Bull. Chem. Soc. Jpn., ***69***, *2349—2354 (1996)*

Reactions of Benzyne with 1,3-Benzodithiole-2-thione and Related Compounds: Formation of Novel Tetracyclic Sulfonium Salts and Their Reactions Leading to Dibenzo-1,3,6,-trithiocin Derivatives

Juzo Nakayama,* Atsuko Kimata, Hideki Taniguchi, and Fumihiko Takahashi

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338

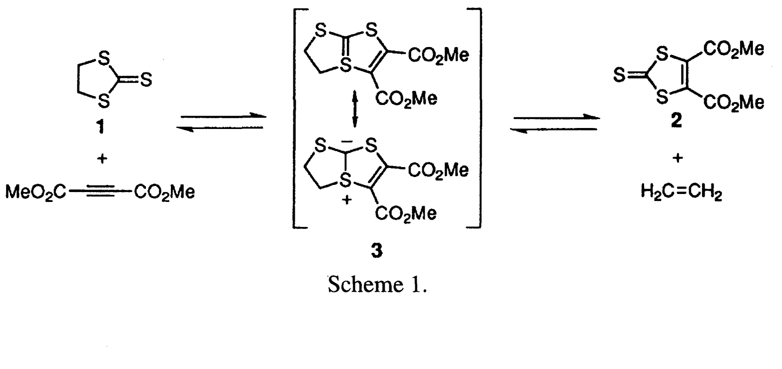
(Received April 9, 1996)

A sulfur ylide intermediate, produced by a 1,3-dipolar cycloaddition of 1,3-benzodithiole-2-thione (**5**) with benzyne, was successfully trapped by hydrogen chloride to give a novel tetracyclic sulfonium salt, 9a*H*-9,10-dithia-4b-thioniaindeno-[1,2-*a*]indene chloride (**7**), in good yield when benzyne was generated by the thermolysis of 2-carboxybenzenediazonium chloride (**4**). The reaction of ethylene trithiocarbonate with excess **4** provided a convenient one-pot synthesis of **7** in large quantities. The reduction of **7** with NaBH$_4$ gave a novel ring compound, dibenzo[*d*,*g*][1,3,6]trithiocin (**15**), in 95% yield, while alkaline hydrolysis produced the 12-oxide derivative of **15**. The treatment of **7** with *t*-BuOK gave 6,6′-bi(dibenzo[*d*,*g*][1,3,6]trithiocinylidene) in 84% yield. Also described are the reactions of benzyne with related compounds of **5**.

It has been long known that dimethyl acetylenedicarboxylate (DMAD) reacts with ethylene trithiocarbonate (**1**) to give ethylene and dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate (**2**).[1] Although the reaction had been recognized as a 1,3-dipolar cycloaddition, no discrete intermediate had been proposed until Lakshmikantham and Cava suggested that the bicyclic tetravalent sulfur heterocycle (a sulfur ylide) **3** is produced initially, and that this unstable species then either reverts reversibly to the starting materials or collapses irreversibly to give the observed products (Scheme 1).[2] There are also a large number of reactions which are synthetically important and will proceed via a similar mechanism.[3] However, sulfur ylide intermediates, such as **3**, have not been spectroscopically detected nor chemically trapped, though the reaction of **1** with bromocyanoacetylene afforded a thioacetyl bromide derivative, which would be derived from a ring-opening of the initial adduct.[3i] Here, we report that the reactions of 1,3-benzodithiole-2-thione (**5**) and related compounds with benzyne, generated from 2-carboxybenzenediazonium chloride (**4**),[4] allow us to trap such intermediates by hydrogen chloride generated from **4** to give the novel tetracyclic sulfonium chloride **7** and related salts. We also report that **7** gives novel eight-membered ring compounds, 1,3,6-trithiocin derivatives upon the reduction with NaBH$_4$ alkaline hydrolysis, and a treatment with bases.[5]

Results and Discussion

The reaction of benzyne with **5** should lead to intermediate **6** by analogy with the reaction of **1** with DMAD. λ^4-Thiabenzenes are species in which one of the carbon atoms of benzene or benzene derivatives are replaced by a tetravalent sulfur atom. Many are stable enough at low temperatures, and have been fully characterized by spectroscopic means.[6] With this in mind, the two five-membered rings of **6**, each of which possesses a formal cyclic 6π-electron structure, correspond to a *thiathiophene*, and might be stabilized in their own right. In addition, the two plausible decomposition pathways of **6**, reversion to the starting materials and a carbon–sulfur bond cleavage leading to the carbene **8**, are seemingly unfavorable endothermic processes. These factors would make the lifetime of **6** longer, and thus enable us to trap **6** chemically. As expected, **6** was effectively trapped



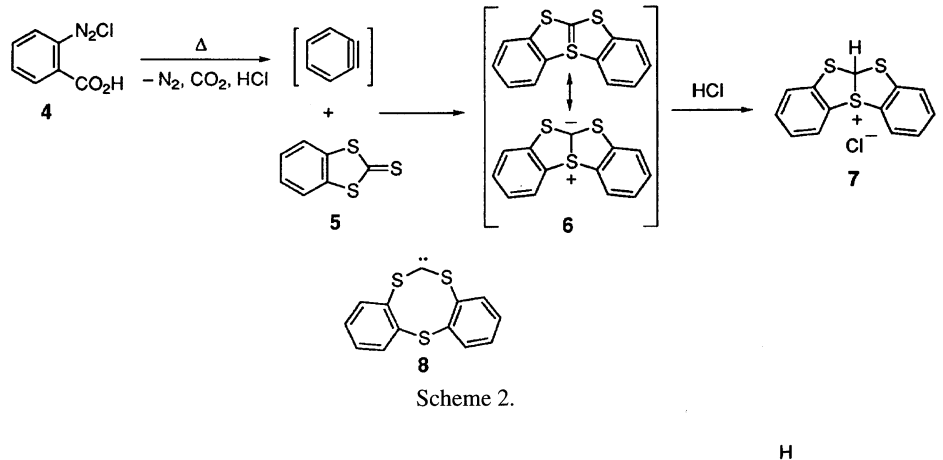
Scheme 1.

by hydrogen chloride to give a novel tetracyclic sulfonium salt, 9a*H*-9,10-dithia-4b-thioniaindeno[1,2-*a*]indene chloride (**7**), when a reaction of **5** with benzyne was carried out using 2-carboxybenzenediazonium chloride (**4**) as the benzyne precursor (Scheme 2). Thus, heating **5** with a slight excess of **4** in refluxing 1,2-dichloroethane gave the sulfonium chloride **7** in 84% yield with an 8% recovery of **5**. The generation of benzyne by the thermal decomposition of **4** is generally carried out in the presence of propylene oxide, which serves as a scavenger of hydrogen chloride liberated from **4**.[4] The reaction of **5** with **4**, carried out in the presence of propylene oxide, also afforded **7** in 76% yield, thus revealing that the reaction of hydrogen chloride with **6** was much faster than that with propylene oxide. It is known that the ylide intermediate produced by the reaction of dimethyl sulfide with benzyne, which was generated by a treatment of *o*-bromochlorobenzene with BuLi, is trapped with perchloric acid to give dimethylphenylsulfonium perchlorate.[7] Also known is that the ylide intermediates produced by the reactions of cyclic and acyclic sulfides with benzyne are captured by hydrogen chloride liberated from the benzyne precursor **4**.[8]

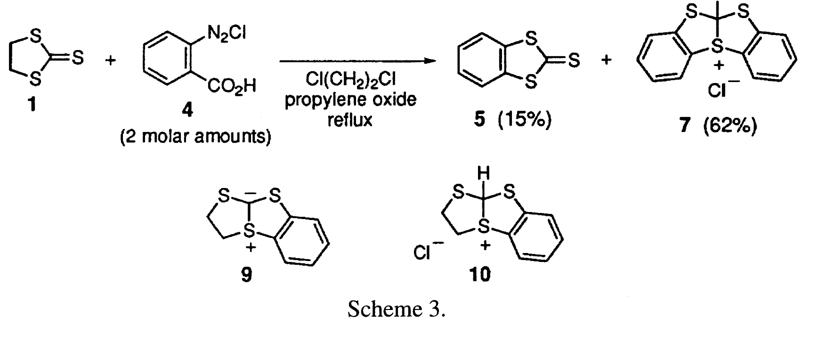
The structure of **7** was determined based on spectroscopic data and chemical transformations. The ^{13}C NMR spectrum showed seven peaks, which were in agreement with the assigned structure, thereby the methine carbon resonating at $\delta = 74.18$. In the ^{1}H NMR spectrum, the methine hydrogen appeared at $\delta = 7.90$.

More important synthetically is the reaction of **1** with **4**. Heating **1** with two molar amounts of **4** in refluxing 1,2-dichloroethane in the presence of propylene oxide afforded **7** directly in 62% yield (Scheme 3). The thione **5** was also formed in 15% yield. This reaction enabled the salt **7** to be easily prepared in one-pot in large quantities from commercially available **1**. These results can be explained as follows: The initial adduct **9**, formed from **1** and benzyne, decomposed to ethylene and **5** more quickly than it was trapped by hydrogen chloride to give the sulfonium salt **10**, while **6**, produced by the reaction of **5** with benzyne, is a more long-lived species and was captured by hydrogen chloride to give **7**. When the reaction of **1** with **4** was carried out in the absence of propylene oxide, a prolonged reaction was required for the complete decomposition of **4** to give less pure **7** in lower yield. Thus, propylene oxide may accelerate a smooth decomposition of **4** by accepting a proton from **4**; the resulting benzenediazonium-2-carboxylate is known to decompose to benzyne more easily at lower temperature than does **4**.[9] It was previously reported that reactions of **1** with benzynes, generated by the thermolysis of diphenyliodonium-2-carboxylate and by the oxidation of 1-aminobenzotriazole, afforded the thione **5** in low yields (9 and 13%, respectively).[1] The low yields of **5** in these cases would mean that **5** further reacted with benzyne to give the ylide **6**, which, in the absence of an appropriate trapping agent, collapsed to give a complex mixture. Actually, also in our own experiment, the reaction of **5** with benzyne, generated from benzenediazonium-2-carboxylate, gave a complex mixture from which any products could not be isolated in a pure form.

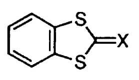
We also examined the reactions of benzyne with some related compounds of **5**. The reaction of 1,3-benzodithiole-2-selone (**11a**) with a slight excess of **4** in refluxing 1,2-dichloroethane for 1.2 h cleanly afforded the sulfonium salt, 9a*H*-9-selena-10-thia-4b-thioniaindeno[1,2-*a*]indene chlo-



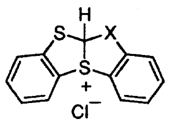
Scheme 2.



Scheme 3.



11a: X = Se
11b: X = O
11c: X = NPh



12a: X = Se
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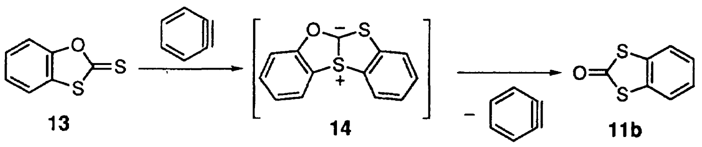
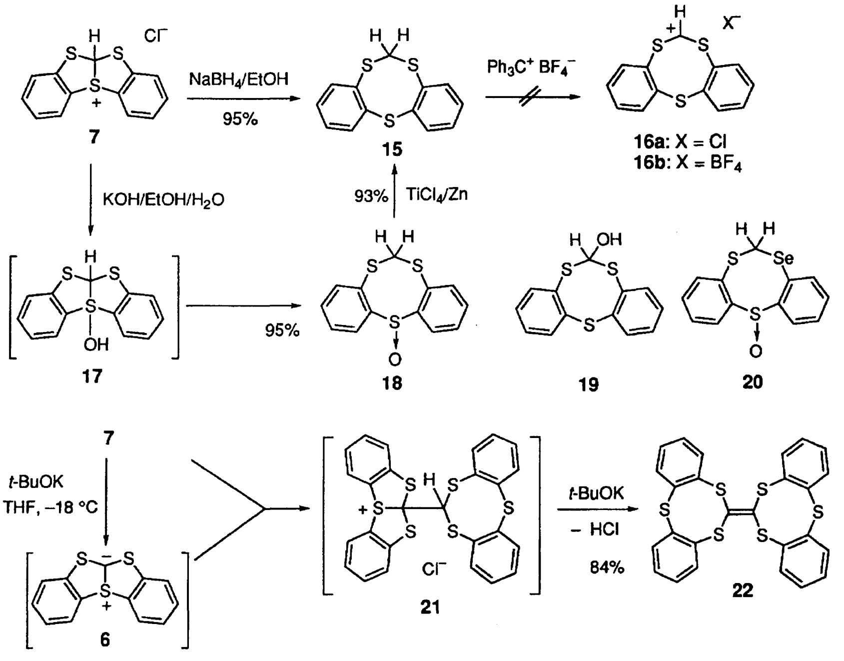
12c: X = NPh



Scheme 4.



Scheme 5.

ride (**12a**), in 82% yield with a 12% recovery of **11a**. 1,3-Benzodithiol-2-one **11b** did not react with benzyne to give the sulfonium salt **12b**; **11b** was recovered nearly quantitatively. The reaction with the imine derivative **11c** gave a complex mixture from which no expected sulfonium salt **12c** could be isolated, **11c** being recovered in 58% yield. The reaction of 1,3-benzoxathiole-2-thione (**13**) with benzyne also did not give the expected sulfonium salt, but brought about an interesting rearrangement to give **11b** in 39% yield, indicating that the initial adduct **14** collapsed to **11b** and benzyne quickly and irreversibly (Scheme 4). This observation is in harmony with the fact that **11b** is inert to benzyne. It is thus concluded that, in the 1,3-benzodithiole and related ring systems, the 1,3-dipolar cycloaddition of benzyne takes place smoothly only when they have a unit of –C(=X)–S– (X = S or Se).

The reactivities of the sulfonium salt **7** that possesses a novel tetracyclic structure should be a matter of next interesting concern. The reduction of **7** with $NaBH_4$ gave the dibenzo[*d*,*g*][1,3,6]trithiocin (**15**) in 95% yield. To our knowledge, this is the first example of 1,3,6-trithiocin derivatives. The reaction probably proceeds via an S_N2 mechanism where a hydride attacks the central carbon, while the sulfide group acts as a leaving group.[10] The eight-membered ring carbocation **16** is an isomer of the sulfonium ion **7**, and has a formal 10π electron system, thus satisfying the Hückel rule. Therefore, if it can adopt a planar conformation, it might be aromatic. However, attempted hydride abstraction from the trithiocin **15** by triphenylcarbenium tetrafluoroborate failed to give the expected salt **16b**.[11] The formation of the salt **7** (BF_4^- instead of Cl^-) was not observed either. This indicates that **16** cannot adopt a planar conformation, because of a steric demand, and is no longer aromatic. This conclusion is also in harmony with the fact that the sulfonium salt **7** does not show any tendency to isomerize the carbonium salt **16a**.

An alkaline hydrolysis of **7** afforded the eight-membered ring sulfoxide **18** in 95% yield. It is thus probable that a hydroxide ion attacked the sulfonium sulfur to give the λ^4-sulfurane intermediate **17**, which underwent a proton transfer along with a concomitant sulfur-carbon bond cleavage to give **18**.[12] The product of the carbon attack by the hydroxide ion,

19 was not formed. The reduction of **18** with a low-valent titanium reagent, prepared from $TiCl_4$ and zinc powder, gave the trithiocin **15** in 93% yield.[13] The alkaline hydrolysis of the selenium analog **12a** also gave the corresponding sulfoxide **20** in 73% yield.

Deprotonation of the salt **7** with a base is expected to regenerate the ylide **6**. Disappointingly, this attempt was unsuccessful. However, interestingly, the treatment of **7** with *t*-BuOK and BuLi gave the dimeric product **22** in 84 and 45% yields (Scheme 5), respectively, whereas the treatment with pyridine and Et_3N at room temperature resulted in a recovery of the starting material. As for the formation of **22**, the most plausible mechanism would involve the initial formation of **6**, whose ylide carbon then attacks the central carbon of **7** via an S_N2 mechanism to give a sulfonium ion intermediate **21**, which then deprotonates to produce the final product **22**. A mechanism involving the ring-opening of **6** to the carbene **8**, followed by a reaction with **7**, and then by deprotonation, is seemingly less probable.

Faint yellow crystals of **22** show a high melting point, and are hardly soluble in common organic solvents. Compound **22** is a hitherto unknown, higher analog of tetrathiafulvalenes, and was expected to form charge-transfer complexes or salts with electron acceptor molecules. However, it failed to form such salts or complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ); solutions of **22** and TCNQ or DDQ in CH_2Cl_2 and CH_3CN did not show any new absorptions in the UV-vis spectra. This is probably due to a lack of the aromaticity of the carbenium ion **16**, which makes it impossible to form a stable radical cation.

Experimental

The melting points were determined on a MEL-TEMP capillary tube apparatus and are uncorrected. The NMR spectra were determined on a Bruker AM-400 spectrometer (at 400 MHz for ^1H and 100 MHz for ^{13}C) or on a Bruker AC-200 spectrometer (at 200 MHz for ^1H and 50 MHz for ^{13}C). Mass spectra were obtained at 70 eV in the EI mode on a JEOL JMS-DX303 or a Shimadzu QP-1000 spectrometer, IR spectra on a Hitachi Model 270-50 spectrophotometer, and UV-vis spectra on a Hitachi 340 spectrophotometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. Column chromatography was performed with Merck Kieselgel 60 (70—230 mesh).

1,3-Benzodithioles **5**,[14] **12a**,[14] **12b**,[15] and **12c**,[16] the benzoxathiole **13**,[17] and 2-carboxybenzenediazonium chloride (**4**)[4] were prepared according to the literature methods.

Reaction of 1,3-Benzodithiole-2-thione (5) with Benzyne Generated from 2-Carboxybenzenediazonium Chloride (4). a) In the Presence of Propylene Oxide. *Great care should be taken when handling the diazonium salt* **4**, *because of its potential explosive nature.* A mixture of 1110 mg (6 mmol) of **4**, 922 mg (5 mmol) of **5**, and 5 ml of propylene oxide in 100 ml of 1,2-dichloroethane was heated under reflux for 45 min. The resulting mixture was cooled and a trace amount of an insoluble material was removed by filtration. The wine-red filtrate was evaporated under reduced pressure, and the residue was triturated with 20 ml of CH_2Cl_2 and set aside overnight. The resulting crystalline solid was collected by filtration to give 1087 mg (73%) of 9a*H*-9,10-dithia-4b-thioniaindeno[1,2-*a*]indene chloride (**7**), mp 197—198.5 °C (decomp), as near-white solid. Concentration of the mother liquor gave another crop (46 mg, 3%) of **7**, mp 190.5—191 °C (decomp). The thus-obtained sulfonium salt **7** was sufficiently pure, and, thus, although colorless leaflets were obtained on crystallization from acetic acid, no increase in the melting point was observed. **7**: Mp 193—195 °C (decomp); colorless leaflets (from AcOH); ^1H NMR (CF_3CO_2D, 400 MHz) $\delta = 7.60$—7.64 (4H, m), 7.74—7.78 (2H, m), 7.90 (1H, s, methine), 7.98—8.00 (2H, m); ^{13}C NMR (CF_3CO_2D, 100 MHz) $\delta = 74.18$ (d, methine), 124.74 (s), 127.23 (d), 131.00 (d), 132.14 (d), 137.81 (d), 145.62 (s); MS *m/z* 298 (M^+; Cl = 37), 296 (M^+; Cl=35), 216, 189, 187, 184. Found: C, 40.37; H, 2.25%. Calcd for $C_{13}H_9ClS_3$: C, 40.21; H, 2.34%.

b) In the Absence of Propylene Oxide. A mixture of 1110 mg of **4** (6 mmol) and 922 mg (5 mmol) of **5** in 100 ml of 1,2-dichloroethane was heated under reflux for 45 min. The resulting mixture was cooled and a trace amount of insoluble material was removed by filtration. The mixture was evaporated under reduced pressure and the residue was triturated with 20 ml of CH_2Cl_2 and set aside overnight. The resulting crystalline solid was collected by filtration to give 1249 mg (84%) of **7**, mp 197—198 °C (decomp), as near-white solid. Purification of the filtrate with silica-gel column chromatography gave 83 mg (10%) of the starting material **5**.

Reaction of Ethylene Trithiocarbonate (1) with Benzyne in the Presence of Propylene Oxide; One-Pot Synthesis of 7 in Large Quantities. A mixture of 8.54 g (62.7 mmol) of **1**, 23.14 g (125.4 mmol) of **4**, and 25 ml of propylene oxide in 800 ml of 1, 2-dichloroethane was heated under reflux for 2 h. Trace amounts of insoluble materials were removed by filtration, and the yellowish orange filtrate was evaporated under reduced pressure; the residue was triturated with 100 ml of CH_2Cl_2 and set aside overnight. The resulting precipitate was collected by filtration to give 11.50 g (62%) of **7**, mp 206—207 °C (decomp), as near-white solid. Chromatographic purification of the filtrate gave 2.77 g (15%) of 1,3-benzodithiole-2-thione (**5**). **Reaction of 1 with benzyne in the absence of propylene oxide** required a longer reaction time to give less pure **7** in a lower yield. Thus, heating 1.36 g (10 mmol) of **1** and 3.70 g (20 mmol) of **4** in refluxing 1,2-dichloroethane (300 ml) for 4 h gave 1.76 g (59%) of less pure **7**, melting at about 170 °C (decomp).

Reaction of 1,3-Benzodithiole-2-selone (11a) with Benzyne. A mixture of 1110 mg (6 mmol) of **4** and 1156 mg (5 mmol) of **11a** in 100 ml of 1,2-dichloroethane was heated for 1.2 h under reflux. A trace amount of insoluble material was removed by filtration, and the red filtrate was evaporated under reduced pressure. The residue was triturated with 25 ml of CH_2Cl_2, set aside overnight, and collected by filtration to give 1405 mg (82%) of 9a*H*-9-selena-10-thia-4b-thioniaindeno[1,2-*a*]indene chloride (**12a**): Mp > 223 °C (decomp); lemon yellow plates (AcOH); ^1H NMR (CF_3CO_2D, 400 MHz) $\delta = 7.60$—7.76 (6H, m), 7.79 (1H, s, methine), 7.83 (1H, d, $J = 8.0$ Hz), 7.97 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (CF_3CO_2D, 100 MHz) $\delta = 60.04$ (methine), 125.57 (C), 127.18 (CH), 127.40 (C), 130.31 (CH), 130.85 (CH), 131.46 (CH), 132.04 (CH), 132.39 (CH), 137.68 (CH), 137.92 (CH), 142.08 (C), 146.97 (C). Found: C, 45.68; H. 2.70%. Calcd for $C_{13}H_9ClS_2Se$: C, 45.42; H, 2.64%.

Reaction of 1,3-Benzoxathiole-2-thione (13) with Benzyne. A mixture of 223 mg (1.2 mmol) of **4** and 170 mg (1 mmol) of **13** in 20 ml of 1,2-dichloroethane was heated under reflux for 1 h. The mixture was evaporated and the residue was purified by silica-gel column chromatography and then by preparative thin-layer chromatography to give 67 mg (39%) of 1,3-benzodithiol-2-one (**11b**), whose spectroscopic data agreed with those of an authentic sample.

Reduction of 7 with NaBH$_4$. To a stirred and ice-cooled suspension of 2.96 g (10 mmol) of **7** in 100 ml of EtOH was added 766 mg (20 mmol) of NaBH$_4$ in small portions over a period of 1 h. After the addition, the mixture was stirred for 1 h and diluted with ice-water (100 ml). The resulting crystalline precipitate was collected by filtration, washed with water, air-dried, and dried under vacuum to give 2.49 g (95%) of dibenzo[*d*,*g*][1,3,6]trithiocin (**15**): Colorless needles (cyclohexane); mp 157—158 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) $\delta = 4.76$ (2H, broad s, CH$_2$), 7.13—7.64 (8H, m); ^{13}C NMR (CDCl$_3$, 50 MHz) $\delta = 39.51$ (CH$_2$), 128.34 (CH, overlapping of two signals), 133.22 (CH), 134.37 (C), 136.20 (CH), 139.58 (C). Found: C, 59.63; H, 3.83%. Calcd for $C_{13}H_{10}S_3$: C, 59.50; H, 3.84%. The treatment of 262 mg (1 mmol) of **15** with 396 mg of triphenylcarbenium tetrafluoroborate in CH$_2$Cl$_2$ (10 ml) did not give the expected salt **16** though triphenylmethane was formed in a low yield.

Alkaline Hydrolysis of 7. An aqueous solution of KOH (20 g) in water (100 ml) was diluted with ethanol (100 ml). The solution was cooled by an ice bath and 2.96 g (10 mmol) of **7** was added in small portions over a period of 20 min. The creamy suspension was stirred at room temperature overnight. The resulting crystalline precipitate was collected by filtration, washed with water, air-dried, and dried under vacuum to give 2.63 g (95%) of dibenzo[*d*,*g*]-[1,3,6]trithiocin 12-oxide (**18**): Lemon yellow needles (AcOEt); mp 221—222 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) $\delta = 3.48$ (1H, d, $J = 15.2$ Hz, CH$_2$), 4.66 (1H, d, $J = 15.2$ Hz, CH$_2$), 7.32—7.36 (2H, m), 7.52—7.58 (4H, m), 8.19 (2H, d, $J = 7.5$ Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) $\delta = 45.28$ (CH$_2$), 124.04 (CH), 129.50 (C), 130.81 (CH), 135.95 (CH), 155.63 (C); IR (KBr) 1067 cm^{-1} (SO). Found:C, 55.82; H, 3.59%. Calcd for $C_{13}H_{10}OS_3$: C, 56.08; H, 3.62%.

Reduction of 18 to 15. To a mixture of 278 mg (1 mmol) of **18** and 392 mg (6 mmol) of zinc powder in 10 ml of THF was added 0.33 ml (3 mmol) of TiCl$_4$ at -18 °C. After the mixture was stirred for 3 h at 0 °C, the reaction was quenched by adding ice-water and then CH$_2$Cl$_2$. The two-phase mixture was filtered with a pad of celite, and the organic layer was washed with water, dried, and evaporated. The resulting crystalline residue was passed though a short column of silica gel with CH$_2$Cl$_2$ as the eluent to give 243 mg (93%) of **15**, mp 156.5—157 °C.

Alkaline Hydrolysis of 12a. An aqueous solution of KOH (2.0 g) in water (10 ml) was diluted with ethanol (10 ml). To this stirred and ice-cooled solution was added 344 mg (1 mmol) of **12a** in small portions over a period of 10 min. The mixture was warmed to room temperature and stirred overnight. The resulting crystalline precipitate was collected by filtration, washed with water, air-dried, and dried under vacuum to give 238 mg (73%) of dibenzo[*d*,*g*]-[1,3,6]dithiaselenocin 12-oxide (**20**): Faint yellow needles (AcOEt); mp > 200°C (decomp); ^{1}H NMR (CDCl$_3$, 400 MHz) $\delta = 3.59$ (broad d, $J = 14.0$ Hz, 1H), 4.65 (d, $J = 14.0$ Hz, 1H), 7.26—7.36 (m, 2H), 7.53—7.67 (m, 4H), 8.18—8.22 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) $\delta = 35.43$ (methylene), 124.58 (overlapping of two peakes), 130.38, 130.70, 130.89, 135.57, 135.60, 135.63, 135.65, 136.62 (overlapping of two peakes), 136.69; IR (KBr) 1055 cm^{-1} (SO). Found: C, 48.03; H, 3.19%. Calcd for $C_{13}H_{10}OS_2Se$: C, 48.00; H, 3.10%.

Treatment of 7 with Bases; 6,6′-Bi(dibenzo[*d*,*g*][1,3,6]trithiocinylidene) (22). a) With *t*-BuOK. A solution of 673 mg (6 mol) of *t*-BuOK in 15 ml of THF was added to a stirred and ice-cooled suspension of 1.48 g (5 mmol) of **7** in 50 ml of THF over a period of 20 min. The mixture was stirred for 4 h at room temperature, and the resulting crystalline precipitate was collected by filtration, washed with water, air-dried, and dried under vacuum to give 1.08 g (84%) of **22**: Faint yellow granules (from DMSO); mp 385—386 °C (decomp); ^{1}H NMR (DMSO-d_6, 400 Hz) $\delta = 7.30$ —7.33 (m), 7.45—7.47 (m), 7.58—7.60 (m) (intensity ratio, 2 : 1 : 1); UV/vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (ε) 340 nm (16750); IR (KBr) 1615, 1562, 1442, 1422, 1245, 1035, 842, 748 cm^{-1}; MS *m*/*z* 520 (M$^+$), 304, 228. Found: C, 59.75; H, 3.14%. Calcd for $C_{26}H_{16}S_6$: C, 59.96; H, 3.10%.

b) With BuLi. To a suspension of 890 mg (3 mmol) of **7** in 25 ml of THF was added a 1.65 M hexane solution ($\mathrm{M = mol\,dm^{-3}}$) of BuLi (2 ml, 3.3 mmol) at -18 °C. The mixture was warmed to 0 °C slowly, and the resulting crystalline precipitate was collected by filtration, washed with water, and dried to give 349 mg (45%) of **22**. An attempted purification of the filtrate did not give any indentifiably pure products.

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