer catalyst, resulted in ring closure to give the desired (*Z*)-3-methylideneselenophthalides **5A** regioselectively as the sole product. The stereochemistry of the olefin moiety of **5A** was determined by the nuclear Overhauser enhancement (NOE) measurement. The NOE was observed between the 3'-H and the aromatic 4-H in the 400 MHz ^1H nmr spectra of **5A**. Thus, the olefin moiety was determined to have (*Z*)-stereochemistry. The stereospecific intermolecular *trans*-addition of phenylselenols and/or alkylselenols or similar compounds to an ethynyl group, forming (*Z*)-vinylselenides, is well known [8]. These results support the proposal that the reaction forming **5A** will probably proceed through an intramolecular *endo*-mode ring closure at the *sp* carbon of the triple bond of intermediates **4** (path a). No six-membered ring closure products, **6A**, were obtained. The reason why no *exo*-mode intramolecular addition reaction (path b) proceeds is not clear at present.

(*Z*)-3-Methylidenetellurophthalides **5B** were similarly obtained by use of sodium hydrotelluride. These results are summarized in Table 1 and the spectral data

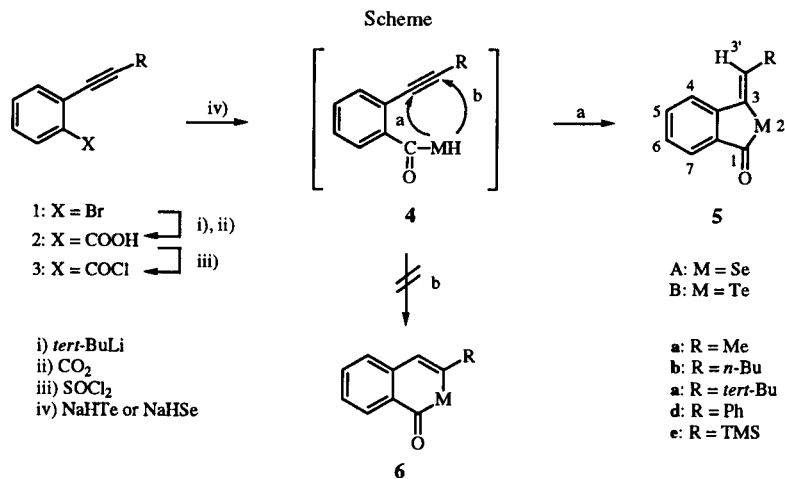


Table 1
(Z)-3-Methylideneselenophthalides **5A** and (Z)-3-Methylidenetellurophthalides **5B**

Compound No.	M	R	Yield (%) [a]	Appearance
5Aa	Se	Me	78	colorless oil
5Ab	Se	<i>n</i> -Butyl	75	pale yellow oil
5Ac	Se	<i>tert</i> -Butyl	70	colorless prisms [b] mp 34-36°
5Ad	Se	Ph	76	colorless prisms [b] mp 80-81°
5Ae	Se	Trimethylsilyl	59	colorless oil
5Ba	Te	Me	59	yellow prisms [b] mp 77-80°
5Bb	Te	<i>n</i> -Butyl	50	yellow oil
5Bc	Te	<i>tert</i> -Butyl	65	yellow oil
5Bd	Te	Ph	64	yellow prisms [b] mp 88-92°
5Be	Te	Trimethylsilyl	47	yellow oil

[a] Isolated yields from **3**. [b] Recrystallized from acetone-*n*-hexane.

for compounds **5A** and **5B** are shown in Table 2, respectively.

EXPERIMENTAL

General Methods.

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. The ir spectra were determined with a Hitachi 270-30 spectrometer. Mass spectra and high resolution mass spectra were recorded on a JEOL JMS-DX300 instrument. The ¹H nmr spectra were determined with a JEOL PMX 60SI (60 MHz), JEOL EX-90A (90 MHz) or JEOL JNM-GSX 400 (400 MHz) spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. Microanalyses were performed in the Microanalytical Laboratory of this Faculty.

General Procedure for the Preparation of *o*-Ethynylbenzoic Acids **2**.

To a stirring solution of *o*-bromoethynylbenzene (1, 10 mmoles) in anhydrous tetrahydrofuran (50 ml) at -80° under an argon atmosphere was slowly added *tert*-butyllithium (1.60 mol/l in pentane solution, 9.38 ml, 15 mmoles). The reaction mixture was stirred under the above conditions for 1 hour. Dry ice (*ca.* 20 g) was added to the mixture in one portion, and then

Table 2
Spectral Data of the (Z)-3-Methylideneselenophthalides **5A** and (Z)-3-Methylidenetellurophthalides **5B**

Compound No.	Formula HRMS Calcd. (Found)	IR cm ⁻¹ (C=O)	¹ H-NMR (90 MHz, J = Hz)		
			3'-H	Ar-H	R-H
5Aa	C ₁₀ H ₈ OSe 223.9741 (223.9730)	1694	6.93 (q) (J = 7.2)	7.26-7.87 (4H, m)	2.05 (3H, d, J = 7.2) R = Me
5Ab	C ₁₃ H ₁₄ OSe 266.0210 (266.0205)	1694	6.86 (t) (J = 7.2)	7.16-7.88 (4H, m)	0.92 (3H, t, J = 6.2) 1.16-1.75 (4H, m) 2.34 (2H, dt, J = 6.2, 7.2) R = <i>n</i> -Butyl
5Ac	C ₁₃ H ₁₄ OSe 266.0210 (266.0208)	1680	7.12 (s)	7.39-7.90 (4H, m)	1.29 (9H, s) R = <i>tert</i> -Butyl
5Ad	C ₁₅ H ₁₀ OSe 285.9897 (285.9897)	1688	7.92 (s)	7.33-8.05 (9H, m)	R = Ph
5Ae	C ₁₂ H ₁₄ OSiSe 281.9979 (281.9977)	1698	7.25 (s)	7.33-7.98 (4H, m)	0.30 (9H, s) R = Trimethylsilyl
5Ba	C ₁₀ H ₈ OTe 273.9638 (273.9634)	1664	7.26 (q) (J = 6.6)	7.29-7.91 (4H, m)	2.05 (3H, d, J = 7.2) R = Me
5Bb	C ₁₃ H ₁₄ OTe 316.0107 (316.0112)	1672	7.15 (t) (J = 7.0)	7.21-7.98 (4H, m)	0.92 (3H, t, J = 6.2) 1.16-1.75 (4H, m) 2.34 (2H, dt, J = 6.2, 7.2) R = <i>n</i> -Butyl
5Bc	C ₁₃ H ₁₄ OTe 316.0107 (316.0110)	1672	7.49 (s)	7.30-7.98 (4H, m)	1.29 (9H, s) R = <i>tert</i> -Butyl
5Bd	C ₁₅ H ₁₀ OTe 335.9795 (335.9793)	1672	8.24 (s)	7.32-8.10 (9H, m)	R = Ph
5Be	C ₁₂ H ₁₄ OSiSe 331.9875 (331.9878)	1678	7.82 (s)	7.36-8.19 (4H, m)	0.28 (9H, s) R = Trimethylsilyl

the cooling bath was removed. The reaction mixture was allowed to rise to room temperature, and stirred for an additional 12 hours. The mixture was quenched by pouring into ice-water, and extracted with saturated aqueous sodium hydrogen carbonate solution (100 ml x 3). After washing with ether, the aqueous layer was acidified with 20% aqueous hydrochloric acid, and extracted with methylene chloride (100 ml x 3). The combined organic fractions were washed with brine (100 ml x 3), dried over magnesium sulfate, and evaporated. The crude product was recrystallized from acetone-*n*-hexane to give pure **2**.

Compound **2a** was obtained in 69% yield, as pale yellow prisms, mp 87-90°; ir (potassium bromide): 3100 (OH), 2240 (C≡C), 1684 (C=O) cm⁻¹; ¹H nmr (60 MHz): 1.14 (3H, s, Me), 7.23-7.30 and 8.07-8.20 (3H, m and 1H, m, phenyl protons), 12.05 (1H, brs, COOH); ms: m/z 160 (M⁺).

Anal. Calcd. for C₁₀H₈O₂: C, 74.99; H, 5.03. Found: C, 75.01; H, 5.02.

Compound **2b** was obtained in 67% yield, as colorless prisms, mp 35-36°; ir (potassium bromide): 3100 (OH), 2232 (C≡C), 1702 (C=O) cm⁻¹; ¹H nmr (60 MHz): 1.04, 1.33-1.90, and 2.55 (3H, t, J = 6 Hz, 4H, m, and 2H, q, J = 6 Hz, *n*-Bu), 7.23-7.73 and 8.08-8.25 (3H, m and 1H, m, phenyl protons), 12.83 (1H, brs, COOH); ms: m/z 202 (M⁺).

Anal. Calcd. for C₁₃H₁₄O₂: C, 77.20; H, 6.98. Found: C, 77.22; H, 6.94.

Compound **2c** was obtained in 68% yield, as colorless prisms, mp 118-122°; ir (potassium bromide): 3100 (OH), 2244 (C≡C), 1698 (C=O) cm⁻¹; ¹H nmr (60 MHz): 1.37 (9H, s, *tert*-Bu), 7.32-7.65 and 8.10-8.27 (3H, m and 1H, m, phenyl protons), 10.89 (1H, brs, COOH); ms: m/z 202 (M⁺).

Anal. Calcd. for C₁₃H₁₄O₂: C, 77.20; H, 6.98. Found: C, 76.97; H, 7.02.

Compound **2d** was obtained in 76% yield, as pale yellow prisms, mp 126-127°; ir (potassium bromide): 3100 (OH), 2212 (C≡C), 1692 (C=O) cm⁻¹; ¹H nmr (60 MHz): 7.37-7.77 and 8.16-8.32 (8H, m and 1H, m, phenyl protons), 11.87 (1H, brs, COOH); ms: m/z 222 (M⁺).

Anal. Calcd. for C₁₅H₁₀O₂: C, 81.06; H, 4.54. Found: C, 80.55; H, 4.52.

Compound **2e** was obtained in 69% yield, as pale yellow prisms, mp 98-99°; ir (potassium bromide): 3100 (OH), 2156 (C≡C), 1706 (C=O) cm⁻¹; ¹H nmr (60 MHz): 0.31 (9H, s, TMS), 7.32-7.78 and 8.07-8.21 (3H, m and 1H, m, phenyl protons), 12.51 (1H, brs, COOH); ms: m/z 218 (M⁺).

Anal. Calcd. for C₁₂H₁₄O₂Si: C, 66.01; H, 6.46. Found: C, 66.00; H, 6.44.

General Procedure for the Reaction of *o*-Ethynylbenzoyl Chlorides **3** with Sodium Hydrotelluride or Sodium Hydroselenide.

Acid **2**, (2.5 mmoles) was heated in thionyl chloride (10 ml) under reflux with stirring for 1 hour. After removal of the excess reagent under reduced pressure, the crude acid chloride **3** was dissolved in toluene (15 ml) and the solution was slowly added to a solution of sodium hydroselenide or sodium hydrotelluride (5.5 mmoles, in water, 10 ml), which was generated from selenium or tellurium powder (5.5 mmoles) and sodium borohydride (418 mg, 11 mmoles) under an argon atmosphere at room temperature. Tetrabutylammonium hydrogen sulfate (60 mg, 0.18 mmole) was then added. The resulting mixture was vigorously stirred under the same conditions for 6-12 hours, and poured into saturated aqueous sodium hydrogen carbonate solution (100 ml). The aqueous mixture was filtrated through a celite pad, and extracted with benzene (50 ml x 3). The combined organic layer was washed with water and brine, dried over magnesium sulfate, and evaporated *in vacuo*. The residue was purified by silica gel chromatography using *n*-hexane:methylene chloride (2:1, v/v) as an eluent to give pure (Z)-3-methylideneselenophthalides **5A** or (Z)-3-methylidenetellurophthalides **5B**.

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