Heteroatom Chemistry
Volume 13, Number 4, 2002

Reactions of Sterically Congested 1,6- and 1,7-Bis(diazo)alkanes with Elemental Sulfur and Selenium: Formation of Cyclohexene, 1,2-Dithiocane, 1,2-Diselenocane, and 1,2,3-Triselenecane Derivatives

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Received 25 September 2001; revised 12 November 2001

ABSTRACT: *The reaction of 3,8-bis(diazo)-2,2,4,4,7,7,9,9-octamethyldecane (**5**) with elemental selenium in 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 130°C yielded 1,2-di-*tert*-butyl-3,3,6,6-tetramethylcyclohexene (**1**) (64%) and* trans*-3,8-di-*tert*-butyl-4,4,7,7-tetramethyl-1,2-diselenocane (**8**) (13%), while that of **5** with elemental sulfur in DBU gave* trans*-3,8-di-*tert*-butyl-4,4,7,7-tetramethyl-1,2-dithiocane (**9**) (77%). The reaction of 3,9-bis(diazo)-2,2,4,4,8,8,10,10-octamethylundecane (**6**) with elemental selenium in DBU at 80°C gave a cyclic triselenide,* cis*-4,10-di-*tert*-butyl-5,5,9,9-tetramethyl-1,2,3-triselenecane (**11**), in 15% yield as the only identifiable product. The structures of **9** and **11** were confirmed by X-ray crystallography.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:351–356, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10046

INTRODUCTION

Recently we reported the synthesis of a sterically congested cyclohexene **1** [1] by a twofold extrusion process [2] of the 1,3,4-selenadiazoline **2** which was prepared by the reaction of dihydrazone **3** with Se_2Cl_2 (Scheme 1). The formation of **2** was explained by an intramolecular cyclization of diazoselenoketone **4** [1,3]. In our continuous study on the chemistry of sterically congested cycloalkenes, we examined the reaction of bis(diazo)alkanes **5** and **6** with elemental sulfur and selenium in expectation of the formation of **1** and a cycloheptene derivative **7**, respectively. Since it has been reported that the reaction of diazoalkanes and elemental selenium provided selenoketones [2,4], the intermediate diazoselenoketone **4** is expected to form by the reaction of **5** with elemental selenium. It was also reported that the reactions of diazoalkanes with elemental sulfur are synthetically useful to prepare alkenes or episulfides [5–7]. We report here the formation of **1** by the reaction of **5** with elemental selenium in good yield and the formation of rare classes of sulfur- and selenium-containing heterocycles.

RESULTS AND DISCUSSION

1,6-Bis(diazo)hexane **5** was prepared from the corresponding dihydrazone **3** [1] by oxidation with nickel peroxide (NiPO) [8]. Compound **5** was heated with an excess amount of elemental selenium (5 molar amounts) in DBU at 130°C for 10 min to yield **1** in 64% yield along with 1,2-diselenocane **8** in 13%

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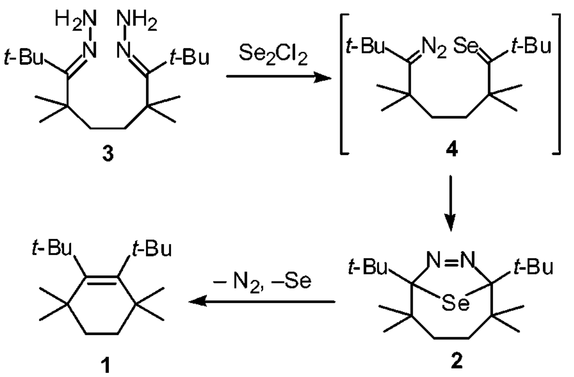
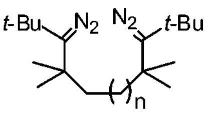
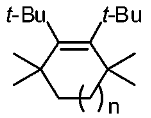
Contract grant sponsor: Ministry of Education, Culture, Sports, Science and Technology, Japan.
Contract grant number: 90193242.



SCHEME 1



5 : n = 1
6 : n = 2



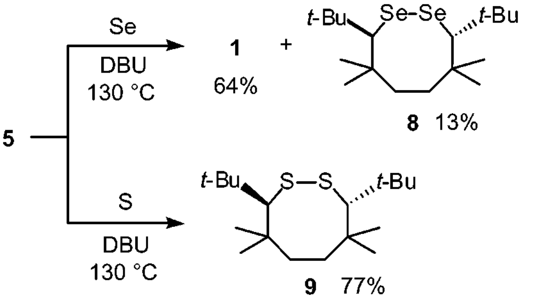
1 : n = 1
7 : n = 2

yield (Scheme 2). The reaction in which a catalytic amount of selenium (10 mol%) was used yielded **1** in a lower yield (28%). In addition, isolation of **1** from the complex reaction mixture was difficult. When the reaction was conducted at 80°C for 30 min, 1,3,4-selenadiazoline **2** [1] was isolated in 61% yield. This strongly suggests that **1**, obtained in the reaction at 130°C, was formed by thermolysis of intermediately generated selenadiazoline **2**, as expected. DBU would act as an activator for elemental selenium [9,10]. In the absence of DBU, the reaction of **5** with elemental selenium (10–20 molar amounts) at 150°C gave **1** in lower yields (ca. 20%).

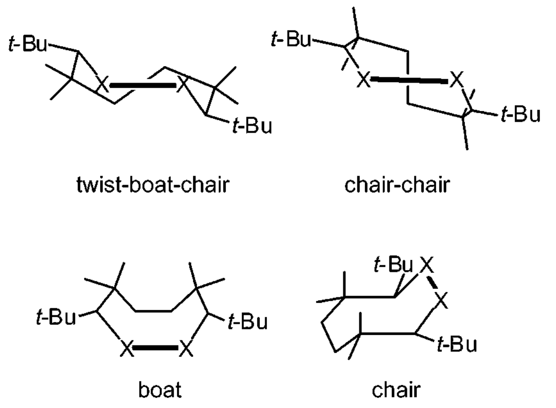
On the other hand, the reaction of **5** with elemental sulfur in DBU at 130°C gave 1,2-dithiocane **9** in 77% yield without formation of **1** (Scheme 2). This implies that the formation of the corresponding bicyclic 1,3,4-thiadiazoline was hampered, probably because of the large ring strain due to the shorter C—S bond compared with the C—Se bond in **2**. Incidentally, neat **5** decomposed with evolution of N_2 over 120°C, but the thermolysate did not contain **1**. Photolysis of **5** in a solvent gave a complex mixture of products.

Compounds **8** and **9** were obtained as a single isomer of two possible cis (*meso*) and trans (*dl*) stereoisomers. In the ^{1}H NMR spectrum of **8**, the two *tert*-butyl groups are equivalent (δ 1.21) as well as the two methine protons (δ 3.47). While the four methyl groups of **8** appeared as two singlets at δ 1.06 and 1.17, the CH_2CH_2 chain resonated as an AA′XX′ system centered at δ 0.914 and 2.225 [$J(AA') = 9.25$ Hz, $J(XX') = 0$ Hz, $J(AX) = -13.6$ Hz, $J(AX') = 9.4$ Hz)] [11]. This is also the case for **9**: coupling constants for the AA′XX′ system of the ethylene chain were simulated to be $J(AA') = 10.15$ Hz, $J(XX') = 0$ Hz, $J(AX) = -14.0$ Hz, and $J(AX') = 9.4$ Hz [11]. These data tell us that (i) if **8** and **9** are the trans isomers, the 1,2-dichalcogenocane rings have the C_2 symmetry corresponding to chair–chair and twist-boat–chair conformations of cyclooctanes [12], or (ii) if they are the cis isomers, the 8-membered rings have a plane of symmetry, which corresponds to boat and chair conformations of cyclooctanes [12] (Scheme 3): both the rotation axes and the symmetry planes pass through the centers of the dichalcogenide (X—X) and the ethylene bonds. Incidentally, the boat and chair conformations of cyclooctanes are less stable by 10.3 and 8.3 kcal mol^{-1}, respectively, than the most stable boat–chair conformation [12].

The structure of **9** was finally determined by X-ray crystallography to be the trans isomer which takes the twist-boat–chair conformation (Fig. 1 and also see Experimental). It was reported that MM2(85) calculations predicted a twist-boat–chair conformation for the parent 1,2-dithiocane [13] and, in addition, a similar conformation was observed for 1,2,5,6-tetrathiacyclooctanes in the solid state [14,15]. In analogy, 1,2-diselenocane (**8**) was assigned to be the trans isomer. In solution, **8** and **9** would take the twist-boat–chair conformation as



SCHEME 2



SCHEME 3

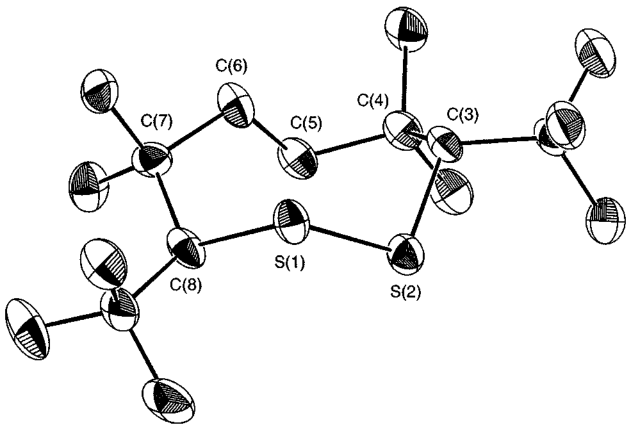
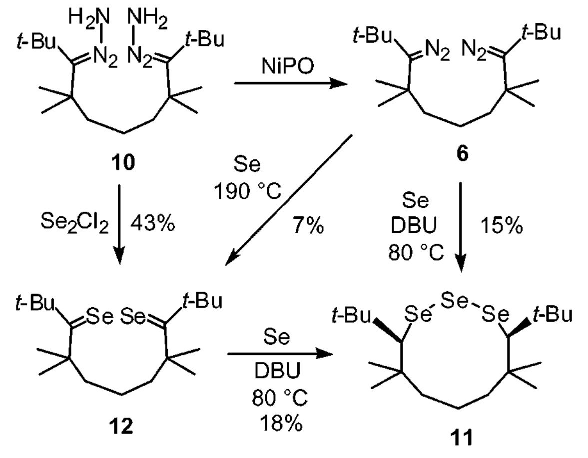


FIGURE 1 ORTEP drawing of one of two independent molecules of **9** (30% ellipsoidal probability). Hydrogen atoms are omitted for clarity.

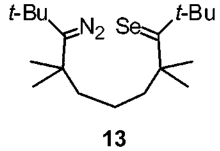
in the solid state: PM3 calculations showed that the twist-boat–chair conformations of **8** and **9** are more stable by 5.4 and 5.9 kcal mol^{-1}, respectively, than the corresponding chair–chair conformations. There is no precedent for 1,2-diselenocanes as far as we know [16,17].

Next, 1,7-bis(diazo)heptane **6**, prepared by oxidation of dihydrazone **10**, was heated with elemental selenium in DBU at 80°C in expectation of the formation of the cycloheptene **7**. Interestingly, the reaction gave the 1,2,3-triselenecane **11** in 15% yield as the only identifiable product (Scheme 4). When the reaction of **6** with elemental selenium was conducted without DBU at higher temperatures, the diselone **12** was isolated in 7% yield. The diselone **12** itself reacted with elemental selenium in DBU at 80°C to give **11** in 18% yield. These results suggest that the diazoselenoketone **13** doesnot undergo cyclization to the corresponding selenadiazoline **14** to give **7**, but further selenation to lead to **12** which reacts with elemental selenium to yield **11**. Although **13** may be in equilibrium with **14** [2,18,19], the equilibrium would lie predominantly towards **13**.

The structure of **11** was determined by the spectroscopic data and finally by X-ray crystallography (Fig. 2). To our knowledge, the compound **11** is the first triselenecane derivative reported in the literature [17]. The X-ray structure indicates that **11** has a plane of symmetry passing through the Se(2A) and C(7A) atoms [Se(2B) and C(7B) atoms], which is in harmony with the symmetry in the NMR data (see Experimental). In the solid state, **13** takes a chair–boat–chair conformation extremely collapsed around the C(6A)—C(7A)—C(8A) chain [C(6B)—C(7B)—C(8B) chain]. In particular, the C(7A) carbon [C(7B) carbon] is moved largely into the inside of the ring, where the C(5A)—C(9A) carbon



SCHEME 4



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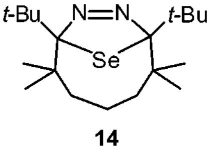

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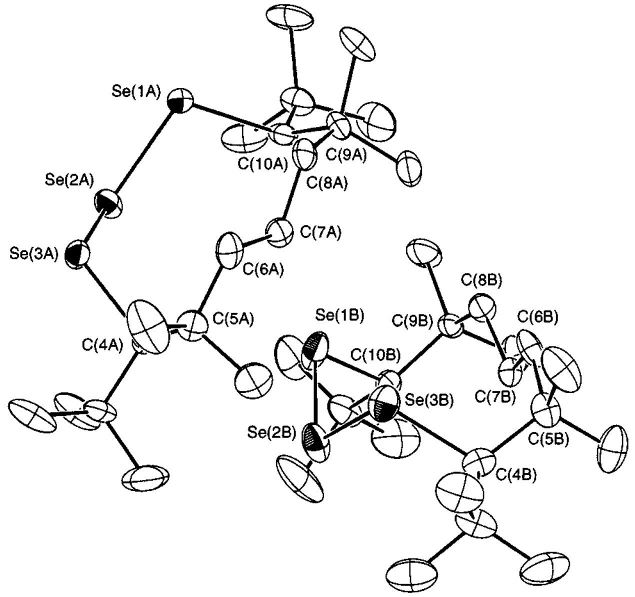

FIGURE 2 ORTEP drawing of two independent molecules of **11** (20% ellipsoidal probability). Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (deg) data: Se(1A)—Se(2A), 2.3208(2); Se(2A)—Se(3A), 2.3050(2); Se(3A)—C(4A), 1.9847(9); C(10A)—Se(1A), 2.015(1); Se(1A)—Se(2A)—Se(3A), 109.6(1); Se(2A)—Se(3A)—C(4A), 105.3(1); C(10A)—Se(1A)—Se(2A), 103.4(1); C(10A)—Se(1A)—Se(2A)—Se(3A), 107.0(1); Se(1A)—Se(2A)—Se(3A)—C(4A), −101.0(1); Se(1B)—Se(2B), 2.3164(2); Se(2B)—Se(3B), 2.3172(2); Se(3B)—C(4B), 2.0155(10); C(10B)—Se(1B), 2.0248(9); Se(1B)—Se(2B)—Se(3B), 109.0(1); Se(2B)—Se(3B)—C(4B), 104.4(1);C(10B)—Se(1B)—Se(2B), 105.2(1); C(10B)—Se(1B)—Se(2B)—Se(3B), 102.6(1); Se(1B)—Se(2B)—Se(3B)—C(4B), −107.2(1).

chain [C(5B)—C(9B) carbon chain] practically takes the trans conformations. The dihedral angles are C(5A)—C(6A)—C(7A)—C(8A), −173.6(2)°; C(6A)—C(7A)—C(8A)—C(9A), 165.7(2)° [C(5B)—C(6B)—C(7B)—C(8B), −168.2(2)°; C(6B)—C(7B)—C(8B)—C(9B), 171.6(2)°].

Although the formation mechanism for **8, 9**, and **11** has not been investigated in detail, it was verified that the hydrogen atoms α to the selenium atoms in **11** were introduced by a radical mechanism. Thus, the yield of **11** increased up to 31% yield by addition of 2-propanol as the hydrogen donor, whereas addition of D_2O decreased the yield (7%) and no deuterium was incorporated into the product.

In conclusion, we could prepare **1** in good yield by the reaction of 1,6-bis(diazo)hexane **5** with elemental selenium in DBU, where the bicyclic 1,3,4-selenadiazoline is the precursor of **1**. We also found the formation of rare classes of compounds, in particular, 1,2-diselenocane **8** and 1,2,3-triselenecane **11**, the structures of which were unambiguously determined.

EXPERIMENTAL

General: Melting points were determined on a capillary tube apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ as the solvent unless otherwise noted. Mass spectra were operated at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

In the workup of the reactions, the extracts were dried over anhydrous magnesium sulfate after washing with water. Column chromatography was performed with silica gel and the eluent is given in parentheses in the text.

*3,8-Bis(diazo)-2,2,4,4,7,7,9,9-octamethyldecane (**5**)*

To a solution of 2,2,4,4,7,7,9,9-octamethyldecane-3,8-dione dihydrazone (**3**) [1] (302 mg, 0.971 mmol) in ether (40 ml) was added nickel peroxide [8] (4.10 mmol g^{-1}, 595 mg, 2.44 mmol), and the mixture was stirred for 2 h at room temperature. The insoluble materials were removed by filtration, and the filtrate was dried and evaporated to dryness to give the 1,6-bis(diazo)hexane **5** (288 mg, 96%) as orange crystals. Because of instability, **5** was recrystallized only once from acetonitrile and then used for the next reactions: mp 61.5–63°C (CH_3CN). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.18 (s, 12H), 1.20 (s, 18H), 1.44 (s, 4H); IR (KBr) 2026 cm^{-1}.

*Reaction of 3,8-Bis(diazo)-2,2,4,4,7,7,9,9-octamethyldecane (**5**) with Elemental Selenium*

At 130°C: To a mixture of **5** (242 mg, 0.784 mmol) and elemental selenium (309 mg, 3.92 mmol) under argon was added DBU (1.0 ml). The mixture was heated at 130°C for 10 min. The resulting black paste was washed with pentane repeatedly. The washings were combined, washed with 1.2 M HCl and then with water, and dried. The solvent was carefully evaporated to semidryness on a warm water bath under atmospheric pressure because of the high volatility of **1**. The residue was subjected to column chromatography (pentane) to give **1** [1] (126 mg, 64%) and *trans*-3,8-di-*tert*-butyl-4,4,7,7-tetramethyl-1,2-diselenocane (**8**) (40 mg, 13%).

8: Yellow crystals, mp 107–108°C (EtOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86–0.97 [m (AA′), 2H], 1.06 (s, 6H), 1.17 (s, 6H), 1.21 (s, 18H), 2.20–2.32 [m (XX′), 2H], 3.47 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.0 (CH_3), 27.4 (CH_3), 31.6 (CH_3), 38.3 (C), 39.3 (C), 43.0 (CH_2), 74.5 (CH); MS *m/z* 412 (M^+). Anal. Calcd for $C_{18}H_{36}Se_2$: C, 52.68; H, 8.84. Found: C, 52.80; H, 8.89.

At 80°C: To a mixture of **5** (51 mg, 0.165 mmol) and elemental selenium (132 mg, 1.68 mmol) under argon was added DBU (0.25 ml). The mixture was heated at 80°C for 30 min. The mixture was treated in the manner as described above to give selenadiazoline **2** [1] (36 mg, 61%).

*Reaction of 3,8-Bis(diazo)-2,2,4,4,7,7,9,9-octamethyldecane (**5**) with Elemental Sulfur*

To a mixture of **5** (153 mg, 0.495 mmol) and elemental sulfur (80 mg, 2.51 mmol) under argon was added DBU (1.0 ml). The mixture was heated at 130°C for 30 min. The resulting paste was treated in the manner as described above to give *trans*-3,8-di-*tert*-butyl-4,4,7,7-tetramethyl-1,2-dithiocane (**9**) (121 mg, 77%): colorless crystals, mp 110–111°C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91–1.00 [m (AA′), 2H), 1.01 (s, 6H), 1.14 (s, 6H), 1.16 (s, 18H), 2.20–2.29 [m (XX′), 2H], 2.97 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 25.6 (CH_3), 27.9 (CH_3), 31.0 (CH_3), 37.7 (C), 39.2 (C), 41.1 (CH_2), 76.1 (CH); MS *m/z* 316 (M^+). Anal. Calcd for $C_{18}H_{36}S_2$: C, 62.28; H, 11.46. Found: C, 68.52; H, 11.65.

X-Ray Crystallographic Analysis of **9**

$C_{18}H_{36}S_2$, M_w 316.61, yellow needles, $0.30 \times 0.18 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$, $a = 11.337(2)$, $b = 14.049(2)$, $c = 14.245(3)$ Å, $\alpha = 89.476(7)$, $\beta = 71.402(7)$, $\gamma = 66.88(2)^\circ$, $V = 1960.1(6)$ Å^3, $Z = 4$,

$\rho_{\text{calcd}} = 1.073$ g cm^{-3}, $F(000) = 704$, μ(Mo Kα) = 0.26 mm^{-1}. Mac Science DIP3000 diffractometer with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data reduction was made by the maXus program system [20]. Intensity data of 6289 unique reflections were collected in the range of $-13 \le h \le 14$, $-16 \le k \le 15$, $0 \le l \le 18$. Refinement was carried out with full-matrix least squares on F^2 using all the unique reflections. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at the calculated positions. Absorption correction was done by SORTAV [21]. For 2707 reflections with $I > 2\sigma I$, 361 parameters: $R = 0.139$, $wR2 = 0.161$ (0.163 for all data); max/min residual electron density = $1.15/-1.14$ e Å^{-3}. Because of the low quality of the crystals, satisfactory R values were not obtained. Therefore, we do not discuss the bond lengths and angles data and show only some relevant data for tentative information: S(1)—S(2), 2.0388(7); S(1)—C(8), 1.836(2); S(2)—C(3), 1.858(2) Å; C(8)—S(1)—S(2), 107.7(1); S(1)—S(2)—C(3), 106.1(2); C(8)—S(1)—S(2)—C(3), 99.4(1); S(2)—C(3)—C(4)—C(5), 40.5(2); C(4)—C(5)—C(6)—C(7), −148.2(3); C(6)—C(7)—C(8)—S(1), 40.4(2)°.

*2,2,4,4,8,8,10,10-Octamethylundecane-3,9-dione Dihydrazone (**10**)*

2,2,4,4,8,8,10,10-Octamethylundecane-3,9-diimine (**15**) (711 mg, 2.41 mmol) was prepared in 91% yield by the reaction of 2,6-dimethyl-2,6-dicyanoheptane [22] (486 mg, 2.73 mmol) with *tert*-BuLi (1.54 M, 10.6 ml, 16.3 mmol) in ether (20 ml) at 0°C. The diimine **15** was dissolved in a mixture of di(ethylene glycol) (50 ml) and hydrazine monohydrate (27.5 g, 0.55 mol), and the mixture was refluxed for 20 h [23]. The resulting mixture was diluted with water and extracted with ether. The extract was washed with water, dried, and evaporated to dryness to give an oily material, which was washed with hexane to give the dihydrazone **10** (732 mg, 90%).

15: Colorless crystals, mp 65.5–66.0°C (hexane). ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.10–1.13 (m, 2H), 1.22 (s, 12H), 1.23 (s, 18H), 1.48–1.56 (m, 4H), 9.36 (br s, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 20.8 (CH$_2$), 28.3 (CH$_3$), 30.2 (CH$_3$), 41.4 (C), 42.8 (CH$_2$), 45.1 (C), 192.8 (C). Anal. Calcd for $C_{19}H_{38}N_2$: C, 77.48; H, 13.01; N, 9.51. Found: C, 77.70; H, 13.22; N, 9.66.

10: Colorless crystals, mp 134–135°C (hexane). ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.17 (s, 20H, 2*t*Bu and CH$_2$), 1.34 (s, 12H), 1.61–1.69 (m, 4H), 5.23 (br s, 4H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 21.6 (CH$_2$), 28.3 (CH$_3$), 30.7 (CH$_3$), 40.9 (C), 41.9 (C), 42.1 (CH$_2$), 158.7 (C); IR (KBr) 3394, 3322, 3248 cm^{-1}; MS (EI) *m/z* 324 (M$^+$). Anal. Calcd for $C_{19}H_{40}N_4$: C, 70.31; H, 12.42; N, 17.26. Found: C, 70.54; H, 12.62; N, 17.40.

*3,9-Bis(diazo)-2,2,4,4,8,8,10,10-octamethylundecane (**6**)*

To a solution of the dihydrazone **10** (100 mg, 0.308 mmol) in ether (15 ml) was added nickel peroxide (4.10 mmol g^{-1}, 232 mg, 0.95 mmol). The suspension was stirred at room temperature for 2 h, and the insoluble materials were removed by filtration. The filtrate was dried and the solvent was removed under reduced pressure to give **6** (88 mg, 89%) as an orange oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.94–1.02 (m, 2H), 1.17 (s, 12H), 1.20 (s, 18H), 1.33–1.39 (m, 4H); IR (KBr) 2028 cm^{-1}. Compound **6** was used for the next reaction without further purification.

*Reaction of 3,9-bis(diazo)-2,2,4,4,8,8,10,10-octamethylundecane (**6**) with Elemental Selenium*

A mixture of **6** (202 mg, 0.631 mmol) and elemental selenium (510 mg, 6.46 mmol) in DBU (1 ml) was heated for 1 h at 80°C under argon. The mixture was cooled to room temperature and then diluted with ether and water. The organic layer was separated, washed with aq. NH$_4$Cl and then with water, dried, and evaporated to dryness. The residue was subjected to column chromatography (pentane) to give a crude product, which was recrystallized from EtOH to give pure *cis*-4,10-di-*tert*-butyl-5,5,9,9-tetramethyl-1,2,3-triselenecane (**11**) (48 mg, 15%): orange needles, mp 111–111.5°C (EtOH). ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.03 (s, 6H), 1.21 (s, 18H), 1.23–1.25 (m, 4H), 1.27 (s, 6H), 2.17 (pseudo t, $J = 13.3$ Hz, 2H), 3.46 (s, 2H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 17.5 (CH$_2$), 27.1 (CH$_3$), 29.1 (CH$_3$), 32.0 (CH$_3$), 39.1 (C), 40.5 (C), 50.7 (CH$_2$), 79.8 (CH); MS *m/z* 504 (M$^+$). Anal. Calcd for $C_{19}H_{38}Se_3$: C, 45.33; H, 7.61. Found: C, 45.55; H, 7.67.

X-Ray Crystallographic Analysis of **11**

$C_{19}H_{38}Se_3$, M_w 503.40. Orange needles, $0.32 \times 0.24 \times 0.22$ mm^3, orthorhombic, space group $P2_12_12_1$, $a = 15.959(3)$, $b = 23.214(6)$, $c = 12.347(2)$ Å, $V = 4574(2)$ Å^3, $\rho_{\text{calcd}} = 1.461$ g cm^{-3}, $Z = 8$, μ(Cu Kα) = 5.81 mm^{-1}, $F(000) = 2031$. Mac Science MXC3KHF diffractometer with graphite-monochromated Cu Kα radiation ($\lambda = 1.54178$ Å), $\theta/2\theta$ scans method in the range $3° < 2\theta < 140°$ ($0 < h < 19$, $0 < k < 28$, $0 < l < 19$), 4829 independent reflections. The structure was solved by direct methods using SIR92 [24] in the maXus program system [20] and refined by a full-matrix least squares method on F^2 using all the independent reflections. Absorption correction was done by a psi-scan method. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at the calculated positions. For 4172 reflections with $I > 2\sigma I$, 398 parameters: $R = 0.054$, $wR2 = 0.026$ (0.025 for all data); max/min residual electron density = 0.75/−0.53 e Å^{-3}.

*2,2,4,4,8,8,10,10-Octamethylundecane-3,9-diselone (**12**)*

The diselone **12** was prepared by the reported method [25]. A solution of the dihydrazone **10** (500 mg, 1.54 mmol) in THF (20 ml) maintained under argon was treated with EtMgBr (0.787 M, 7.9 ml, 6.22 mmol) and the mixture was heated at 60°C for 2 h. After removal of the solvent under reduced pressure, benzene (20 ml) and Bu_3N (1.43 g, 7.7 mmol) were added. All the following manipulations were carried out in the dark as far as possible because of the susceptibility of the diselone **12** to light. To the mixture was added a solution of Se_2Cl_2 (1.23 g, 5.38 mmol) in benzene (5 ml) at 0°C, and the resulting mixture was stirred for 0.5 h at room temperature and then for 3 h at 60°C. The mixture was cooled to room temperature and diluted with aq. NH_4Cl. The organic layer was separated, washed with water, dried, and evaporated to dryness. The residue was subjected to column chromatography (hexane–CH_2Cl_2 3:1) to give diselone **12** (318 mg, 49%): Green oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.82–0.91 (m, 2H), 1.46 (s, 18H), 1.48 (s, 12H), 1.81–1.87 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.1 (CH_2), 31.4 (CH_3), 32.6 (CH_3), 45.0 (CH_2), 60.4 (C), 63.6 (C), 291.8 (C); UV/Vis (CH_3CN) λ_{max} 708 nm (ε36); MS (EI) m/z 424 (M^+); HRMS calcd for $[C_{19}H_{36}Se_2]^+$ 424.1200, found 424.1147.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-173915 (**9**) and CCDC-173914 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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