OXIDATION OF 1*H*-2-BENZOSELENOPYRANS. GENERATION OF BENZOSELENOPHENES, BENZALDEHYDES, AND BENZOPHENONES

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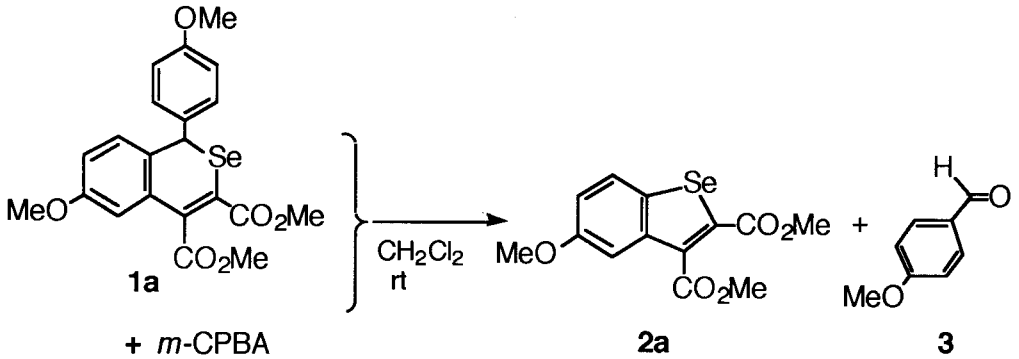
Abstract—Oxidation of 1*H*-2-benzoselenopyrans bearing electron-withdrawing substituents gave benzoselenophenes, benzaldehydes, and benzophenone derivatives *via* the corresponding selenoxides followed by Pummerer and [3,3]sigmatropic rearrangements.

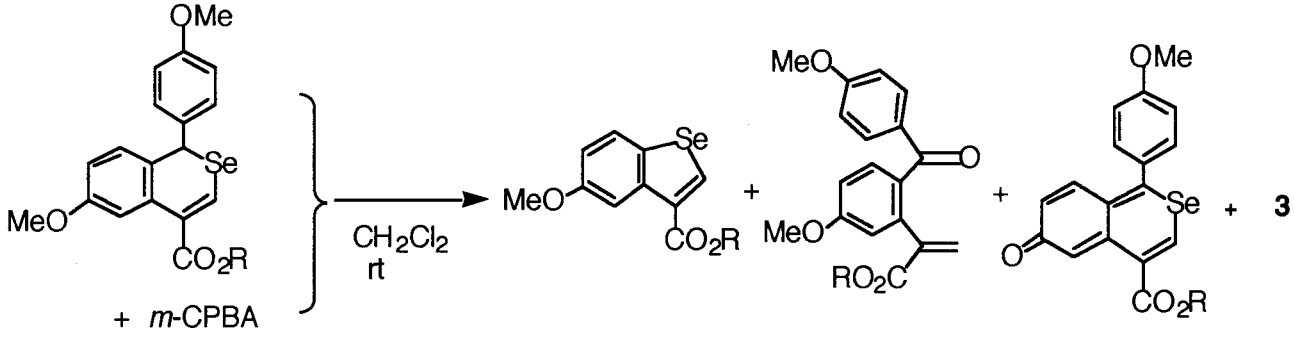
Recently, much attention has been paid for the oxidative metabolism of thiophenes and molecular orbital calculation of thiophenes and benzo[*c*]thiophene.[1] Hori *et al.* have reported the unusual formation of benzo[*c*]thiophenes by the reaction of thiochromene oxide derivatives with active methylene compounds.[2] They have also reported the formation of 2-selenanaphthalene, which is easily oxidized to give the ring-opened methyl selenoether.[3] Kataoka *et al.* have reported that the oxidation of dihydroselenopyranes by *m*-chloroperbenzoic acid (*m*-CPBA) afforded the corresponding m-chloroperbenzoates (Pummerer rearranged products).[4] We have reported that the reaction of selenobenzophenones with dimethyl acetylenedicarboxylate gave 1*H*-2-benzoselenopyrans (**1**).[5] We have also reported that oxidation of bicyclic diselenides, which were obtained from selenobenzophenones and cyclopentadiene, afforded diphenylfulvenes.[6] In view of these results, we have become interested in the reactivity of 1*H*-2-benzoselenopyrans. In this communication, we report herein the oxidation of **1**.

In contrast with selenanaphthalenes, dimethyl 1*H*-2-benzoselenopyran-3,4-dicarboxylate (**1a**) is stable in the air.[3] Thus, oxidation of **1a** was carried out using *m*-CPBA as an oxidizing agent. When **1a** was treated with *m*-CPBA at room temperature, two main products were obtained. MS spectrum of the one indicated formula $C_{11}H_{10}O_3Se$, which was found to be 2,3-dicarbomethoxy-5-methoxy-benzo[*b*]selenophene (**2a**) by its NMR analysis. The other product was *p*-methoxybenzaldehyde (**3a**), which is identical with the authentic sample (Scheme 1).



Scheme 1.

When **1b** was oxidized under similar conditions, additional two products (**4b** and **5b**) were obtained along with **2b** and **3b**. One of them was found to be a benzophenone derivative (**4b**). The structure of **4b** was confirmed by its ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of **4b** displayed signals at δ 3.51, 3.87, and 3.89 for three methoxy protons, 5.87 and 6.61 for two geminal olefinic protons (J=1.2 Hz). The ^{13}C NMR spectrum of **4b** showed three methoxy carbons, twelve olefinic and aromatic carbons, one ester and one ketone carbonyl carbons (Scheme 2). The structure of **5b** was also confirmed by its NMR analysis along with HRMS. The results were shown in Table 1.



1b R=Me
1c R=Et

2b R=Me
2c R=Et

4b R=Me
4c R=Et

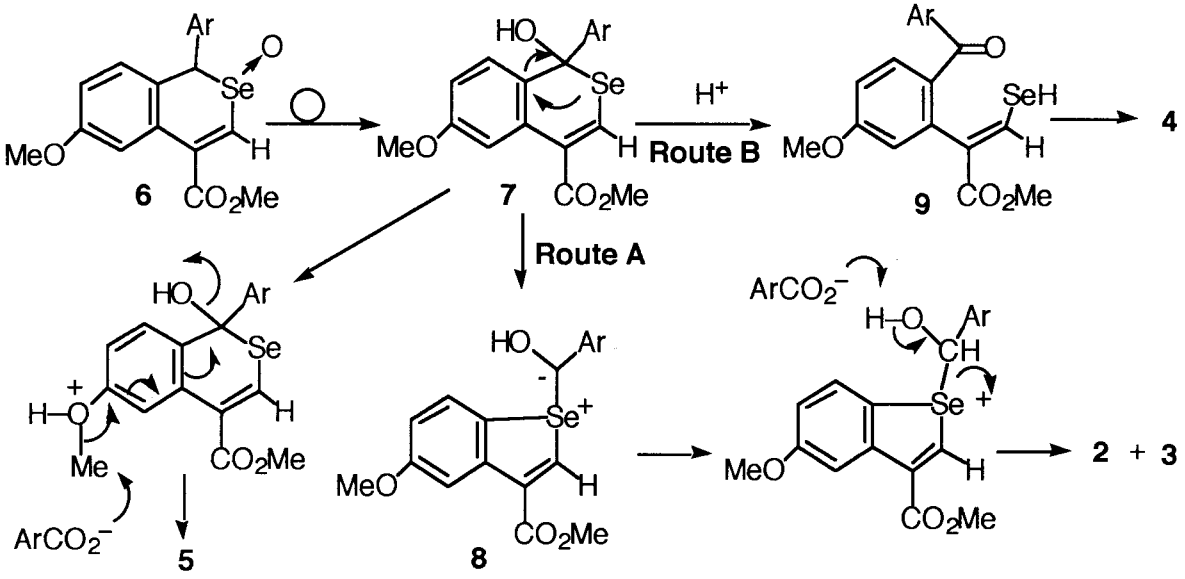
5b R=Me
5c R=Et

Scheme 2.

Table 1. Oxidation of **1**.

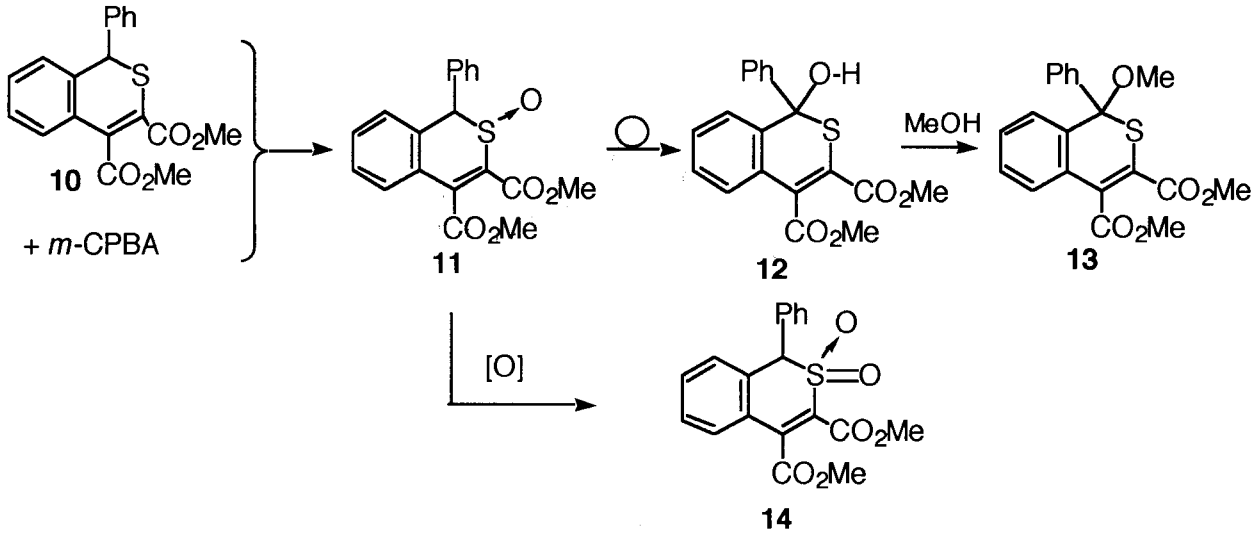
1	*m*-CPBA (eq)	Products (Yields/%)[7] **2**	**3**	**4**	**5**
1a	1.1	**2a**: 23	25	**4a**: 0	**5a**: 0
1a	1.4	**2a**: 32	33	**4a**: 0	**5a**: 0
1b	1.1	**2b**: 33	30	**4b**: 17	**5b**: 15
1b	1.4	**2b**: 37	38	**4b**: 17	**5b**: 12
1c	1.1	**2c**: 31	29	**4c**: 24	**5c**: 0
1c	1.4	**2c**: 37	35	**4c**: 34	**5c**: 0

It is noteworthy that normal Pummerer rearranged products (*m*-chloroperbenzoates) were not obtained in all reactions. The present result is different from that of Kataoka's. It has been found that the molar ratio of **2** to **3** is always very close to unity. Thus, the reaction most likely proceeds as follows. Oxidation of **1** gave the corresponding selenoxides (**6**), which rearranged to give the α-hydroxy selenides (**7**) by Pummerer reaction. Intermediate (**7**) further rearranged to give the corresponding selenonium ylides (**8**), protonation of the ylides by benzoic acid followed by an attack of benzoate to give **2** and **3** (Route A in Scheme 3). This result is mechanistically similar to that reported by Hori *et al.*[2] They observed that the oxidation of 1*H*-2-benzothiopyran gave the ring contracted substituted benzothiophene *via* the corresponding sulfonium ylide. Intermediate (**7**) gave the eneselenol (**9**) by the action of an acid, which extruded selenium finally to give **4** (Route B in Scheme 3). The present result is quite different from that of selenanaphthalene and 1-selenochromene.[8] 1-Selenochromene was found to be oxidized by *m*-CPBA to give benzophenone derivative *via* selenoxide intermediate. The reason why route A only proceeds by the use of **1a** as a substrate is unclear, but 3-carbomethoxy group plays an important role for this rearrangement. The 3,4-dicarboxylate moiety might more stabilize the selenonium ylides than the 4-carboxylate moiety. Compound (**5**) would be produced form the intermediate (**7**) by acid catalyzed demethylation.[9]



Scheme 3.

To support the above reaction mechanism, oxidation of dimethyl 1*H*-2-benzothiopyran-3,4-dicarboxylate (**10**), thia-analogue of **1**,[10] was carried out. The reaction of **10** with 1.2 eq of *m*-CPBA in dichloromethane gave relatively unstable sulfoxide (**11**), which is easily rearranged to give Pummerer rearranged product (**12**) without any ring contraction (Scheme 4). Interestingly, methyl ether (**13**) was obtained in the presence of a small amount of methanol in dichloromethane. Thus, the above reaction *via* 7 proceed through Pummerer rearrangement. When this reaction was carried out by using 2.4 eq of *m*-CPBA, sulfone (**14**) was obtained in 76 % yield.



Scheme 4.

This result is different from that of Hori *et al.*[2] They isolated stable 1*H*-2-benzothiopyran 2-oxide by oxidation of the corresponding thiopyran. Electron withdrawing carbomethoxy group of **10** made the sulfoxide more reactive than 1,2-dihydro-2-thianaphthalene oxide. Isolation of the Pummerer rearranged product (**12**) also confirms the formation of intermediate (**7**) in Scheme 3.

Ruwet *et al.* reported that SeO_2 oxidation of 1-selenochromenes in pyridine afforded 2-formylbenzo[*b*]selenophenes,[8] in which formyl group still remained. Compounds (**1**) are benzo analogues of selenopyran. The reaction of 3,6-dihydro-2*H*-selenopyrans with sodium periodate gave the

ring contraction products, selenophenes, *via* selenopyrans,[11] suggesting that the behavior of **1** toward oxidizing reagents is similar to the simple selenopyrans.

In summary, oxidation of **1** gave the corresponding benzoselenophenes along with *p*-methoxybenzaldehyde. The reaction might proceed through two types of rearrangements *via* selenoxides. Efforts to explore the chemistry of 1,2-dihydroselenanaphthalenes are continuing in our laboratories.

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7. Satisfactory elemental analyses and/or high resolution MS were obtained for all new compounds. Spectral data of **2b**, **4c** and **5b: 2b**: ^{1}H NMR ($CDCl_3$) δ=3.92 (s, 3 H), 3.94 (s, 3 H, OMe), 7.02 (dd, 1 H, *J*=8.8 and 2.8 Hz, Ar), 7.76 (d, 1 H, *J*=8.8 Hz, Ar), 8.25 (d, 1 H, *J*=2.8 Hz, Ar), 9.06 (s, 1 H, with ^{77}Se satellite J_{Se-H}=44.8 Hz, SeCH). ^{13}C NMR ($CDCl_3$) δ=51.73 (OMe), 55.51 (OMe), 108.95, 115.44, 125.83, 129.83, 133.31, 139.95, 142.64, 158.35, 163.48 (COO). **4c**: ^{1}H NMR ($CDCl_3$) δ=1.08 (t, 3 H, *J*=7.2 Hz, Me), 3.87 (s, 3 H, OMe), 3.89 (s, 3 H, OMe), 4.01 (q, 2 H, *J*=7.2 Hz, CH_2), 5.84 (d, 1 H, *J*=1.2 Hz, =CH), 6.40 (d, 1 H, *J*=1.2 Hz, =CH), 6.87-6.92 (m, 3 H, Ar), 7.45 (d, 1H, *J*=8.4 Hz, Ar), 7.77 (d, 2 H, *J*=7.2 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ=13.94 (Me), 55.44 (MeO), 55.48 (MeO), 61.02 (CH_2), 112.04, 113.36, 116.85, 127.46, 130.86, 130.93, 131.99, 132.49, 139.91, 141.79, 161.27, 163.05, 165.81 (COO), 195.38 (CO). **5b**: ^{1}H NMR ($CDCl_3$) δ=3.81 (s, 3 H, OMe), 4.00 (s, 3 H, OMe), 6.73 (s, 1 H, =CH), 6.79 (d, 1 H, *J*=7.6 Hz, =CH), 6.88 (d, 2 H, *J*=9.2 Hz, Ar), 6.95 (d, 1 H, *J*=7.6 Hz, =CH), 7.23 (d, 2 H, *J*=9.2 Hz, Ar), 9.12 (s, 1 H, with ^{77}Se satellite J_{Se-H}=45.6 Hz, SeCH).
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