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Ring-Opening and Ring-Expansion Study of 3,4-Di(1-adamantyl)-1,2-dithiete

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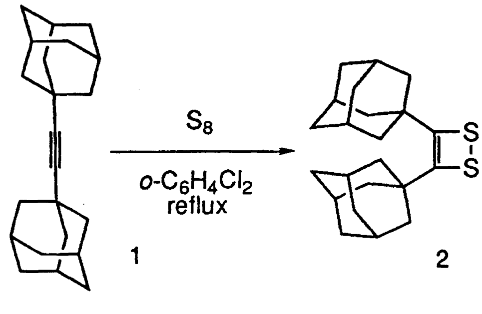
Reduction of 3,4-di(1-adamantyl)-1,2-dithiete (**2**) with $LiEt_3BH$, followed by treatment with MeI, gave (*E*)-1,2-di(1-adamantyl)-1,2-bis(methylthio)ethene (**7-E**) in 87% yield. Configuration of the double bond part of **7-E** was determined by X-ray diffraction analysis. Treatment of **2** with MeLi and then with MeI also gave the same alkene **7-E** in 90% yield, whereas treatment of **2** with MeLi followed by acidification afforded thermally labile (*E*)-1,2-di(1-adamantyl)-2-methylthioethenethiol in a good yield. Reduction of **2** with $LiEt_3BH$ followed by treatment with CS_2, $SOCl_2$, and $PhBCl_2$ gave 4,5-di(1-adamantyl)-1,3-dithiole-2-thione, 4,5-di(1-adamantyl)-1,2,3-trithiole 2-oxide, and 4,5-di(1-adamantyl)-2-phenyl-1,3,2-dithiaborole, respectively, in moderate yields. The CuCl(I)-catalyzed decomposition of Ph_2CN_2 in the presence of **2** afforded 4,5-di(1-adamantyl)-2,2-diphenyl-1,3-dithiole quantitatively, whereas that of tosyl azide produced 1,2-di(1-adamantyl)-2-(*p*-tolylsulfonyl)iminoethane-1-thione in 10% yield.

1,2-Dithietes are structurally interesting compounds which possess one carbon–carbon double bond and one disulfide linkage in the four-membered ring. Most of them are highly reactive and have eluded isolation at room temperature. However, they become stable enough to be isolated when 3- and 4-positions are substituted by bulky[1,2] or electron-withdrawing[3] groups. Recently, we have reported the preparation of a range of 1,2-dithietes which are stabilized by introduction of bulky substituents.[1] A typical example is 3,4-di(1-adamantyl)-1,2-dithiete (**2**) which is easily obtainable by mere heating of di(1-adamantyl)ethyne (**1**) and elemental sulfur in refluxing *o*-dichlorobenzene (Scheme 1).[1] The dithiete **2**, which carries two bulky 1-adamantyl groups in cis-configuration, is of both structural and synthetic importance. To our knowledge, 3,4-di(1-adamantyl)thiophene and *o*-di(1-adamantyl)benzene are the only other examples that carry two 1-adamantyl groups on the vicinal sp^2 carbons in cis-configuration.[4] We have therefore investigated the synthetic use of **2** with research efforts being focused on the followings; 1) preparation of congested compounds where two 1-adamantyl groups are placed on vicinal sp^2 carbons in cis-orientation and 2) preparation of congested compounds in which a labile functional group is kinetically stabilized.

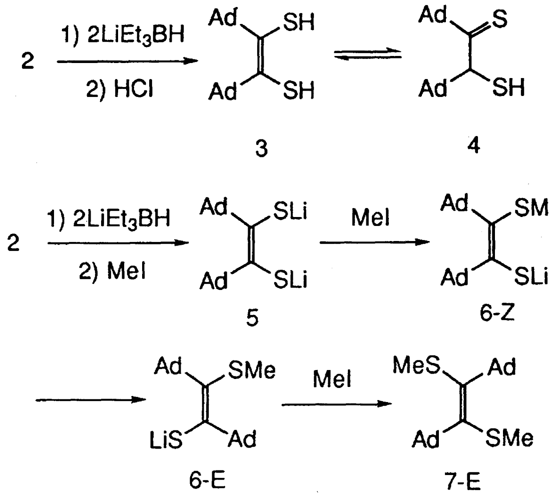


(Ad denotes 1-adamantyl hereafter)

Scheme 1.

Results and Discussion

Preparation of the enedithiol **3** or its tautomer dithioacyloin **4** was first examined by reductive cleavage of the disulfide bond of **2** (Scheme 2). Thus, **2** was treated with 2 molar amounts of $LiEt_3BH$ in tetrahydrofuran (THF)[5] and the reaction was quenched by addition of 1 M HCl (1 M = 1 mol dm^{-3}). The pale yellow reaction mixture turned blue on acidification, but the color faded soon. The origin of the color is apparently ascribable to the dithioacyloin **4**. However, neither **3** nor **4** could be isolated in spite of repeated attempts and careful workup. Repeatedly, **2** was recovered in 35—40% yields, despite complete consumption of **2** on



Scheme 2.

reduction. In some cases, (*E*)-1,2-di(1-adamantyl)-1-(ethylthio)ethene (**9b**) was isolated in small amounts in addition to **2**. Reduction of **2** with 2 molar amounts of $LiEt_3BH$ followed by treatment with excess MeI gave (*E*)-1,2-di(1-adamantyl)-1,2-bis(methylthio)ethene (**7-E**) in 87% yield. No expected (*Z*)-isomer **7-Z** was formed. Configuration of the double bond part of **7-E** was determined by X-ray diffraction analysis. The exclusive formation of **7-E** indicates that the second methylation is so slow, because of steric hindrance, that isomerization of the monomethylated **6-Z** to **6-E** takes place by contribution of the canonical structure **8**. These results stand in a marked contrast to those of dimethylation of (*Z*)-1,2-dicyano-1,2-dithiolate which takes place with retention of configuration.[6)] The recovery of **2** in 35—40% yield, despite complete consumption on reduction, suggests that both **3** and **4** are susceptible to oxidation to give **2**. Successive treatment of the reaction mixture, obtained by reduction of **2** with 2 molar amounts of $LiEt_3BH$, with 1 M HCl, 1 M NaOH, and MeI, gave **7-E** (12%), (*E*)-1,2-di(1-adamantyl)-1-(methylthio)ethene (**9a**) (19%), **9b** (8%), and **2** (36%). The formation of **7-E**, though in a low yield, suggests that **3** or **4** can survive for a short period of time. The formation of **9a** and **9b** is indicative of the occurrence of the over-reduction leading to **10** (Chart 1). The origin of the ethyl group of **9b** is apparently ascribable to Et_3B formed from $LiEt_3BH$, though the mechanism of the reaction remains uncertain. The assignment of (*E*)-configuration for **9a** and **9b** is in harmony with the exclusive formation of **7-E**. In addition, no NOE was observed between methyl and alkenic hydrogen signals in the ^1H NMR. Figure 1 shows the X-ray molecular structure of the alkene **7-E**.[7)]

It is well documented that the S–S bond of disulfides ($R^1S–SR^2$) is cleaved by organometallic reagents (R^3M, M = Li, MgX) to give sulfides (R^1SR^3) and thiolates (R^2SM).[8)] Such an S–S bond cleavage also took place for **2**. Thus, treatment of **2** with MeLi at 0 °C and then with MeI gave the alkene **7-E** in 90% yield. In this case, the initial product **6-Z**, produced by nucleophilic attack of MeLi on the S–S bond, would isomerize to **6-E**, and then would be methylated to give **7-E** (Scheme 3). These findings are in harmony with the timing of isomerization presented for the formation of **7-E** in the $LiEt_3BH$ reduction followed by methylation. Acidification of the mixture, obtained by treatment of **2** with MeLi, gave the enethiol **11**[9)] in a good yield as an amorphous solid. The ^1H NMR spectrum ($CDCl_3$) of **11** showed the signal due to SH at $\delta = 3.49$ which disappeared on addition of D_2O, and the ^{13}C NMR spectrum showed two signals due to sp^2 carbons at $\delta = 145.4$ and 148.5. In the IR spectrum, the SH stretching absorption appeared at 2494 cm^{-1}. The thiol **11** is thermally labile and afforded the thioketone **12** and alkene **9a** (53 and 35% yields based on **2**, respectively) on standing at room temperature for a short period of time. The methine hydrogen of **12**, which appeared at $\delta = 4.04$ in the ^1H NMR, was deuterated very slowly on addition of D_2O, indicating the existence of a slow equilibrium between **11** and **12**, though it lies far to the thioketone side. The formation of **9a** is rather unexpected and is tentatively explained by cyclization of **11** to **13**, followed by loss of sulfur.

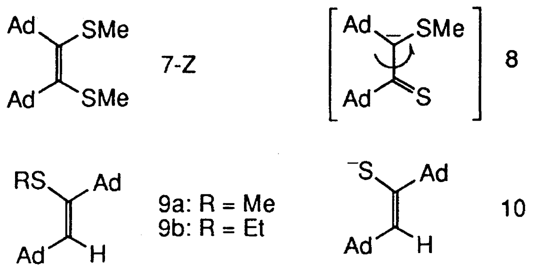


Chart 1.

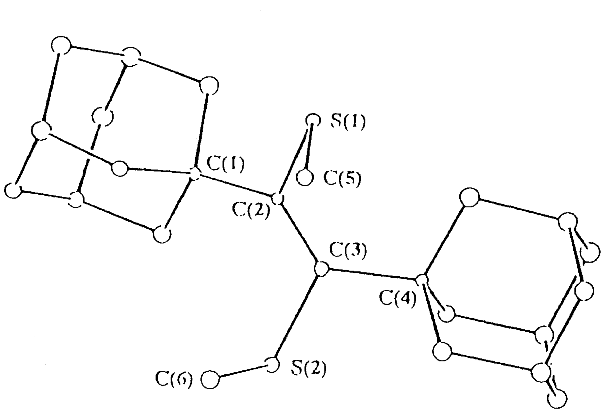
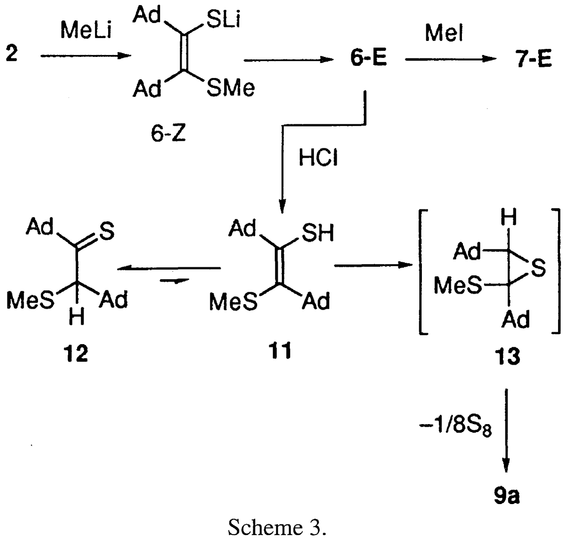
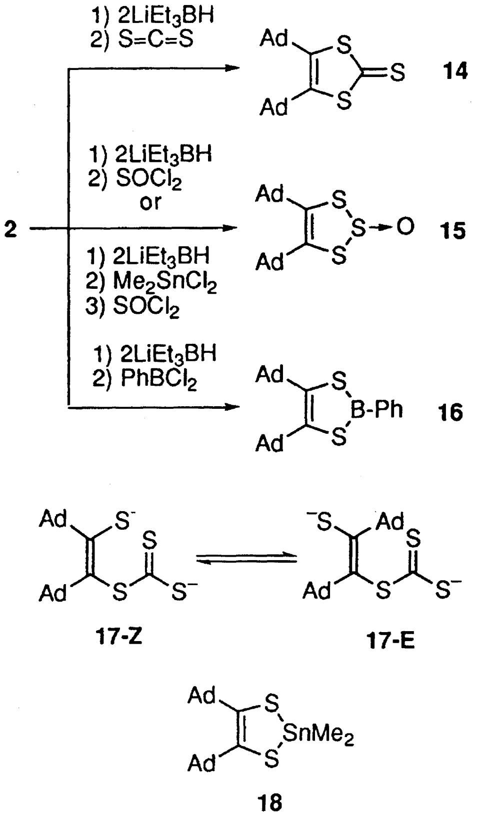


Fig. 1. X-Ray molecular structure of the alkene **6-E**.

Next, derivation of five-membered heterocycles, where two bulky 1-adamantyl groups are substituted in cis-configuration on vicinal sp^2 carbon atoms, was examined through reduction of **2** to the enedithiolate **5** (Scheme 4). Condensation of CS_2 with **5** gave the expected 1,3-dithiole-2-thione **14** in 45% yield.[10)] The satisfactory formation of **14** suggests that, although the initial adduct **17-Z** may isomerize the (*E*)-isomer **17-E**, these are in an equilibrium and hence cyclization to **14** can take place via **17-Z**, though slowly. The enedithiolate **5** also condensed with $SOCl_2$ to give the 1,2,3-trithiole 2-oxide **15** in 6% yield.[11)] The yield of **15** was improved to 37% when **5** was allowed to react with Me_2SnCl_2 and then condensed with $SOCl_2$. Attempted isolation of the proba-



Scheme 3.

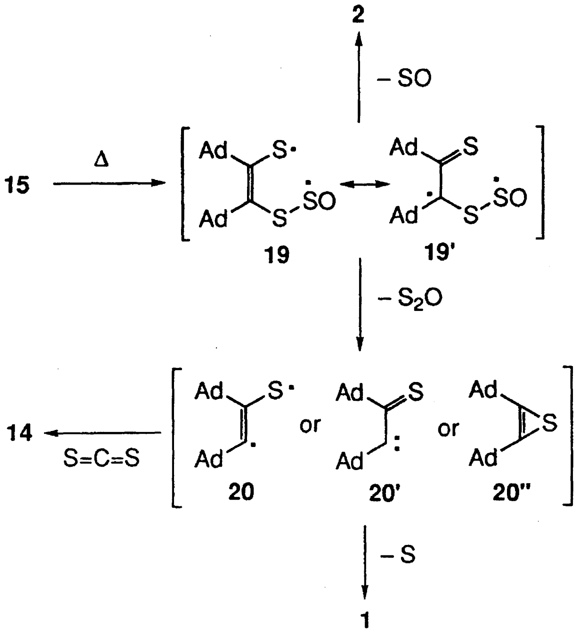


Scheme 4.

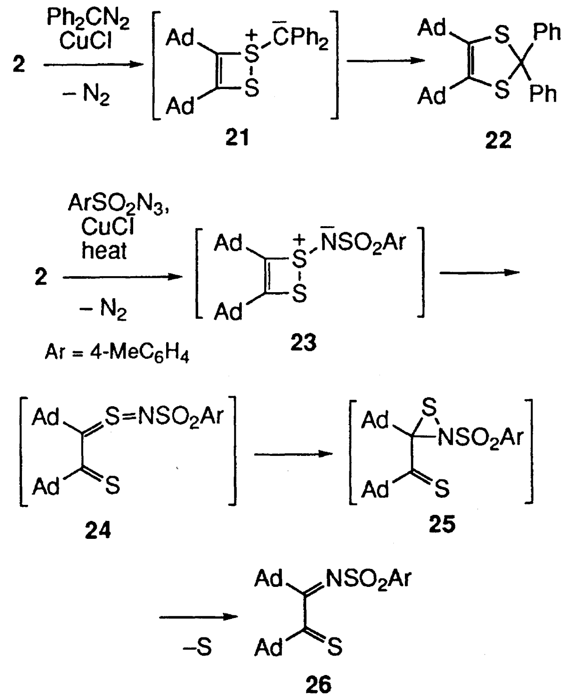
ble intermediate 1,3,2-dithiastannole **18**[12] was unsuccessful. The enedithiolate **5** failed to react with SO_2Cl_2 to give the expected 1,2,3-dithiole 2,2-dioxide derivative. Condensation of **5** with $PhBCl_2$ gave the expected 1,3,2-dithiaborole **16** in 18% yield.[13] However, neither $PhPCl_2$ nor $PhP(O)Cl_2$ gave the corresponding 1,3,2-dithiaphosphole derivatives on reactions with **5**.

The 1,2,3-trithiole 2-oxide **15** is rather thermally labile and afforded the dithiete **2** and ethyne **1** in 39 and 37% yields, respectively, when heated in refluxing toluene.[14] The homolytic cleavage of the weakest bond S–S(O) would initiate the decomposition of **15** to give the biradical **19** (Scheme 5). Extrusion of SO from **19** explains the formation of **2**. This agrees with the observation that $[M-SO]^+$ is the most intense peak in the MS spectrum. Meanwhile, extrusion of S_2O from **19** would produce a reactive intermediate **20** (or its equivalent **20′** or **20″**): Contribution of the canonical structure **19′** may weaken the C–S bond of the CSSO side to favor this fragmentation. Extrusion of sulfur from **20** (**20′**,**20″**) explains the formation of **1**. Actually, when the thermolysis of **15** was carried out in CS_2 at 120 °C in a sealed tube, the dithiole-2-thione **14**, the adduct of the intermediary reactive species with CS_2, was obtained in 70% yield.[15]

Finally, reactions of **2** with carbenes (carbenoids) and nitrenes were examined in the expectation of obtaining 1,3-dithioles and 1,3,2-dithiazoles (Scheme 6). However, both CH_2I_2/Zn–Cu and CH_2I_2/Et_2Zn failed to react with **2** to give the expected insertion product, 4,5-di(1-adamantyl)-1,3-dithiole; **2** was recovered quantitatively. Disappointingly, Cu(I)-catalyzed decomposition of CH_2N_2 and EtO_2CCHN_2 in the presence of **2** also did not give the expected products, 1,3-dithioles.[16] In these cases, complex mixtures containing **2** were formed, from which no pure product was isolated in a sufficient amount. Curiously, however, only Cu(I)-catalyzed decomposition of Ph_2CN_2 gave the 1,3-dithiole **22** quantitatively probably via the ylide intermediate **21**. Interestingly, Cu(I)-catalyzed decomposition of tosyl azide in refluxing toluene gave a low yield (10%) of the α-iminothioketone **26** as violet crystals with 90% recovery of **2**. Initially, the tosyl nitrene would add to the sulfur to give **23**, which in



Scheme 5.



Scheme 6.

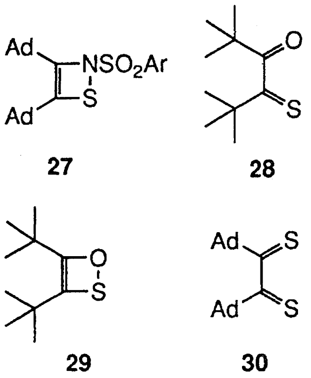


Chart 2.

turn undergoes a ring opening to produce the thione-*S*-imide interemediate **24**. Ring-closure of **24** and extrusion of sulfur from the resulting **25** would explain the formation of **26**.[17] Direct formation of **25** from **23** should be less probable since 3,4-di(1-adamantyl)-1,2-dithiete 1-oxide undergoes a thermal ring-opening similar to that from **23** to **24**.[1c]

The α-iminothioketone **26** did not show any tendency to form a 1,2-thiazete **27** by ring-closure (Chart 2). It is also known that an α-thioxoketone **28** does not undergo a ring-closure to form a 1,2-oxathiete **29**.[18,19] On the other hand, no tautomerization between the 1,2-dithiete **2** and the α-di(thioketone) **30** was observed. Similarly, other 1,2-dithietes do not isomerize to the the corresponding α-dithioxo compounds at room temperature, except in a few cases.[1a,1b,20] These results lead to the conclusion that, when four-membered rings are constituted by a combination of one S–X (X = N, O, S) and one carbon-carbon double bonds, probably 1,2-dithietes are the only species that can adopt a ring-closed structure as the predominant isomeric form.

Experimental

General. Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H- and ^{13}C NMR spectra were determined on a Bruker AM400, a Bruker ARX400, a Bruker AC300P, and a Bruker AC200 spectrometer using $CDCl_3$ as the solvent with TMS as the internal standard (400, 300, and 200 MHz for ^{1}H and 100.6, 75.5, and 50 MHz for ^{13}C, respectively). IR spectra were taken on a Hitachi 270-50 spectrometer. UV-vis spectra were determined using a JASCO V-560 spectrophotometer. Mass spectra were determined on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. HPLC was performed on a Japan Analytical Industry LC-908. 3,4-Di(1-adamantyl)-1,2-dithiete (**2**) was prepared by the method developed by us.[1a,1b] All of the reactions were carried out under argon. Silica-gel column chromatography was performed on Kiesel-gel Art 7734 (Merck, 70—230 mesh).

Reduction of the Dithiete 2. a) Treatment with 1 M HCl. To a solution of 72 mg (0.2 mmol) of **2** in 4 mL of THF cooled at 0 °C was slowly added 0.4 mL (0.4 mmol) of a 1 M THF solution of $LiEt_3BH$ (Aldrich). After the resulting pale yellow mixture was stirred at 0 °C for 1 h, the reaction was quenched by addition of 2 mL of a 1 M deaerated HCl. This caused a violet coloration of the mixture. However, the color faded during extraction with ether. The ether extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel with hexane as the eluent to give a small amount of (*E*)-1, 2-di(1-adamantyl)-1-(ethylthio)ethene (**9b**) and 27 mg (38%) of **2**.

b) Treatment with MeI. The dithiete **2** (72 mg, 0.2 mmol) was treated with $LiEt_3BH$ (0.4 mmol) in the same manner as described above. To the resulting solution containing **5**, MeI (2 mmol) was slowly added at 0 °C. The mixture was stirred for 1 h at 0 °C. The reaction was quenched by addition of cold water. The mixture was extracted with ether and purified by silica-gel column chromatography to give 68 mg (87%) of (*E*)-1,2-di(1-adamantyl)-1,2-bis(methylthio)ethene (**7-E**) and 2 mg (3%) of **2**.

c) Successive Treatment with 1 M HCl, 1 M NaOH, and MeI. The dithiete **2** (216 mg, 0.6 mmol) was treated with $LiEt_3BH$ (1.2 mmol) in the same manner as described above. The resulting mixture containing **5** was successively treated with 1 M HCl (1.5 mL), 1 M NaOH (3 mL), and MeI (0.63 mL, 10 mmol). Purification of the mixture by silica-gel column chromatography gave 40 mg (19%) of (*E*)-1,2-di(1-adamantyl)-1-(methylthio)ethene (**9a**), 18 mg (8%) of **9b**, 28 mg (12%) of **7-E**, and 77 mg (36%) of **2**.

7-E: Mp 179—180 °C; colorless plates (hexane); ^{1}H NMR (400 MHz) $\delta = 1.66$—1.71 (12H, m), 2.02 (6H, broad s), 2.15 (12H, broad s), 2.17 (6H, s, SMe); ^{13}C NMR (100.6 MHz) $\delta = 26.2$, 29.4, 36.6, 41.7, 45.7, 154.1 (sp^2 C); MS *m*/*z* 388 (M^+), 373, 341, 294, 135 (100%). Found: C, 74.30; H, 9.40%. Calcd for $C_{24}H_{36}S_2$: C, 74.17; H, 9.34%.

9a: Mp 151—152 °C; colorless plates (ethanol); ^{1}H NMR (200 MHz) $\delta = 1.55$—1.76 (18H, m), 1.95—2.00 (12H, m), 2.19 (3H, s, SMe), 5.60 (1H, s, =CH); ^{13}C NMR (50 MHz) $\delta = 23.8$, 26.2, 28.9, 36.3, 36.8, 36.9, 41.8, 42.2, 42.7, 144.6 (sp^2 C), 145.7 (sp^2 C); MS *m*/*z* 342 (M^+), 327, 135 (100%). Found: C, 80.52; H, 10.05%. Calcd for $C_{23}H_{34}S$: C, 80.64; H, 10.00%.

9b: Mp 134—136 °C; colorless powder (hexane); ^{1}H NMR (200 MHz) $\delta = 1.22$ (3H, t, $J = 7.5$ Hz, $CH_2C\underline{H}_3$), 1.66—1.75 (18H, m), 1.93—1.99 (12H, m), 2.63 (2H, q, $J = 7.5$ Hz, $C\underline{H}_2CH_3$), 5.60 (1H, s, =CH); ^{13}C NMR (50 MHz) $\delta = 28.6$, 29.0, 34.4, 36.3, 36.5, 36.9, 37.0, 41.7, 41.9, 42.8, 143.7 (sp^2 C), 145.7 (sp^2 C); MS *m*/*z* 356 (M^+), 327, 135 (100%). HRMS. Found: M^+, *m*/*z* 356.2515. Calcd for $C_{24}H_{36}S$: M, 356.2538.

Reaction of the Dithiete 2 with MeLi. a) Treatment with MeI. To a solution of **2** (72 mg, 0.2 mmol) in 4 mL of THF was added 0.3 mL (0.32 mmol) of a 1.05 M ether solution of MeLi at 0 °C. After the mixture was stirred for 1 h at 0 °C, 0.2 mL (3 mmol) of MeI was added. The reaction was quenched by addition of cold water after the mixture had been stirring for 1 h at 0 °C. The resulting mixture was extracted with ether and the ether extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel with hexane as the eluent to give 70 mg (90%) of **7-E** and 1 mg (1.4%) of **2**.

b) Treatment with 2 M HCl. The dithiete **2** (108 mg, 0.3 mmol) was allowed to react with MeLi (0.45 mmol) in the same manner as described above. The reaction was quenched by addition of 2 M HCl (2 ml) at 0 °C. The resulting mixture was extracted with ether and the pale yellow ether extracts were washed with water, dried over $MgSO_4$, and evaporated to leave the enethiol **11** as an orange-to-brown amorphous solid: ^{1}H NMR (200 MHz) $\delta = 1.60$—1.82 (12H, m), 2.05—2.25 (18H, m), 2.19 (3H, s, SMe), 3.48 (1H, s, SH; disappeared on addition of D_2O); ^{13}C NMR (50 MHz) $\delta = 145.5$, 148.5 (considerable decomposition took place during determination; signals due to sp^2 carbons were only given here); IR (KBr) 2494 cm^{-1} (SH). In a separate experiment, a fresh solution of **11** in CH_2Cl_2, prepared from **2** (108 mg, 0.3 mmol), was allowed to stand at room temperature for 1 h. The resulting purple solution was evaporated and chromatographed on a column of silica gel with hexane as the eluent to give 36 mg (35%) of **9a** and 60 mg (53%) of 1,2-di(1-adamantyl)-2-(methylthio)ethane-1-thione (**12**): Mp 143—144 °C; fine purple needles (from ethanol); ^{1}H NMR (200 MHz) $\delta = 1.56$—1.80 (15H, m), 1.92—2.23 (15H, m), 2.11 (3H, s, SMe), 4.04 (1H, s, methine); ^{13}C NMR (50 MHz) $\delta = 18.2$, 28.7, 28.9, 36.4, 36.9, 40.2, 40.4, 42.6, 54.7, 65.8, 264.5 (C=S); UV-vis ($CHCl_3$) $\lambda_{\max}$ (ε) 331 (1070), 541 nm (20). Found: C, 73.76; H, 9.26%. Calcd for $C_{23}H_{34}S_2$: C, 73.74; H, 9.15%.

4,5-Di(1-adamantyl)-1,3-dithiole-2-thione (14). The dithiete **2** (72 mg, 0.2 mmol) was treated with 0.4 mmol of $LiEt_3BH$ in the same manner as described above. To the resulting solution containing **5** was added 0.12 mL (2 mmol) of CS_2 at 0 °C, and the mixture was stirred for 3 h at the same temperature. After the reaction was quenched by addition of water, the mixture was extracted with CH_2Cl_2 and the extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel and eluted with hexane to give 8 mg (11%) of **2** and then with hexane/CH_2Cl_2 (1/1) to give 36 mg (45%) of **14**: Mp 277—278 °C; fine yellow needles (cyclohexane); ^{1}H NMR (200 MHz) $\delta = 1.71$—1.75 (12H, m), 2.11 (6H, broad s), 2.18—2.23 (12H, m); ^{13}C NMR (75.5 MHz) $\delta = 29.0$, 36.0, 41.5, 43.9, 152.9 (sp^2 C), 209.3 (C=S); MS *m/z* 402 (M$^+$; 100%), 326, 294, 135. Found: C, 68.75; H, 7.63%. Calcd for $C_{23}H_{30}S_3$: C, 68.60; H, 7.51%.

4,5-Di(1-adamantyl)-1,2,3-trithiole 2-Oxide (15). a) Without Treatment with Me_2SnCl_2. The dithiete **2** (72 mg, 0.2 mmol) was treated with 0.4 mmol of $LiEt_3BH$ in the same manner as described above. To the resulting solution containing **5** was added 0.15 mL (2 mmol) of $SOCl_2$ at 0 °C, and the mixture was stirred for 6 h at the same temperature. After the reaction was quenched by addition of water, the mixture was extracted with ether and the extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel. The column was eluted with hexane to give 51 mg (71%) of **2** and then with hexane/CH_2Cl_2 (1/2) to give 5 mg (6%) of **15**: Mp 147—149 °C (decomp); fine pale yellow needles (cyclohexane); ^{1}H NMR (200 MHz) $\delta = 1.73$ (12H, broad s), 2.01 (6H, broad s), 2.26—2.34 (12H, m); ^{13}C NMR (75.5 MHz) $\delta = 29.1$, 29.5, 36.1, 44.3, 139.4 (sp^2 C); IR (KBr) 1125 cm^{-1} (S=O); MS *m/z* 358 (M−SO)$^+$, 326, 294, 135 (100%). Found: C, 64.95; H, 7.49%. Calcd for $C_{22}H_{30}OS_3$: C, 64.98; H, 7.44%.

b) With Treatment with Me_2SnCl_2. The dithiete **2** (216 mg, 0.6 mmol) was treated with 1.2 mmol of $LiEt_3BH$ in the same manner as described above. To the resulting solution of **5** was added a solution of 132 mg (0.6 mmol) of Me_2SnCl_2 in 2 mL of THF at 0 °C. After the mixture was stirred for 3 h at 0 °C, 0.45 mL (0.6 mmol) of $SOCl_2$ was added at 0 °C, and the mixture was stirred for an additional 4.5 h at the same temperature. After the reaction was quenched by addition of water, the mixture was extracted with ether and the extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel. The column was eluted with hexane to give 116 mg (54%) of **2** and then with hexane/CH_2Cl_2 (1/2) to give 91 mg (37%) of **15**.

4,5-Di(1-adamantyl)-2-phenyl-1,3,2-dithiaborole (16). The dithiete **2** (72 mg, 0.2 mmol) was treated with 0.4 mmol of $LiEt_3BH$ in the same manner as described above. To the resulting solution of **5** was added 32 mg (0.2 mmol) of $PhBCl_2$ at 0 °C. After the mixture was stirred for 3 h at 0 °C, the solvent was evaporated. The residue was stirred with 20 mL of hexane and the insoluble material was removed by filtration. The filtrate was evaporated and the residue was chromatographed on a column of silica gel with hexane as the eluent to give 11 mg (15%) of **9b**, 16 mg (18%) of **16**, and 25 mg (35%) of **2** in this order.

16: Mp 162—165 °C (decomp); fine colorless plates (hexane); ^{1}H NMR (300 MHz) $\delta = 1.66$—1.92 (12H, m), 2.13 (6H, broad s), 2.31—2.48 (12H, m), 7.32—7.47 (3H, m), 7.71—7.82 (2H, m); ^{13}C NMR (50 MHz) $\delta = 29.6$, 36.5, 42.2, 44.8, 128.1, 130.2, 133.3, 133.5, 149.6. Found: C, 75.13; H, 7.93%. Calcd for $C_{28}H_{35}BS_2$: C, 75.32; H, 7.90%.

Thermolysis of 4,5-Di(1-adamantyl)-1,2,3-Trithiole 2-Oxide (15). a) In Refluxing Toluene. A solution of 255 mg (0.63 mmol) of **15** in 10 mL of toluene was heated at reflux for 4 h. The mixture was evaporated and the residue was chromatographed on a column of silica gel. Elution of the column with hexane gave 21 mg of elemental sulfur, 69 mg (37%) of the ethyne **1**, and 88 mg (39%) of **2**.

b) In CS_2 at 120 °C. A solution of 81 mg (0.2 mmol) of **15** in 14 mL of CS_2 was heated at 120 °C for 4 h in a sealed glass tube. The mixture was evaporated and the residue was chromatographed on a column of silica gel. Elution with hexane gave 8 mg of elemental sulfur, 1.5 mg (3%) of **1**, and 6.5 mg (9%) of **2**. Further elution of the column with hexane/CH_2Cl_2 (1/2) gave 56 mg (70%) of **14**.

4,5-Di(1-adamantyl)-2,2-diphenyl-1,3-dithiole (22). A mixture of 72 mg (0.2 mmol) of **2**, 155 mg (0.8 mmol) of Ph_2CN_2, and a catalytic amount of CuCl(I) (2 mg) in 5 ml of CH_2Cl_2 was stirred for 2 h at room temperature. The CuCl was removed by filtration and the filtrate was evaporated. The residue was chromatographed on a column of silica gel with hexane as the eluent to give 101 mg (100%) of **22**: Mp 219—220 °C; fine colorless plates (hexane); ^{1}H NMR (400 MHz) $\delta = 1.61$—1.73 (12H, m), 1.98 (6H, broad s), 2.07—2.18 (12H, m), 7.01—7.12 (2H, m), 7.18—7.32 (4H, m), 7.58—7.66 (4H, m); ^{13}C NMR (100.6 MHz) $\delta = 29.2$, 36.4, 40.5, 43.4, 64.2 ($\underline{C}Ph_2$), 126.3, 126.9, 127.58, 127.64, 131.2, 137.8, 140.9, 143.6, 143.7. Found: C, 80.21; H, 7.76%. Calcd for $C_{35}H_{40}S_2$: C, 80.10; H, 7.68%.

1,2-Di(1-adamantyl)-2-(*p*-tolylsulfonyl)iminoethane-1-thione (26). A mixture of 72 mg (0.2 mmol) of **2**, 80 mg (0.4 mmol) of tosyl azide, and a catalytic amount of CuCl(I) (2 mg) in 4 mL of toluene was heated at reflux for 8 h. The CuCl was removed by filtration and the filtrate was evaporated. The residue was chromatographed on a column of silica gel. Elution with hexane gave 65 mg (90%) of **2**. Further elution of the column with hexane/CH_2Cl_2 (1/2) gave 10 mg (10%) of **26**: Mp 251—252 °C; purple plates (ethanol); ^{1}H NMR (400 MHz) $\delta = 1.58$—2.36 (30H, m), 2.42 (3H, s, Me), 7.29 (2H, d, $J = 8.2$ Hz), 7.73 (2H, d, $J = 8.2$ Hz); ^{13}C NMR (100.6 MHz) $\delta = 21.6$, 28.5, 28.9, 36.1, 36.2, 41.5, 42.6, 44.3, 55.4, 127.2, 129.4, 137.6, 143.5, 193.7 (C=N), 265.9 (C=S); MS *m/z* 495 (M$^+$), 316, 179 (100%), 135; UV-vis ($CHCl_3$) $\lambda_{\max}$ (ε) 328 (1290), 544 (60) nm. Found: C, 70.03; H, 7.54; N, 2.77%. Calcd for $C_{29}H_{37}NO_2S_2$: C, 70.26; H, 7.52; N, 2.83%.

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