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Preparation of Sydnone Compounds Substituted by Thio and Seleno Functional Groups at the 4-Positions

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The introduction of thio and seleno functional groups to the 4-position of a sydnone ring was successfully attempted using 4-lithiosydnones (**2**) and 4-bromosydnones (**3**) as starting compounds. The reaction of **2** with tetraalkylthiuram disulfides, bis[alkoxy(thiocarbonyl)] disulfides, and bis[alkylthio(thiocarbonyl)] disulfides provided 4-sydnonyl dithiocarbamates, *O*-alkyl *S*-(4-sydnonyl) dithiocarbonates, and dialkyl 4-sydnonyl trithiocarbonates, respectively in good yields. In addition, treatment of **2** with thiocyanogen and selenocyanogen gave rise to bis(4-sydnonyl) sulfides (**11**) and bis(4-sydnonyl) selenides (**12**), respectively. These products, **11** and **12** were also formed by the reaction of **3** with potassium thiocyanate and selenocyanate, respectively. Furthermore, it was found that **3** reacted with selenourea and potassium *O*-ethyl dithiocarbonate under heating to provide **12** and **11**, respectively. It was also found that the reactivity of these sydnone compounds **2** and **3** was quite different in many cases from that of the corresponding ordinary aromatic analogues, though the sydnone ring has a somewhat aromatic nature.

Although a typical mesoionic compound, sydnone (**1**) has been investigated extensively because of its unique electronic structure and biological activities, a few studies on the direct substitution by heteroatoms and hetero functional groups at the 4-position have been reported.[1)]

In our previous paper,[2)] we have reported a general method for the introduction of heteroatoms such as sulfur, selenium, phosphorus and arsenic to the 4-position. For example, we found that 4-thio and 4-selenosydnone compounds were successfully prepared by the reaction of 4-lithiosydnones (**2**) with disulfides and diselenides, respectively. In these cases, reaction proceeded under mild conditions and almost pure products could be obtained directly. Since sydnones are known to be unstable to acid, alkali, heat, oxidation, and reduction, quite mild reaction conditions are necessary for the successful synthesis of sydnone derivatives in general.[3)] Therefore, the previous method for the introduction of thio and seleno groups seems to be applicable to more complicated disulfides and selenides bearing carbonyl, thiocarbonyl, and cyano groups to provide sydnone compounds having hetero functional groups containing sulfur and selenium atoms.

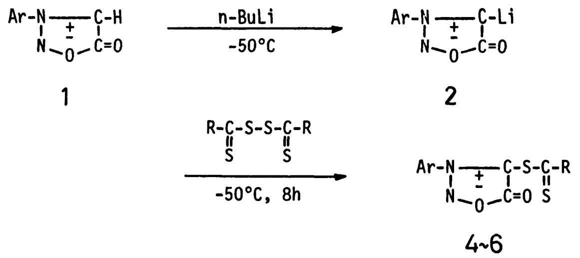
4-Bromosydnones (**3**) are easily prepared by both chemical and electrochemical halogenation of 4-unsubstitued sydnones.[4)] Although **3** is known to be useful starting compounds for the preparation of sydnone derivatives, only one paper dealing with the reaction of **3** with heteroatom compounds such as hydrogen sulfide, thiophenol, and thiourea has been reported.[5)]

From these aspects, preparation of sydnone compounds substituted by hetero functional groups at the 4-positions was attempted using **2** and **3** as starting materials.

Results and Discussion

Preparation of Sydnones Having Thiocarbonylthio Groups at the 4-Positions. It was found that the initial lithiation of sydnones (**1**) and the subsequent reaction of the resulting 4-lithiosydnones (**2**) with tetraalkylthiuram disulfides, bis[alkoxy(thiocarbonyl)] disulfides, and bis[alkylthio(thiocarbonyl)] disulfides could be run in sequence in THF below −50 °C (Scheme 1).

As shown in Table 1, 4-sydnonyl dithiocarbamates (**4**), *O*-alkyl-*S*-(4-sydnonyl) dithiocarbonates (**5**), and alkyl 4-sydnonyl trithiocarbonates (**6**) were successfully prepared in good yields.



Scheme 1.

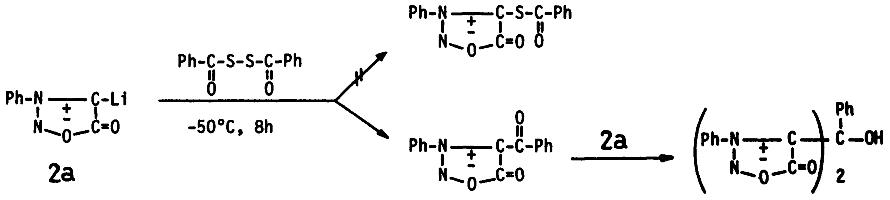
The structures of the products **4**, **5**, and **6** were confirmed by elemental analyses and various spectral studies. In the IR spectra, C–H absorption bands (3140—3160 cm^{-1}) of the starting **1** disappeared after the reaction, while those of thiocarbonyl groups (1050—1200 cm^{-1}) newly appeared. In the MS spectra, most sydnone derivatives showed their molecular ion peaks together with their characteristic fragment peaks due to the elimination of CO and NO. The sydnones bearing an isopropyl group showed fragment peaks due to elimination of the isopropyl group but did not show their molecular ion peaks.

It is known that the reaction of ordinary aryllithiums

Table 1. Preparation of Sydnone Compounds **4**, **5**, and **6**

Compd	Ar	R	Yield[a)] %	Mp θ_m/°C	IR (KBr) $\nu_{C=O}$/cm^{-1}	IR (KBr) $\nu_{C=S}$/cm^{-1}
4a	Ph	Me$_2$N	99	148—150	1790 1775	1150
4b	Ph	*i*-Pr$_2$N	95	151—152	1795 1775	1150
4c	*p*-Tolyl	Me$_2$N	92	156—158	1795 1775	1160
4d	*p*-Tolyl	*i*-Pr$_2$N	100	118—119	1780	1150
5a	Ph	*i*-PrO	84	75—76	1790	1090
5b	*p*-Tolyl	*i*-PrO	74	95—96	1790 1770	1090
6	*p*-Tolyl	MeS	82	100—101	1785 1770	1080

a)Crude yield.



Scheme 2.

with such sulfides always gives a mixture of products because of a competing nucleophilic attack at both the sulfur atoms of the disulfide bond and the carbon atoms of the thiocarbonyl group. Recently, Cava et al.[6] have reported that an aryllithium reacts exclusively at a disulfide bond of tetraisopropylthiuram disulfide to provide aryl dithiocarbamate because the thiocarbonyl group is highly hindered to nucleophilic attack. From these points, it is noticeable that the reaction always took place at the disulfide bond selectively, regardless of the bulkiness of the alkyl substituents in the case of **2**. These results indicate that the reactivity of 4-sydnonyl anions is different from that of ordinary aryl anions.

Next, we extended this process to the preparation of 4-(benzoylthio)sydnone. The reaction was carried out in a similar manner using equimolar **2a** and dibenzoyl disulfide. However, no expected product was obtained and Phenylbis(3-phenyl-4-sydnonyl)methanol (**7**) was formed in a low yield. In this case, a large amount of the disulfide was recovered. Since **7** should be stoichiometrically formed from two mole of **2a** and one mole of the disulfide, the reaction was carried out using two equiv of **2a** to provide **7** in a moderate yield.

It is noticeable that 4-sydnonyl anions attack at a carbonyl group but do not attack the thiocarbonyl group of the disulfides used in these reactions. In order to confirm this fact further, the reaction of **2** with carbon disulfide was examined. However, the reaction did not proceed at all, though it is well-known that **2** readily reacts with carbon dioxide to provide 4-sydnonecarboxylic acid in a good yield.[7] Since carbon disulfide is much more reactive to nucleophiles than carbon dioxide, the reactivity of 4-sydnonyl anions is quite unique.

Since dithiocarbamates are known to be easily hydrolyzed by alcoholic alkali to give the corresponding thiols,[6] hydrolysis of **4**, **5**, and **6** were attempted in order to obtain 4-mercaptosydnone (**8**) which are hitherto unknown compounds. However, our attempts were unsuccessful owing to the decomposition of the sydnone ring.

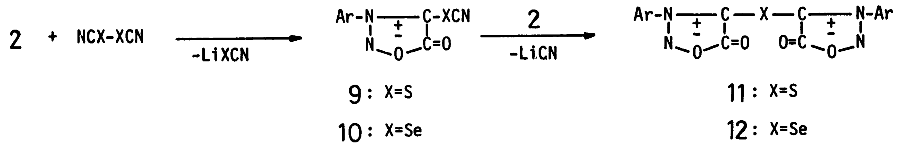
Reaction of 4-Lithiosydnones (2) with Thiocyanogen and Selenocyanogen. Since the reaction of **2** with disulfides bearing a thiocarbonyl group was found to be useful for the introduction of thiocarbonylthio groups to the 4-positions of sydnones, we applied this procedure to the preparation of 4-sydnonyl thio- and selenocyanates (**9** and **10**) from thio- and selenocyanogens. Thio- and selenocyanogens were generated from potassium thio- and selenocyanates and bromine in dry THF at −50 °C and the resulting solution was directly used for the reaction with **2**. When the solution of thiocyanogen was added gradually to the solution of **2** [procedure (a)], bis(4-sydnonyl) sulfide (**11**) was unexpectedly formed instead of 4-sydnonyl thiocyanate (**9**). In order to obtain the desired **9**, the reverse procedure (b) was attempted as follows: **2** was added to the solution of thiocyanogen, however the same product, **11** was obtained. No remarkable differene in the yield of **11** was observed between these two procedures employed.

In a similar manner, the reaction of **2** with seleno-

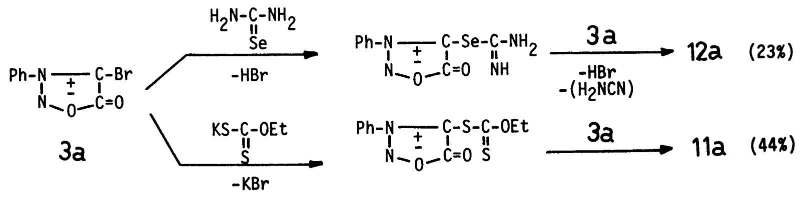
Table 2. Reaction of 4-Lithiosydnone (**2**) with Thiocyanogen and Selenocyanogen

Compd	Ar	X	Procedure	Yield[a]	Mp	IR (KBr)
				%	θ_m/°C	$\nu_{C=O}$/cm^{-1}
11a	Ph	S	(a)	57	165—166 (164—165)[5] (169—171)[14]	1780, 1750
11a	Ph	S	(b)	51	165—166	1780, 1750
11b	*p*-Tolyl	S	(b)	42	218—219 (201—203)[14]	1770
12a	Ph	Se	(a)	34	180—181	1770, 1750
12b	*p*-Tolyl	Se	(a)	64	209—211 (decomp)	1770, 1750

a) After recrystallization.



Scheme 3.



Scheme 4.

cyanogen also provided bis(4-sydnonyl) selenide (**12**) in a moderate yield as shown in Table 2.

Aryl tellurocyanates are known to be unstable and disproportionate to diaryl tellurides and tellurium dicyanate in some cases,[8] whereas aryl thio- and selenocyanates are stable and such disproportionation has not been reported. A probable mechanism for the reaction involves the formation of 4-sydnonyl thio- and selenocyanates (**9** and **10**) as primary products, which reacted further with 4-sydnonyl anions to give rise to **11** and **12**, respectively.[9]

These results clearly indicate that the reactivity of 4-sydnonyl anions is quite different from that of ordinary aromatic analogues though the sydnone ring has a somewhat aromatic nature.

Reaction of 4-Bromosydnone (3) with Selenourea. 4-Bromo-3-phenylsydnone (**3a**) was found to react with selenourea under refluxing in ethanol to give bis(3-phenyl-4-sydnonyl)selenide (**12a**). During the reaction, the precipitation of selenium metal was observed. Since ordinary aryl bromides do not react with selenourea, this reaction seems to be quite interesting.

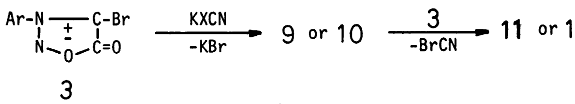
Kato and Ohta found that 4-iodo- and bromosydnones have weak oxidizing power whereas 4-chlorosydnone does not.[5,10] Since oxidative deselenylation of selenourea is known to take place very often as well as that of thiourea, the elimination of selenium metal clearly indicates that the bromosydnone **3a** acted as oxidizing reagent in this reaction.

Table 3. Reaction of 4-Bromosydnone (**3**) with Potassium Thiocyanate and Selenocyanate

Compd	Ar	X	Reaction time/h	Yield[a]
				%
11a	Ph	S	4	61
11b	*p*-Tolyl	S	6.5	51
12a	Ph	Se	8	54
12b	*p*-Tolyl	Se	24	50

a) After recrystallization.

Reaction of 4-Bromosydnone with Potassium Thio- and Selenocyanates and Potassium *O*-Ethyl Dithiocarbonate. Because the thio- and selenocyanation of sydnones from **2** and thio- and selenocyanogen was unsuccessful, the reaction of **3** with potassium thio- and selenocyanates was attempted in order to obtain **9** and **10**, respectively. However, the reaction in DMF under heating provided sulfides **11** and selenides **12** instead of the desired products (**9** and **10**) as shown in Scheme 5. The results are summarized in Table 3.



Scheme 5.

In our earlier work,[11] we found that *N*-[α-(chloroimino)benzyl]sulfilimine easily reacted with potassium thiocyanate to provide heterocyclic sulfilimine. Although this sulfilimine has a positive halogen, such elimination of the cyanate ion was not observed.

The products **11** and **12** seem to be formed by the further reaction of 4-sydnonyl thio- or selenocyanates (**9** or **10**) once formed with additional 4-bromosydnones as shown in Scheme 5.

It was found that the sulfide **11a** was also formed by the reaction of **3a** with potassium *O*-ethyl dithiocarbonate in a similar manner. The reaction may proceed similarly to the reaction of the thio- and selenocyanate ions (Secheme 4).

It was reported that the bromine atom of bromomalonic acids could be substituted by the thiocyanate ion, although their bromine atom has a positive character.[12] These unusual reactions (Schemes 4 and 5) have never been known in the case of the corresponding ordinary aryl bromides, therefore it can be stated that 4-bromosydnone **3** has quite intriguing reactivities.

The new type of sydnone compounds thus prepared are expected to be pharmacologically active and screening tests of several biological activities of these sydnones are currently under investigation.

Experimental

NMR spectra were recorded at 60 MHz on a Varian EM-360 spectrometer using $\mathrm{Me_4Si}$ as an internal standard. IR spectra were obtained on a Hitachi 295 infrared spectrometer. Electron impact mass spectra were determined at 30 eV on a JEOL JMS-D100 mass spectrometer by direct introduction via solid probe.

Typical Procedure for the Preparation of Sydnones Having Thiocarbonylthio Groups at the 4-Positions (4, 5, and 6). 3-Phenyl-4-sydnonyl Dimethyldithiocarbamate (4a): To a stirred suspension of 1.00 g (6.2 mmol) of 3-phenylsydnone in 10 ml of anhydrous THF, under a dry nitrogen atmosphere, was added dropwise 4.0 ml (6.5 mmol) of a solution of butyllithium in hexane (15%) below −50 °C. After about 1 h of stirring, a solution of 1.48 g (6.2 mmol) of tetramethylthiuram disulfide in 7 ml of THF was added dropwise to the resulting brown solution below −50 °C. After additional 8 h of stirring, the yellow-brown reaction mixture was poured into ice-water. The pricipitated yellow solid was collected by filtration, washed with water, and dried: yield 1.71 g (99%); mp 145—147 °C. Recrystallization from ethanol provided 1.55 g (89%) of the pure product **4a** as yellow plates: Mp 148—150 °C; NMR ($\mathrm{CDCl_3}$) δ=3.30 (s, 3H, $\mathrm{C\underline{H}_3}$), 3.35 (s, 3H, $\mathrm{C\underline{H}_3}$), and 7.63 (s, 5H, $\mathrm{C_6\underline{H}_5}$); MS, *m/z* 281 ($\mathrm{M^+}$) and 223 ($\mathrm{M^+}$—NO-CO). Found: C, 46.98; H, 3.92; N, 14.93; S, 22.47%. Calcd for $\mathrm{C_{11}H_{11}N_3O_2S_2}$: C, 46.96; H, 3.94; N, 14.93; S, 22.79%.

3-Phenyl-4-sydnonyl Diisopropyldithiocarbamate (4b): A yellow solid (from ethanol); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.31 (d, 12H, $\mathrm{C\underline{H}_3}$), 4.0—5.0 (m, 2H, $\mathrm{C\underline{H}}$), and 7.63 (s, 5H, $\mathrm{C_6\underline{H}_5}$); MS, *m/z* 337 ($\mathrm{M^+}$), 294 ($\mathrm{M^+}$—*i*-Pr), and 236 ($\mathrm{M^+}$—*i*-Pr-NO-CO). Found: C, 53.37; H, 5.71; N, 12.32; S, 18.98%. Calcd for $\mathrm{C_{15}H_{19}N_3O_2S_2}$: C, 53.39; H, 5.67; N, 12.45; S, 19.00%.

3-(*p*-Tolyl)-4-sydnonyl Dimethyldithiocarbamate (4c): A yellow solid (from ethanol); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=2.45 (s, 3H, *p*-$\mathrm{C\underline{H}_3C_6H_4}$), 3.35 (s, 3H, $\mathrm{NC\underline{H}_3}$), 3.40 (s, 3H, $\mathrm{NC\underline{H}_3}$), 7.30 (d, 2H, Ar-H), and 7.50 (d, 2H, Ar-H); MS, *m/z* 295 ($\mathrm{M^+}$) and 149 ($\mathrm{M^+}$—NO-CO-C(S)$\mathrm{NMe_2}$). Found: C, 48.98; H, 4.77; N, 14.10; S, 21.65%. Calcd for $\mathrm{C_{12}H_{13}N_3O_2S}$: C, 48.80; H, 4.44; H, 14.23; S, 21.71%.

3-(*p*-Tolyl)-4-sydnonyl Diisopropyldithiocarbamate (4d): Pale pink plates (from ethanol); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.40 (d, 12H, $\mathrm{CH(C\underline{H}_3)_2}$), 2.45 (s, 3H, *p*-$\mathrm{C\underline{H}_3C_6H_4}$), 4.10—4.90 (br. m, 2H, $\mathrm{C\underline{H}}$), 7.30 (d, 2H, Ar-H), and 7.50 (d, 2H, Ar-H); MS, *m/z* 308 ($\mathrm{M^+}$—*i*-Pr), and 250 ($\mathrm{M^+}$—*i*-Pr-NO-CO). Found: C, 54.87; H, 6.12; N, 11.73; S, 18.45%. Calcd for $\mathrm{C_{16}H_{21}N_3O_2S_2}$: C, 54.68; H, 6.02; N, 11.96; S, 18.24%.

***O*-Isopropyl *S*-(3-phenyl-4-sydnonyl) Dithiocarbonate (5a):** A yellow solid (from ethanol); ^{1}H NMR (DMSO-d_6) δ=1.28 (d, 6H, $\mathrm{C\underline{H}_3}$), 5.50 (m, 1H, $\mathrm{C\underline{H}}$), and 7.70 (s, 5H, $\mathrm{C_6\underline{H}_5}$); MS, *m/z* 253 ($\mathrm{M^+}$—*i*-Pr), and 195 ($\mathrm{M^+}$—*i*-Pr-NO-CO). Fond: C, 48.62; H, 4.02; N, 9.46; S, 21.39%. Calcd for $\mathrm{C_{12}H_{12}N_2O_3S_2}$: C, 48.63; H, 4.08; N, 9.45; S, 21.64%.

***O*-Isopropyl *S*-[3-(*p*-Tolyl)-4-sydnonyl] Dithiocarbonate (5b):** A yellow solid (from ethanol); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.33 (d, 6H, $\mathrm{CH(C\underline{H}_3)_2}$), 2.50 (s, 3H, *p*-$\mathrm{C\underline{H}_3C_6H_4}$), 5.57 (m, 1H, $\mathrm{C\underline{H}}$), and 7.37 (s, 4H, Ar-$\underline{\mathrm{H}}$); MS, *m/z* 310 ($\mathrm{M^+}$), 267 ($\mathrm{M^+}$—*i*-Pr), and 209 ($\mathrm{M^+}$—*i*-Pr-NO-CO). Found: C, 50.32; H, 4.53; N, 8.98; S, 20.96%. Calcd for $\mathrm{C_{13}H_{14}N_2O_3S_2}$: C, 50.31; H, 4.55; N, 9.03; S, 20.66%.

Methyl [3-(*p*-Tolyl)-4-sydnonyl] Trithiocarbonate (6): A yellow solid (from ethanol); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=2.40 (s, 3H, *p*-$\mathrm{C\underline{H}_3C_6H_4}$), 2.70 (s, 3H, $\mathrm{C\underline{H}_3S}$), and 7.40 (s, 4H, Ar-$\underline{\mathrm{H}}$); MS, *m/z* 298 ($\mathrm{M^+}$) and 240 ($\mathrm{M^+}$—NO-CO). Found: C, 44.22; H, 3.26; N, 9.49; S, 32.32%. Calcd for $\mathrm{C_{11}H_{10}N_2O_2S_3}$: C, 44.28; H, 3.38; N, 9.39; S, 32.23%.

Phenylbis(3-phenyl-4-sydnonyl)methanol (7): In a manner similar to the preparation of **4**—**6**, **7** was obtained in 66% yield using two equiv of 4-lithio-3-phenylsydnone and dibenzoyl disulfide. Recrystallization from ethanol provided pure **7** as a pale yellow solid (58%); mp 199—201 °C (decomp) (lit,[13] mp 203—205 °C); IR (KBr): 3240 (νOH), 3070 (νCH of aromatic), 1790 and 1710 cm^{-1} (νC=O); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=6.15 (s, 1H, $\mathrm{O\underline{H}}$), 7.10 (s, 5H, $\mathrm{C_6\underline{H}_5COH}$), and 7.20—7.60 (m, 10H, $\mathrm{C_6\underline{H}_5}$). Found: C, 64.48; H, 3.51; N, 13.06%. Calcd for $\mathrm{C_{23}H_{16}N_4O_5}$: C, 64.48; H, 3.76; N, 13.08%.

Reaction of 4-Lithiosydnones (2) with Thiocyanogen and Selenocyanogen. General Procedure (a). To a stirred solution of 6 mmol of 4-lithiosydnone **2** in 10 ml of THF under dry nitrogen atmosphere below −50 °C, was added dropwise a solution of thiocyanogen or selenocyanogen in 15 ml of THF, which was prepared by the treatment of potassium thiocyanate or selenocyanate (20—24 mmol) with 10—12 mmol of bromine below −50 °C. After ca. 8h of stirring, the colored (violet or orange color) reaction mixture was poured into a large amount of ice-water. After the mixture had been allowed to stand for 1h, the resulting precipitates were collected by filtration and washed with water. The crude product was dissolved in ethanol-acetone (10:1) and the solution was treated with activated charcoal powder. The solution was concentrated and the remaining solution was allowed to stand overnight. The precipitated pure product was obtained by filtration.

Bis(3-phenyl-4-sydnonyl)sulfide (11a): ^{1}H NMR ($\mathrm{CDCl_3}$) δ=7.40—7.93 (m, $\mathrm{C_6\underline{H}_5}$). MS, *m/z* 354 ($\mathrm{M^+}$), 296 ($\mathrm{M^+}$—NO-

CO), and 238 (M^+−2NO-2CO). Found: C, 54.17; H, 2.63; N, 15.66; S, 8.94%. Calcd for $C_{16}H_{10}N_4O_4S$: C, 54.24; H, 2.84; N, 15.81; S, 9.05%.

Bis[3-(*p*-tolyl)-4-sydnonyl]sulfide (11b): ^{1}H NMR ($CDCl_3$) δ=2.50 (s, 6H, $C\underline{H}_3$), 3.37 (d, 4H, Ar-$\underline{H}$), and 7.70 (d, 4H, Ar-$\underline{H}$). MS, *m/z* 324 (M^+−NO-CO) and 266 (M^+−2NO-2CO). Found: C, 56.40; H, 3.61; N, 14.59; S, 8.50%. Calcd for $C_{18}H_{14}N_4O_4S$: C, 56.54; H, 3.69; N, 14.65; S, 8.38%.

Bis(3-phenyl-4-sydnonyl)selenide (12a): ^{1}H NMR ($CDCl_3$) δ=7.40—8.10 (m, $C_6\underline{H}_5$). MS, *m/z* 402, 400 (M^+) and 344, 342 (M^+−NO-CO). Found: C, 47.83; H, 2.23; N, 13.93%. Calcd for $C_{16}H_{10}N_4O_4Se$: C, 47.90; H, 2.51; N, 13.96%.

Bis[3-(*p*-tolyl)-4-sydnonyl]selenide (12b): ^{1}H NMR ($CDCl_3$) δ=2.55 (s, 6H, $C\underline{H}_3$), 7.43 (d, 4H, Ar-$\underline{H}$), and 7.73 (d, 4H, Ar-H). MS, *m/z* 430, 428 (M^+) and 372, 370 (M^+−NO-CO). Found: C, 50.27; H, 3.13; N, 13.02%. Calcd for $C_{18}H_{14}N_4O_4Se$: C, 50.36; H, 3.29; N, 13.05%.

Reaction of 4-Bromo-3-phenylsydnone (3a) with Selenourea. To a stirred solution of 1.90 g (7.8 mmol) of **3a** in 20 ml of anhydrous ethanol was added 1.00 g (8.1 mmol) of selenourea and the mixture was refluxed for 8 h. After cooling, the precipitating selenium metal (0.44 g, 69%) was filtered. The filtrate was concentrated and the remaining solution was allowed to stand overnight. The resulting precipitates were collected by filtration and 0.36 g (23%) of pure **12a** was obtained as a yellow solid.

Reaction of 4-Bromosydnones (3) with Potassium Thiocyanate and Selenocyanate. General Procedure. A stirred mixture of 4.1 mmol of **3** and 4.1 mmol of potassium thiocyanate or selenocyanate in 10 ml of anhydrous DMF was heated at 80—90 °C. After 1—1.5h (reaction with potassium thiocyanate) or 4—6h (reaction with selenocyanate) of heating, the reaction mixture was cooled and poured into ice-water. The precipitated solid was collected by filtration and recrystallized from ethanol-acetone (10:1) to provide pure **11** or **12** (Table 3).

Reaction of 4-Bromo-3-phenylsydnone (3a) with Potassium *O*-Ethyl Dithiocarbonate. To a stirred solution of 1.00 g (4.2 mmol) of **3a** in 15 ml of anhydrous DMF was added 0.67 g (4.2 mmol) of potassium *O*-ethyl dithiocarbonate and then the mixture was heated at 80—90 °C. After ca. 0.5h, potassium bromide began to precipitate. After 4h, the reaction mixture was cooled and was poured into ice-water and then the precipitates were collected by filtration; 0.32 g (44%); mp 156—150 °C. Recrystallization from ethanol provided 0.30 g (41%) of pure **11a** as a yellow solid.

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