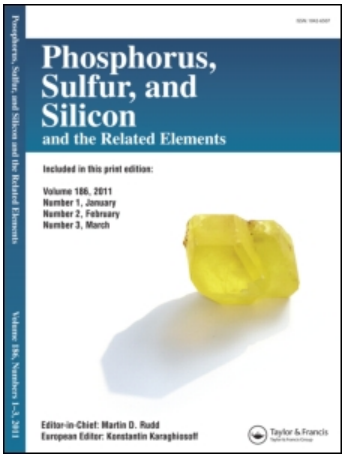

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OXIDATION OF SELENOPHENES

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OXIDATION OF SELENOPHENES

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Oxidation of a series of selenophenes (**1**) with a variety of oxidizing agents was investigated. Oxidation of **1** with 2 molar amounts of dimethyldioxirane (DMD) generally gave the corresponding selenophene 1,1-dioxides (**2**) in good yields except for a few cases where **1** carry electron-withdrawing substituents. Isolation of selenophene 1-oxide intermediates on oxidation with an equimolar amount of DMD was difficult because of their thermally labile nature, only oxidation of benzo[*b*]selenophene gave the isolable 1-oxide in a good yield. Meanwhile, oxidation of **1** with *m*-chloroperbenzoic acid did not give the selenophene 1,1-dioxides **2**, but led instead to oxidation products containing no selenium atoms, resulting from ring opening of the selenophene. Thus, for example, oxidation of tetraarylselenophenes gave (*Z*)-1,2,3,4-tetraaryl-2-butene-1,4-diones as the principal product. Also in this oxidation, the only exception was the oxidation of benzo[*b*]selenophene which afforded the corresponding 1-oxide.

Keywords: Selenophenes; selenophene 1-oxides; selenophene 1,1-dioxides, oxidation; dimethyldioxirane; x-ray diffraction

INTRODUCTION

Thiophene 1,1-dioxides are compounds of great importance both from synthetic and mechanistic points of view.[1] They act either as 2π- or 4π-components and thus undergo a range of cycloadditions with 2π-, 4π-, and 6π-components thermally or photochemically in addition to 1,3-dipolar cycloadditions with 1,3-dipoles.[2] They also undergo ring-opening on reaction with nucleophiles.[3] Thiophene 1-oxides are more reactive species than the corresponding 1,1-dioxides and thus until now only a few isolable monocyclic thiophene 1-oxides

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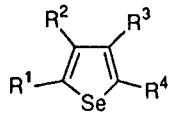
are known.[4] These compounds are also of interest in connection with stereochemistry[4] and cycloaddition chemistry.[5] Keeping this in mind, the chemistry of selenophene 1-oxides and 1,1-dioxides is expected to provide a new fruitful field of heterocyclic and heteroatom chemistry. However, dibenzoselenophene 5-oxides are the only example of selenophenes that carry an oxygen atom on selenium,[6,7] and selenophene 1,1-dioxides still remain an unknown class of compounds. The most straightforward way to these compounds apparently involves the oxidation of the corresponding selenophenes with appropriate oxidizing agents. However, no detailed oxidation study on selenophenes has been reported. To our knowledge, peracid[6] and electrochemical[7] oxidations of dibenzoselenophenes which afforded dibenzoselenophene 5-oxides are the only example of an oxidation study of selenophenes. We report here an oxidation study of a series of selenophenes with a variety of oxidizing reagents including dimethyldioxirane (DMD) and *m*-chloroperbenzoic acid (MCPBA).[8] Oxidation with DMD generally afforded the corresponding selenophene 1,1-dioxides in good yields, whereas oxidation with MCPBA generally led to oxidation products resulting from the ring opening of the selenophenes and containing no selenium atoms. In the present study, oxidation of ten selenophenes (**1a–j**), most of which had become readily obtainable by the methods developed by the authors' group,[9–12] was investigated.



1a: R^1, R^2, R^3, R^4 = Ph
1b: R^1, R^2, R^3, R^4 = 4-MeC_6H_4
1c: R^1, R^2, R^3, R^4 = 4-$MeOC_6H_4$
1d: R^1, R^2, R^3, R^4 = 2-thienyl
1e: R^1, R^2, R^3, R^4 = 4-ClC_6H_4
1f: R^1 = R^4 =Me, R^2 = R^3 = Ph
1g: R^1 = R^3 = *t*-Bu, R^2 = R^4 = H
1h: R^1, R^2 = -CH=CH-CH=CH-, R^3 = R^4 = H
1i: R^1 = R^4 = benzoyl, R^2 = R^3 = H
1j: R^1 = R^4 = CO_2Me, R^2 = R^3 = H

CHART I

RESULTS AND DISCUSSION

1. Oxidation with Dimethyldioxirane (DMD)

Recently it was reported that oxidation of thiophenes with DMD afforded the corresponding thiophene 1,1-dioxides in good yields.[13] We have then investigated the oxidation of selenophenes with DMD. An acetone solution of DMD was prepared according to the literature method by oxidation of acetone with Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) and its concentration was determined prior to use by oxidizing thioanisole to its sulfoxide with this solution.[14] Treatment of tetraphenylselenophene (**1a**) with 1 molar amount of DMD resulted in nearly complete consumption of **1a**. Evaporation of the solvent at 0 °C gave a yellow glassy oil which probably contained tetraphenylselenophene 1-oxide. However, the compound is thermally labile and decomposed to give **1a** as the principal product on attempted purification by silica-gel column chromatography or by crystallization. For this reason, further investigation of this material was interrupted for a while. On the other hand, treatment of **1a** with 2.2 molar amounts of DMD in acetone at 0 °C for 1 h afforded the expected tetraphenylselenophene 1,1-dioxide (**2a**) as a yellow, nicely crystalline compound in 97% yield. Similarly, oxidation of tetraarylselenophenes such as tetra-*p*-tolyl-, tetrakis(4-methoxyphenyl)- and tetrakis(4-chlorophenyl)selenophenes (**1b,c,e**) with a 2.2 molar amount of DMD gave the corresponding selenophene 1,1-dioxides **2b,c,e** in good yields (Table I). Oxidation of 2,5-dimethyl-3,4-diphenyl- and 2,4-di-*t*-butylselenophenes (**1f** and **1g**) also proceeded cleanly to give the corresponding selenophene 1,1-dioxides (**2f** and **2g**), respectively, in high yields. On oxidation of tetra-2-thienylselenophene (**1d**), the corresponding 1,1-dioxide **2d** could not be isolated in pure form because of its thermally labile nature, although the oxidation probably took place selectively on the selenium atom, and not on the sulfur atom of the 2-thienyl groups. Although oxidation of 2,5-dibenzoylselenophene (**1i**) with 2.2 molar amounts of DMD also resulted in consumption of the starting material, decomposition of the resulting products took place during purification to give **1i** as the sole identifiable product in 40% yield. Oxidation of dimethyl selenophene-2,5-dicarboxylate (**1j**) with DMD is sluggish at room temperature, though excess DMD was used, and did not give any identifiable products except the starting material in 52% yield.

Most oxidations with equimolar amounts of DMD, described above, resulted in the nearly complete consumption of the starting selenophenes, but the corresponding 1-oxides could not be isolated in pure form because of their labile nature. However, the oxidation of benzo[*b*]selenophene (**1h**) enabled us to iso-

TABLE I Preparation of selenophene 1,1-dioxides **2** by oxidation of the corresponding selenophenes **1** with DMD

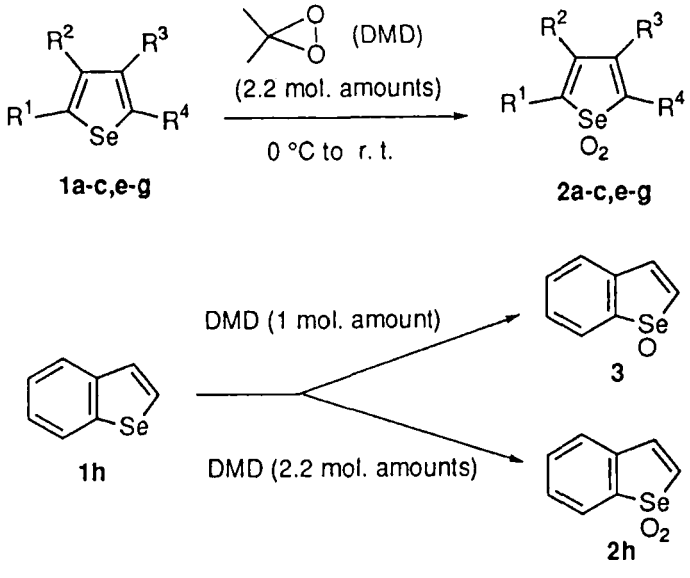
Selenophene dioxides	R^1	R^2	R^3	R^4	*Yields (%)*	*Mp(°C) (decomp.)*	$\delta(^{77}Se)^{a)}$ *(ppm)*	*ν(Se (cm*⁻¹*)*
	C_6H_5	C_6H_5	C_6H_5	C_6H_5	97	>148	1036	876
	4-MeC_6H_4	4-MeC_6H_4	4-MeC_6H_4	4-MeC_6H_4	89	>145	1035	875
	4-$MeOC_6H_4$	4-$MeOC_6H_4$	4-$MeOC_6H_4$	4-$MeOC_6H_4$	99	>140	1035	900
	4-ClC_6H_4	4-ClC_6H_4	4-ClC_6H_4	4-ClC_6H_4	69	>155	1032	909
	Me	C_6H_5	C_6H_5	Me	97	>155	1042	880
	t-Bu	H	*t*-Bu	H	97	>152	1054	877
	-CH=CH-CH=CH-		H	H	71	>135	1018	880

a) Determined with D_2SeO_3 (δ 1282) as the external standard for $CDCl_3$ solutions (76 MHz). b) Taken for KBr disks.

late benzo[*b*]selenophene 1-oxide (**3**) in 88% yield.[15] This is the only example where we could isolate the selenophene 1-oxide throughout this study. Prolonged oxidation of **1h** with 2.2 molar amounts of DMD gave the expected benzo[*b*]selenophene 1,1-dioxide **2h** in 71% yield.

We next developed a method to synthesize the selenophene 1,1-dioxide **2a** on a larger scale, without using an isolated acetone solution of DMD. Thus, the selenophene **1a** was oxidized with DMD which was generated *in situ* by oxidation of acetone with Oxone® in a mixture of water and CH_2Cl_2. This enabled the dioxide **2a** to be prepared in high yield in several grams quantities with a very simple workup. As will be described later, Oxone® oxidizes **1a** to give non-selenium containing oxidation products, and not **2a**. This indicates that both the oxidation of acetone, which exists in large excess, with Oxone® and the oxidation of **1a** with DMD took place much faster than the oxidation of **1a** by Oxone®.

All of the selenophene 1,1-dioxides prepared above decompose gradually on heating without showing distinct melting points (Table I). Their structures were determined spectroscopically (^1H, ^{13}C, and ^{77}Se NMR, IR, UV-Vis, and MS) and also, in the case of **2a**, by X-ray single-crystal structure analysis. In ^{13}C NMR, signals due to 10 nonequivalent sp^2 carbon atoms of **2a** appeared as 9 peaks because of an accidental overlap of two peaks. The ^{77}Se NMR signal of **2a** appeared at δ 1036 with D_2SeO_3 as the external standard, while that of the



SCHEME 1

selenophene **1a** appeared at the much higher field of δ 605. ^{77}Se NMR signals of the other selenophene 1,1-dioxides appeared in the range of δ 1018–1054 (Table I). Reportedly, alkyl phenyl selenones and dialkyl selenones exhibit a ^{77}Se NMR signal in the range of δ 980–1040.[16] The dioxide **2a** consists of yellow crystals and its UV-Vis spectrum, λ_{max} (log ε) (CH_3CN) 330 (3.8), 375 nm (3.8), closely resembles that of tetraphenylthiophene 1,1-dioxide (**4**), λ_{max} (log ε) (CH_3CN) 310 (3.8), 371 nm (3.7) (Fig. 1). In the IR spectra, characteristic absorptions of the -SeO_2- moiety of the selenophene dioxides **2** appeared as two signals in the ranges 875–909 and 927–938 cm^{-1} (Table I). It is known that a selenone group shows a characteristic IR absorption in the ranges of 860–970 and 912–1059 cm^{-1}.[17]) In the mass spectrum of **2a** in the EI mode, the most intense peak was observed at *m/z* 372, which resulted from the loss of SeO from the molecular ion and corresponds to the tetraphenylfuran radical cation, although weak peaks due to the molecular ion are also observed. This is the most characteristic fragmentation pattern of selenophene dioxides **2**.[18]

The selenophene 1-oxide **3** is a rather thermally labile, crystalline compound and decomposes above 76 °C. The ^{77}Se NMR signal of **3** appeared at δ 943, while that of the dioxide **2g** was found at a lower field of δ 1018. In the IR spectrum, $\nu_{Se\text{-}O}$ appeared at 780 cm^{-1}. It is soluble in aqueous NaOH probably because the hydrate of **3** behaves as a protonic acid. It is easily reduced to **1h** by treatment with aqueous $NaHSO_3$ and, in addition, we have often encountered the reduction of **2h** to **1h** on standing in solution by an unknown process.

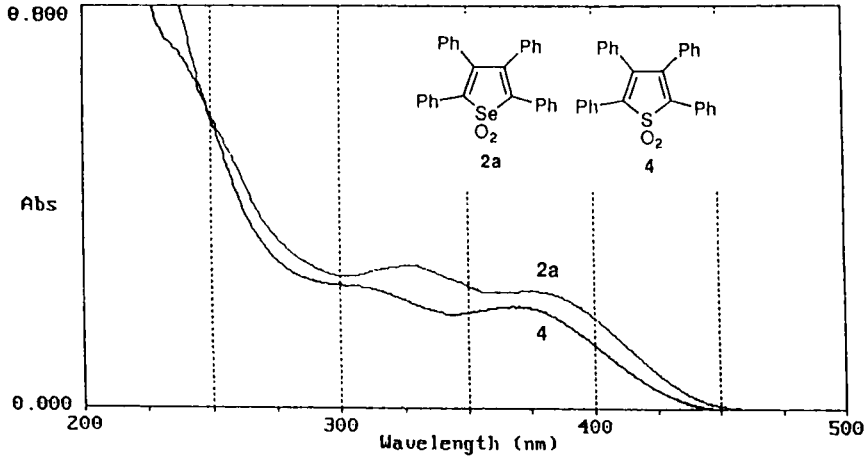


FIGURE 1 UV-Vis Spectra of Tetraphenylselenophene 1,1-Dioxide (**2a**) and Tetraphenylthiophene 1,1-Dioxide (**4**).

2. Molecular Structure of 2a

A yellow needle of **2a** obtained on crystallization from CH_2Cl_2/hexane was subjected to X-ray single-crystal structure analysis. An ORTEP drawing of the structure (Fig. 2), crystal and structure analysis data (Table II), selected bond lengths, bond angles, and torsion angles data (Table III), and fractional coordinates and equivalent isotropic displacement parameters (Table IV) are given below. The five-membered ring of **2a** retains a nearly planar structure regardless of the loss of aromaticity. However, occurrence of bond fixation is apparent from the bond length data. Thus, the C1–C2 and C3–C4 bond lengths (1.354 and 1.345 Å, respectively) are close to common carbon-carbon double bond lengths, whereas the C2–C3 bond length (1.515 Å) is comparable with common carbon-carbon single bond lengths. The C1–C2 and C3–C4 bond lengths of the parent selenophene were reported to be 1.369 and 1.433 Å, respectively.[19] Even the C1-Se and C4-Se bonds (1.920 and 1.930 Å, respectively) are much longer than those of the parent selenophene (1.855 Å) probably because of the loss of aromaticity. These bond length values are seemingly comparable with those observed with common selenones; the C(Me)-Se and C(Ph)-Se bond lengths of methyl phenyl selenone are 1.927 and 1.899 Å, respectively.[16] The phenyl

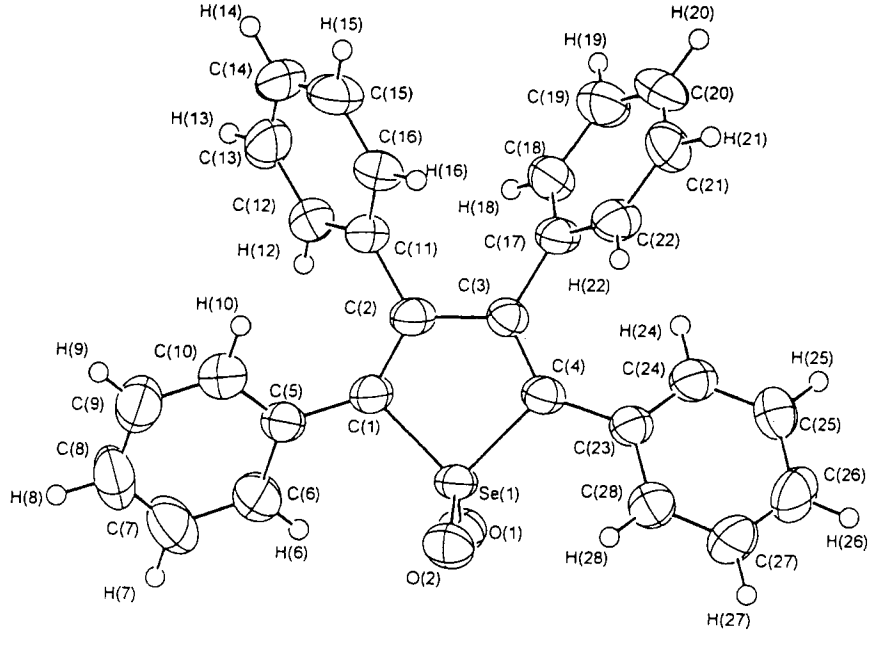


FIGURE 2 Molecular Structure of Tetraphenylselenophene 1,1-Dioxide (**2a**) Showing Atom Labeling.

TABLE II Crystal and structure analysis data of **2a**

Crystal:	
Mol formula	$C_{28}H_{20}O_2Se$
Mol wt	467.43
Crystal syst	Triclinic
Space group	*P*1
a/Å	10.232(2)
b/Å	10.234(3)
c/Å	12.106(2)
α/deg	87.74(4)
β/deg	74.41(3)
γ/deg	64.29(5)
V/Å^3	1095.7(6)
Z	2
D_{calcd}/g cm^{-3}	1.42
Cryst dimens/mm	0.2 × 0.2 × 0.1
Data collection:	
Diffractometer used	Mac Science DIP3000
Radiation	Mo *K*α (λ = 0.71073 Å)
Measured reflns	13710
Reflns used in L. S.	3519
Reflns (hkl) limits	$0 < h < 14$, $-12 < k < 14$, $-14 < l < 14$
Unique reflns	5214
Internal Consistency: Rint	0.00
Refinement:	
L. S. refinement method	Full matrix
Function minimized	$\Sigma[w(\|Fo\| - \|Fc\|)^2]$
Weight method	$w = 1/(\sigma^2(Fo) + 0.003\|Fo\|^2)$
F (000)	238
Linear abs coeff/cm^{-1}	17.174
R	0.0486
*R*w	0.0673

TABLE III Selected bond lengths (Å), bond angles (°), and torsion angles (°) data of **2a**

Bond lengths		*Bond angles*		*Torsion angles*	
Se-O1	1.614(3)	O1-Se-O2	114.9(2)	C4-Se-C1-C2	2.5(3)
Se-O2	1.603(3)	O1-Se-C1	112.4(2)	Se-C1-C2-C3	−1.8(3)
Se-C1	1.920(4)	O1-Se-C4	109.0(2)	C1-C2-C3-C4	−0.3(4)
C1-C2	1.354(5)	O2-Se-C1	112.1(2)	C2-C3-C4-Se	2.2(3)
C2-C3	1.516(5)	O2-Se-C4	115.0(2)	C1-Se-C4-C3	−2.6(3)
C3-C4	1.345(5)	C1-Se-C4	91.1(2)	Se-C1-C5-C6	−34.6(4)
C4-Se	1.930(4)	Se-C1-C2	107.2(3)	C1-C2-C11-C12	−54.1(5)
		C1-C2-C3	117.2(4)	C2-C3-C17-C18	−58.8(5)
		C2-C3-C4	117.1(4)	C3-C4-C23-C24	−28.3(5)
		Se-C4-C3	107.3(3)		

TABLE IV Fractional coordinates and equivalent isotropic parameters of **2a**

Atom	*x/a*	*y/b*	*z/c*	U_{eq} [a)]
Se(1)	0.43256(4)	0.17018(4)	0.79090(4)	0.056
O(1)	0.4452(3)	0.2780(3)	0.6919(3)	0.078
O(2)	0.2984(3)	0.2463(3)	0.9069(3)	0.074
C(1)	0.6227(4)	0.0549(4)	0.8216(4)	0.059
C(2)	0.6707(4)	−0.0837(3)	0.7792(3)	0.055
C(3)	0.5681(4)	−0.1135(4)	0.7250(3)	0.052
C(4)	0.4368(4)	0.0000(4)	0.7237(3)	0.056
C(5)	0.6801(4)	0.1264(4)	0.8849(3)	0.060
C(6)	0.6533(6)	0.2698(5)	0.8689(5)	0.090
C(7)	0.7050(7)	0.3402(6)	0.9301(5)	0.112
C(8)	0.7858(6)	0.2684(7)	1.0047(5)	0.108
C(9)	0.8107(6)	0.1273(6)	1.0225(5)	0.093
C(10)	0.7569(5)	0.0553(5)	0.9651(4)	0.075
C(11)	0.8197(4)	−0.2010(4)	0.7807(3)	0.055
C(12)	0.9493(4)	−0.1817(4)	0.7317(4)	0.065
C(13)	1.0896(5)	−0.2892(6)	0.7317(4)	0.081
C(14)	1.1023(6)	−0.4163(5)	0.7802(5)	0.089
C(15)	0.9740(7)	−0.4353(5)	0.8295(5)	0.096
C(16)	0.8334(5)	−0.3292(4)	0.8298(4)	0.075
C(17)	0.6136(4)	−0.2606(4)	0.6722(4)	0.057
C(18)	0.7437(5)	−0.3274(4)	0.5828(4)	0.068
C(19)	0.7789(5)	−0.4623(5)	0.5298(5)	0.089
C(20)	0.6847(6)	−0.5258(5)	0.5641(5)	0.096
C(21)	0.5554(6)	−0.4601(5)	0.6532(5)	0.092
C(22)	0.5188(5)	−0.3269(4)	0.7079(4)	0.071
C(23)	0.3155(4)	0.0243(4)	0.6700(4)	0.059
C(24)	0.3424(4)	−0.0523(4)	0.5684(4)	0.068
C(25)	0.2276(5)	−0.0221(5)	0.5176(4)	0.079
C(26)	0.0829(5)	0.0888(6)	0.5696(5)	0.095
C(27)	0.0559(5)	0.1651(5)	0.6698(5)	0.085
C(28)	0.1704(5)	0.1324(5)	0.7209(4)	0.072

a) Equivalent isotropic U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

groups of **2a** are no longer coplanar with the five-membered ring and exist in a propeller-like conformation to avoid steric repulsion. The O-Se-O bond angle is 114.9° and is bisected by the plane of the five-membered ring.

3. Oxidation with *m*-Chloroperbenzoic Acid (MCPBA) and Other Reagents

It is well documented that peracid oxidation of thiophenes generally produces the corresponding thiophene 1,1-dioxides as the final product via thiophene 1-oxide intermediates.[1] In rare cases, the 1-oxide intermediates could be isolated[4] and also, in some cases, products arising from dimerization of these

intermediates were produced.[1] Moreover, selenides are known to be oxidized with peracids to give the corresponding selenoxides and selenones.[16,20] Next we then examined the oxidation of selenophenes with *m*-chloroperbenzoic acid (MCPBA).

In contrast to the oxidation with DMD, oxidation of the selenophene **1a** with 2.2 molar amounts of MCPBA in CH_2Cl_2 at room temperature gave (*Z*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**5a**) (42%), (*E*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**6a**) (3%), and benzil (**7a**) (0.3%) with recovery of **1a** in 52% yield. The oxidation with the same amount of MCPBA in refluxing CH_2Cl_2 also produced **5a** (39%), **6a** (3%), and **7a** (1%) with 53% recovery of **1a**. Even the oxidation, carried out under basic conditions with Na_2CO_3 as the additive, with expectation of obtaining selenium-containing products, brought about no dramatic change in the products. The oxidation with 4.4 molar amounts of MCPBA at room temperature raised the yield of **5a** to 69% with decreased recovery of **1a** (14%). The oxidation in refluxing CH_2Cl_2 also gave a similar result (Table V). In all the experiments described above, no products retaining the selenium atom of **1a** was obtained. When the reaction mixture, obtained by oxidation of **1a** with 4.4 molar amounts of MCPBA, was stirred with water and the aqueous layer was evaporated under reduced pressure, a crystalline residue, which partially turned red on standing, was obtained. The ^{77}Se NMR spectrum of this residue in D_2O showed a singlet at δ 1282, thus revealing that the residue was H_2SeO_3 in 67% yield and thus the selenium atom of **1a** was transformed into SeO_2 on the oxidation. These results are in marked contrast to the oxidation with DMD

TABLE V Oxidation of tetraarylselenophenes (**1**) with *m*-chloroperbenzoic acid and oxone®

1 (Ar)	*Oxidizing Reagents (Mol. Amounts)*	*Solvents (Temperature)*	*Time (h)*	*Products: Yield (%)*			*Recovery of* **1** (%)
				5	6	7	
C_6H_5	MCPBA (2.2)	CH_2Cl_2 (r. t.)[c]	50	42	3	0.3	52
C_6H_5	MCPBA (2.2)	CH_2Cl_2 (reflux)	30	39	3	1	53
C_6H_5	MCPBA (1.8)[a]	CH_2Cl_2 (r. t.)	50	26	2	1	66
C_6H_5	MCPBA (4.4)	CH_2Cl_2 (r. t.)	27	69	2	3	14
C_6H_5	MCPBA (4.4)	CH_2Cl_2 (reflux)	12	72	2	2	16
C_6H_5	Oxone® (3.0)[b]	C_6H_6/H_2O (reflux)	40	30	(+)	(+)	63
4-MeC_6H_4	MCPBA (4.4)	CH_2Cl_2 (r. t.)	5	65	0	10	10
4-$MeOC_6H_4$	MCPBA (4.4)	CH_2Cl_2 (r. t.)	2	85	0	8	0
4-ClC_6H_4	MCPBA (4.4)	CH_2Cl_2 (reflux)	7	66	3	0	24

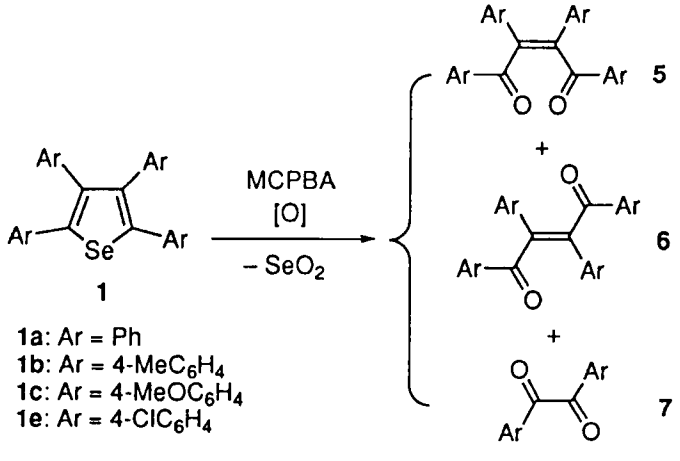
a) Na_2CO_3 as the additive. b) Methyltrioctylammonium chloride was used as the phase transfer agent. c) r. t. stands for room temperature.

which gave the selenophene 1,1-dioxide **2a** in high yield and also to the MCPBA oxidation of tetraphenylthiophene which affords the corresponding 1,1-dioxide **4** nearly quantitatively.[21]

In order to examine the generality of this oxidation, some other tetraarylselenophenes were oxidized with 4.4 molar amounts of MCPBA. Results, summarized in Table V, show that the formation of (E)-1,2,3,4—tetraaryl-2-butene-1,4-diones (**5**) in general (the *Z*-isomers **6** are also formed along with benzils **7** in small amounts) and that the oxidation is decelerated by an electron-withdrawing substituent on the benzene ring. Oxidation of 2,5-dimethyl-3,4-diphenylselenophene (**1f**) with 4.4 molar amounts of MCPBA gave a complex mixture from which an unknown crystalline product was isolated. 2,5-Dibenzoylselenophene (**1i**), deactivated by electron-withdrawing benzoyl groups, was inert to MCPBA oxidation.

A competition study revealed that **1a** was oxidized by MCPBA much faster than tetraphenylthiophene; oxidation of a 1 : 1 mixture of **1a** (0.5 mmol) and tetraphenylthiophene (0.5 mmol) with MCPBA (0.5 mmol) at room temperature gave only oxidation products derived from **1a**.

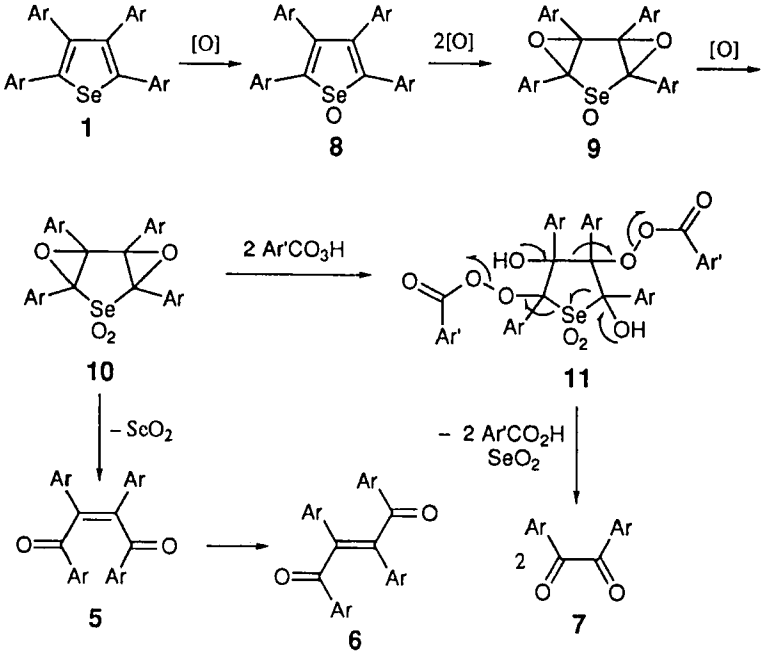
The mechanism of the MCPBA oxidation is not fully understood: one of the tentative mechanisms, which is based mainly on the fact that the oxidation of **1** to the final products **5** requires at least 4 molar amounts of MCPBA, is given below. The first oxidation of **1** will take place on the selenium atom to give the selenoxides **8** as the oxidation with DMD did. However, further oxidation with MCPBA would occur at the carbon-carbon double bonds, in contrast to the oxidation with DMD, to give the bis-epoxides **9**. If the subsequent oxidation of



SCHEME 2

8 takes place on the selenium atom, the corresponding selenophene 1,1-dioxides should be isolated because a separate experiment revealed that the selenophene 1,1-dioxide **2a** was inert to MCPBA oxidation and also did not decompose under the conditions of MCPBA oxidation. Further oxidation of **9** would give rise to the epoxyselenones **10**. Extrusion of SeO_2 from **10** affords *Z*-1,2-diaroyl-1,2-diarylethylenes **5**, which will partly isomerize to the *E*-isomers **6** during the oxidation or workup. Addition of two molecules of MCPBA to **10** followed by thermal decomposition of the resulting adducts **11** would lead to benzils **7** along with SeO_2 and *m*-chlorobenzoic acid.

Finally the oxidation of benzo[*b*]selenophene (**1h**) with an equimolar amount of MCPBA afforded benzo[*b*]selenophene 1-oxide (**3**) in 50–60% yield in harmony with the oxidation with an equimolar amount of DMD. This is the only instance that the selenium atom of selenophenes could be retained by oxidation with MCPBA. The oxidation of **1h** with 2 molar amounts of MCPBA gave a complex mixture from which no products could be isolated in pure form.



SCHEME 3

Other oxidizing agents such as $NaIO_4$ and alkaline hydrogen peroxide were inert to **1a**, whereas Oxone® afforded **5a** in 30% yield with recovery of **1a** in 63% yield.

In conclusion, the oxidation of selenophenes with DMD affords the corresponding selenophene 1,1-dioxides in good yields, whereas the oxidation with other reagents such as MCPBA does not give the selenium-containing products except in case of the benzoselenophene **1h**. The selenophene 1,1-dioxide synthesis developed here may contribute to open a new fruitful field in heterocyclic and heteroatom chemistry. Continuing effort to isolate thermally labile selenophene 1-oxide intermediates in pure form is under way in our laboratories.

EXPERIMENTAL

Melting points were determined on a MEL-TEMP capillary tube apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were determined on a Bruker AM-400 spectrometer, a Bruker ARX-400 (at 400 MHz for ^1H and 100 MHz for ^{13}C), or on a Bruker AC-200 spectrometer (at 200 MHz for ^1H and 50 MHz for ^{13}C). ^{77}Se NMR spectra were determined on a Bruker AM-400 spectrometer (76 MHz) with D_2SeO_3 as the external standard. $CDCl_3$ was used as the NMR solvent throughout this work. Mass spectra were obtained at 70 eV in the EI mode on a JEOL JMS-DX303 or a Shimadzu QP-1000 spectrometer. IR spectra were taken with KBr disks on a Hitachi Model 270-50 or a Perkin Elmer System 2000 FT-IR spectrophotometer and UV-Vis spectra on a Shimadzu UV-160A or JASCO V-560 spectrophotometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. Column chromatography was performed with Merck Kieselgel 60 (70–230 mesh).

An acetone solution of dimethyldioxirane (DMD) was prepared according to the literature method and its concentration was determined prior to use by oxidation of thioanisole to its sulfoxide with this reagent.[14] *m*-Chloroperbenzoic acid (MCPBA) was purchased from Tokyo Kasei and purified prior to use by washing with a buffer solution and then water. Oxone® was used as purchased. Tetraphenyl-, tetra-4-tolyl-, tetrakis(4-methoxyphenyl)-, tetra-2-thienyl-, and tetrakis(4-chlorophenyl)selenophenes (**1a–1e**),[9] 2,5-dimethyl-3,4-diphenyl- and 2,4-di-*t*-butylselenophenes (**1f** and **1g**),[10] benzo[*b*]selenophene (**1h**),[22] 2,5-dibenzoylselenophene (**1i**),[11] and dimethyl selenophene-2,5-dicarboxylate (**1j**)[12] were prepared according to literature methods. Throughout this study, CH_2Cl_2 used as solvent is freed of methanol.

*Oxidation of Tetraphenylselenophene (**1a**)*

1) Oxidation with DMD.

a) With 2 Molar Amounts. To a stirred and ice-cooled solution of **1a** (67.9 mg, 0.16 mmol) in acetone (5 ml) containing molecular sieves (Zeolite, synthetic, A-4, beads, 8–12 mesh) was added an acetone solution of DMD (3.4 ml, 0.34 mmol). After being stirred for 1 h at 0 °C, the mixture was evaporated under reduced pressure. The resulting crystalline residue was dissolved in CH_2Cl_2, dried over $MgSO_4$, and evaporated to leave 70.8 mg (97%) of practically pure tetraphenylselenophene 1,1-dioxide (**2a**): mp (dec) > 148 °C; yellow needles (CH_2Cl_2/hexane); ^1H NMR (200 MHz) δ = 6.90–6.95 (m, 4H), 7.12–7.35 (m, 12H), 7.45–7.50 (m, 4H); ^{13}C NMR (50 MHz) δ = 127.5, 128.7, 129.0, 129.4, 129.5, 130.3, 132.1, 137.8, 140.0; ^{77}Se NMR (76 MHz) δ = 1036; IR 876, 937 cm^{-1} (SeO_2); MS *m/z* 468, 466 (M^+), 436, 434, 372; UV (CH_3CN) λ_{max} (ε) 326 (8100), 373 nm (6600). Anal. Calcd for $C_{28}H_{20}O_2Se$: C, 71.95; H, 4.31. Found: C, 71.90; H, 4.28. *b) Synthesis of **2a** in Large Quantities.* Oxone® (31.0 g, 50 mmol) was added in small portions over a period of 2 h to a vigorously stirred mixture of **1a** (4.35 g, 10 mmol), $NaHCO_3$ (14.5 g, 173 mmol), CH_2Cl_2 (40 ml), acetone (40 ml), and water (40 ml) at room temperature. After being stirred for 3 h at room temperature, the mixture was diluted with CH_2Cl_2 (300 ml) and the insoluble materials were removed by filtration. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to leave 4.63 g (99%) of practically pure **2a**, mp (dec) > 148 °C.

2) Oxidation of 1a with m-Chloroperbenzoic Acid (MCPBA)

a) With 4.4 Molar Amounts of MCPBA at Room Temperature. To a stirred and ice-cooled solution of **1a** (435 mg, 1 mmol) in CH_2Cl_2 (5 ml) was added a solution of MCPBA (759 mg, 4.4 mmol) in CH_2Cl_2 (15 ml) over a period of 15 min. After the mixture had been stirred at room temperature for 27 h, CH_2Cl_2 (75 ml) was added to dissolve the crystalline precipitate of *m*-chlorobenzoic acid. The mixture was washed with aqueous $NaHSO_3$ and $NaHCO_3$ solutions and then with water, dried over Na_2SO_4, and evaporated. The resulting solid residue was chromatographed on a column of silica gel. Elution with benzene gave **1a** (62 mg, 14%), benzil (**7a**) (14 mg, 3%), mp 94–95 °C, (*E*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**6a**) (8 mg, 2%), mp 232–233°C (lit.,[23] mp 232–234 °C), and (*Z*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**5a**) (269 mg, 69%), mp 215–217.5 °C (lit.,[24] mp 216–217 °C); ^{13}C NMR (100 MHz) δ = 128.2, 128.3, 128.6, 129.8, 130.0, 132.9, 135.2, 136.3, 144.5, 196.9, in this order. Oxidation of **1a** (435 mg, 1 mmol) with 4.4 molar amounts of MCPBA, extrac-

tion of the mixture with water, and evaporation of the water under reduced pressure gave 86 mg (67%) of H_2SeO_3 whose ^{77}Se NMR spectrum showed a singlet at δ 1282; a D_2O solution of commercial SeO_2 also showed a singlet at δ 1282. *b) Oxidation of* ***1a*** *(435 mg) with 4.4 molar amounts of MCPBA in refluxing* CH_2Cl_2 for 12 h gave **1a** (69 mg, 16%), **7a** (10 mg, 2%), **6a** (8 mg, 2%), and **5a** (280 mg, 72%). *c) Oxidation of* ***1a*** *(435 mg) with 2.2 molar amounts of MCPBA at room temperature* for 50 h gave **1a** (227 mg, 52%), **7a** (1 mg, 0.3%), **6a** (10 mg, 3%), and **5a** (162 mg, 42%). *d) Oxidation of* ***1a*** *(435 mg) with 2.2 molar amounts of MCPBA in refluxing* CH_2Cl_2 for 30 h gave **1a** (233 mg, 53%), **7a** (5 mg, 1%), **6a** (10 mg, 3%), and **5a** (150 mg, 39%). *e) Oxidation of* ***1a*** *(435 mg) with 1.8 molar amounts of MCPBA in the presence of* $NaHCO_3$ at room temperature for 50 h gave **1a** (288 mg, 66%), **7a** (5 mg, 1%), **6a** (7 mg, 2%), and **5a** (102 mg, 26%).

3) Oxidation of 1a with Oxone®

A mixture of **1a** (435 mg, 1 mmol), Oxone® (1.85 g, 3 mmol), C_6H_6 (20 ml), water (10 ml), and methyltrioctylammonium chloride (60 mg) was refluxed for 40 h. The resulting mixture was purified by silica-gel column chromatography to give **1a** (274 mg, 63%) and **5a** (118 mg, 30%) contaminated with a trace amount of **6a**.

4) Competitive Oxidation of 1a and Tetraphenylthiophene

A mixture of **1a** (212 mg, 0.5 mmol), tetraphenylthiophene (191 mg, 0.5 mmol), MCPBA (86 mg, 0.5 mmol) in CH_2Cl_2 (40 ml) was stirred for 27 h at room temperature. Workup of the mixture with silica-gel column chromatography gave 350 mg of a mixture of **1a** and tetraphenylthiophene (**1a** and tetraphenylthiophene are not separable even by use of HPLC) and 47 mg (24%) of **5a**. Formation of any other products was not detected.

Oxidation of Tetra-p-tolylselenophene (1b)

a) With DMD. Selenophene **1b** (143 mg, 0.29 mmol) was oxidized with DMD (0.68 mmol) in acetone (21 ml) at 0 °C for 2 h and then at room temperature for 5 h. Purification of the mixture with silica-gel column chromatography gave 136 mg (89%) of tetra-*p*-tolylselenophene 1,1-dioxide (**2b**): mp (dec) > 145 °C; yellow needles (CH_2Cl_2/hexane); ^1H NMR (200 MHz) δ = 2.28 (s, 6H), 2.31 (s, 6H), 6.79 (d, J = 8.0 Hz, 4H), 7.00 (d, J = 8.0 Hz, 4H), 7.09 (d, J = 8.0 Hz, 4H), 7.35 (d, J = 8.0 Hz, 4H); ^{13}C NMR (50 MHz) δ = 21.3, 21.5, 124.9,

129.3, 129.4, 129.7, 137.2, 138.8, 138.9, 139.6, 140.5; ^{77}Se NMR (76 MHz) δ = 1035; IR 875, 933 cm^{-1} (SeO_2); MS *m/z* 491, 428; UV (CH_3CN) λ_{max} (ε) 341 nm (11800). Anal. Calcd for $C_{32}H_{28}O_2Se$: C, 73,42; H, 5.39. Found: C, 73.14; H, 5.40. *b) With MCPBA.* Selenophene **1b** (245 mg, 0.5 mmol) was oxidized with MCPBA (385 mg, 2.2 mmol) in CH_2Cl_2 (30 ml) at room temperature for 5 h. Purification of the mixture with silica-gel column chromatography gave **1b** (25 mg, 10%), 4,4′-dimethylbenzil (**7b**) (24 mg, 10%), mp 104–105 °C, and (*Z*)-1,2,3,4-tetrakis(4-methylphenyl)-2-butene-1,4-dione (**5b**) (146 mg, 65%), mp 187–189 °C (lit.,[25] mp 180 °C).

Oxidation of Tetrakis(4-methoxyphenyl)selenophene (1c)

a) With DMD. Selenophene **1c** (70 mg, 0.13 mmol) was oxidized with DMD (0.27 mmol) in a mixture of acetone (10 ml) and CH_2Cl_2 (7 ml) at 0 °C for 2 h to give 74 mg (99%) of tetrakis(4-methoxyphenyl)selenophene 1,1-dioxide (**2c**): mp (dec) > 145 °C; orange needles (CH_2Cl_2/hexane); ^{1}H NMR (200 MHz) δ = 3.74 (s, 6H), 3.77 (s, 6H), 6.68–6.82 (m, 12H), 7,41 (d, *J* = 8.9 Hz, 4H); ^{13}C NMR (50 MHz) δ = 55.0, 55.2, 114.1, 114.5, 120.2, 124.3, 131.0, 136.2, 138.3, 159.8, 160.7; ^{77}Se NMR (76 MHz) δ = 1035; IR 900, 933 cm^{-1} (SeO_2); MS *m/z* 556, 554 (M^+-2O), 482; UV (CH_3CN) λ_{max} (ε) 336 (8900), 381 nm (9400). Anal. Calcd for $C_{32}H_{28}O_6Se$: C, 65.42; H, 4.80. Found: C, 65.60; H, 4.85. *b) With MCPBA.* Selenophene **1c** (280 mg, 0.5 mmol) was oxidized with MCPBA (385 mg, 2.2 mmol) in CH_2Cl_2 (30 ml) at room temperature for 2 h. Purification of the mixture with silica-gel column chromatography gave 4,4′-dimethoxybenzil (**7c**) (22 mg, 8%), mp 131–132 °C, and (*Z*)-1,2,3,4-tetrakis(4-methoxyphenyl)-2-butene-1,4-dione (**5c**) (216 mg, 84%), mp 185.5–187 °C (lit.,[26] mp 183–184 °C).

Oxidation of Tetrakis(4-chlorophenyl)selenophene (1e)

a) With DMD. Selenophene **1e** (144 mg, 0.25 mmol) was oxidized with DMD (0.54 mmol) in a mixture of acetone (10 ml) and CH_2Cl_2 (90 ml) at room temperature for 38 h. Purification of the mixture by silica-gel column chromatography with CH_2Cl_2/hexane (7/3) as the eluent gave 22 mg (15%) of **1e** and 105 mg (69%) of tetrakis(4-chlorophenyl)selenophene 1,1-dioxide (**2e**): mp (dec) > 155 °C; yellow needles (CH_2Cl_2/hexane); ^{1}H NMR (200 MHz) δ = 6.84 (d, *J* = 8.5 Hz, 4H), 7.22 (d, *J* = 8.5 Hz, 4H), 7.27 (d, *J* = 8.8 Hz, 4H), 7,34 (d, *J* = 8.8 Hz, 4H); ^{13}C NMR (50 MHz) δ = 125.4, 129.5, 129.7, 130.7, 136.1, 137.2, 137.6, 138.8; ^{77}Se NMR (76 MHz) δ = 1032; IR 909, 938 cm^{-1}

(SeO_2); MS *m/z* 577, 575, 573 (M^+-2O), 512, 510, 508; UV (CH_3CN) λ_{max} (ϵ) 337 (12700), 377 nm (11200, sh). Anal. Calcd for $C_{28}H_{16}Cl_4O_2Se$: C, 55.57; H, 2.67. Found: C, 55.56; H, 2.69. *b) With MCPBA.* Oxidation of **1e** (287 mg, 0.5 mmol) with MCPBA (385 mg, 2.2 mmol) was done by heating in refluxing CH_2Cl_2 (45 ml) for 7 h. Purification of the mixture with silica-gel column chromatography with CCl_4 as the eluent gave **1e** (24 mg, 24%), (*E*)-1,2,3,4-tetrakis(4-chlorophenyl)-2-butene-1,4-dione (**6e**) (8 mg, 3%), and (*Z*)-1,2,3,4-tetrakis(4-chlorophenyl)-2-butene-1,4-dione (**5e**) (174 mg, 66%). **6e**: mp 195.0–196.5°C (hexane); ^1H NMR (400 MHz) δ = 7.16 (d, *J* = 8.6 Hz, 4H), 7.32 (d, *J* = 8.6 Hz, 4H), 7.33 (d, *J* = 8.6 Hz, 4H), 7.84 (d, *J* = 8.6 Hz, 4H); ^{13}C NMR (100 MHz) δ = 129.1 (d), 129.2 (d), 129.8 (d), 131.0 (d), 132.9 (s), 133.7 (s), 135.3 (s), 140.2 (s), 140.7 (s), 194.9 (s); HRMS Found: *m/z* 525.9893. Calcd for $C_{28}H_{16}{}^{35}Cl_3{}^{37}ClO_2$: M^+, 525.9876. **5e**: mp 174.5–175.0 (hexane); ^1H NMR (400 MHz) δ = 7.06 (d, *J* = 8.5 Hz, 4H), 7.20 (d, *J* = 8.5 Hz, 4H), 7.31 (d, *J* = 8.5 Hz, 4H), 7.72 (d, *J* = 8.5 Hz, 4H); ^{13}C NMR (100 MHz) δ = 128.9 (d), 129.4 (d), 130.9 (d), 131.3 (d), 132.8 (s), 134.2 (s), 135.2 (s), 139.9 (s), 143.7 (s), 195.1 (s); IR 1659 cm^{-1} (C=O). Anal. Calcd for $C_{28}H_{16}Cl_4O_2$: C, 63.91; H, 3.04. Found: C, 63.57; H, 3.25.

Oxidation of 2,5-Dimethyl-3,4-diphenylselenophene (1f) with DMD

Selenophene **1f** (94 mg, 0.3 mmol) was oxidized with DMD (0.66 mmol) in acetone (24 ml) at 0°C for 5 h gave 100 mg (97%) of 2,5-dimethyl-3,4-diphenylselenophene 1,1-dioxide (**2f**): mp (dec) > 155°C; colorless needles (CH_2Cl_2/hexane); ^1H NMR (200 MHz) δ = 2.32 (s, 6H), 6.86–6.90 (m, 4H), 7.22–7.28 (m, 6H); ^{13}C NMR (50 MHz) δ = 10.9, 128.4, 128.9, 129.0, 131.2, 135.8, 141.0; ^{77}Se NMR (76 MHz) δ = 1042; IR 880, 928 cm^{-1} (SeO_2); MS *m/z* 312, 310 (M^+-2O), 248; UV (CH_3CN) λ_{max} (ϵ) 292 nm (4600). Anal. Calcd for $C_{18}H_{16}O_2Se$: C, 63.00; H, 4.70. Found: C, 62.97; H, 4.72.

Oxidation of 2,4-Di-t-butylselenophene (1g) with DMD

Selenophene **1g** (86 mg, 0.35 mmol) was oxidized with DMD (0.81 mmol) in acetone (15 ml) at room temperature for 3 h gave 94 mg (97%) of 2,4-di-*t*-butylselenophene 1,1-dioxide (**2g**): mp (dec) > 152°C; colorless needles (CH_2Cl_2/hexane); ^1H NMR (200 MHz) δ = 1.22 (s, 9H), 1.63 (s, 9H), 6.55 (s, 1H), 6.69 (s, 1H); ^{13}C NMR (50 MHz) δ = 27.4, 29.3, 35.0, 36.5, 119.4, 121.3, 155.7, 158.1; ^{77}Se NMR (76 MHz) δ = 1054; IR 877, 932 cm^{-1} (SeO_2); MS

m/z 244, 242 (M^+-2O), 180; UV (CH_3CN) λ_{max} (ϵ) 244 (3500), 294 nm (1800). Anal. Calcd for $C_{12}H_{20}O_2Se$: C, 52.36; H, 7.32. Found: C, 52.51; H, 7.39.

Oxidation of Benzo[b]selenophene (1h)

a) With 1 Molar Amount of DMD. Selenophene **1h** (104 mg, 0.58 mmol) was oxidized with DMD (0.64 mmol) in acetone (11 ml) at 0°C for 2 h gave 100 mg (88%) of benzo[*b*]selenophene 1-oxide (**3**): mp (dec) > 76°C; colorless needles (acetone); ^{1}H NMR (400 MHz) δ = 7.40 (d, *J* = 6.4 Hz, 1H), 7.49 (d, *J* = 6.4 Hz, 1H), 7.43–7.56 (m, 3H), 7.88 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (50 MHz) δ = 126.4 (d), 128.0 (d), 130.0 (d), 132.1 (d), 138.5 (d), 140.8 (d), 141.5 (s), 146.4 (s); ^{77}Se NMR (76 MHz) δ = 943; IR 780 cm^{-1} (SeO); MS *m/z* 182, 180 (M^+-O). Anal. Calcd for C_8H_6OSe: C, 48.75; H, 3.08. Found: C, 48.56; H, 3.02. Stirring a two phase mixture of a CH_2Cl_2 solution of **3** and an aqueous $NaHSO_3$ solution for a few minutes resulted in the quantitative reduction of **3** to **1h**. *b) With 2 Molar Amounts of DMD.* Selenophene **1h** (108 mg, 0.59 mmol) oxidized with DMD (1.3 mmol) in acetone (42 ml) at 0°C for 12 h and then at room temperature for 17 h gave 90 mg (71%) of benzo[*b*]selenophene 1,1-dioxide (**2h**): mp (dec) > 135°C; yellow prisms ($CHCl_3$); ^{1}H NMR (400 MHz) δ = 7.21 (d, *J* = 6.6 Hz, 1H), 7.52–7.54 (m, 1H), 7.70–7.72 (m, 2H), 7.73 (dd, *J* = 6.5/0.8 Hz, 1H), 7.91–7.93 (m, 1H); ^{13}C NMR (50 MHz) δ = 125.1, 127.7, 129.7, 131.1, 132.9, 134.9, 135.5, 135.8; ^{77}Se NMR (76 MHz) δ = 1018; IR 880, 927 cm^{-1} (SeO_2); MS *m/z* 182, 180 (M^+-2O), 170, 168, 118. Anal. Calcd for $C_8H_6O_2Se$: C, 45.09; H, 2.84. Found: C, 45.09; H, 2.75. *c) With 1.5 Molar Amount of MCPBA.* A mixture of selenophene **1h** (198 mg, 1.1 mmol) and MCPBA (270 mg, 1.6 mmol) in CH_2Cl_2 (15 ml) was stirred at 0°C for 1 h. The resulting mixture was washed with 2*M* NaOH (8 ml) and a small amount of water and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure and washing with hexane gave 159 mg (70%) of practically pure **2h**, recrystallization of which from CH_2Cl_2/hexane gave an analytically pure sample, mp (dec) > 76°C.

Oxidation of 2,5-Dibenzoylselenophene (1i) and Dimethyl Selenophene-2,5-dicarboxylate (1j)

A solution of **1i** (100 mg, 0.3 mmol) and DMD (0.72 mmol) in acetone (22 ml) was stirred at 0 °C for 2 h. Although analysis of the mixture by tlc revealed complete consumption of the starting material, attempted purification of the mixture at room temperature resulted in decomposition of the products to give **1i**

as the sole identifiable product in 40% yield. Oxidation of **1j** with DMD is sluggish at room temperature, though exess DMD was used, and did not give any identifiable products except the starting material (52%).

X-Ray Single-Crystal Structure Analysis of 2a

A yellow crystal of **2a** was mounted on a Mac Science DIP3000 diffractometer with a graphite monochrometer. Oscillation and nonscreen Weissenburg photographs were recorded on the imaging plates of the diffractometer by using Mo $K\alpha$ radiation and the data collection was made by the MAC-DENZO program system. Cell parameters were determined and refined by using the MAC-DENZO for all observed reflections. The structure was solved by direct methods using SIR[27] in the CRYSTAN-GM program system. The atomic coordinates and anisotropic thermal parameters of the non-H atoms were refined by full-matrix least squares[28] to minimize the functions, $\Sigma(|Fo| - |Fo|)^2$, for 3519 reflections with $|Fo| > 3\sigma(|Fo|)$. Structure determination and refinements were made by using the CRYSTAN-GM program system. All the calculations were carried out on a SUN SPARC 10 workstation.

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