First Synthesis of Selenophene 1,1-Dioxides

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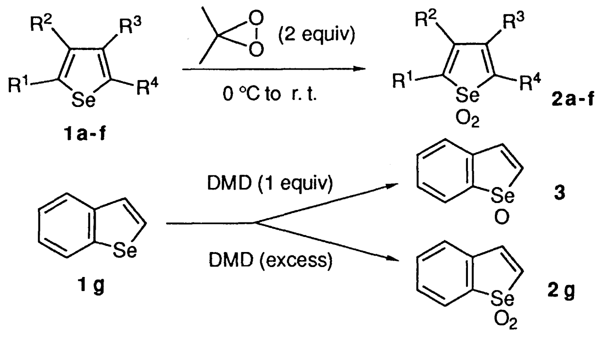
Oxidation of four tetraarylselenophenes, 2,5-dimethyl-3,4-diphenylselenophene, 2,4-di-*t*-butylselenophene, and benzo[*b*]selenophene with dimethyldioxirane produces the corresponding selenophene 1,1-dioxides in high yields.



Thiophene 1,1-dioxides are compounds of great importance both from synthetic and mechanistic points of view.[1] They act either as a 2π- or a 4π-component 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 reactions with nucleophiles.[3] Keeping this background in mind, the chemistry of selenophene 1,1-dioxides is expected to provide a new fruitful field of heterocyclic and heteroatom chemistry. Nevertheless, no successful synthesis of selenophene 1,1-dioxides has been reported. The most straightforward way to selenophene 1,1-dioxides apparently involves the oxidation of the corresponding selenophenes. However, no detailed study on the oxidation of selenophenes had appeared. To our knowledge, peracetic acid[4] and electrochemical[5] oxidations of dibenzoselenophene which afford dibenzoselenophene 5-oxide had been the only examples of oxidation of selenophenes until we have recently reported the oxidation of a series of selenophenes with *m*-chloroperbenzoic acid (m-CPBA).[6] However, this oxidation failed to give the corresponding selenophene 1,1-dioxides and led to the formation of oxidation products having no selenium atoms, which resulted from the opening of the selenophene ring. Thus, for example, oxidation of tetraarylselenophenes with m-CPBA gives *cis*-1,2-diaroyl-1,2-diarylethylenes as the principal product along with *trans*-1,2-diaroyl-1,2-diarylethylenes and diaroyls in small amounts.[6] Oxidation of benzo[*b*]selenophene was the only case to give the selenium-retained product, benzo[*b*]selenophene 1-oxide. Here we report the first synthesis of selenophene 1,1-dioxides by oxidation of the corresponding selenophenes with dimethyldioxirane (DMD)[7] and their characterization.

Treatment of tetraphenylselenophene **1a**[8] with 2.2 equiv. of DMD in acetone at 0 °C for 1 h afforded tetraphenylselenophene 1,1-dioxide **2a** in 97% yield. Similarly, oxidation of tetraarylselenophenes such as tetra-*p*-tolyl-, tetra-*p*-anisyl- and tetrakis-*p*-chlorophenylselenophenes **1b-d**[8] with 2.2 equiv. of DMD gave the corresponding selenophene 1,1-dioxides **2b-d** in good yields (Table 1). Oxidation of 2,5-dimethyl-3,4-diphenyl- and 2,4-di-*t*-butylselenophenes, **1e** and **1f**,[9] also proceeded cleanly to give the corresponding selenophene 1,1-dioxides, **2e** and **2f**, respectively, in high yields.

Oxidation of all of the selenophenes described above with an equimolar amount of DMD 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

Table 1. Preparation of selenophene 1,1-dioxides **2** by oxidation of the corresponding selenophenes **1** with dimethyldioxirane (DMD)[a]

Selenophene 1,1-dioxides	R^1	R^2	R^3	R^4	Yields (%)	M.p.(°C)[b] (decomp.)	δ (^{77}Se)[c] (ppm)	ν (SeO_2)[d] (cm^{-1})
2a	C_6H_5	C_6H_5	C_6H_5	C_6H_5	97	>148	1036	876, 937
2b	4-MeC_6H_4	4-MeC_6H_4	4-MeC_6H_4	4-MeC_6H_4	89	>145	1035	875, 933
2c	4-MeOC_6H_4	4-MeOC_6H_4	4-MeOC_6H_4	4-MeOC_6H_4	99	>140	1035	900, 933
2d	4-ClC_6H_4	4-ClC_6H_4	4-ClC_6H_4	4-ClC_6H_4	69	>155	1032	909, 938
2e	Me	C_6H_5	C_6H_5	Me	97	>155	1042	880, 928
2f	*t*-Bu	H	*t*-Bu	H	97	>152	1054	877, 932
2g	-CH=CH-CH=CH-		H	H	71	>135	1018	880, 927

[a] All of **2** gave satisfactory elemental analysis results. [b] None of **2** show clear melting points, but they begin to decompose at the temperatures given here. [c] Determined with D_2SeO_3 (δ 1282) as the external standard for $CDCl_3$ solutions (76 MHz). [d] Taken for KBr disks.

nature. However, the oxidation of benzo[*b*]selenophene **1g** enabled us to isolate benzo[*b*]selenophene 1-oxide **3** in 88% yield in harmony with the fact that the oxidation of **1g** with m-CPBA allowed to isolate **3**.[6] Prolonged oxidation of **1g** with excess DMD gave the expected benzo[*b*]selenophene 1,1-dioxide **2g** in 71% yield.

Structure of **2a-g** was determined spectroscopically (^{1}H, ^{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** resonated at δ 1036 with D_2SeO_3 as the external standard, while that of **1a** appeared at a much higher field of δ 605. ^{77}Se NMR signals of other selenophene 1,1-dioxides **2b-g** appear in the range of δ 1018-1054 (Table 1). Reportedly, alkyl phenyl selenones and dialkyl selenones exhibit a ^{77}Se NMR signal in the range of δ 980-1040.[10] The dioxide **2a** is 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, λ_{max} (log ε) (CH_3CN) 310 (3.8), 371 nm (3.7). In the IR spectra, characteristic absorptions of the $-SeO_2-$ moiety of **2** appear as two signals in the ranges 875-909 and 927-938 cm^{-1} (Table 1). It is known that a selenone group shows a characteristic IR absorption in the ranges of 860-970 and 912-1059 cm^{-1}.[11] In the mass spectrum of **2a**, the most intense

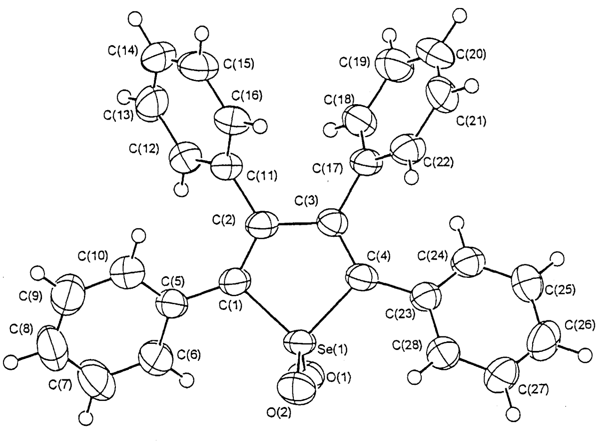


Figure 1. Molecular structure of **2a** showing atom labelling. Bond lengths (Å): Se(1)-O(1) 1.614(3), Se(1)-O(2) 1.603(3), Se(1)-C(1) 1.920(4), C(1)-C(2) 1.354(5), C(2)-C(3) 1.516(5), C(3)-C(4) 1.345(5), C(4)-Se(1) 1.930(4); bond angles (°): O(1)-Se(1)-O(2) 114.9(2), O(1)-Se(1)-C(1) 112.4(2), O(1)-Se(1)-C(4) 109.0(2), O(2)-Se(1)-C(1) 112.1(2), O(2)-Se(1)-C(4) 115.0(2), C(1)-Se(1)-C(4) 91.1(2), Se(1)-C(1)-C(2) 107.2(3), C(1)-C(2)-C(3) 117.2(4), C(2)-C(3)-C(4) 117.1(4), Se(1)-C(4)-C(3) 107.3(3); torsion angles (°): C(4)-Se(1)-C(1)-C(2) 2.5(3), Se(1)-C(1)-C(2)-C(3) –1.8(3), C(1)-C(2)-C(3)-C(4) –0.3(4), C(2)-C(3)-C(4)-Se(1) 2.2(3), C(1)-Se(1)-C(4)-C(3) –2.6(3), Se(1)-C(1)-C(5)-C(6) –34.6(4), C(1)-C(2)-C(11)-C(12) –54.1(5), C(2)-C(3)-C(17)-C(18) –58.8(5), C(3)-C(4)-C(23)-C(24) –28.3(5).

peak was observed at *m/z* 372, which results 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. In accordance with this observation, thermolysis of **2a** in refluxing toluene gave tetraphenylfuran in 85% yield.

Recrystallization of **2a** from CCl_4/CH_2Cl_2 formed an inclusion complex with CCl_4, while recrystallization from CH_2Cl_2/hexane gave the solvent-free crystals. X-Ray single crystal structure analyses were performed both for the inclusion complex and for the solvent free crystals. Figure 1 gives an ORTEP drawing obtained with the solvent-free crystal.[12] The five-membered ring of **2a** is nearly planar, but the bond length data (C1-C2 1.354 Å, C3-C4 1.345 Å, and C2-C3 1.516 Å) reveal that bond fixing was brought about by loss of aromaticity. All of the phenyl groups are not coplanar to the five-membered ring and exist in a propeller like conformation. The O-Se-O bond angle is 114.9° and bisected by the plain of the five-membered ring.

References and Notes

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12 Crystal data for **2a**: $C_{28}H_{20}O_2Se$; M = 467.43, triclinic, $P\bar{1}$ (No. 2), a = 10.232(2), b = 10.234(3), c = 12.106(2) Å, α = 87.74(4), β = 74.41(3), γ = 64.29(5) °, V = 1095.7(6) Å^3, Z = 2, D_c = 1.42 g cm^{-3}, μ = 1.717 mm^{-1}, crystal dimensions 0.2 x 0.2 x 0.1 mm, Mo-$K\alpha$ (λ = 0.71073 Å), $R(R_w)$ = 0.0486 (0.0673) for 5214 unique reflections.