

125°C under inert atmosphere. The mixture was poured into ice water (100 ml) and extracted with methylene chloride. The organic phase was washed with water, dried over MgSO_4 and the solvent removed under reduced pressure. Distillation of the resulting oil, gave pure olivetol, 3.5 g (76 %), b.p. 160–170°C/3–4 mm, characterized by its IR and NMR spectra.⁶

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Mass Spectrometric Studies on Organic Selenium-Oxygen Compounds

2. Mass Spectra of Diphenyl Selenoxide and 4,4'-Dimethyl-diphenyl Selenoxide

ERIK REBANE

Chemical Institute, University of Uppsala, S-751 21 Uppsala 1, Sweden

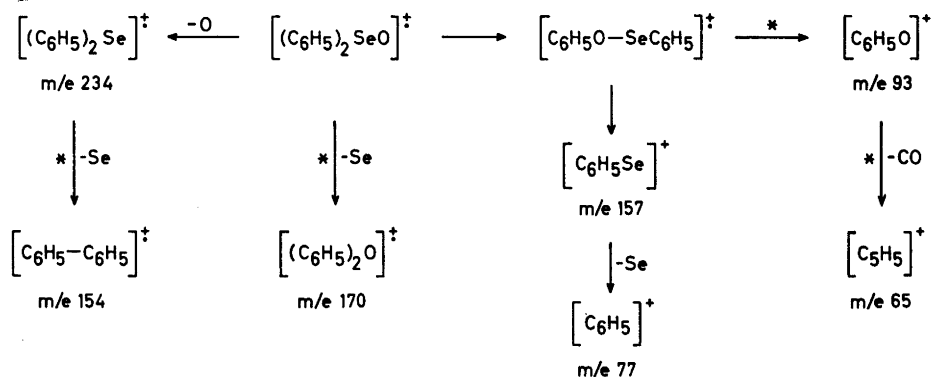
The behaviour of sulphoxides on electron impact has been thoroughly investigated and a survey showing the principles of their fragmentation is given by Budzikiewicz, Djerassi and Williams.¹ Up to now, however, nothing seems to be reported in the literature on mass spectrometric studies on selenoxides. In connection with work in progress on the behaviour of different kinds of organic selenium-oxygen compounds on electron impact the mass spectra of diphenyl selenoxide (I) and 4,4'-dimethyldiphenyl selenoxide (II) are given and briefly discussed here.



The discussion is limited to fragments containing the main selenium isotope ⁷⁸Se. The final fragmentation of the different non-selenious ions, proceeding along well-known routes,² is not considered here. The main fragmentation paths mentioned below are summarized in the scheme for the case of I. Transitions supported by appropriate metastable peaks are indicated by asterisks.

An initial skeletal rearrangement of the molecular ion to a selenenic acid ester ion, involving a migration of a phenyl group from selenium to oxygen, and followed by a cleavage of the Se–O bond to the ions $(\text{C}_6\text{H}_5\text{O})^+$ at m/e 93 and $(\text{C}_6\text{H}_5\text{Se})^+$ at m/e 157 forms a characteristic feature of the spectrum of I, Fig. 1. Such a 1,2-shift of a phenyl group on electron impact is well-known in the case of certain sulphoxides and some other types of sulphur-oxygen compounds¹ and has recently also been observed in esters of aromatic selenonic acids³ and diaryl selenones.⁴

A noteworthy fragmentation process, supported by the appropriate metastable peak, is the elimination of the selenium



atom from the molecular ion of I, giving the ion at m/e 170, tentatively described as the ion of diphenyl ether. No analogous transition has been observed in the case of the corresponding sulphoxide.⁵

A third prominent process observed in the spectrum of I is the simple cleavage of the Se—O bond of the molecular ion forming $((\text{C}_6\text{H}_5)_2\text{Se})^{\dagger}$ at m/e 234. This fragment is then decomposed by loss of the selenium atom along routes described by Agenäs⁶ and Bergman.⁷

In addition to these main fragmentation paths a minor peak at m/e 222,

$(\text{C}_{11}\text{H}_{10}\text{Se})^{\dagger}$, may be interpreted as caused by the elimination of CO from the molecular ion of I. The transition is supported by a metastable peak. Diphenyl sulphoxide exhibits a rearrangement of the molecular ion followed by loss of CO.⁵ The process mentioned may be the initial step of an alternative fragmentation pattern of I: $\text{M}-\text{CO}-\text{C}_6\text{H}_5-\text{Se}$, leading to the peaks at m/e 222, 145, and 65. The ion at m/e 145 may be formulated as a selenium analogue to the thiopyrylium cation reported in the mass spectrum of diphenyl sulphoxide.⁵

The mass spectrum of II, Fig. 2, shows

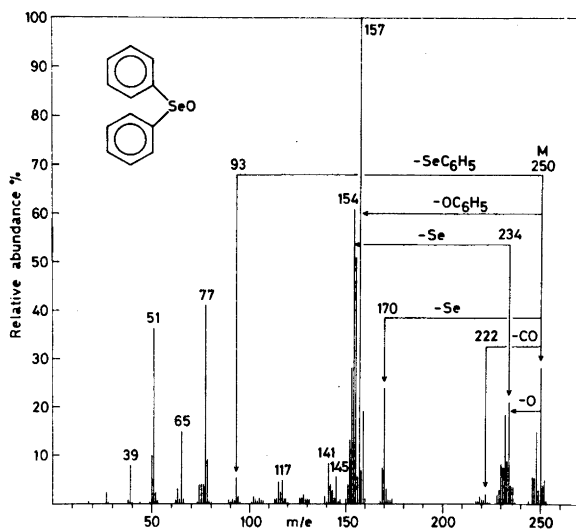


Fig. 1. Mass spectrum of diphenyl selenoxide, recorded with the inlet system at 65°.

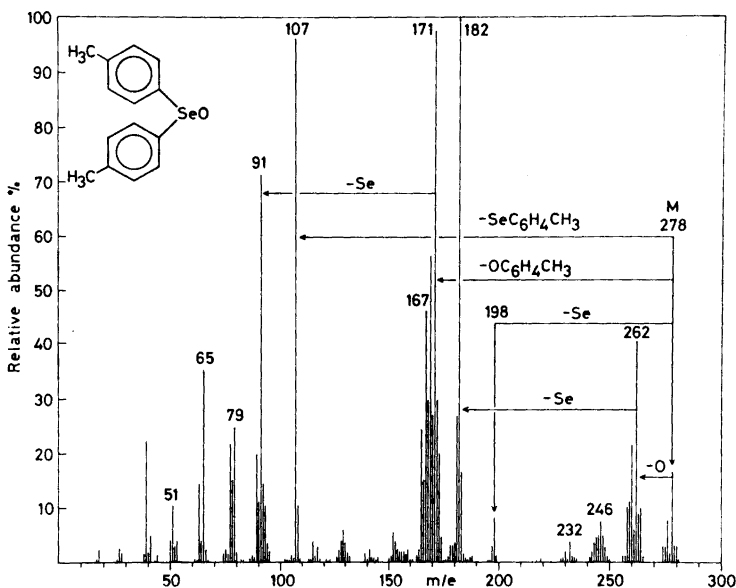


Fig. 2. Mass spectrum of 4,4'-dimethyl-diphenyl selenoxide, recorded with the inlet system at 70°.

the same principal features as that of I, thus supporting the fragmentation pattern formulated in the scheme. Here, however, no elimination of CO from the molecular ion has been observed. In this connection it is worth mentioning that the same is valid for the corresponding sulphoxide.⁵ The groups of peaks around m/e 246 and 232 in Fig. 2, also recognized in the mass spectrum of 4,4'-dimethyl-diphenyl selenide, are assigned to side chain fragmentations of the ion at m/e 262, $((p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Se})^+$.

Experimental. The mass spectra were recorded on an LKB model 9000A gas chromatograph-mass spectrometer, operating at 70 eV, using the direct inlet technique.

Diphenyl selenoxide was prepared according to Rheinboldt and Giesbrecht,⁸ but instead of diphenylselenium dibromide the corresponding dichloride⁹ (m.p. 185–187°) was used. After repeated recrystallizations from petroleum ether-ether and benzene the pure product was obtained, m.p. 112–113.5°.

4,4'-Dimethyl-diphenyl selenoxide was prepared via the corresponding dichloride, m.p. 182–184°, analogously to diphenyl selenoxide. M.p. 87–88° was obtained after repeated recrystallizations from benzene.

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