

Oxidation of Tetraarylselenophenes and Benzo[*b*]selenophene with *m*-Chloroperbenzoic Acid

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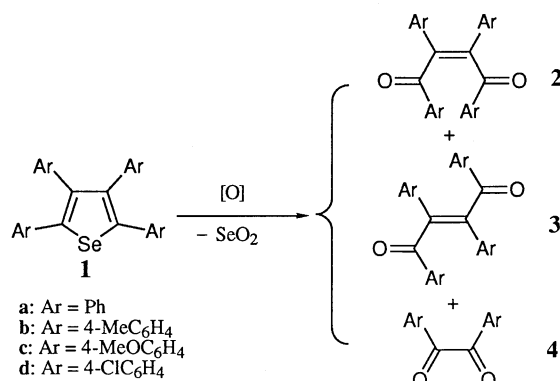
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Oxidation of tetraarylselenophenes with *m*-chloroperbenzoic acid produces *cis*-1,2-diaroyl-1,2-diarylethylenes and SeO<sub>2</sub> as the principal product, while the oxidation of benzo[*b*]selenophene affords benzo[*b*]selenophene 1-oxide.

It is well documented that peracid oxidation of thiophenes produces the corresponding thiophene 1,1-dioxides as the final product, even though, in some cases, products arising from dimerization of the thiophene 1-oxide intermediates may form.<sup>1,2</sup> Meanwhile, oxidation of selenophenes has been scarcely investigated; the only one report is concerned with the formation of dibenzoselenophene 1-oxide on oxidation of dibenzoselenophene with peracetic acid.<sup>3</sup> We report here the preliminary results on oxidation of tetraarylselenophenes and benzo[*b*]selenophene with *m*-chloroperbenzoic acid (MCPBA).

Tetraarylselenophenes, which had become readily obtainable<sup>4</sup> and are expected to give crystalline products on oxidation, were chosen as the substrate in the present study. Thus, oxidation of tetraphenylselenophene (**1a**) with 2.2 equivolar amounts of MCPBA in CH<sub>2</sub>Cl<sub>2</sub> at room temperature gave *cis*-1,2-dibenzoyl-1,2-diphenylethylene (**2a**) (42%), *trans*-1,2-dibenzoyl-1,2-diphenylethylene (**3a**) (3%), and benzil (**4a**) (0.3%) with 52% recovery of **1a**. The oxidation with the same amount of MCPBA in refluxing CH<sub>2</sub>Cl<sub>2</sub> also produced **2a** (39%), **3a** (3%), and **4a** (1%) with 53% recovery of **1a**. The oxidation in the presence of Na<sub>2</sub>CO<sub>3</sub> gave a similar result. The oxidation with 4.4 equivolar amounts of MCPBA at room temperature raised the yield of **2a** to 69% with 14% recovery of **1a**. The oxidation in refluxing CH<sub>2</sub>Cl<sub>2</sub> also gave a similar result (Table 1). In all the experiments described above, no products retaining the selenium atom of **1a** was formed; aqueous workup of the mixture followed by <sup>77</sup>Se NMR analysis revealed that the selenium atom of **1a** was

transformed into SeO<sub>2</sub> on the oxidation.<sup>5</sup> These results are in marked contrast to the MCPBA oxidation of tetraphenylthiophene (**5**), which affords tetraphenylthiophene 1,1-dioxide nearly quantitatively.<sup>1c</sup>



In order to examine the generality of the reaction, some other tetraarylselenophenes were oxidized with 4.4 equivolar amounts of MCPBA. Results summarized in Table 1 show that the formation of *cis*-1,2-diaroyl-1,2-diarylethylenes (**2**) on oxidation is quite general (the *trans*-isomers **3** are formed along with benzils in small amounts) and that the oxidation is accelerated by an electron-donating substituent on the benzene ring; a separate experiment has shown that 2,5-dibenzoylselenophene deactivated by electron-withdrawing benzoyl groups is inert to MCPBA oxidation.

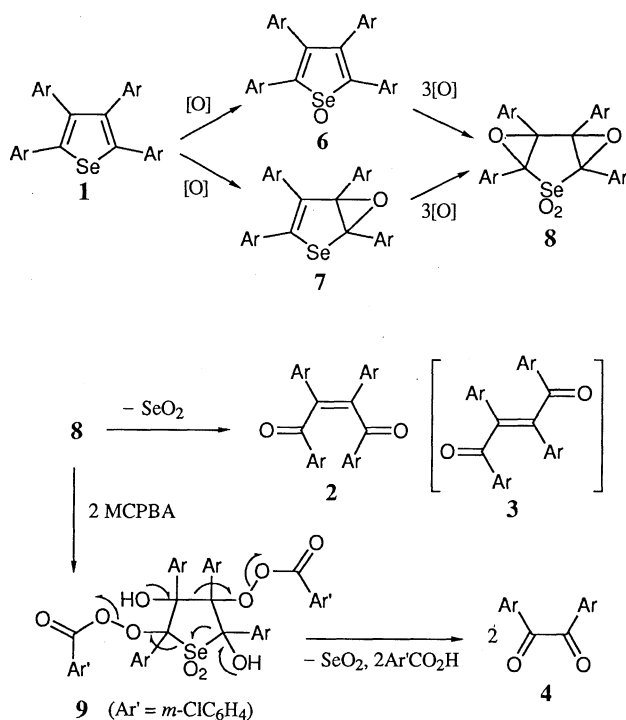
Table 1. Oxidation of tetraarylselenophenes (**1**) with *m*-chloroperbenzoic acid (OXONE®)

<b>1</b> (Ar)	Oxidizing Reagents (Equiv.)	Solvents (Temperature)	Time (h)	Products: Yield (%)			Recovery of <b>1</b> (%)
				<b>2</b>	<b>3</b>	<b>4</b>	
C <sub>6</sub> H <sub>5</sub>	MCPBA (2.2)	CH <sub>2</sub> Cl <sub>2</sub> (r. t.) <sup>c</sup>	50	42	3	0.3	52
C <sub>6</sub> H <sub>5</sub>	MCPBA (2.2)	CH <sub>2</sub> Cl <sub>2</sub> (reflux)	30	39	3	1	53
C <sub>6</sub> H <sub>5</sub>	MCPBA (1.8) <sup>a</sup>	CH <sub>2</sub> Cl <sub>2</sub> (r. t.)	50	26	(+)	(+)	66
C <sub>6</sub> H <sub>5</sub>	MCPBA (4.4)	CH <sub>2</sub> Cl <sub>2</sub> (r. t.)	27	69	2	3	14
C <sub>6</sub> H <sub>5</sub>	MCPBA (4.4)	CH <sub>2</sub> Cl <sub>2</sub> (reflux)	12	72	2	2	16
C <sub>6</sub> H <sub>5</sub>	OXONE® (3.0) <sup>b</sup>	C <sub>6</sub> H <sub>6</sub> /H <sub>2</sub> O (reflux)	40	30	(+)	(+)	63
4-MeC <sub>6</sub> H <sub>4</sub>	MCPBA (4.4)	CH <sub>2</sub> Cl <sub>2</sub> (r. t.)	5	65	0	10	10
4-MeOC <sub>6</sub> H <sub>4</sub>	MCPBA (4.4)	CH <sub>2</sub> Cl <sub>2</sub> (r. t.)	2	85	0	8	0
4-ClC <sub>6</sub> H <sub>4</sub>	MCPBA (4.4)	CH <sub>2</sub> Cl <sub>2</sub> (reflux)	7	66	3	0	24

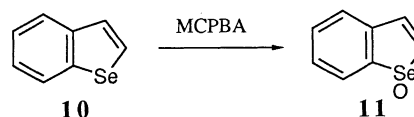
<sup>a</sup>Na<sub>2</sub>CO<sub>3</sub> as the additive. <sup>b</sup>Methyltriocetylammmonium chloride was used as the phase transfer agent. <sup>c</sup>r. t. stands for room temperature.

Competition study revealed that **1a** is oxidized much faster than tetraphenylthiophene (**5**); oxidation of an equimolar mixture of **1a** and **5** with an equimolar amount of MCPBA at room temperature gave only oxidation products of **1a**. Other oxidizing reagents such as NaIO<sub>4</sub> and alkaline hydrogen peroxide were inactive toward **1a**, whereas the oxidation with OXONE® (2KHSO<sub>5</sub>•KHSO<sub>4</sub>•K<sub>2</sub>SO<sub>4</sub>) afforded **2a** in 30% yield with 63% recovery of **1a**.

The mechanism of the present oxidation is not fully understood; one of tentative mechanisms, which is based on the fact that the oxidation of **1** to the final products (**2**, **3**, and **4**) would require at least 4 equimolar amounts of MCPBA, is given below. The first oxidation of **1** probably takes place on the selenium atom to give the selenoxides **6** (the oxidation might first give the epoxides **7**, though less possible). Further oxidation of **6** (or **7**) with three molecules of MCPBA would give rise to **8**. Extrusion of SeO<sub>2</sub> from **8** affords *cis*-1,2-diaroyl-1,2-diarylethylenes **2**, which may partly isomerize to the *trans*-isomers **3** during the oxidation or workup. Addition of two molecules of MCPBA to **8** followed by thermal decomposition of the resulting adducts would lead to benzils **4** along with SeO<sub>2</sub> and *m*-chlorobenzoic acid.



Finally oxidation of benzo[*b*]selenophene (**10**) with an equimolar amount of MCPBA affords the benzo[*b*]selenophene



1-oxide (**11**)<sup>6</sup> in 50-60% yield. This is the only compound that the selenium atom of selenophenes could be retained throughout the present oxidation study. The crystalline selenoxide **11** is soluble in aqueous NaOH probably because the hydrate of **11** behaves as a proton acid. The selenoxide is also rather thermally labile and thus heating **11** neat at its melting point gives **10** as the principal product.<sup>7</sup> Reduction of **11** to **10** is also readily attained by treatment with aqueous NaHSO<sub>3</sub>.

#### References and Notes

- a) S. Rajappa, "Comprehensive Heterocyclic Chemistry," ed by C. W. Bird and G. W. H. Cheeseman, Pergamon Press, Oxford, 1984, Vol. 4, Chap. 3.14; b) J. L. Melles and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **72**, 314 (1953); c) J. Nakayama, M. Kuroda, and M. Hoshino, *Heterocycles*, **24**, 1233 (1986); d) J. Nakayama, S. Yamaoka, and M. Hoshino, *Tetrahedron Lett.*, **29**, 1161 (1988); e) J. Nakayama and R. Hasemi, *J. Am. Chem. Soc.*, **112**, 5654 (1990).
- For the formation of 1,2-dibenzoyl ethylenes by oxidation of 2,5-diphenylthiophenes with other reagents, see: P. S. Bailey and H. H. Hwang, *J. Org. Chem.*, **50**, 1778 (1985); P. Pouzet, I. Erdelmeier, D. Ginderow, J. -P. Mornon, P. Dansette, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, **1995**, 473.
- J. D. McCullough, T. W. Campbell, and E. S. Gould, *J. Am. Chem. Soc.*, **72**, 5753 (1950).
- K. Sawada, K. S. Choi, M. Kuroda, T. Taniguchi, A. Ishii, M. Hoshino, and J. Nakayama, *Sulfur Lett.*, **15**, 273 (1993).
- After the reaction mixture was stirred with water, the aqueous layer was evaporated under reduced pressure to give the crystalline residue (67% yield as H<sub>2</sub>SeO<sub>3</sub>), which partially turned red on standing. <sup>77</sup>Se NMR of the residue in D<sub>2</sub>O showed the singlet at δ 1282 (a D<sub>2</sub>O solution of commercial SeO<sub>2</sub> also showed the singlet at δ 1282).
- 11**: mp 76-77 °C (dec); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 (1H, d, *J*=6.4 Hz), 7.49 (1H, d, *J*=6.4 Hz), 7.43-7.56 (3H, m), 7.88 (1H, d, *J*=7.6 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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); <sup>77</sup>Se NMR (76 MHz, CDCl<sub>3</sub>) δ 943; IR (KBr) 780 cm<sup>-1</sup> (Se-O); MS *m/z* 180, 182 (M<sup>+</sup>-O). Anal. Calcd for C<sub>8</sub>H<sub>6</sub>OSe: C, 48.75; H, 3.08. Found: C, 48.56; H, 3.02.
- Although disproportionation of **11** could explain the formation of **10**, no evidence for the formation of its counterpart, benzo[*b*]selenophene 1,1-dioxide, is available currently.