

Novel Oxidative Ring Contraction of Dihydroselenopyrans to Selenophenes

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Oxidation of 3,6-dihydro-2*H*-selenopyrans with an electron-withdrawing group at the 2 position proceeded *via* an unprecedented ring-contraction to afford selenophenes.

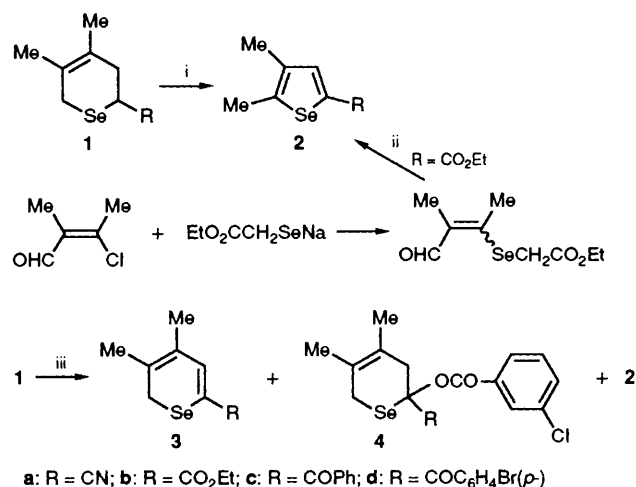
Selenides are easily oxidised to selenoxides by common oxidising agents.¹ The selenoxides without α - or β -hydrogen can be isolated, but those selenoxides bearing a β -hydrogen readily undergo β -*cis*-elimination even at room temperature to form alkenes. The β -*cis*-eliminations are widely used for

synthesis of alkenes.^{1,2} Oxidation of the selenides bearing an α -electron-withdrawing group with peracids did not give selenoxides but gave diselenides and the Pummerer rearrangement products.³ Selective oxidation of 1-selenochromenes with selenium dioxide in pyridine underwent a ring

Table 1 Oxidation of dihydroselepyrans **1** with NaIO₄

	NaIO ₄ (equiv.)	Product ^a (%)
1a	2	2a (21)
1a	4	2a (30)
1b	2	2b (15)
1c	2	2c (15)
1c	4	2c (25)
1d	1	2d (22)
1d	2	2d (37)
1d	4	2d (46)

^a The dihydroselepyrans **1a-d** were recovered.



Scheme 1 Reagents: i, NaIO₄, H₂O-MeOH; ii, EtONa, EtOH; iii, MCPBA, CH₂Cl₂

contraction to afford 2-formylbenzo[*b*]selenophenes.⁴ In the course of our synthesis of selenabenzene, we found a novel ring contraction of dihydroselepyrans bearing an electron-withdrawing group at the 2 position. We report here this unprecedented reaction.

Dihydroselepyrans⁵ **1** were oxidised with sodium periodate with the following general procedure: a solution of sodium periodate (0.86 g, 4 mmol) in water (6 ml) was added to a solution of **1** (1 mmol) in methanol (5 ml), with cooling in an ice-bath. The reaction mixture was stirred for 12 h at room temp. and the precipitate was filtered off. The filtrate was poured into water and extracted with dichloromethane. The extracts were dried (MgSO₄) and evaporated under reduced pressure. The product **2** was separated by preparative TLC on silica gel using hexane-dichloromethane (2 : 1). The structures of **2** were characterised by NMR, IR and mass spectroscopy and microanalysis. The structure of **2b** was assigned as 2-(ethoxycarbonyl)-4,5-dimethylselenophene by spectral data.[†] An authentic sample of **2b** was synthesised from 3-chloro-2-methylbut-2-enal and ethylselenoglycolate as shown in Scheme 1.⁶ The product **2b** was identical with the authentic sample. Oxidation products of **1** with sodium periodate and their yields are listed in Table 1.

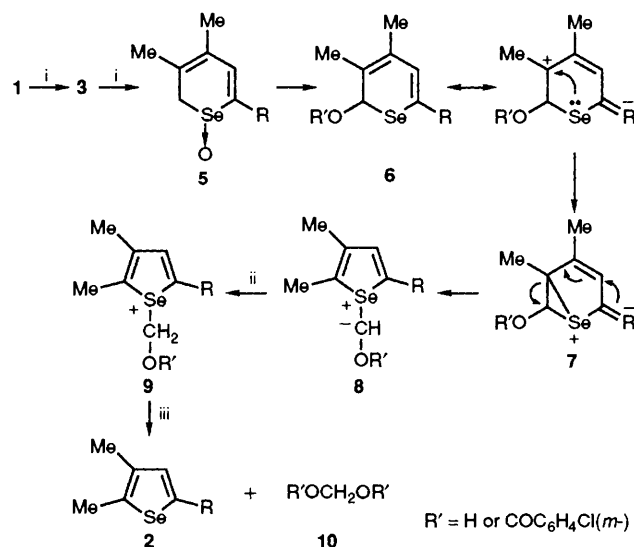
The oxidation was then conducted with 1.5 equiv. of *m*-chloroperbenzoic acid (MCPBA) in dichloromethane and

[†] Spectral data for **2b**: ¹H NMR (CDCl₃) δ 1.34 (3H, t, *J* 7.3 Hz, OCH₂Me), 2.11, 2.42 (each 3H, s, Me), 4.29 (2H, q, *J* 7.3 Hz, OCH₂Me), 7.76 (1H, s, CH=C); ¹³C NMR (CDCl₃) δ 14.2 (q), 14.4 (q), 16.0 (q), 80.8 (t), 133.0 (s), 136.1 (s), 139.3 (d), 147.7 (s), 163.4 (s); Found: C, 46.6; H, 5.2, C₉H₁₂O₂Se requires C, 46.8, H, 5.2%.

Table 2 Oxidation of dihydroselepyrans **1** with MCPBA

	Base (equiv.)	Products ^a (%)
1a	None	3a (41), 4a (29)
1a	NaHCO ₃ (1.5)	3a (24), 4a (31)
1a	MeCOONa (1.5)	3a (32), 4a (28)
1a	K ₂ CO ₃ (1.5)	3a (19), 4a (23)
1b	MeCOONa (1.5)	3b (7), 4b (20)
1c	MeCOONa (1.5)	3c (38), 4c (14)
1d	None	3d (48), 4d (22)
1d	NaHCO ₃ (1.5)	3d (56), 4d (21)
1d	MeCOONa (1.5)	3d (55), 4d (26)
1d	Et ₃ N (10)	No reaction
1d	(CF ₃ CO) ₂ O(2)	Complex mixture

^a The dihydroselepyrans **1a-d** were obtained in very small quantities.

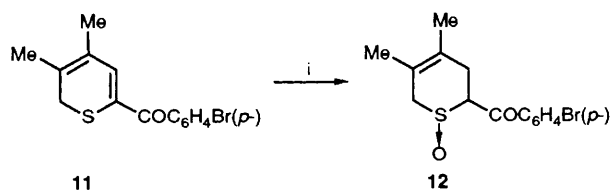


Scheme 2 Reagents: i, NaIO₄ or MCPBA; ii, protonation; iii, R'OH

obtained selenopyrans **3**, benzoates **4** and a trace amount of selenophenes **2**. It is interesting that the Pummerer reaction predominates the alkenation with the C-Se bond cleavage (β -*cis*-elimination) in the oxidation of selenides bearing a β -hydrogen. Yields of **3** were not improved by oxidation of **1** with MCPBA in the presence of a base. Oxidation of **1d** with MCPBA in the presence of trifluoroacetic anhydride, which causes the Pummerer reaction even at 0 °C,⁷ gave only a complex mixture.

Various reactions were conducted to elucidate the reaction mechanism of the ring contraction. Since trace amounts of **2** were obtained from the MCPBA oxidation described above, oxidation of **1d** with 4 equiv. of MCPBA was carried out, giving **2d** in 8.5% yield. This implies that the ring transformation proceeds *via* selenopyrans **3**. Therefore, **1a** was treated with 2 equiv. of sodium periodate or 2 equiv. of MCPBA and **2a** was obtained in 33 and 41% yields, respectively.

From the evidence described here, a plausible mechanism for the ring contraction is proposed in Scheme 2. Selenopyrans **3**, formed initially by oxidation of dihydroselepyrans **1** are further oxidised to give selenopyran Se-oxides **5**, which easily undergo the Pummerer rearrangement because of an electron-withdrawing group R to give acetals **6**.³ The R group makes the 5-carbon electron deficient and the episelenonium betaines **7** would be formed. The betaines **7** are transformed into the selenophenium ylides **8**. Protonation of the ylides **8** by a benzoic acid or a solvent followed by hydrolysis of a selenophenium ion **9** yields selenophenes **2** and acetals **10**. Detection of the acetals **10** was unsuccessful.



Scheme 3 Reagents: i, NaIO₄, H₂O-MeOH

In contrast with the above result, oxidation of 2-(*p*-bromobenzoyl)-3,6-dihydro-2*H*-thiopyran **11** with 2 equiv. of sodium periodate did not give a thiophene derivative but gave the sulfoxide **12** in 31% yield. The MCPBA oxidation of 3,6-dihydro-2*H*-thiopyrans had produced the sulfoxides.⁸

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