

trometry.<sup>10</sup> The results are summarised in Table 1, column A.

*Partial hydrolysis.* The fucogalactan (20 mg) was dissolved in 0.05 M sulphuric acid (10 ml) and kept at 100° for 1.5 h. The hydrolysate was dialysed overnight against tap-water and concentrated to dryness. The polymeric residue,  $[\alpha]_{578}^{20} + 140^\circ$  (c 0.1, H<sub>2</sub>O), was subjected to methylation analysis as described above. The results are summarised in Table 1, column B.

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## Mass Spectrometric Studies on Organic Selenium-Oxygen Compounds

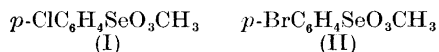
### 1. Mass Spectra of Methyl *p*-Chlorobenzene Selenonate and Methyl *p*-Bromobenzene Selenonate

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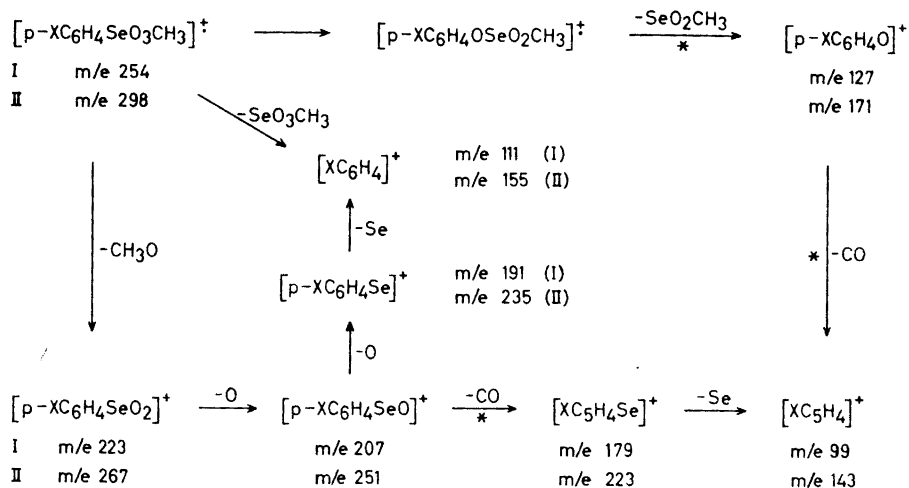
Recently it has been shown by several workers that a variety of sulphur-oxygen compounds, such as sulphoxides,<sup>1,2</sup> sulphones,<sup>1-6</sup> sulphonamides,<sup>7,8</sup> sulphonyl chlorides,<sup>7</sup> sulphonyl hydrazones<sup>9</sup> and sulphonylureas,<sup>10</sup> in most of the cases studied with the sulphur atom bonded to an aromatic carbon, are subjected to skeletal rearrangements upon electron impact with formation of C—O bonds.

No reports are, however, found in the literature on mass spectrometric studies in the domain of selenium-oxygen compounds. An investigation of the behaviour of different types of compounds in this field upon electron impact has been started at this Institute and in this first paper the mass spectra of the methyl esters of *p*-chlorobenzene and *p*-bromobenzene selenonic acids, I and II, are briefly discussed.



In the following discussion only fragment ions of higher masses are mentioned because the final fragmentation of the non-selenious ions intermediately obtained, gives peaks well-known for aromatic compounds.<sup>11</sup> Moreover, only peaks corresponding to the main isotopes of selenium, <sup>78</sup>Se, and of the halogens in question, <sup>35</sup>Cl and <sup>79</sup>Br, are considered. Transitions supported by appropriate metastable peaks are indicated in the scheme by asterisks.

The spectra of I and II, Figs. 1 and 2, show a series of very characteristic groups of peaks. Generally speaking, the principal ions are derived from cleavages around the selenium containing group. Alternative routes possible for the formation of the non-selenious ions are summarized in the scheme below.



One prominent fragmentation path shows an initial rearrangement of the molecule involving a 1,2-shift of the phenyl group from selenium to oxygen, probably analogous to the rearrangements found by several workers in certain sulphur-oxygen compounds.<sup>1-6</sup> However, no elimination of CO from the molecular ions of I and II seems to occur. This process is observed in the case of sulphoxides and sulphones,<sup>1</sup> but not in the case of sulphonamides.<sup>7</sup> The molecular ions of I and II fragment by the loss of  $\text{H}_3\text{COSeO}$  to  $m/e$  127 and

$m/e$  171, respectively ( $\text{XC}_6\text{H}_4\text{O}^+$ ), which are the base peaks. These ions then eliminate CO to give the abundant ions ( $\text{XC}_5\text{H}_4^+$ ) at  $m/e$  99 and  $m/e$  143, respectively.

Another prominent process is the simple cleavage of the C-Se bond to give the ions ( $\text{XC}_6\text{H}_4^+$ ) at  $m/e$  111 in the spectrum of I and at  $m/e$  155 in the case of II.

A series of peaks from selenium containing fragment ions at  $m/e$  223, 207, and 191 in Fig. 1 and  $m/e$  267, 251, and 235 in Fig. 2 is also observed indicating the

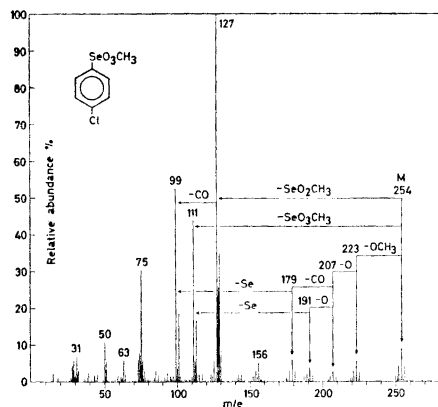


Fig. 1. Mass spectrum of methyl *p*-chlorobenzene selenonate, recorded with the inlet system at 70°.

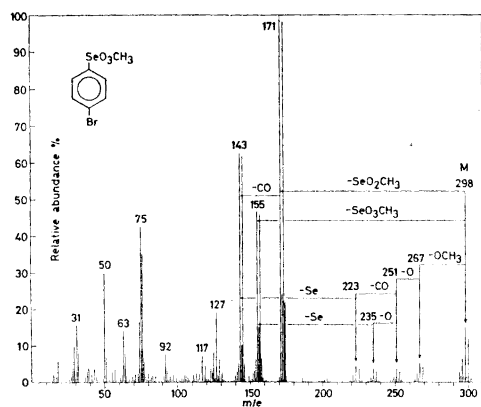


Fig. 2. Mass spectrum of methyl *p*-bromobenzene selenonate, recorded with the inlet system at 80°.

process  $M-CH_3O-O-O$  to operate and leading to the ions  $(XC_6H_4Se^+)$ . The next step is a simple cleavage of the C-Se bond to  $m/e$  111 and  $m/e$  155 in Fig. 1 and Fig. 2, respectively.

Instead of the fragmentation mentioned above of the  $m/e$  207 and  $m/e$  251 ions,  $(XC_6H_4SeO^+)$  or  $(XC_6H_4OSe^+)$ , a competitive process involving a rearrangement, followed by elimination of CO, occurs giving the ions at  $m/e$  179 in the case of I and at  $m/e$  223 in the case of II,  $(XC_5H_4Se^+)$ , possibly structurally similar to the thiopyrylium cations considered by Bowie *et al.* to be formed during mass spectrometric fragmentation of certain sulphoxides.<sup>1</sup>

*Experimental.* The mass spectra were recorded on an LKB model 9000A gas chromatograph-mass spectrometer, operating at 70 eV, using the direct inlet technique. The selenium analyses were performed by a microanalytical method developed by Bengtsson.<sup>13</sup>

*p-Chlorobenzene selenonic acid.* 3.35 g of *p*-Chlorobenzene seleninic acid<sup>12</sup> was oxidized with 1.58 g potassium permanganate as described earlier.<sup>14</sup> The free acid was obtained by using Amberlite IR 100 ion exchange resin. 2.60 g, m.p. 146–147.5°C. (Found: Se 32.81. Calc. for  $C_6H_5ClO_3Se$ : Se 32.97).

*p-Bromobenzene selenonic acid* was prepared analogously to the compound above. M.p. 156–158°C. (Found: Se 27.75. Calc. for  $C_6H_5BrO_3Se$ : Se 27.61).

The methyl esters I and II were obtained from the acids by using a distilled and dried ether solution of diazomethane. The esters were obtained as white solids which, however, turned green after a while. The spectra were recorded using freshly prepared esters.

A more detailed report on the preparation of these and other esters of this type will be published elsewhere.

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