Formation and Reactions of Novel Heterocycles: 1,3,4-Oxadithiolane, 1,3,4-Oxadiselenolane, 1,3-Oxathietane, and 1,3-Oxaselenetane Derivatives

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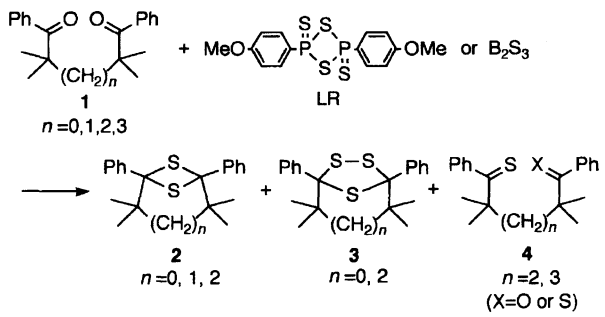
The reactions of 2,2,4,4-tetramethyl-1,5-diphenyl-1,5-pentanedione monohydrazone with S_2Cl_2 and Se_2Cl_2 gave 2,2,4,4-tetramethyl-1,5-diphenyl-8-oxa-6,7-dithiabicyclo[3.2.1]octane (**9**) and 2,2,4,4-tetramethyl-1,5-diphenyl-8-oxa-6,7-diselenabicyclo[3.2.1]octane (**10**), respectively. Dechalcogenation of **9** or **10** with triphenylphosphine in boiling toluene yielded an equilibrium mixture of 2,2,4,4-tetramethyl-1,5-diphenyl-6-oxa-7-thiabicyclo[3.1.1]-heptane (**11**) and 2,2,4,4-tetramethyl-1,5-diphenyl-5-thioxo-1-pentanone (**13**) or 2,2,4,4-tetramethyl-1,5-diphenyl-6-oxa-7-selenabicyclo[3.1.1]heptane (**12**), respectively. On the other hand, the reaction of **10** with hexamethylphosphorous triamide [$P(NMe_2)_3$] in boiling toluene gave **12**, 3-methyl-3-(2,2-dimethyl-3-oxo-3-phenylpropyl)-2-phenylselenetanes (**18**), 5-benzoyl-3,3,5-trimethyl-2-phenylselenanes (**19**), 6,6,8,8-tetramethyl-9-phenyl-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (**20**), and 3,3,5,5-tetramethyl-1,2-diphenylcyclopentene (**21**), while that of **9** afforded **11**, **13**, 3-(2-benzoyl-2-methylpropyl)-3-methyl-2-phenylthietanes, **20**, and **21**. The reaction of **12** with $P(NMe_2)_3$ also gave **18**, **19**, **20**, and **21**. A single-electron transfer mechanism seems to be operative in the reaction of **9** or **10** with $P(NMe_2)_3$. Compounds **11** and **13** are in equilibrium with each other at room temperature, while a ring-opening of **12** to 2,2,4,4-tetramethyl-1,5-diphenyl-5-selenoxo-1-pentanone is observed on heating by the UV-vis and ^1H NMR spectra.

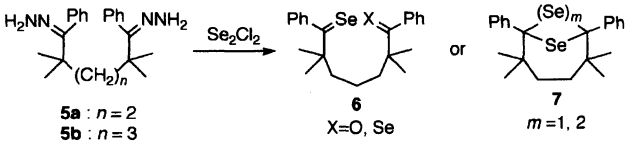
The chemistry of four- and five-membered cyclic compounds containing two or more chalcogen atoms has been attracting considerable attention.[1,2] We have recently reported in detail that the reaction of nonenolizable α,ω-diketones **1** with sulfurizing reagents such as Lawesson's reagent (LR) or B_2S_3 affords bicyclic dithietanes **2**, trithiolanes **3**, and thiones **4**, the ratio of which depends on the length of methylene chains separating two functional groups (Scheme 1).[3] In extension of this study we have already reported two preliminary works. Thus, the reaction of the dihydrazones **5a** of 1,6-diketone **1** ($n=2$) with Se_2Cl_2 affords bicyclic diselenetane (**7**: $m=1$) and triselenolane (**7**: $m=2$), while that of the dihydrazone **5b** produces the selenoxo ketone (**6**: X=O) and diselone (**6**: X=Se) (Scheme 2).[4] The other work reports that the reaction of the monohydrazone **8** of 1,5-diketone (**1**: $n=1$) with S_2Cl_2 and Se_2Cl_2[5,6] produces novel heterocycles, 1,3,4-oxadithiolane (**9**) and 1,3,4-oxadiselenolane (**10**) derivatives, and that desulfurization of **9** with hexamethylphosphorous triamide [$P(NMe_2)_3$] gives an equilibrium mixture of the 1,3-oxathietane **11** and 5-thioxo-1-pentanone **13** and the deselenation of **10** yields the 1,3-oxaselenetane **12** together with other products (Scheme 3).[7] The present article is concerned with the full accounts of the above latter communication and includes (1) the mechanistic feature of these novel reactions, (2) the formation of new products not described in the preliminary form, and (3) equilibriums between compounds **11** and **13** and also between **12** and the corresponding selenoxo ketone.



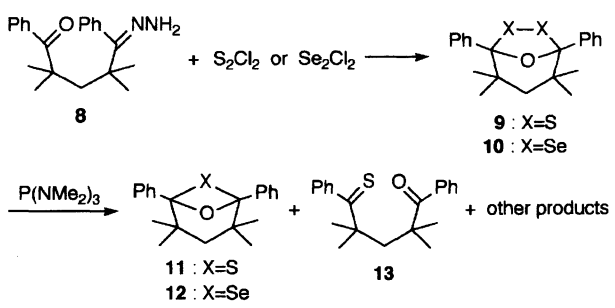
Scheme 1.

Results and Discussion

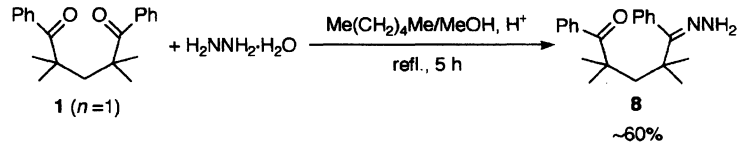
Reaction of Hydrazone 8 with Se_2Cl_2 and S_2Cl_2. Hydrazone **8** was prepared in about 60%



Scheme 2.



Scheme 3.



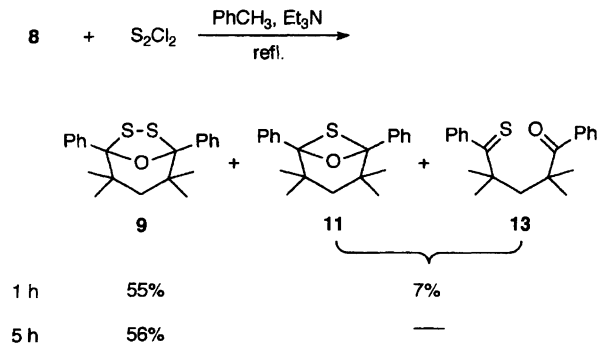
Scheme 4.

yield by treatment of 1,5-diketone **1** (n=1) with excess hydrazine monohydrate in a boiling mixed solvent of hexane and methanol in the presence of an acid catalyst (Scheme 4). The corresponding dihydrazone was not formed even by either prolongation of the reaction time or further treatment of **8** with hydrazine monohydrate.

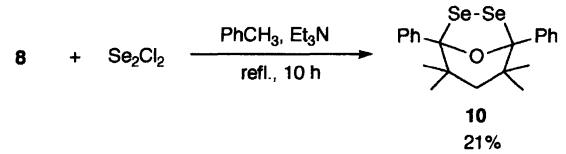
Hydrazone **8** was treated with 2 molar amounts of Se_2Cl_2 in boiling toluene in the presence of triethylamine to give a bicyclic compound **10** in 21% yield (Scheme 5). The structure of **10** was assigned to 2,2,4,4-tetramethyl-1,5-diphenyl-8-oxa-6,7-diselenabicyclo[3.2.1]octane by elemental analysis and spectroscopic data. Compound **10** is red-orange needles and its absorption maxima appear at 443 (ε 151) and 350 (ε 143) nm in the UV-vis spectrum, indicating the existence of a diselenide bond.[8] The ^{1}H NMR spectrum of **10** displays two singlets for methyls at δ=0.99 and 1.38, a set of two doublets for two methylene protons at δ=1.32 and 2.39 with J=14.2 Hz of a geminal coupling constant, and a multiplet for two equivalent phenyls. In the ^{13}C NMR spectrum, a peak due to two bridgehead carbons (O–C–Se) appears at δ=111.4 with other requisite ones. These observations consist with the assigned structure **10**.

On the other hand, treatment of **8** with 2 molar amounts of S_2Cl_2 in the presence of triethylamine in boiling toluene for 5 h yielded 2,2,4,4-tetramethyl-1,5-diphenyl-8-oxa-6,7-dithiabicyclo[3.2.1]octane (**9**) in 56% yield (Scheme 6). The use of an equimolar amount of S_2Cl_2 gave **9** in decreased yield (25%). The structure of **9** was determined by elemental analysis and spectroscopic means. Its ^{1}H and ^{13}C NMR spectrum patterns are similar to those of **10**. Interestingly, quenching of the reaction after 1 h afforded 2,2,4,4-tetramethyl-1,5-diphenyl-6-oxa-7-thiabicyclo[3.1.1]heptane (**11**) and 2,2,4,4-tetramethyl-1,5-diphenyl-5-thioxo-1-pentanone (**13**) in 7% combined yield together with **9** (55%). The compounds **11** and **13** could not be isolated in pure form by chromatography because they are in equilibrium with each other in solution. Pure crystalline **11** could be obtained only by recrystallization of the mixture from hexane. Details about the equilibrium are described later in this article. The structure elucidations of **11** and **13** were made by elemental analysis (for **11**) and spectroscopic means.

Compounds **9** and **10** contain 1,3,4-oxadithiolane and 1,3,4-oxadiselenolane ring systems, respectively, which are previously unknown ozonide analogs where two oxygen atoms are replaced with two sulfur and selenium atoms, respectively, although the formation of a 1,3,4-oxadithiolane derivative was previously suggested.[9] The formation of **9** and **10** suggested the generation of thioxo ketone *S*-sulfide **14** and selenoxo ketone *Se*-selenide **15**, respectively, as intermediates (Fig. 1). While mechanistic feature of the reaction of hydrazones with Se_2Cl_2 is generally complex,[6b,10] the generation of a thioxo ketone *S*-sulfide was assumed as an intermediate leading to a thione in the reaction of a hydrazone with S_2Cl_2.[5b] Therefore, also in the reaction of **8** with S_2Cl_2, the primarily formed thioxo ketone *S*-sulfide **14** might give **9** by an intramolecular cyclization before collapse to 1-oxo-5-thione **13**. Recently, successful trapping experiments of thioxo ketone *S*-sulfide were reported by Huisgen[11] and Saito.[12] So we attempted trapping of thioxo ketone *S*-sulfide **14** with dimethyl acetylenedicarboxylate (DMAD), which, however, resulted in failure. In this reaction, only **9** was obtained in 33% yield as an identifiable compound. This may, however, imply that the intramolecular cyclization of **14** to **9** is much faster than the intermolecular reaction of **14** with DMAD. On



Scheme 6.



Scheme 5.

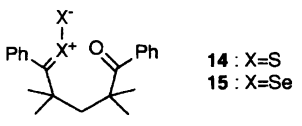


Fig. 1. Structures of thioxo ketone *S*-sulfide **14** and selenoxo ketone *Se*-selenide **15**.

the other hand, treatment of **13** with S_2Cl_2 (3.8 molar amounts) in boiling toluene for 1 h also gave **9** in 30% yield along with unidentified materials. The observed yield of **9** is not high enough to account for the formation of **9** only in terms of the secondary reaction of **13** with S_2Cl_2. We therefore conclude that thioxo ketone *S*-sulfide intermediate **14** leading to **9** would be formed both by the reaction of **8** with S_2Cl_2 directly and the secondary reaction of **13** with S_2Cl_2.

Reaction of 1,3,4-Oxadiselenolane 10 and 1,3,4-Oxadithiolane 9 with Trivalent Phosphorus Reagents. Treatment of **10** with an equimolar amount of triphenylphosphine in refluxing toluene for 10 h provided a novel heterocyclic compound, 2,2,4,4-tetramethyl-1,5-diphenyl-6-oxa-7-selenabicyclo[3.1.1]-heptane (**12**) in 72% yield along with unchanged **10** (17%) (Scheme 7). Under similar conditions, desulfurization of 1,3,4-oxadithiolane **9** proceeded to afford an equilibrium mixture of 1,3-oxathietane **11** and 5-thioxo-1-pentanone **13** (43%) and unchanged **9** (57%) (Scheme 8). In the both reactions, the dechalcogenation would be initiated by the attack of PPh_3 on a chalcogen atom (X) leading to a zwitterionic intermediate **16**, followed by the elimination of $Ph_3P{=}X$ (X=S or Se) (Scheme 9).[13] The resulting 5-selenoxo-1-pentanone **17** may cyclize to give **12** when the reaction solution was cooled to ambient temperature. The ring opening and closure between **12** and **17** was actually observed when a solution of **12** in toluene was heated and then cooled. Thus, a slightly yellowish solution of **12** at room temperature gradually turned blue on heating to reflux and turned pale yellow on cooling. The UV-vis spectrum of the hot solution of **12** displayed the longest absorption maximum at 690 nm that is comparable with that of 2,2,6,6-tetramethyl-1,7-diphenylheptane-1,7-diselone (**6**).[4] There is no precedent, to our knowledge, for an equilibrium among selenocarbonyl, carbonyl groups, and their cycloadduct, oxaselenetane.

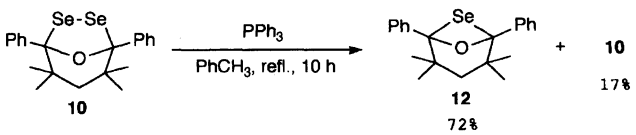
An alternative trivalent phosphorus reagent we examined is $P(NMe_2)_3$. While $P(NMe_2)_3$ is known as a useful reagent to desulfurize disulfides to sulfides,[14] it was reported that abnormal reactions took place in the reaction of sterically protected thio- and selenobenzaldehydes with $P(NMe_2)_3$, where a single-electron transfer mechanism may be operative (Scheme 10).[15] Since intervention of 5-thioxo-1-pentanone **13** or 5-selenoxo-1-pentanone **17** is considered in the present case, it is of interest to examine the reaction of **9** and **10** with $P(NMe_2)_3$. Thus, treatment of 1,3,4-oxadiselenolane **10** with $P(NMe_2)_3$ in refluxing toluene gave 1,3-oxaselenetane **12** (14%), selenetane derivatives **18a** and **18b** (6 and 3%, respectively), selenane derivatives **19a** and **19b** (0.6 and 1%, respectively), a benzosuberone derivative **20** (14%), and 3,3,5,5-tetramethyl-1,2-diphenylcyclopentene (**21**, 5%) (Scheme 11). Although there are two separable isomers (cis and trans) for each of the selenetanes and the selenanes, it was difficult to determine which was cis or trans unequivocally by spectroscopic means. So, for convenience, one isomer having a larger R_f value on silica-gel thin-layer chromatography is represented by suffix **a** and the other suffix **b**; this expression is also the case for **22a** and **22b** (vide infra). Structure elucidations of **12**, **20**, and **21** were easily performed with elemental analyses and spectroscopic data. The selenane structure of **19a, b** was identified by the existence of a long-range W-shape coupling in their ^{1}H NMR spectra, which is, on the other hand, absent in **18a, b**. Selected ^{1}H NMR spectral data of **18a** and **19a** are depicted in Fig. 2. Meanwhile, treatment of 1,3,4-oxadithiolane **9** with 2 molar amounts of $P(NMe_2)_3$ in boiling toluene for 5 h afforded an equilibrium mixture of 1,3-oxathietane **11** and 5-thioxo-1-pentanone **13** (40%), thietane derivatives **22a** and **22b** (two stereoisomers, 4 and 3%), benzosuberone **20** (4%), and cyclopentene **21** (2%) (Scheme 12).

Dechalcogenation of **10** or **9** with $P(NMe_2)_3$ would initially provide **12** and **17** or **11** and **13**, respectively, and other products would be derived from them. To examine this speculation, we carried out the reaction of oxaselenetane **12** with $P(NMe_2)_3$. Thus, heating **12** with $P(NMe_2)_3$ (equimol) in boiling toluene for 10 h gave selenetanes **18a** and **18b** (11 and 8%, respectively), selenanes **19a** and **19b** (5 and 3%, respectively), **20** (16%), and **21** (6%) (Scheme 13), indicating the speculation to be reasonable. Moreover, since heating **12** alone resulted in the quantitative recovery of the starting material, the isomerization of **12** to **18a, b** and **19a, b** must be catalyzed by $P(NMe_2)_3$.

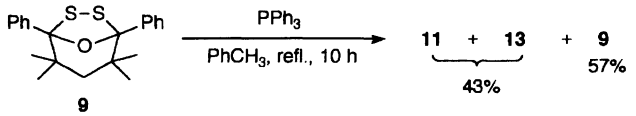
Thus, also in the present case, it seems that a single-electron transfer from $P(NMe_2)_3$ to 5-selenoxo-1-pentanone **17** took place (Scheme 14). The resulting anion radical **23** should isomerize to **24** or **25** by a 1,3- or a 1,5-hydrogen shift, respectively. Then, intramolecular cyclizations of the anion radicals followed by giving back of an electron to $[P(NMe_2)_3]^{+\cdot}$ would provide selenetanes **18** and selenanes **19**.

On the other hand, **20** might be derived from intramolecular radical addition of **23** as shown in Scheme 15.[16]

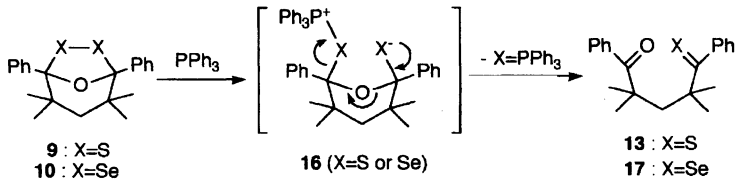
By the way, it can be considered that a zwitterionic intermediate **28** was formed by coupling of anion rad-



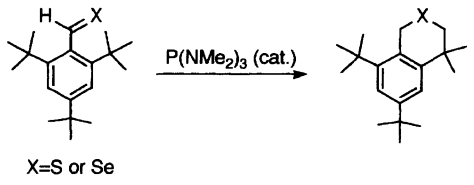
Scheme 7.



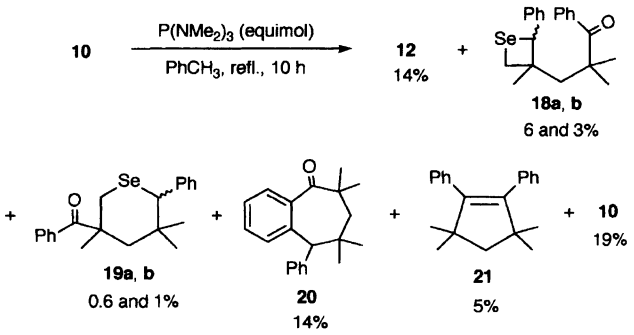
Scheme 8.



Scheme 9.



Scheme 10.



Scheme 11.

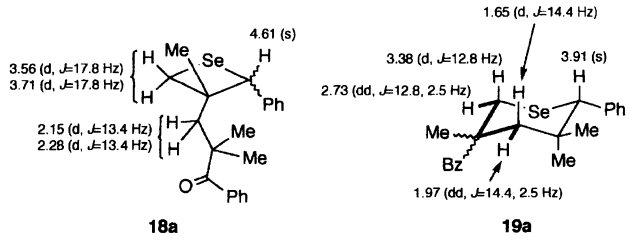
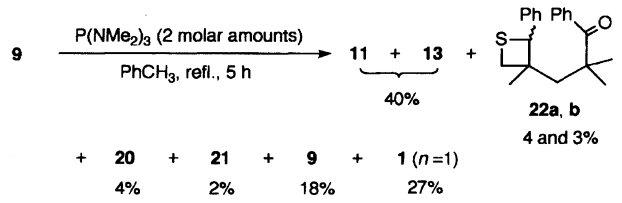


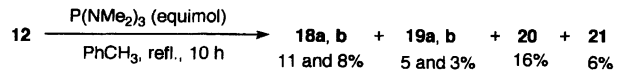
Fig. 2. Selected ^{1}H NMR data (δ) of **18a** and **19a**.

ical **23** with $[P(NMe_2)_3]^{+\bullet}$. Intramolecular addition of the carbanion center to the carbonyl carbon giving **29** followed by elimination of $O{=}P(NMe_2)_3$ would yield selenirane **30**,[17] which further reacts with $P(NMe_2)_3$ to give cyclopentene **21**. These mechanisms would be also the case for the reaction of 1,3,4-oxadithiolane **9** with $P(NMe_2)_3$ (Scheme 16).

Equilibriums between 1,3-Oxathietane 11 and 5-Thioxo-1-pentanone 13 and between 1,3-Oxaselenetane 12 and 5-Selenoxo-1-pentanone 17. The process of attaining equilibrium from both a **13**-rich mixture and pure **11** were monitored by ^{1}H NMR and the ratios of **13** and **11** were estimated from the integral ratios. Thus, a $CDCl_3$ solution of a **13**-rich mixture (**13** : **11**=1 : 0.2) in an NMR tube under argon was allowed to stand at 25 °C. The ratio became 1 : 0.56 after 24 h and 1 : 0.85 after 194 h. On the other hand, starting from pure **11**, the ratio of **13** and **11** became



Scheme 12.

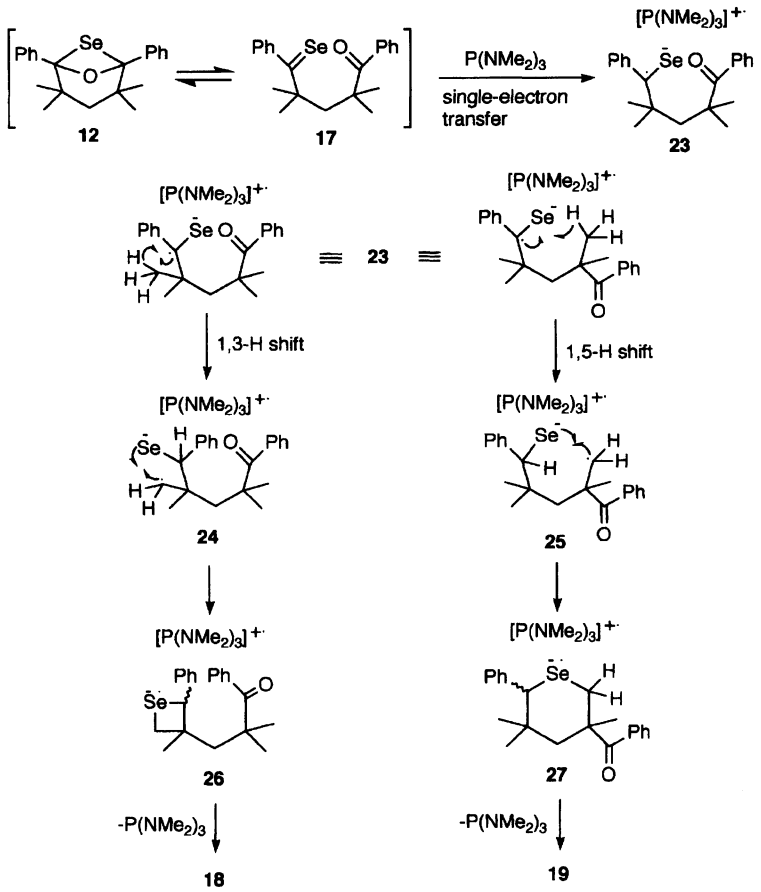


Scheme 13.

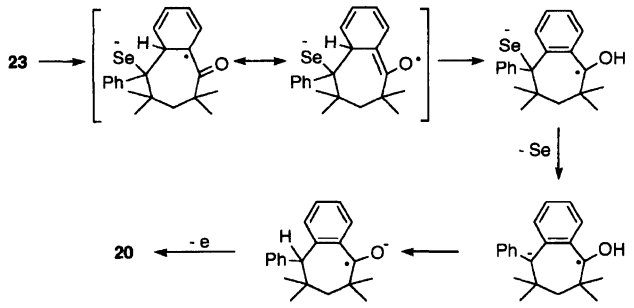
0.78 : 1 after 261 h. These observations indicate that it takes long time to attain equilibrium at 25 °C. Unfortunately, because of partial decomposition of the materials, we could not follow the process until the mixture came to equilibrium.

Interestingly, the cyclization of 2,2,5,5-tetramethyl-1, 6-diphenyl-6-thioxo-1-hexanone (**31**) to the corresponding 1,3-oxathietane **32** was not observed in our previous study (Scheme 17).[3] Steliou recently reported computer-aided evaluation of enthalpic stability of **31** and **32**, which showed that the latter was slightly more stable ($\Delta H_R = -1.5$ kcal mol^{-1}).[18] The intramolecular cyclization of **13** to **11** forming 6-membered rings may be more favorable than that of **31** to **32** giving 7-membered rings.[19] To our knowledge, the present observation is the first example of the head-to-tail [2+2] cycloaddition of thiocarbonyl and carbonyl groups.

As described above, ring opening of 1,3-oxaselenetane **12** to **17** was observed in boiling toluene. In the ^{1}H NMR determined in toluene-d_8 at 105 °C, a new set of peaks assignable to **17** appeared at δ=1.39 (2Me), 1.52 (2Me), 2.98 (CH_2), 7.37 (*ortho*-H of PhC(=Se), d, J=7.9 Hz), and 7.68 (*ortho*-H of PhC(=O), d, J=7.4 Hz) (other aromatic protons overlapped with those of **12**). The ratio of **17** to **12** was 1 : 4.8 at this temperature. The peaks due to **17** were barely observed at room temperature although the ratio to **12** was less than 1%. In addition to the spectroscopic proof, we examined trapping of the selenoxo ketone. Heating **12** with DMAD in boiling toluene for 6 h provided an adduct **33** in 30% yield along with **10** (20%) (Scheme 18). A plausible mechanism for **33** is depicted in Scheme 19. Thus, [4+2] cyclization provides an adduct **34**, whose intramolecular cyclization accompanied with rearomaization would yield **33**.[20] The mechanism of the formation of **10** is



Scheme 14.



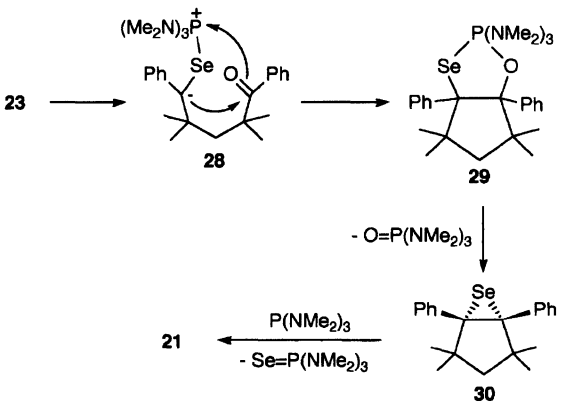
Scheme 15.

not clear at present.

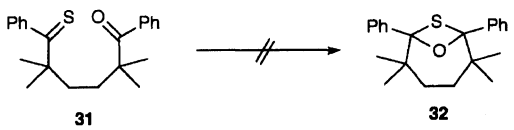
In summary, we obtained novel heterocycles containing oxygen and sulfur or selenium, 1,3,4-oxadithiolane **9**, 1,3,4-oxadiselenolane **10**, 1,3-oxathietane **11**, and 1,3-oxaselenetane **12**, by the reactions of hydrazone **8** with X_2Cl_2 (X=S, Se) and related reactions. Moreover, we observed previously unknown equilibriums; thiocarbonyl + carbonyl ⇌ 1,3-oxathietane and selenocarbonyl + carbonyl ⇌ 1,3-oxaselenetane.

Experimental

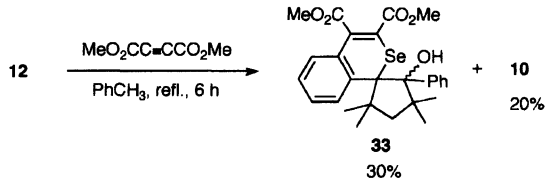
Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H NMR spectra were determined at 400 MHz and ^{13}C NMR spectra were deter-



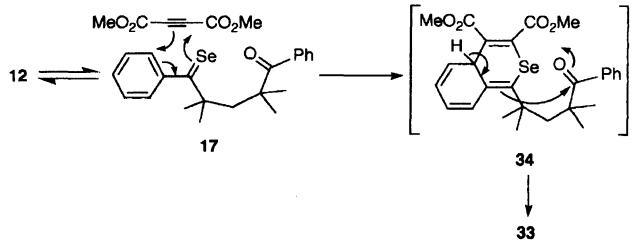
Scheme 16.



Scheme 17.



Scheme 18.



Scheme 19.

mined at 100.6 MHz using $CDCl_3$ as the solvent on a Bruker AM-400 spectrometer. Low- and high-resolution mass spectra were measured at 70 eV in the EI mode on either a JEOL JMS-DX303 or a Shimadzu QP-1000 spectrometer. IR spectra were obtained on a Hitachi Model 270-50 spectrometer, and UV-vis spectra were determined on a Hitachi Model 340 spectrometer. Dry column chromatography was performed with a 1:5 mixture of Merck Kieselgel 60 F_{254} (70—230 mesh) and Merck Kieselgel 60 (70—230 mesh) packed in a seamless cellulose tubing and visualized with a 254-nm UV lamp. Elemental analyses were performed by the Analytical Center of Saitama University. The diselenium dichloride Se_2Cl_2 was prepared according to the literature.[21]

Preparation of 2,2,4,4-Tetramethyl-1,5-diphenyl-1, 5-pentanedione Monohydrazone (8). A solution of 2, 2,4,4-tetramethyl-1,5-diphenyl-1,5-pentanedione (**1**: n=1)[22] (474 mg, 1.47 mmol) and hydrazine monohydrate (0.75 mL, 15.5 mmol) in hexane (10 mL) and methanol (2 mL) was refluxed for 5 h in the presence of three drops of sulfuric acid. The solvents were removed under reduced pressure and the residue was purified by dry column chromatography (silica gel containing 10% w/w water, CH_2Cl_2) to afford **8** (361 mg, 66%).

8: Colorless needles, mp 87—88 °C (hexane); ^{1}H NMR δ=1.08 (s, 6H), 1.40 (s, 6H), 2.37 (s, 2H), 4.70 (br s, 2H), 7.09—7.11 (m, 2H), 7.31—7.43 (m, 6H), 7.71—7.73 (m,2H); ^{13}C NMR δ=28.6 (q, two peaks overlapped), 40.8 (s), 48.0 (s), 48.9 (t), 127.7 (d), 128.0 (d), 128.06 (d), 128.14 (d), 128.8 (d), 130.3 (d), 133.7 (s), 139.2 (s), 157.7 (s), 209.4 (s); IR (CCl_4) 1674 cm^{-1} (C=O), 3400 (N–H). Found: C, 77.82; H, 8.00; N, 8.48%. Calcd for $C_{21}H_{26}N_2O$: C, 78.22; H, 8.13; N, 8.69%.

Reaction of Hydrazone 8 with Se_2Cl_2. A solution of Se_2Cl_2 (300 mg, 1.3 mmol) in toluene (1 mL) was added into a solution of **8** (212 mg, 0.66 mmol) in toluene (10 mL) in the presence of triethylamine (266 mg, 2.6 mmol) under N_2. After refluxing for 1.5 h, the resulting mixture was filtered and the filtrate was concentrated under reduced pressure. The resdue was purified by dry column chromatography (silica gel, dichloromethane–hexane 1:1) to give 2,2,4, 4-tetramethyl-1,5-diphenyl-8-oxa-6,7-diselenabicyclo[3.2.1]-octane (**10**) (62 mg, 21%).

10: Red-orange needles, mp 237—238 °C (hexane); ^{1}H NMR δ=0.99 (s, 6H), 1.32 (d, J=14.2 Hz, 1H), 1.38 (s, 6H), 2.39 (d, J=14.2 Hz, 1H), 7.25—7.29 (m, 2H), 7.34—7.38 (m, 4H), 7.55—7.57 (m, 4H); ^{13}C NMR δ=26.2 (q), 31.1 (q), 42.0 (s), 50.0 (t), 111.4 (s), 125.9 (d), 127.6 (d), 127.7 (d), 141.9 (s); MS m/z 452 (M^+); UV-vis (CH_3CN) λ_{max} 444 nm (ε 151), 350 (143). Found: C, 56.21; H, 5.30%. Calcd for $C_{21}H_{24}OSe_2$: C, 56.01; H, 5.37%.

Reaction of Hydrazone 8 with S_2Cl_2. (a) Reflux for 5 h. S_2Cl_2 (169 mg, 1.25 mmol) was added into a solution of **8** (192 mg, 0.59 mmol) in toluene (10 mL) in the presence of triethylamine (249 mg, 2.4 mmol) at room temperature under N_2. The mixture was refluxed for 5 h and then the solvent was removed under reduced pressure. The residue was purified by dry column chromatography (silica gel, dichloromethane–hexane 1:1) to give 2,2,4,4-tetramethyl-1,5-diphenyl-8-oxa-6,7-dithiabicyclo[3.2.1]octane (**9**) (119 mg, 56%).

9: Pale yellow needles, mp 226—227 °C (hexane) (decomp); ^{1}H NMR δ=1.01 (s, 6H), 1.26 (s, 6H), 1.31 (d, J=14.2 Hz, 1H), 2.38 (d, J=14.2 Hz, 1H), 7.27—7.31 (m, 2H), 7.33—7.37 (m, 4H), 7.54—7.56 (m, 4H); ^{13}C NMR δ=26.7 (q), 29.3 (q), 42.0 (s), 48.7 (t), 111.8 (s), 126.3 (d), 127.5 (d), 127.7 (d), 140.0 (s); MS m/z 356 (M^+); UV-vis (hexane) λ_{max} 372 nm (ε 129), 308 (165). Found: C, 70.58; H, 6.76%. Calcd for $C_{21}H_{24}OS_2$: C, 70.74; H, 6.78%.

(b) Reflux for 1 h. S_2Cl_2 (253 mg, 1.9 mmol) was added into a solution of **8** (222 mg, 0.69 mmol) in toluene (10 mL) in the presence of triethylamine (380 mg, 3.8 mmol) at room temperature under argon. The mixture was refluxed for 1 h. After the solvent was removed under reduced pressure, the residue was purified by dry column chromatography (silica gel, dichloromethane–hexane 1:1) to give **9** (123 mg, 55%) and a mixture of 2,2,4,4-tetramethyl-1,5-diphenyl-6-oxa-7-thiabicyclo[3.1.1]heptane (**11**) and 2,2,4, 4-tetramethyl-1,5-diphenyl-5-thioxo-1-pentanone (**13**) (15.7 mg, 7%).

11: Colorless needles, mp 144—145 °C (hexane) (decomp); ^{1}H NMR δ=0.99 (s, 6H), 1.19 (s, 6H), 1.75 (d, J=13.9 Hz, 1H), 2.59 (d, J=13.9 Hz, 1H), 7.16—7.19 (m, 4H), 7.21—7.23 (m, 2H), 7.26—7.30 (m, 4H); ^{13}C NMR δ=22.7 (q), 26.7 (q), 40.9 (s), 53.0 (t), 98.8 (s), 124.9 (d), 127.19 (d), 127.23 (d), 141.0 (s); MS m/z 324 (M^+). Found: C, 77.83: H, 7.45%. Calcd for $C_{21}H_{24}OS$: C, 77.73; H, 7.46%.

13: Purple oil; ^{1}H NMR δ=1.34 (s, 6H), 1.36 (s, 6H), 2.84 (s, 2H), 7.26—7.47 (m, 8H), 7.64—7.66 (m, 2H); ^{13}C NMR δ=28.7 (q), 31.2 (q), 48.4 (s), 51.7 (t), 55.4 (s), 125.5 (d), 127.4 (d), 128.08 (d), 128.12 (d), 128.5 (d), 130.9 (d), 138.9 (s), 150.9 (s), 209.3 (s), 265.5 (s); IR (neat) 1676 cm^{-1} (C=O); MS m/z 324 (M^+); UV-vis (hexane) λ_{max} 569 nm (ε 71); HRMS Found: m/z 324.1548. Calcd for $C_{21}H_{24}OS$: M, 324.1552.

Reaction of Hydrazone 8 with S_2Cl_2 in the Presence of Dimethyl Acetylenedicarboxylate (DMAD). S_2Cl_2 (41 mg, 0.3 mmol) was added to a solution of **8** (97 mg, 0.3 mmol) and triethylamine (61 mg, 0.6 mmol) in toluene (15 mL) at 0—5 °C under N_2. When the solution turned purple, DMAD (116 mg, 0.8 mmol) was added into this solution at 0—5 °C. The purple color disappeared after 5 min and the mixture was allowed to warm to ambient temperature and stirred for 1 h. The solvent was removed under

reduced pressure and the residue was purified by column chromatography (silica gel, dichloromethane–hexane 1 : 1) to afford 35 mg (33%) of 1,3,4-oxadithiolane **9**.

Deselenation of 1,3,4-Oxadiselenolane 10 with Triphenylphosphine. A solution of **10** (200 mg, 0.44 mmol) and triphenylphosphine (120 mg, 0.46 mmol) in toluene (20 mL) was heated under reflux for 10 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, dichloromethane–hexane 2 : 3) to afford 2,2,4,4-tetramethyl-1,5-diphenyl-6-oxa-7-selenabicyclo[3.1.1]heptane (**12**) (119 mg, 72%) and unchanged **10** (34 mg, 17%).

12: Pale yellow needles, mp 161—162 °C (hexane); ^{1}H NMR δ=1.09 (s, 6H), 1.15 (s, 6H), 1.81 (d, J=14.0 Hz, 1H), 2.71 (d, J=14.0 Hz, 1H), 7.18—7.22 (m, 6H), 7.25—7.29 (m, 4H); ^{13}C NMR δ=21.4 (q), 27.8 (q), 41.4 (s), 54.8 (t), 92.6 (s), 124.9 (d), 127.1 (d), 127.2 (d), 141.6 (s); MS m/z 372 (M^+). Found: C, 67.91: H, 6.35%. Calcd for $C_{21}H_{24}OSe$: C, 67.92; H, 6.51%.

Desulfurization of 1,3,4-Oxadithiolane 9 with Triphenylphosphine. A solution of **9** (172 mg, 0.48 mmol) and triphenylphosphine (127 mg, 0.48 mmol) in toluene (20 mL) was refluxed for 10 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, dichloromethane–hexane 2 : 3) to give a mixture of 1,3-oxathietane **11**, 5-thioxo-1-pentanone **13** (68 mg, 43%), and unchanged **9** (101 mg, 57%).

Reaction of 1,3,4-Oxadiselenolane 10 with Hexamethylphosphorous Triamide [P(NMe$_2$)$_3$]. P(NMe$_2$)$_3$ (90 mg, 0.55 mmol) was added into a solution of **10** (277 mg, 0.50 mmol) in toluene (20 mL) under argon and the mixture was heated under reflux for 10 h. The solvent was removed under reduced pressure and the residue was subjected to dry column chromatography (silica gel, dichloromethane–hexane 1 : 1) to give 3,3,5,5-tetramethyl-1,2-diphenylcyclopentene (**21**) (6 mg, 5%), 1,3-oxaselenetane **12** (26 mg, 14%), unchanged **10** (42 mg, 19%), 6,6,8,8-tetramethyl-9-phenyl-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (**20**) (21 mg, 14%), and a mixture of 3-(2-benzoyl-2-methylpropyl)-3-methyl-2-phenylselenetanes (**18**) and 5-benzoyl-3,3,5-trimethyl-2-phenylselenanes (**19**). The mixture of **18** and **19** was further separated by preparative thick-layer chromatography (hexane–diethyl ether 15 : 1) to give **18a** (12 mg, 6%), **18b** (6 mg, 3%), **19a** (1 mg, 0.6%), and **19b** (2 mg, 1%) (the R_f values decrease in this order).

21: Colorless crystals, mp 117.5—118.5 °C (hexane); ^{1}H NMR δ=1.16 (s, 12H), 1.93 (s, 2H), 6.99—7.01 (m, 4H), 7.04—7.08 (m, 2H), 7.10—7.14 (m, 4H); ^{13}C NMR δ=29.7 (q), 46.3 (s), 56.1 (t), 125.9 (d), 127.2 (d), 129.8 (d), 137.8 (s), 146.8 (s); MS m/z 276 (M^+). Found: C, 91.06; H, 8.82%. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75%.

20: Colorless crystals, mp 86—87 °C (MeOH); ^{1}H NMR δ=0.94 (s, 3H), 1.10 (s, 3H), 1.40 (s, 3H), 1.42 (d, J=15.4 Hz, 1H), 1.48 (s, 3H), 2.22 (d, J=14.1 Hz, 1H), 4.68 (s, 1H), 6.86—6.88 (m, 1H), 7.00—7.02 (m, 1H), 7.20—7.25 (m, 1H), 7.42—7.44 (m, 1H), 7.48—7.52 (m, 2H), 7.56—7.60 (m, 1H), 8.05—8.08 (m, 2H); ^{13}C NMR δ=29.2 (q), 29.8 (q), 33.6 (s), 33.7 (q), 33.9 (s), 34.9 (q), 47.7 (t), 56.3 (d), 125.3 (d), 127.2 (d), 127.6 (d), 128.6 (d), 128.7 (d), 129.1 (d), 132.9 (d), 134.1 (s), 139.8 (s), 145.7 (s), 202.0 (s); IR (neat) 1682 cm^{-1} (C=O); MS m/z 292 (M^+); HRMS Found: m/z 292.1812. Calcd for $C_{21}H_{24}O$: M, 292.1827. Found: C, 85.84; H, 8.20%. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27%.

18a: Colorless crystals, mp 89—91 °C; ^{1}H NMR δ=1.07 (s, 3H), 1.10 (s, 3H), 1.89 (s, 3H), 2.15 (d, J=13.4 Hz, 1H), 2.28 (d, J=13.3 Hz, 1H), 3.56 (d, J=17.8 Hz, 1H), 3.71 (d, J=17.8 Hz, 1H), 4.61 (s, 1H), 7.21—7.29 (m, 3H), 7.42—7.48 (m, 4H), 7.54—7.58 (m, 1H), 7.95—7.97 (m, 2H); ^{13}C NMR δ=23.7 (q), 28.3 (q), 31.3 (q), 47.0 (s), 48.5 (s), 50.1 (t), 59.5 (d), 61.0 (t), 127.0 (d), 127.8 (d), 127.9 (d), 128.6 (d), 129.9 (d), 133.0 (d), 137.4 (s), 138.0 (s), 198.2 (s); IR (neat) 1690 cm^{-1} (C=O); MS m/z 372 (M^+); HRMS Found: m/z 372.1016. Calcd for $C_{21}H_{24}OSe$: M, 372.0992.

18b: Colorless crystals, mp 90—92 °C; ^{1}H NMR δ=1.05 (s, 3H), 1.09 (s, 3H), 1.80 (s, 3H), 2.02 (d, J=13.6 Hz, 1H), 2.30 (d, J=13.7 Hz, 1H), 3.61 (d, J=18.0 Hz, 1H), 3.85 (d, J=18.1 Hz, 1H), 4.59 (s, 1H), 7.20—7.26 (m, 3H), 7.36—7.38 (m, 2H), 7.46—7.50 (m, 2H), 7.56—7.60 (m, 1H), 7.98—8.00 (m, 2H); ^{13}C NMR δ=23.8 (q), 28.3 (q), 33.9 (q), 46.4 (s), 48.8 (s), 52.8 (t), 58.2 (d), 60.8 (t), 127.0 (d), 127.8 (d), 127.9 (d), 128.6 (d), 129.9 (d), 133.1 (d), 137.2 (s), 138.2 (s), 198.2 (s); IR (neat) 1688 cm^{-1} (C=O); MS m/z 372 (M^+); HRMS Found: m/z 372.0993. Calcd for $C_{21}H_{24}OSe$: M, 372.0992.

19a: Colorless crystals, mp 97—98 °C; ^{1}H NMR δ=0.86 (s, 3H), 1.31 (s, 3H), 1.65 (d, J=14.4 Hz, 1H), 1.79 (s, 3H), 1.97 (dd, J=14.4 and 2.5 Hz, 1H), 2.73 (dd, J=12.8 and 2.5 Hz, 1H), 3.38 (d, J=12.8 Hz, 1H), 3.91 (s, 1H), 7.23—7.27 (m, 5H), 7.40—7.52 (m, 3H), 7.64—7.67 (m, 2H); ^{13}C NMR δ=23.4 (q), 24.1 (q), 31.9 (q), 32.7 (t), 37.1 (s), 48.4 (s), 50.8 (t), 52.2 (d), 127.1 (d), 127.8 (d), 127.9 (d), 128.2 (d), 129.1 (d), 130.9 (d), 138.6 (s), 139.9 (s), 208.1 (s); IR (neat) 1668 cm^{-1} (C=O); MS m/z 372 (M^+); HRMS Found: m/z 372.1039. Calcd for $C_{21}H_{24}OSe$: M, 372.0992.

19b: Colorless crystals, mp 110—111 °C; ^{1}H NMR δ=0.84 (s, 3H), 0.88 (s, 3H), 1.42 (d, J=14.4 Hz, 1H), 1.52 (s, 3H), 2.74 (dd, J=14.4 and 2.7 Hz, 1H), 2.81 (d, J=12.9 Hz, 1H), 3.27 (dd, J=13.1 and 3.0 Hz, 1H), 3.95 (s, 1H), 7.16—7.24 (m, 5H), 7.41—7.52 (m, 3H), 7.81—7.83 (m, 2H); ^{13}C NMR δ=22.5 (q), 30.7 (q), 31.4 (q), 31.9 (t), 37.0 (s), 48.7 (s), 52.9 (d), 53.2 (t), 127.0 (d), 127.8 (d), 128.0 (d), 128.1 (d), 129.3 (d), 130.9 (d), 139.1 (s), 139.7 (s), 206.3 (s); IR (neat) 1674 cm^{-1} (C=O); MS m/z 372 (M^+); HRMS Found: m/z 372.1033. Calcd for $C_{21}H_{24}OSe$: M, 372.0992.

Reaction of 1,3,4-Oxadithiolane 9 with P(NMe$_2$)$_3$. P(NMe$_2$)$_3$ (133 mg, 0.81 mmol) was added to a solution of **9** (144 mg, 0.41 mmol) in toluene (20 mL) under N_2 at ambient temperature. The solution was refluxed for 5 h. After the solvent was removed, the residue was subjected to column chromatography (silica gel, dichloromethane–hexane 2 : 3) to afford cyclopentene **21** (2 mg, 2%), a mixture of **11** and **13** (53 mg, 40%), benzosuberone **20** (5 mg, 4%), 3-(2-benzoyl-2-methylpropyl)-3-methyl-2-phenylthietanes **22a** (6 mg, 4%) and **22b** (4 mg, 3%), 1,5-dione **1** (n=1) (34 mg, 27%), and unchanged **9** (26 mg, 18%).

22a: Colorless oil; ^{1}H NMR δ=0.95 (s, 3H), 1.07 (s, 3H), 1.69 (s, 3H), 2.00 (d, J=13.6 Hz, 1H), 2.32 (d, J=13.5 Hz, 1H), 3.51 (d, J=17.5 Hz, 1H), 3.68 (d, J=17.5 Hz, 1H), 4.38 (s, 1H), 7.21—7.28 (m, 3H), 7.34—7.37 (m, 2H), 7.46—7.50 (m, 2H), 7.56—7.60 (m, 1H), 7.98—8.01 (m, 2H); ^{13}C NMR δ=23.4 (q), 28.0 (q), 32.9 (q), 47.6 (s), 50.4 (s), 51.8 (t), 58.6 (t), 62.6 (d), 127.2 (d), 127.7 (d), 128.0 (d), 128.6 (d), 129.2 (d), 133.1 (d), 137.1 (s), 137.4 (s), 198.0 (s); IR (neat) 1690 cm^{-1} (C=O); MS m/z 324 (M^+); HRMS Found: m/z 324.1564. Calcd for $C_{21}H_{24}OS$: M, 324.1548.

22b: Colorless oil; ^{1}H NMR δ=1.02 (s, 3H), 1.03 (s, 3H), 1.75 (s, 3H), 2.19 (d, J=13.5 Hz, 1H), 2.24 (d, J=13.4 Hz, 1H), 3.48 (d, J=17.2 Hz, 1H), 3.55 (d, J=17.3 Hz, 1H), 4.40 (s, 1H), 7.22—7.30 (m, 3H), 7.38—7.40 (m, 2H), 7.44—7.47 (m, 2H), 7.53—7.57 (m, 1H), 7.96—8.00 (m, 2H); ^{13}C NMR δ=23.1 (q), 27.8 (q), 30.6 (q), 47.6 (s), 50.7 (s), 54.7 (t), 58.5 (t), 63.7 (d), 127.3 (d), 127.7 (d), 128.0 (d), 128.5 (d), 129.2 (d), 133.0 (d), 136.9 (s), 137.6 (s), 198.2 (s); IR (neat) 1690 cm^{-1} (C=O); MS m/z 324 (M^+); HRMS Found: m/z 324.1547. Calcd for $C_{21}H_{24}OS$: M, 324.1548.

Reaction of 1,3-Oxaselenetane 12 with $P(NMe_2)_3$. To a solution of **12** (160 mg, 0.43 mmol) in toluene (20 mL) was added $P(NMe_2)_3$ (72 mg, 0.44 mmol) under argon and the mixture was refluxed for 10 h. After the solvent was removed under reduced pressure, the residue was purified by dry column chromatography (silica gel, dichloromethane–hexane 2:3) to give cyclopentene **21** (7 mg, 6%), unchanged **12** (35 mg, 22%), benzosuberone **20** (20 mg, 16%), and a mixture of selenetanes **18** and selenanes **19** (41 mg). The yields of **18a**, **18b**, **19a**, and **19b** were estimated by the ^{1}H NMR spectrum to be 11, 8, 5, and 3%, respectively.

Trapping of 5-Selenoxo-1-pentanone 17 with DMAD. A solution of 1,3-oxaselenetane **12** (79 mg, 0.21 mmol) and DMAD (116 mg, 0.81 mmol) in toluene (10 mL) was heated under reflux for 6 h. The color of the solution changed from initial pale yellow to blue and finally to yellow during the reaction. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, dichloromethane) to afford dimethyl 2′-hydroxy-3′,3′,5′,5′-tetramethyl-2′-phenylspiro[1*H*-2-benzoselenin-1,1′-cyclopentane]-3,4-dicarboxylate (**33**) (32 mg, 30%) and 1,3,4-oxadiselenolane **10** (19 mg, 20%).

33: Yellow needles, mp 184.5—185.5 °C (hexane); ^{1}H NMR δ=0.87 (s, 3H), 1.41 (s, 3H), 1.50 (s, 3H), 1.70 (s, 3H), 1.91 (d, J=13.6 Hz, 1H), 1.99 (d, J=13.6 Hz, 1H), (s, 1H, –OH), 3.81 (s, 3H), 3.85 (s, 3H), 7.09—7.20 (m, 6H), 7.28—7.30 (m, 1H), 7.61—7.63 (m, 2H); ^{13}C NMR δ=29.5 (q), 30.4 (q), 30.9 (q), 33.0 (q), 45.4 (s), 47.1 (s), 52.5 (q), 52.7 (q), 57.8 (t), 75.1 (s), 92.2 (s), 125.2 (s), 126.9 (d), 127.2 (d), 127.4 (d), 127.96 (d), 128.02 (d), 129.1 (d), 130.6 (d), 134.5 (s), 135.9 (s), 138.4 (s), 143.0 (s), 165.8 (s), 169.0 (s); MS m/z 514 (M^+). Found: C, 62.93; H, 5.89%. Calcd for $C_{27}H_{30}O_5Se$: C, 63.15; H, 5.89%.

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