One - Pot Synthesis of Novel Sulfur and Selenium Heterocycles by Directed *ortho*-Lithiation

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Received October 23, 2000

A procedure for the synthesis of benzo[*e*][1,3]thiazine-2,4-diones from benzamides by directed lithiation and sequential treatment with sulfur and phosgene is reported. Use of thiophosgene afforded 2-thioxo-2,3-dihydro-benzo[*e*][1,3]thiazin-4-ones. Application of this methodology to benzenesulfonamides afforded the previously unknown 1,1-dioxo-1,2-dihydro-1,4-dithia-2-aza-naphthalen-3-one ring system with phosgene and the 1,2-dioxo-2-phenyl-2,3-dihydrobenzo[*e*][1,4,2]dithiazine-3-one ring system with thiophosgene. Use of selenium in place of sulfur afforded the novel analogous selenium heterocycles, however in the case of benzamides the use of selenium and phosgene afforded benzo[*d*]isoselenazol-3-ones unexpectedly.

J. Heterocyclic Chem., **38**, 723 (2001).

Directed *ortho*-metalation methodology offers a predictable and widely applicable synthetic strategy for the regiospecific construction of substituted aromatic compounds [1]. This methodology has previously been used for the construction of heterocyclic systems containing sulfur and selenium, such as benzo[*d*]isoselenazol-3-one **1** and benzo[*d*]isothiazol-3-ones **2** (Figure 1) [2]. These ring systems have been of biological interest as anti-inflammatory agents and as inhibitors of matrix metalloproteases [3]. Ebselen (**1a**) is a particularly well known selenium heterocycle that has been the subject of extensive study as a small molecule mimic of the enzyme glutathione peroxidase (GPx) [4]. Many analogs of Ebselen, incorporating a variety of selenium heterocycles, have been prepared and studied for the treatment of diseases in which reactive oxygen species are thought to play a role [5].

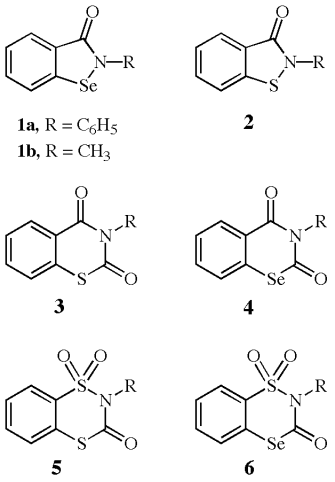
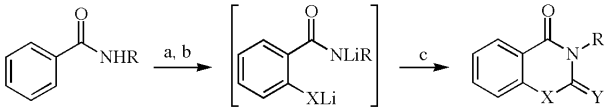


Figure 1

We sought to prepare related sulfur and selenium containing heterocyclic compounds which might have similar biological properties, in which the chalcogen atom was incorporated in a six - membered ring, for example the benzo[*e*][1,3]thiazine-2,4-dione ring system (**3**) and the benzo[*e*][1,3]selenazine-2,4-dione ring system (**4**). An examination of the literature revealed that these ring systems are relatively obscure. Benzo[*e*][1,3]thiazine-2,4-diones have been prepared previously from methyl thiosalicylate by reaction with an isocyanate, or by the reaction of a benzo[*d*]isothiazol-3-one with phosgene, followed by subsequent reaction with a substituted formamide and acid hydrolysis [6]. Alternatively, benzo[*e*][1,3]thiazine-2,4-diones have been prepared by the reaction of a thiosalicylic acid amide with phosgene [7]. The few benzo[*e*]-[1,3]selenazine-2,4-diones that have been reported were prepared by more circuitous routes, for example by the reaction of 2-(benzylseleno)-*N*-trimethylsilyl benzanilide with phosgene and by the ring expansion of a benzo[*d*]-isoselenazol-3-one [8].

We sought a more general approach that would proceed in a minimum number of synthetic steps from readily available commercial starting materials with a broad range of potential substituents, and which would avoid the need to isolate and perform synthetic manipulations upon sensitive thiosalicylic acid derivatives or their selenium counterparts. Our attention turned quickly to the use of directed metalation, which would allow the functionalization of a wide range of readily prepared benzamides in an operationally simple and regiochemically predictable manner. This would allow the efficient preparation of analogs of known ring systems, such as **3** and **4**. We were further attracted by the possibility that this methodology would allow access to entirely unknown heterocyclic systems, for example 1,1-dioxo-2,3-dihydrobenzo[*e*][1,4,2]dithiazine-3-one **5** and 1,1-dioxo-2,3-dihydrobenzo[*e*][1,4,2]thiaselenazine-3-one **6**. The possibility of carrying out the entire reaction sequence, from directed metalation through to the final heterocyclic product in one reaction flask was also attractive, despite the variety of potential difficulties that can be encountered in attempting to carry out multiple synthetic steps in a one - pot manner. We anticipated that the reaction of the dilithiated benzamide with sulfur or selenium would afford the corresponding chalcogenide/amide dianion, which should cyclize upon treatment with a suitable bifunctional electrophile (Scheme 1).

Scheme 1

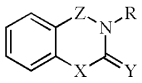


(a) *n*-BuLi, THF, -78 to 0 °C; (b) X = S or Se, 50 °C; (c) Cl_2C = Y, 0 °C

In a typical experiment, the benzamide derivative was treated with 2 equivalents of *n*-butyllithium in tetrahydrofurane (THF) at 0 °C for 1 hour, after which 1 equivalent of sulfur or selenium powder was added. The reaction mixture was heated at 50 °C until the starting amide was consumed as judged by tlc analysis of aliquots removed and quenched into dilute acetic acid. The mixture was then cooled thoroughly in ice and 1 equivalent of phosgene dissolved in toluene was added. The reaction mixture was stirred overnight at ambient temperature prior to extractive workup. Crude products were in most cases > 70% pure by ^{1}H NMR analysis. Purification was readily effected in most cases by recrystallization. In certain cases chromatography proved to be more effective due to high solubility of the product in the usual recrystallization solvents.

The reaction proved to be generally successful for most of the combinations of substrate benzamide and chalcogen (sulfur or selenium) that were examined (Table 1). The directed *ortho*-lithiation and subsequent reaction with sulfur or selenium was uneventful, providing the desired 2-mercapto or 2-seleno benzamide intermediate with little or no by-product formation as judged by tlc analysis. Tellurium was introduced successfully using the directed metalation strategy, as evidenced by trapping the intermediate tellurobenzamide dianion with iodomethane [9]. Subsequent derivatization with phosgene afforded intractable mixtures of unidentified products as well as a precipitate of black tellurium. The methodology was extended successfully to benzenesulfonamides to afford products **5**, **6**, **9**, and **10**. The method was not of preparative value when thiobenzamides were employed as substrates for the directed *ortho*-metalation. These afforded complex mixtures of products, in which relatively small amounts (< 20%) of the desired heterocyclic targets (Figure 2) were present.

Table 1



Substrate	Product	X	Y	R	Z	Yield [a]	mp, °C
Benzanilide	**3a**	S	O	Ph	CO	56%	144 - 146 [b]
N-Methylbenzamide	**3b**	S	O	Me	CO	74%	122 - 124 [c]
Benzenesulfonanilide	**5a**	S	O	Ph	SO_2	80%	164 – 166
N-Methylbenzenesulfonamide	**5b**	S	O	Me	SO_2	72%	101 – 103
Benzenesulfonanilide	**6a**	Se	O	Ph	SO_2	69%	152 – 154
N-Methylbenzenesulfonamide	**6b**	Se	O	Me	SO_2	62%	96 - 97
Benzanilide	**7a**	S	S	Ph	CO	65%	157 - 159 [d]
N-Methylbenzamide	**7b**	S	S	Me	CO	78%	142 - 143 [e]
Benzanilide	**8a**	Se	S	Ph	CO	66%	156 - 157
N-Methylbenzamide	**8b**	Se	S	Me	CO	72%	145 - 147
Benzenesulfonanilide	**9a**	S	S	Ph	SO_2	70%	175 - 177
N-Methylbenzenesulfonamide	**9b**	S	S	Me	SO_2	69%	140 - 142
Benzenesulfonanilide	**10a**	Se	S	Ph	SO_2	57%	192 - 193
N-Methylbenzenesulfonamide	**10b**	Se	S	Me	SO_2	90%	129 – 131

[a] All yields refer to analytically pure products; [b] lit. mp. 145 – 146 °C: H. Boeshagen, W. Geiger, H. Hulpke and C. Wunsche, *Chem. Ber.* **104**, 3757 (1971); [c] lit. mp. 119 – 121 °C: H. Boeshagen, W. Geiger, H. Hulpke and C. Wunsche, *Chem. Ber.* **104**, 3757 (1971); [d] lit. mp. 155 – 157 °C: G. Wagner and P. Richter, *Pharmazie*, **22**, 611 (1967); [e] lit. mp. 144 – 146 °C: G. Wagner and P. Richter, *Pharmazie*, **22**, 611 (1967).

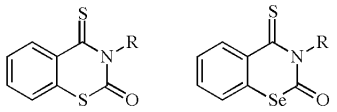


Figure 2

The cyclization of the intermediate 2-thio- or 2-selenobenzamide to the target heterocycle was found to require the use of a very reactive electrophile. Other synthetic equivalents to phosgene, such as ethyl chloroformate, 1,1'-carbonyldiimidazole, and dimethyl carbonate, were tried without success. Thiophosgene was found to react equally well as phosgene. As anticipated, the use of thionyl chloride or sulfuryl chloride in place of phosgene did not afford a new six-membered heterocycle, but instead served to oxidize the intermediate 2-selenobenzamide or 2-thiobenzamide dianion to the corresponding benzo[*d*]isoselena-

zol-3-ones **1** and benzo[*d*]isothiazol-3-ones **2**. However, the reaction of phosgene with the intermediate 2-selenobenzamide dianion also afforded the corresponding benzo[*d*]-isoselenazol-3-ones **1** in high yield. This unexpected result was confirmed by combustion analysis and comparison of spectroscopic data and melting points for these products with those of authentic samples of **1a** and **1b**.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen. The starting materials listed in Table 1 were commercial reagents and were used as received without additional purification. Sublimed sulfur powder meeting USP specifications (Fisher S594) and 100 mesh selenium powder (Aldrich 20,965-1) were used. Phosgene solution (20% in toluene, *ca.* 1.9 *M*) was obtained from Fluka. Commercial anhydrous grade solvents were used without further drying. All solutions were dried over anhydrous magnesium sulfate prior to evaporation on a rotary evaporator at *ca*. 30 Torr. Chromatography was performed using a Biotage Flash 40 pressure chromatography apparatus fitted with a 40S silica gel cartridge. Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. NMR spectra were recorded on Varian Unity Inova 400 spectrometers. Mass spectra were recorded on a Hewlett Packard Model 5989 mass spectrometer using chemical ionization with ammonia. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York, USA.

General Procedure for the Preparation of Sulfur and Selenium Heterocycles.

To a stirred solution of the appropriate benzamide or benzenesulfonamide (6.25 mmol) in 40 mL of dry THF was added *n*-butyllithium (5 mL of a 2.5 *M* solution in hexanes, 12.5 mmol) with cooling in a Dry Ice - acetone bath. Upon completion of the addition, the bath was removed and the mixture was allowed to warm spontaneously to 0 °C. The mixture was then stirred in an ice bath for 1 hour before the addition of sulfur (0.200 g, 6.25 mmol) or selenium (0.492 g, 6.25 mmol). The ice bath was removed and the mixture was stirred for 1 hour at 50 °C, or until all of the element had dissolved and tlc analysis of an aliquot quenched with 1 *M* aqueous acetic acid indicated that the starting benzamide had been consumed. The reaction flask was then cooled in ice for 30 minutes, after which phosgene (3.4 mL of a 1.9 *M* solution in toluene, 6.25 mmol) or thiophosgene (0.48 mL, 6.25 mmol) was added. The ice bath was removed and the mixture was stirred for 18 hours at 20 °C before being poured into water (75 mL) and ethyl acetate (75 mL). The mixture was stirred for 10 minutes, separated, and the ethyl acetate phase was washed with water, twice with brine, dried, and concentrated to afford the crude product, which was purified by silica gel chromatography using 5:1 hexanes - ethyl acetate to elute the column or by recrystallization from the indicated solvent(s).

3-Phenyl-benzo[*e*][1,3]thiazine-2,4-dione (**3a**).

This compound was obtained in 56% yield from benzanilide as colorless crystals following recrystallization from 1-chlorobutane, mp 144 – 146 °C. ^{1}H NMR (deuteriochloroform): δ 8.39 (d, J = 8.0 Hz, 1 H), 7.64 (m, 1 H); 7.51 (m, 4 H); 7.38 (m, 1 H); 7.22 (m, 2 H); ms: (NH_3 CI) m/z = 256 (MH^+).

Anal. Calcd. for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49. Found: C, 65.83; H, 3.51; N, 5.35.

3-Methylbenzo[*e*][1,3]thiazine-2,4-dione (**3b**).

This compound was obtained in 74% yield from *N*-methylbenzamide as light tan crystals following recrystallization from toluene - hexane, mp 122 – 124 °C. ^{1}H NMR (deuteriochloroform): δ 8.37 (d, J = 7.9 Hz, 1 H), 7.58 (d of d, J = 7.9, 8.3 Hz, 1 H), 7.42 (d of d, J = 7.9, 8.3 Hz, 1 H), 7.28 (d, J = 7.9 Hz, 1 H), 3.51 (s, 3 H); ms: (EI) m/z = 193 (M^+).

Anal. Calcd. for $C_9H_7NO_2S$: C, 55.95; H, 3.65; N, 7.25. Found: C, 56.22; H, 3.70; N, 7.08.

1,1-Dioxo-2-phenyl-2,3-dihydrobenzo[*e*][1,4,2]dithiazine-3-one (**5a**).

This compound was obtained in 80% yield from benzenesulfonanilide as white crystals following recrystallization from 1-chlorobutane, mp 164 – 166 °C. ^{1}H NMR (deuteriochloroform): δ 8.08 (d, J = 8.0 Hz, 1 H), 7.73 (m, 1 H), 7.58 (m, 2 H), 7.49 (m, 3 H), 7.32 (m, 2 H); ms: (NH_3 CI) m/z = 292 (MH^+).

Anal. Calcd. for $C_{13}H_9NO_3S_2$: C, 53.59; H, 3.11; N, 4.81. Found: C, 53.41; H, 2.97; N, 4.67.

1,1-Dioxo-2-methyl-2,3-dihydrobenzo[*e*][1,4,2]dithiazine-3-one (**5b**).

This compound was obtained in 72% yield from *N*-methylbenzenesulfonamide as white crystals following trituration with diethyl ether - acetone, mp 101 – 103 °C. ^{1}H NMR (deuteriochloroform): δ 8.01 (d, J = 8.0 Hz, 1 H), 7.63 (d of d, J = 8.0, 7.7 Hz, 1 H), 7.51 (d of d, J = 8.0, 7.7 Hz, 1 H), 7.47 (d, J = 8.0 Hz, 1 H), 3.39 (s, 3 H); ms: (EI) m/z = 229 (M^+).

Anal. Calcd. for $C_8H_7NO_3S_2$: C, 41.91; H, 3.08; N, 6.11. Found: C, 42.10; H, 3.18; N, 6.02.

1,1-Dioxo-2-phenyl- 2,3-dihydrobenzo[*e*][1,4,2]thiaselenazine-3-one (**6a**).

This compound was obtained in 69% yield from benzenesulfonanilide as white crystals following recrystallization from 1-chlorobutane:hexane, mp 152 – 154 °C. ^{1}H NMR (deuteriochloroform): δ 8.14 (d, J = 8.0 Hz, 1 H), 7.66 (m, 2H), 7.54 (m, 1 H), 7.47 (m, 3 H), 7.28 (m, 2 H); ms: (NH_3 CI) m/z = 340 (MH^+).

Anal. Calcd. for $C_{13}H_9NO_3SSe$: C, 46.16; H, 2.68; N, 4.14. Found: C, 46.58; H, 2.67; N, 4.11.

2-Methyl-1,1-dioxo-1,2-2,3-dihydrobenzo[*e*][1,4,2]thiaselenazine -3-one (**6b**).

This compound was obtained in 62% yield from *N*-methylbenzenesulfonamide as white crystals following chromatography on silica gel, mp 96 – 97 °C. ^{1}H NMR (deuteriochloroform): δ 8.05 (d, J = 7.9 Hz, 1 H), 7.59 (m, 2 H), 7.50 (d of d, J = 7.9 Hz, 6.9 Hz, 1 H), 3.40 (s, 3 H); ms: (EI) m/z = 277 (M^+).

Anal. Calcd. for $C_8H_7NO_3SSe$: C, 34.79; H, 2.55; N, 5.07. Found: C, 34.98; H, 2.59; N, 5.09.

3-Phenyl-2-thioxo-2,3-dihydrobenzo[*e*][1,3]thiazine-4-one (**7a**).

This compound was obtained in 65% yield from benzanilide as pale yellow crystals following recrystallization from 1-chlorobutane, mp 157 – 159 °C. ^{1}H NMR (deuteriochloroform): δ 8.37 (d, J = 7.9 Hz, 1 H), 7.63 (m, 1 H); 7.56 (m, 4 H); 7.22 (m, 3 H); ms: (NH_3 CI) m/z = 272 (MH^+).

Anal. Calcd. for $C_{14}H_9NOS_2$: C, 61.97; H, 3.34; N, 5.16. Found: C, 61.97; H, 3.26; N, 5.11.

3-Methyl-2-thioxo-2,3-dihydrobenzo[*e*][1,3]thiazine-4-one (**7b**).

This compound was obtained in 78% yield from *N*-methylbenzamide as off - white crystals following recrystallization from acetic acid - water, mp 142 – 143 °C. ^{1}H NMR (deuteriochloroform): δ 8.33 (d, J = 8.1 Hz, 1 H), 7.59 (d of d, J = 8.1, 7.9 Hz, 1 H), 7.43 (d of d, J = 8.1, 7.9 Hz, 1 H), 7.18 (d, J = 7.9 Hz, 1 H); ms: (EI) m/z = 209 (M^+).

Anal. Calcd. for $C_9H_7NOS_2$: C, 51.65; H, 3.37; N, 6.69. Found: C, 51.49; H, 3.31; N, 6.60.

3-Phenyl-2-thioxo-2,3-dihydro-benzo[*e*][1,3]selenazine-4-one (**8a**).

This compound was obtained in 66% yield from benzanilide as pale yellow crystals following recrystallization from 1-chlorobutane, mp 156 – 157 °C. ^{1}H NMR (deuteriochloroform): δ 8.40 (d, J = 8.1 Hz, 1 H), 7.62 – 7.41 (m, 5 H); 7.34 (d, J = 7.9 Hz, 1 H), 7.19 (m, 2 H); ms: (NH_3 CI) m/z = 320 (MH^+).

Anal. Calcd. for $C_{14}H_9NOSSe$: C, 52.84; H, 2.85; N, 4.40. Found: C, 52.75; H, 3.11; N, 4.38.

3-Methyl-2-thioxo-2,3-dihydro-benzo[*e*][1,3]selenazine-4-one (**8b**).

This compound was obtained in 72% yield from *N*-methylbenzamide as brick - red crystals following recrystallization from 1-chlorobutane, mp 145 – 147 °C. ^{1}H NMR (deuteriochloroform): δ 8.42 (d, J = 7.6 Hz, 1 H), 7.55 (d of d, J = 9.6, 7.6 Hz, 1 H), 7.42 (d of d, J = 9.6, 7.6 Hz, 1 H), 7.27 (d, J = 9.6 Hz, 1 H), 3.95 (s, 3 H); ms: (EI) m/z = 257 (M^+).

Anal. Calcd. for C_9H_7NOSSe: C, 42.20; H, 2.75; N, 5.47. Found: C, 42.45; H, 2.72; N, 5.30.

1,1-Dioxo-2-phenyl-2,3-dihydrobenzo[*e*][1,4,2]dithiazine-3-thione (**9a**).

This compound was obtained in 70% yield from benzenesulfonanilide as dark tan crystals following recrystallization from toluene, mp 175 – 177 °C. ^{1}H NMR (deuteriochloroform): δ 8.01 (d, J = 7.9 Hz, 1 H), 7.72 (m, 1 H), 7.57 (m, 1 H), 7.50 (m, 4 H), 7.29 (m, 2 H); ms: (EI) m/z = 307 (M^+).

Anal. Calcd. for $C_{13}H_9NO_2S_3$: C, 50.79; H, 2.95; N, 4.56. Found: C, 50.60; H, 3.09; N, 4.30.

1,1-Dioxo-2-methyl-2,3-dihydrobenzo[*e*][1,4,2]dithiazine-3-thione (**9b**).

This compound was obtained in 69% yield from *N*-methylbenzenesulfonamide as yellow crystals following trituration with diethyl ether, mp 140 – 142 °C. ^{1}H NMR (deuteriochloroform): δ 8.00 (d, J = 7.9 Hz, 1 H), 7.65 (m, 1 H), 7.53 (m, 1 H), 7.40 (d, J = 7.9 Hz, 1 H), 3.71 (s, 3 H); ms: (EI) m/z = 245 (M^+).

Anal. Calcd. for $C_8H_7NO_2S_3$: C, 39.17; H, 2.88; N, 5.71. Found: C, 39.50; H, 3.07; N, 5.62.

1,1-Dioxo-2-phenyl-2,3-dihydrobenzo[*e*][1,4,2]thiaselenazine-3-thione (**10a**).

This compound was obtained in 57% yield from benzenesulfonanilide as yellow crystals following recrystallization from toluene, mp 192 – 193 °C. ^{1}H NMR (deuteriochloroform): δ 8.07 (d, J = 7.9 Hz, 1 H), 7.68 (m, 1 H), 7.62 (m, 1 H), 7.54 (m, 1 H), 7.48 (m, 3 H), 7.25 (m, 2 H); ms: (EI) m/z = 355 (M^+).

Anal. Calcd. for $C_{13}H_9NO_2S_2Se$: C, 44.07; H, 2.56; N, 3.95. Found: C, 44.23; H, 2.57; N, 3.86.

1,1-Dioxo-2-methyl-2,3-dihydrobenzo[*e*][1,4,2]thiaselenazine-3-thione (**10b**).

This compound was obtained in 90% yield from *N*-methylbenzenesulfonamide as dark yellow crystals following chromatography on silica gel, mp 129 – 131 °C. ^{1}H NMR (deuteriochloroform): δ 8.06 (d, J = 7.9 Hz, 1 H), 7.62 (m, 1 H), 7.53 (m, 2 H), 3.74 (s, 3 H); ms: (EI) m/z = 293 (M^+).

Anal. Calcd. for $C_8H_7NO_2S_2Se$: C, 32.88; H, 2.41; N, 4.79. Found: C, 33.09; H, 2.38; N, 4.73.

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