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

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Abstract—Oxidation of 1H-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 thiocromene oxide derivatives with active methylene compounds.² They have also reported the formation of 2-selenanapthalene, which is easily oxidized to give the ring-opened methyl selenoether.³ Kataoka et al. have reported that the oxidation of dihydrobenzoselenopyranes 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 1H-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 1H-2-benzoselenopyrans. In this communication, we report herein the oxidation of 1.

In contrast with selenanaphthalenes, dimethyl 1H-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_{3}Se, which was found to be 2,3-dicarbomethoxy-5-methoxybenzo[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.](image-url)
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 $\delta$ 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.

![Chemical structure diagram]

Table 1. Oxidation of 1.

<table>
<thead>
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<th>1</th>
<th>m-CPBA (eq)</th>
<th>2</th>
<th>Products (Yields/%)</th>
<th>3</th>
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<th>5</th>
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<tr>
<td>1a</td>
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<td>25</td>
<td>4a:</td>
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<td>2a:</td>
<td>32</td>
<td>33</td>
<td>4a:</td>
<td>0</td>
</tr>
<tr>
<td>1b</td>
<td>1.1</td>
<td>2b:</td>
<td>33</td>
<td>30</td>
<td>4b:</td>
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<tr>
<td>1b</td>
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<td>2b:</td>
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<td>1.4</td>
<td>2c:</td>
<td>37</td>
<td>35</td>
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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 $\alpha$-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 1H-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-carboxymethoxy 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 1H-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. They isolated stable 1H-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 SeO₂ oxidation of 1-selenochromenes in pyridine afforded 2-formylbenzo[b]selenophenes, in which formyl group still remained. Compounds (1) are benzo analogues of selenopyran. The reaction of 3,6-dihydro-2H-selenopyrans with sodium periodate gave the
ring contraction products, selenophenes, via selenopyrans,\textsuperscript{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 \textit{p}-methoxybenzaldehyde. The reaction might proceed through two types of rearrangements \textit{via} selenoxides. Efforts to explore the chemistry of 1,2-dihydroselenanaphthalenes are continuing in our laboratories.

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REFERENCES AND NOTE


7. Satisfactory elemental analyses and/or high resolution MS were obtained for all new compounds. Spectral data of 2b, 4c and 5b: 2b: \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \textdelta=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 \textsuperscript{77}Se satellite J\textsubscript{Se,H}=44.8 Hz, SeCH). \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \textdelta=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: \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \textdelta=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\textsubscript{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). \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \textdelta=13.94 (Me), 55.44 (MeO), 55.48 (MeO), 61.02 (CH\textsubscript{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: \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \textdelta=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 \textsuperscript{77}Se satellite J\textsubscript{Se,H}=45.6 Hz, SeCH).


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