Electronolysis of Some Derivatives of Selenochromane

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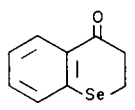
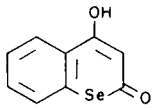
The mass spectra of 4-selenochromanone, 4-hydroxyselenocoumarin, and 3,3′-methylene bis(4-hydroxyselenocoumarin) have been determined, and the fragmentation pathways of these substances under electron-impact are discussed. A strong tendency to form the benzoselenophen ring was noted in all three cases.

Selenium-containing heterocyclic compounds of the selenochromane series are still scarcely investigated, and it was therefore thought interesting to determine the mass spectra of some of these substances, with a view to ascertaining the degree of stability of molecules of that type and to identifying the pathways of their decomposition under electron-impact. The presence of the constellation of selenium isotopes and the pattern of their distribution greatly facilitates the identification of the various fragments involved in the electronolysis.

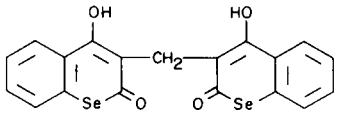
Three selenochromane derivatives were selected for this investigation: 4-selenochromanone (I), 4-hydroxyselenocoumarin (II), and 3,3′-methylene bis(4-hydroxyselenocoumarin) (III).



I



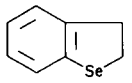
II



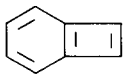
III

4-Selenochromanone (I).

The mass spectrum of this compound (Figure 1) showed that it readily loses carbon dioxide under electron-impact, the base peak being at m/e = 184, which is the species M-28 corresponding to ^{80}Se; another selenium-containing fragment is compound V, whose formation from benzo[*b*]selenophen (IX) through extrusion of ethylene has recently been established (1). Loss of the heteroatom leads to the formation of benzocyclobutadiene (VI), of the ion (VII), and finally of benzyne (VIIIa) and its dehydrogenation-product (VIIIb); the fact that these various species are also formed in the electronolysis of benzo[*b*]selenophen suggests that the decarbonylation-product of selenochromanone is 3,4-dihydrobenzo[*b*]-selenophen (IV).

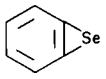


IV

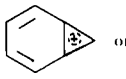


VI;
m/e = 102

VIIIa;
m/e = 76



V



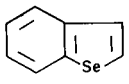
VIIa;
m/e = 89

VIIb

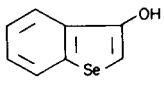
VIIIb;
m/e = 75

4-Hydroxyselenocoumarin (II).

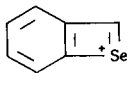
Figure 2 shows that the base peak does not correspond to a molecular ion either, but to a benzo[*b*]selenophen ion (m/e = 182), which was formed by loss of carbon monoxide and oxygen, an intermediate in this process being 3-hydroxybenzo[*b*]selenophen (X), which was formed by



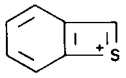
IX



X



XI



XII

XIII;
m/e = 63

simple extrusion of carbon monoxide and which also gave rise to prominent peaks. As could be expected from analogy with the naphthols, which readily lose carbon monoxide (2), 3-hydroxybenzo[*b*]selenophen was fragmented to the species XI, which is the selenium analog of the ion XII already encountered in the decomposition of methylthianaphthenes (3). Here again, the presence of peaks corresponding to the species V indicates that benzo[*b*]selenophen is a capital step in the electronolysis of 4-hydroxyselenocoumarin. Selenium-free fragments included the ions VII, VIIIa, VIIIb, and XIII; the last had already been identified in the mass spectra of several benzo[*b*]selenophens (2).

TABLE I

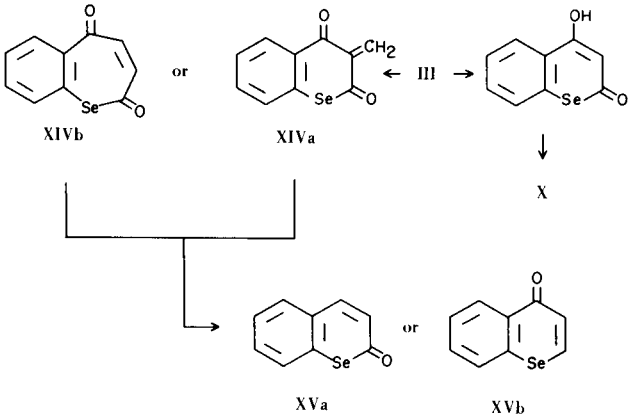
Relative Importance of Peaks Observed (a)

Compound I		Compound II		Compound III (b)	
m/e	%	m/e	%	m/e	%
214	20	228	8.4	240	9.5
213	7	227	5.1	239	4.6
212	62.5	226	39.1	238	21.4
211	0.5	225	0.8	237	2.1
210	40.2	224	22.2	236	10.2
209	19.5	223	6.7	235	5.1
208	20	222	2.4	234	5.2
186	28.3	200	8.5	228	4.5
185	10.2	199	3.1	226	26.5
184	100	198	42.5	225	2.2
183	9.8	197	2.2	224	14.3
182	74.8	196	22.2	223	5.2
181	24.9	195	8.3	222	5.2
180	25.2	194	9.5	212	10.3
158	15.2	184	18.6	211	6.7
157	10.3	183	8.7	210	5.7
156	65.2	182	100	209	28.5
155	7.5	181	4.7	208	2.5
154	35.5	180	35.4	207	16.8
153	19.2	179	18.5	206	7.5
152	20.2	178	19.2	205	7.6
117	22.5	170	6.8	200	7.5
115	20.1	169	17	199	5.2
106	10.8	168	2.5	198	33.2
105	8.7	167	6.7	197	3.1
102	15.5	158	11.8	196	14.3
89	10.8	157	5.7	195	7.3
76	20.1	156	57.5	194	7.2
75	22.2	155	3.7	186	19.2
		154	30.2	185	9.2
		153	8.4	184	100
		152	11.8	183	2.4
		113	11.9	182	52.4
		111	6.7	181	30.5
		102	6.2	180	23.8
		89	2.5	158	15.2
		76	8.5	156	52.5
		75	7.2	154	23.6
		63	13.6	102	18.5
				89	20.2
				76	21.2
				75	19.1
				63	19.2

(a) Base peaks underlined. (b) Metastable peaks observed for the following transitions: XIV → XV, XIV → [XIV-HCO], and IX → V.

3,3′-Methylene bis(4-hydroxyselenocoumarin) (III).

The fragmentation pattern of this compound is remarkably simple and is dominated by the decomposition of the molecule into the 4-hydroxyselenocoumarin moiety (II) and the species XIVa (or, more likely, its heptagonal rearrangement-product XIVb) through hydrogen displacement. Thereafter, 4-hydroxyselenocoumarin undergoes



fragmentation following the pattern reported above, whilst the other moiety (XIV) sheds either carbon dioxide (leading to the species XV, a or b) or formaldehyde, both fragmentations being evidenced by the corresponding systems of metastable peaks. Here again, the benzo[*b*]-selenophen ions feature prominently in the spectrum, and their further fragmentation into the species V is underlined by a system of metastable peaks.

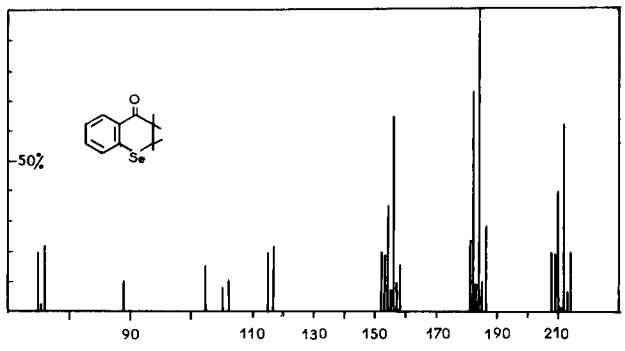


Figure 1

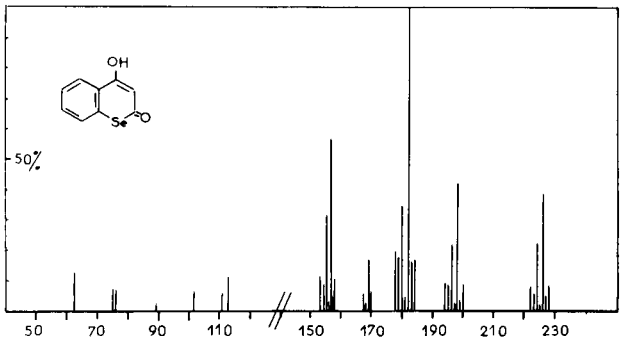


Figure 2

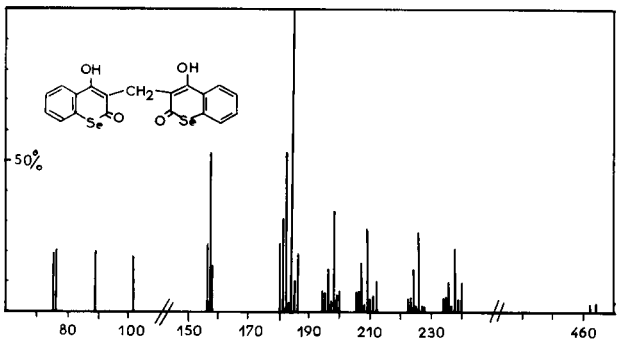


Figure 3

As 3,3′-methylene bis(4-hydroxyselenocoumarin) (III) is a selenium analog of the antivitamin K Dicumarol, it was of interest to determine its anticoagulant activity. This was conducted in Wistar rats, the compound being administered orally at the dose of 300 mg./kg.; determination of the Quick prothrombin time after 4, 8, and 24 hours showed the compound to be devoid of anticoagulant activity at this dose-level.

EXPERIMENTAL

Preparation of Compounds.

4-Selenochromanone (I) and 4-hydroxyselenocoumarin (II) were prepared according to the literature (4, 5, 6). 3,3′-Methylene bis(4-hydroxyselenocoumarin) (III) was obtained by treating an ethanolic solution of 4-hydroxyselenocoumarin with a small excess of an aqueous solution of formaldehyde. The precipitate which formed instantaneously was collected and recrystallized from propionic acid to give compound III as fine colorless needles which darkened after exposure to the air, m.p. inst. 283-284° (dec. >223° on progressive heating); lit. (5), m.p. 253-254°.

Anal. Calcd. for $C_{19}H_{12}O_4Se_2$: C, 49.4; H, 2.6; O, 13.8. Found: C, 49.2; H, 2.8; O, 14.0.

Determination of Mass Spectra.

These were taken on an Atlas CH-4 spectrometer (70 eV), the temperature of injection being 140° for compounds I and II and 220° for compound III.

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