THERMOLYSIS OF SELENOPHENE 1,1-DIOXIDES

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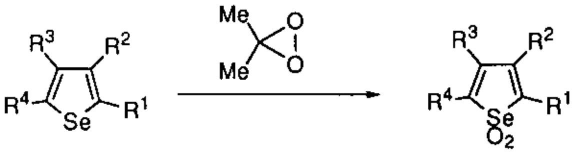
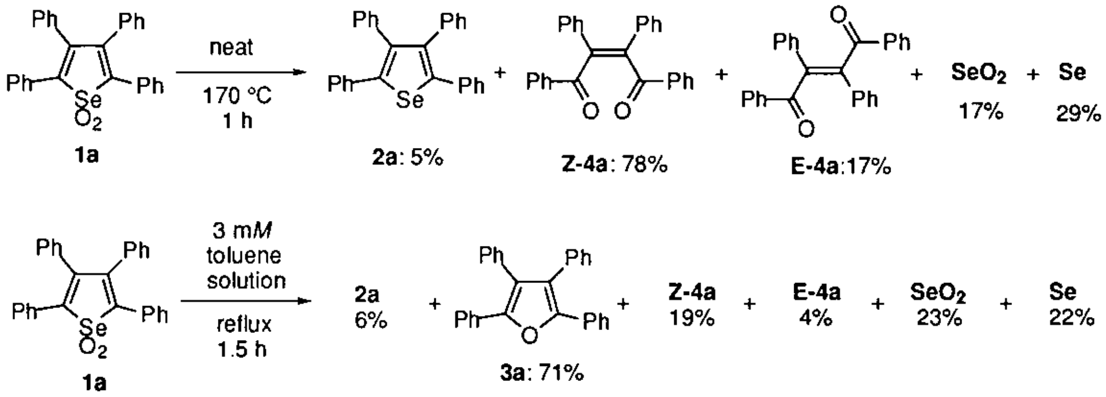
Abstract – Selenophene 1,1-dioxides are thermally far labile than the corresponding thiophene 1,1-dioxides. Even heavily substituted tetraphenylselenophene 1,1-dioxide (**1a**) decomposed, by a process not involving cyclodimerization, when heated above its melting point or heated in refluxing toluene. Thus, the thermolysis of **1a** in refluxing toluene afforded tetraphenylselenophene (**2a**, 6%), tetraphenylfuran (**3a**, 71%), (*Z*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**Z-4a**, 19%), (*E*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**E-4a**, 4%), SeO_2 (23%), and Se (22%), while that of the neat sample gave **2a** (5%), **Z-4a** (78%), **E-4a** (17%), SeO_2 (17%), and Se (29%). Similar results were also obtained on thermolyses of a series of selenophene 1,1-dioxides. The experimental observations (influence of solvents, oxygen, and additive such as diene to the decomposition rate and the presence of induction period) revealed that the mechanism of the decomposition is highly complex. A tentative mechanism that can explain the observed products is presented.

Thiophene 1,1-dioxides are both synthetically and theoretically important compounds since they act as 2π- or 4π-component in a range of cycloadditions. A recent literature survey revealed that more than three hundred papers had appeared on their chemistry.[1] Taking this into account, their selenium analogs, selenophene 1,1-dioxides, are expected to provide a rich field of heterocyclic and heteroatom chemistry. However, no monocyclic selenophene 1,1-dioxides had been known until, after much effort, we succeeded in their synthesis by oxidation of the corresponding selenophenes with dimethyldioxirane (Scheme 1).[2-4] During this study, we have learned that selenophene 1,1-dioxides are thermally far labile than the corresponding thiophene 1,1-dioxides. We therefore investigated their thermal properties as a part of our study on the chemistry of selenophene 1-oxides[5] and 1,1-dioxides[2-4] and report here the product analysis study of the thermal decomposition of these dioxides. Thermolyses of thiophene 1,1-dioxides have been investigated in considerable detail.[6-14] Therefore, the present study is described with emphasis being placed on the comparison of the results with thiophene 1,1-dioxides.



Scheme 1

Even heavily substituted tetraphenylselenophene 1,1-dioxide (**1a**) decomposed above 150°C when heated neat,[3,4] whereas tetraphenylthiophene 1,1-dioxide is thermally stable and melts at 282.0-283.5 °C without decomposition.[15] The thermolysis of the latter dioxide was investigated under forcing conditions. Thus, thermolyses at 340 °C in dibutyl phthalate, 300-400 °C in the presence of $NiBr_2{\bullet}3H_2O$, and 350 °C in the presence of CuBr, produced hydrocarbons such as naphthalene, azulene, and indene derivatives as the major products, whereas the neat thermolysis at 500-550 °C gave tetraphenylthiophene and tetraphenylfuran in 10 and 17% yields, respectively.[6] The flash vacuum pyrolysis at 880 °C/0.01 mmHg afforded diphenylacetylene in 75% yield.[7] We have now found that the thermolysis products of **1a** differ much from those of tetraphenylthiophene 1,1-dioxides. Thus, thermolysis of **1a** at 170 °C without solvent produced tetraphenylselenophene (**2a**), (*Z*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**Z-4a**), (*E*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**E-4a**), SeO_2, and elemental selenium in 5, 78, 17, 17, and 29% yields, respectively. Decomposition of **1a** took place even in refluxing toluene. Thus, heating a 3 m*M* toluene solution of **1a** at reflux for 1.5 h under argon gave **2a** (6%), tetraphenylfuran (**3a**) (71%), **Z-4a** (19%), **E-4a** (4%), SeO_2 (23%), and selenium (22%) (Scheme 2). Thermolysis of **1a** in refluxing toluene was also investigated under a series of concentrations. These results are summarized in Table 1.



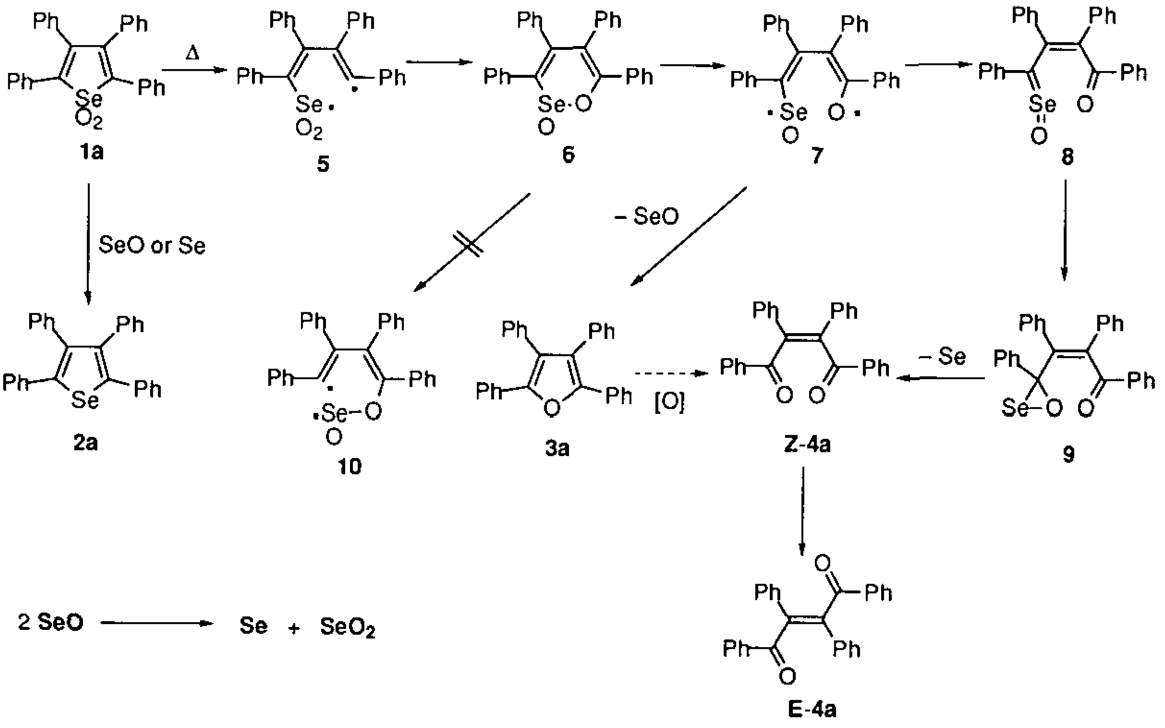
Scheme 2

Table 1. Products of thermal decomposition of the selenophene 1,1-dioxide (**1a**) under a variety of concentrations in toluene

Products	Concentration of **1a** in toluene and yield of products (%)[a]						
	neat[b]	3 mM[c]	5 mM[c]	10 mM[c]	20 mM[c]	40 mM[c]	80 mM[c]
Selenophene **2a**	5	6	6	11	13	19	18
Furan **3a**	0	71	75	74	68	65	61
Diketone **Z-4a**	78	19	17	14	15	8	15
Diketone **E-4a**	17	4	2	1	3	2	3
SeO_2[d]	17	23	14	36	38	33	45
Se[d]	29	22	32	21	14	28	27

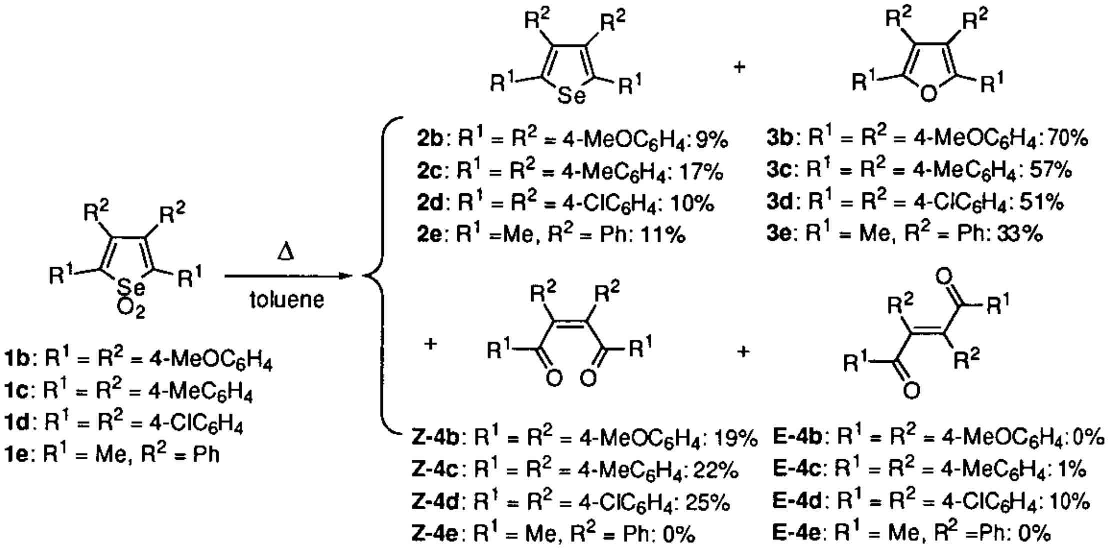
[a] Yields based on isolated products. [b] 170 °C, 1 h. [c] Reflux, 1.5 h. [d] Yields are not accurate because of handling problem.

The following characteristic features emerge from Table 1. 1) Reduction of the dioxide (**1a**) to the selenophene (**2a**) is always observed. Although, with increase of concentration of **1a**, **2a** is formed in slightly increased yields, curiously the yield becomes the lowest on decomposition of the neat sample. 2) The destination of the selenium atom excluded from **1a** is SeO_2 and Se (low material balance is mainly due to the difficulty of the collection of Se by filtration). 3) On decomposition in solution, the furan (**3a**) is consistently the major product (61-75%), and the yield is independent from concentration of **1a**. Flash vacuum pyrolysis of monocyclic thiophene 1,1-dioxides are known to give the corresponding furans as one of the major products.[7-9] 4) On decomposition of the neat sample, no furan (**3a**) forms, but instead the diketone (**Z-4a**) is the major product (78%). When **3a** was heated with SeO_2 above the melting point of **3a** (168 °C), a 5:3.5 mixture of **Z-4a** and **E-4a** was formed in 85% yield, whereas **3a** was inert to SeO_2 in refluxing toluene. It is well documented that **3a** is oxidized to **Z-4a** by many oxidants.[16-21] Thus it is probable that, in the decomposition of the neat sample, **Z-4a** is formed *via* oxidation of **3a** by SeO_2 and, in turn, **E-4a** by isomerization of **Z-4a**.[22] Based on these observations, the mechanism of the thermolysis can be tentatively sketched as shown in the Scheme 3. The initial process should be the C-Se bond cleavage yielding the diradical (**5**), which then cyclizes to give **6**. Then the Se-O bond cleavage gives another diradical (**7**) where the radical centers are stabilized by conjugation with the double bond part. Extrusion of SeO of the diradical (**7**) produces the furan **3a**. Alternatively, **7** might afford the selone *Se*-oxide (**8**) which gives the diketone (**Z-4a**) through cyclization to the oxaselenirane intermediate (**9**). The C-Se bond cleavage of **6** yielding the σ-diradical (**10**) would be less favorable than the Se-O bond cleavage. Disproportionation of the SeO liberated above may explain the formation of SeO_2 and Se. In the decomposition of neat sample, the SeO_2, thus formed, would oxidize **3a** to give the diketone (**Z-4a**), some of which isomerizes to **E-4a** during the reaction. On the thermolysis in solution, **Z-4a** would be mostly formed from **9** *via* **8** since **3a** was inert to SeO_2 in refluxing toluene. The selenophene **2a** would be formed by reduction of **1a** with SeO or Se. However, there is a possibility that **2a** is formed by replacement of SeO_2 of **1a** with Se in analogy with the conversion of 3,4-di-*tert*-butythiophene 1,1-dioxide to 3,4-di-*tert*-butylselenophene by reaction with elemental selenium.[9] As for the formation of furans and other products by thermolysis of thiophene 1,1-dioxides, a mechanism involving the C-S bond cleavage yielding a diradical intermediate was previously presented.[7,12]



Scheme 3

Next, thermolyses of tetra-*p*-anisyl-, tetra-*p*-tolyl-, tetrakis(*p*-chlorophenyl)-, and 2,5-dimethyl-3,4-diphenylselenophene 1,1-dioxides (**1b-e**) were examined in solution. For **1b-d**, 5 m*M* toluene solutions were heated at reflux for 1 h, and for **1e**, a 5 m*M* toluene solution was heated at 100 °C for 1 h. In every case, the products corresponding to those from **1a** were formed with complete decomposition of the starting dioxides as shown in the Scheme 4, revealing the generality of the decomposition mode; only in case of **1e**, no butene-1,4-dione (**Z-4e** or **E-4e**) was formed.

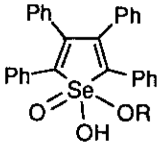


Scheme 4

In the solid state, benzo[*b*]selenophene 1,1-dioxide (**1f**) and 2,4-di-*tert*-butylselenophene 1,1-dioxide (**1g**) decompose above 135 and 152 °C, respectively, without showing a clear melting point, and thus their thermal stability is seemingly comparable with dioxides **1a-1e**, which decompose in the range of 140-150 °C.[3,4] However, **1f** and **1g** were inert to thermolysis in refluxing toluene for 1 h and recovered quantitatively, although **1a-1e** decomposed completely under the same conditions. In case of **1g**, decomposition did not take place even when heated at 150 °C in toluene for 1 h in a sealed tube. This indicates that induced decomposition may take place in the solid state.

The predominant formation of the furan **3a** from **1a** is suggestive of the formation of selenium monoxide "SeO" as the counterpart. Selenium monoxide would be a reactive species like sulfur monoxide "SO" which is generated by thermolysis of thiirane 1-oxides and trapped by dienes to give 2,5-dihydrothiophene 1-oxides.[23] We therefore investigated the decomposition of **1a** in the presence of 2,3-dimethyl-1,3-butadiene with expectation of obtaining the adduct of SeO with the diene. However, disappointingly but interestingly, **1a** did not decompose in the presence of this diene (6 equivalents) even on prolonged heating (24 h) in refluxing toluene under argon. This might be indicative of the involvement of radical species in the decomposition of **1a**, thereby the diene acting as a radical scavenger. However, the radical scavengers such as 1,1-diphenyl-2-picrylhydrazyl (DPPH) and galvinoxyl did not retard the decomposition of **1a**.

In connection with these observations, the influence of solvents was also examined. These led to the following facts: 1) water retarded the decompositon; heating **1a** in a 1:1 mixture of toluene and water resulted in the quantitative recovery even after refluxing for 24 h, 2) the decomposition did not proceed in alcohols; heating **1a** in refluxing 1-butanol for 24 h resulted in the quantitative recovery, 3) the decomposition also did not take place in acetonitrile even when heated at reflux for 74 h. Therefore, decomposition of **1a** is apparently retarded in polar solvents. Increased stability in alcohols and water should be ascribed to the hydrogen bonding between the SeO_2 and OH groups. Alternatively, although addition of H_2O or ROH, which yields **11**, might stabilize **1a**, no evidence for the presence of such species was obtained by spectroscopic means.



11
R = H or O^{n}Bu

Finally, the kinetics of the decomposition of **1a** in toluene led to the observations given below. 1) Induction period, which was longer under argon than was under oxygen, was observed. With decreasing concentration of **1a**, the induction period became longer (for example, 1 m*M* in toluene, 95 °C, > 550 min; 5 m*M* in toluene, 90 °C, 170 min). 2) Once decomposition takes place, it obeys first-order kinetics in **1a** with correlation coefficients in the range 0.98-0.99 at the early stage of the decomposition, and the rate constant is larger under oxygen than is under argon. The typical rate constant values are, for example, 1.88×10^{-4} sec^{-1} (5 m*M* in toluene, 90 °C, under argon), 1.92×10^{-4} sec^{-1} (5 m*M* in toluene, 90 °C, under air) , 5.88×10^{-4} sec^{-1} (5 m*M* in toluene, 100 °C, under air), and 7.41×10^{-4} sec^{-1} (5 m*M* in toluene, 100 °C, under oxygen).

These observations (e.g., retardation of the decomposition by the diene, increased stability by water and alcohols, effect of oxygen, and the presence of induction period) indicate that the decomposition mechanism of **1a** is highly complex. Therefore, at the present stage, we cannot elucidate the mechanism that can accommodate itself to all of the experimental observations, though we have given a sketchy mechanism which is partly in harmony with these observations and can explain the decomposition products.

EXPERIMENTAL

Melting points are uncorrected. Column chromatography was performed with Merck Kieselgel 60 (70-230 mesh). Unless otherwise noted, ^{1}H- and ^{13}C-NMR spectra were determined in $CDCl_3$ as the solvent and with tetramethylsilane as the internal standard. Selenophene 1,1-dioxides were prepared by oxidation of the corresponding selenophenes with dimethyldioxirane.[3,4] Toluene, acetonitrile, and 1-butanol as the solvent were dried by appropriate ways and distilled under argon prior to use.

Thermolysis of Tetraphenylselenophene 1,1-Dioxide (1a). *a) Thermolysis of Neat **1a**.* The dioxide (**1a**) (281 mg, 0.6 mmol) was heated at 170 °C for 1 h in a 30 mL of a round-bottomed flask. The mixture was stirred with 20 mL of CH_2Cl_2 and the insoluble material was collected by filtration to give a mixture of SeO_2 and Se (the presence of SeO_2 was proved by comparison of IR spectrum with that of a commercial material). The mixture was washed with a small amount of water to separate SeO_2 and Se, which ultimately gave 12 mg (17%) of SeO_2 and 14 mg (29%) of selenium. The soluble part in CH_2Cl_2 was chromatographed on a column of silica gel. Elution with hexane gave 13 mg (5%) of tetraphenylselenophene (**2a**) whose spectroscopic properties agreed with those of an authentic sample.[24] Further elution of the column with CH_2Cl_2 gave 39 mg (17%) of (*E*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**E-4a**), mp 232-234 °C (lit.,[25] mp 232-234 °C) and 183 mg (78%) of (*Z*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**Z-4a**), mp 215.0-217.5 °C (lit.[26] mp 216-217 °C) in this order.

*b) Thermolysis of **1a** in Toluene (3 mM Solution).* A solution of 234 mg (0.5 mmol) of **1a** in 167 mL of toluene was heated at reflux for 1.5 h. The insoluble material was collected by filtration to give a mixture of SeO_2 and Se, which was treated as described above to give 9 mg (22%) of Se and 12 mg (23%) of SeO_2. The filtrate was evaporated and the residue was chromatographed on a column of silica gel. Elution with CCl_4 gave 149 mg of a 12:1 mixture of tetraphenylfuran (**3a**, 71%) and the selenophene (**2a**, 6%) (the relative ratio was determined by a 400 MHz ^1H NMR analysis). Recrystallization of the mixture from hexane gave pure **3a**, mp 167-168 °C (lit.,[27] mp 170-171 °C). Further elution of the column with EtOAc gave 46 mg of a 5:1 mixture of **Z-4a** (19%) and **E-4a** (4%); the relative ratio was determined by ^1H NMR. In a similar way, a varying concentration of **1a** in toluene was heated at reflux to give the results in Table 1.

*c) Attempted Thermolyses of **1a** under a Variety of Conditions.* Heating **1a** (164 mg, 0.35 mmol) with 2,3-dimethyl-1,3-butadiene (175 mg, 2.13 mmol) in toluene (70 mL) for 24 h, **1a** (164 mg, 0.35 mmol) in 1-butanol (70 mL) for 24 h , **1a** (234 mg, 0.5 mmol) in a 1:1 mixture of toluene and water (50 mL) for 24 h, and **1a** (164 mg, 0.35 mmol) in acetonitrile (70 mL) for 74 h under reflux all gave the starting material unchanged in 90-100% yields.

*d) Kinetics of Thermolysis of **1a**.* A solution of **1a** in toluene was heated under argon, air, or oxygen at constant temperature (±1 °C). An aliquot was taken from the mixture at regular intervals and the consumption of **1a** was followed by UV using λ_{max} (ε) at 420 nm (435).

Thermolysis of Tetra-*p*-anisylselenophene 1,1-Dioxide (1b). A solution of **1b** (111 mg, 0.19 mmol) in toluene (38 mL) was heated at reflux for 1 h under argon. The mixture was evaporated and the residue was chromatographed on a column of silica gel. Elution with CH_2Cl_2 gave 74 mg of a 8:1 mixture of tetra-*p*-anisylfuran (**3b**) (70%) and tetra-*p*-anisylselenophene (**2b**) (9%). The structure of **2b** was identified by comparison of ^1H and ^{13}C-NMR spectra with an authentic sample.[24] Recrystallization of the mixture from hexane/C_6H_6 gave pure **3b**, 214.0-214.5 °C (lit.,[28] mp 216-218 °C). Further elution of the column with 3:1 CH_2Cl_2/EtOAc gave 18 mg (19%) of (*Z*)-1,2,3,4-tetra-*p*-anisyl-2-butene-1,4-dione (**Z-4b**), mp 185.5-187.0 °C (lit.,[29] mp 183-184 °C).

Thermolysis of Tetra-*p*-tolylselenophene 1,1-Dioxide (1c). A solution of **1c** (112 mg, 0.21 mmol) in toluene (43 mL) was heated at reflux for 1 h under argon. The mixture was treated as described above to give tetra-*p*-tolylselenophene (**2c**) (17 mg, 17%), tetra-*p*-tolylfuran (**3c**) (51 mg, 57%), 1,2,3,4-tetra-*p*-tolyl-2-butene-1,4-dione (**E-4c**) (1 mg, 1%), and (*Z*)-1,2,3,4-tetra-*p*-tolyl-

2-butene-1,4-dione (**Z-4c**) (21 mg, 22%). Structure of **2c** was identified by comparison of ^{1}H- and ^{13}C-NMR spectra with an authentic sample.[24] The furan (**3c**) and the 1,4-diones (**Z-4c**) and (**E-4c**) melted at 187.5-188.5 °C (lit.,[27] mp 185.0-186.5 °C), 183.0-184.5 °C (lit.,[30a] mp 180 °C, lit.,[30b] mp 182-184 °C), and 245.5-247.5 °C (lit.,[31] mp 247 °C), respectively.

Thermolysis of Tetrakis(*p*-chlorophenyl)selenophene 1,1-Dioxide (1d). A solution of **1c** (128 mg, 0.21 mmol) in toluene (43 mL) was heated at reflux for 1 h under argon. The mixture was treated as described above to give tetrakis(*p*-chlorophenyl)selenophene (**2d**) (13 mg, 10%), tetrakis(*p*-chlorophenyl)furan (**3d**) (54 mg, 51%), 1,2,3,4-tetrakis(*p*-chlorophenyl)-2-butene-1,4-dione (**E-4d**) (12 mg, 10%), and (*Z*)-1,2,3,4-tetrakis(*p*-chlorophenyl)-2-butene-1,4-dione (**Z-4d**) (28 mg, 25%). Structures of **2d**,[24] **Z-4d**,[4] and **E-4d**[4] were identified by comparison of ^{1}H- and ^{13}C-NMR spectra with authentic samples. The furan (**3d**) melted at 206.0-208.5 °C (lit.,[27] mp 205-207 °C).

Thermolysis of 2,5-Dimethyl-3,4-diphenylselenophene 1,1-Dioxide (1e). A solution of **1c** (267 mg, 0.78 mmol) in toluene (157 mL) was heated at 100 °C for 1 h under argon. The mixture was treated as described above to give 2,5-dimethyl-3,4-diphenylselenophene (**2e**) (27 mg, 11%), 2,5-dimethyl-3,4-diphenylfuran (**3e**) (64 mg, 33%), and a small amount of an unidentified compound, mp 105-106 °C. Structure of **2e** was identified by comparison of ^{1}H- and ^{13}C-NMR spectra with an authentic sample.[32] The furan (**3e**) melted at mp 60-61 °C (lit.,[33] mp 60-62 °C).

REFERENCES

1. J. Nakayama and Y. Sugihara, to appear in *Organosulfur Chemistry (Synthetic Aspects),* ed. by P. Page, Academic Press, New York, 1998.
2. J. Nakayama, T. Matsui, and N. Sato, *Chem. Lett.*, 1995, 485.
3. J. Nakayama, T. Matsui, Y. Sugihara, A. Ishii, and S. Kumakura, *Chem. Lett.*, 1996, 269.
4. T. Matsui, Y. Sugihara, A. Ishii, S. Kumakura, and J. Nakayama, *Phosphorus, Sulfur, Silicon*, 1996, **118**, 227.
5. Very recently we have succeeded in the preparation of selenophene 1-oxides which are more thermally labile than the corresponding 1,1-dioxides; T. Umezawa, Y. Sugihara, A. Ishii, and J. Nakayama, unpublished results.
6. J. F. W. McOmie and B. K. Bullimore, *J. Chem. Soc., Chem. Commun.*, 1965, 63.
7. W. J. M. van Tilborg and R. Plomp, *Rec. Trav. Chim. Pays-Bas*, 1977, **96**, 282.
8. U. E. Wiersum, *Rec. Trav. Chim. Pays-Bas*, 1982, **101**, 365.
9. J. Nakayama, Y. Sugihara, K. Terada, and E. L. Clennan, *Tetrahedron Lett.*, 1990, **31**, 4473.
10. M. S. Raasch, *J. Org. Chem.*, 1980, **45**, 856.
11. T. G. Squires, C. G. Venier, B. A. Hodgson, L. W. Chang, F. A. Davis, and T. W. Panunto, *J. Org. Chem.*, 1981, **46**, 2373.

12. W. J. M. van Tilborg and R. Plomp, *J. Chem. Soc., Chem. Commun.*, 1977, 130.
13. E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, 1966, **88**, 2836.
14. R. D. Chambers and J. A. Cunningham, *J. Chem. Soc., Chem. Commun.*, 1967, 583.
15. Y. Miyahara and T. Inazu, *Tetrahedron Lett.*, 1990, **31**, 5955; O. Hinsberg, *Ber.*, 1915, **48**, 1611.
16. R. K. Haynes, J. M. Peters, and I. D. Wilmot, *Aust. J. Chem.*, 1980, **33**, 2653.
17. D. H. R. Barton, R. K. Haynes, G. Leclerc, P. D. Magnus, and I. D. Menzies, *J. Chem. Soc., Perkin Trans. 1*, 1975, 2055.
18. G. O. Schenk, *Z. Electrochem.*, 1960, **64**, 997.
19. A. A. Gorman, G. Lovering, and M. A. J. Rodgers, *J. Am. Chem. Soc.*, 1979, **101**, 3050.
20. K. D. Gundermann and M. Steinfatt, *Angew. Chem.*, 1975, **87**, 546.
21. M. Libert and C. Caullet, *Bull. Soc. Chim. Fr.*, 1974, 804.
22. R. E. Lutz, C. R. Bauer, R. G. Lutz, and J. S. Gillespie, *J. Org. Chem.*, 1955, **20**, 218.
23. I. A. Abu-Yousef and D. N. Harpp, *Tetrahedron Lett.*, 1995, **36**, 201 and references cited therein.
24. K. Sawada, K. S. Choi, M. Kuroda, T. Taniguchi, A. Ishii, M. Hoshino, and J. Nakayama, *Sulfur Lett.*, 1993, **15**, 273.
25. C. S. Foote, A. Wexler, and W. Ando, *J. Am. Chem. Soc.*, 1968, **90**, 975.
26. R. M. Wilson, A. C. Hengge, A. Ataei, and D. M. M. Ho, *J. Am. Chem. Soc.*, 1991, **113**, 7240.
27. L. R. Krepski, S. M. Heilmann, J. K. Rasmussen, M. L. Tumey, and H. K. Smith, II, *Synth. Commun.*, 1986, **16**, 377.
28. W. Adam, H. Platsch, and E. Schmidt, *Chem. Ber.*, 1985, **118**, 4385.
29. R. C. Hartnedy and D. C. Dittmer, *J. Org. Chem.*, 1984, **49**, 4752.
30. a) M. Libert, C. Caullet, and G. Barbey, *Bull. Soc. Chim. Fr.*, 1973, 536; b) A. P. Rudenko and A. V. Vasil'ev, *Zh. Org. Khim.*, 1995, **31**, 1502.
31. H. Fauduet and R. Burgada, *Nouv. J. Chim.*, 1979, **3**, 555.
32. J. Nakayama, F. Murai, M. Hoshino, and A. Ishii, *Teterahedron Lett.*, 1988, **29**, 1399.
33. E. Bartmann and R. Gompper, *Synth. Commun.*, 1987, **17**, 263.

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