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The electron impact mass spectrometric behaviour of 2-(methoxycarbonylmethyl)-2-phenyl-1,3-benzoxathiole 3a and 2-acetonyl-2-phenyl-1,3-benzoxathiole 3b has been studied in detail. The structures of the more interesting fragment ions have been confirmed with the aid of accurate mass measurements, linked scans and collisional activation experiments. In addition to the ionic species already described in the general fragmentation pattern of 1,3-benzoxathiole derivatives, other fragments arising from the interaction of the carboxycontaining chain with the sulfur atom of these compounds have been observed and evidence presented.

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#### Introduction.

It has previously been reported [1] that 2-(methoxycarbonylmethyl)-2-phenyl-1,3-benzoxathiole 3a and 2-acetonyl-2-phenyl-1,3-benzoxathiole 3b were obtained synthetically by the reaction of 1,2-hydroxybenzenethiole 1 with acetylenic compounds 2a,b (Scheme 1). Compounds 3a,b were purified by column chromatography. Pursuing our interest in the mass spectrometric characterization of 1,3-benzoxathiole and 1,3-benzodioxole derivatives [2-5], in the present paper we discuss the mass spectrometric behaviour of 2-(methoxycarbonylmethyl)-2-phenyl-1,3-benzoxathiole 3a and 2-acetonyl-2-phenyl-1,3-benzoxathiole 3b as obtained with the aid of accurate mass measurements, linked scans [6] and collisionally activated decomposition (CAD) mass analyzed ion kinetic energy (MIKE) spectra [7].

# Scheme 1

### Results and Discussion.

The most of the mass spectrometric data on 1,3-benzoxathiole derivatives are mainly related to 2,2-dialkyl- or 2-alkyl-2-aryl derivatives [3]. The only example of a carboxy containing chain in the position 2 of the oxathiole ring was discussed by us [2]. In that case most of the fragmentation products arise from cleavage of the ester bond with and without rearrangement, while the formation of 2hydroxybenzenethiol, usually observed as a EI induced retrosynthetic pathway of 2,2-dialkyl-1,3-benzoxathioles, was in that case completely absent.

In the present paper we wish to discuss the EI induced fragmentation pattern of 3a and 3b, with the aim to in-

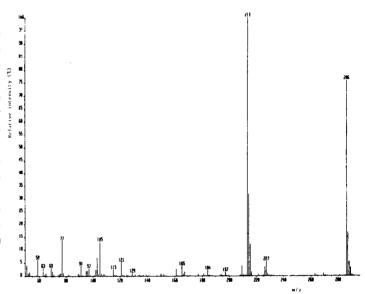


Figure 1. 70 eV EI mass spectrum of compound 3a.

vestigate the possible interreaction between the phenyl group and the carboxy-containing side chain in position 2.

The spectra of compounds 3a and 3b are reported in Figures 1 and 2 respectively, while the common fragmentation pattern, as obtained by B/E and B<sup>2</sup>/E linked scans [6], and accurate mass measurements are reported in Scheme 2.

The most favourable decomposition route is due to the loss of the -CH<sub>2</sub>CO-R chain, which leads to the already well described ionic species at m/z 213, highly stabilized by resonance phenomena. It is worth noting that these ionic species have already been described in condensed phase [8-10].

The primary methyl loss is observed for compound 3b only, leading to ions at m/z 255. The same ionic species

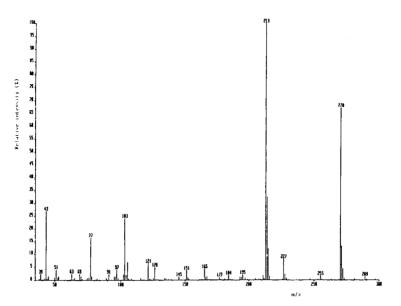


Figure 2. 70 eV EI mass spectrum of compound 3b.

are not present for compound 3a, showing that the methoxy loss, usually observed in methyl ester mass spectrometry, is in this case not favoured. The cleavage in an

 $\alpha$ -position to carboxy group gives rise, for both the compounds, to easily detectable ionic species at m/z 227. For these ionic species the structure of benzoxathiane derivatives can be reasonably proposed, looking at the higher thermodynamic stability of such a six-membered ring.

These ions can also originate by CO loss from the ionic species at m/z 255 described above, as proved by B/E linked scans [6] of such ions.

From compound **3b** the primary formation of 2-hydroxybenzenethiol has been detected. This unexpected behaviour can be explained by the mechanism shown in Scheme 3. The first hydrogen rearrangement on the sulfur

#### Scheme 3

atom, through the four-center mechanism already proposed by us for other 1,3-benzoxathiole derivatives [3], leads to the molecular ion in an "open" structure. From these species, through a McLafferty rearrangement, ionic species at m/z 126 can be easily obtained. Collisional spectroscopy indicates for these ions the structure of o-hydroxy-benzenethiol: in fact the collisional spectrum of the ionic species at m/z 126 originating from 3b and that of M\* of o-hydroxybenzenethiol are completely superimposable. We emphasize the lack of this fragmentation pattern for compound 3a. This behaviour can be ascribed both to the

different chain length (the analogous structure a involves a seven-membered ring instead the six-membered one invoked in the McLafferty rearrangement occurrence) and to the presence of the electron-withdrawing oxygen in the ester chain.

The last primary fragmentation pathway leads to ionic species at m/z 103 (particularly abundant for 3b). Accurate mass measurements give for them the molecular formula C<sub>6</sub>H<sub>7</sub>. The B/E linked scans [6] of such an ion (see Figure 3), identical for both compounds, shows loss of H. and C<sub>2</sub>H<sub>2</sub>, together with the usually observed phenyl fragment ions at m/z 63, 51 and 39. These results are in agreement with the structure of the vinvl cation. Its formation originates from a four-center mechanism (see upper part of Scheme 4) leading in this case to the transfer of the CO-R group on the sulfur atom, followed by the cleavage of the S(3)-C(2) bond. The further rupture, in species **b**, of the O(1)-C(2) bond leads to the vinyl ion at m/z 103. The B<sup>2</sup>/E linked scans [6] of these [C<sub>8</sub>H<sub>7</sub>]<sup>+</sup> ions shows another possible precursor at m/z 131 which in the 70 eV mass spectra are shown to be particularly scarce.

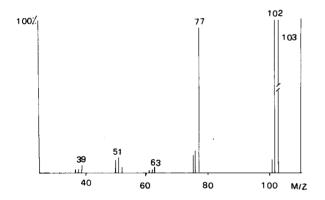


Figure 3. B/E linked scan of ionic species at m/z 103 originating from EI of compound 3a.

Hence another decomposition mechanism can be proposed which should be slower than that above described (in fact, metastable ion data describe processes with lower decomposition rates). For such a slow mechanism the formation of an intermediate as c of the lower part of Scheme 4 can explain the presence of the  $[C_9H_7O]^+$  (m/z 131) species which easily gives rise, through CO loss, to the  $[C_8H_7]^+$  ones above described. The ions at m/z 213 further decompose through the fragmentation pattern already described for other 1,3-benzoxathiole derivatives [3].

In conclusion the presence of a carboxy-containing chain in position 2 of a 1,3-benzoxathioles leads on one hand to the fragmentation products already described for other 1,3-benzoxathiole derivatives, so confirming the general mass spectrometric behaviour of these compounds, on the other hand to decomposition products due to interaction of the side chain with the sulfur atom, thus giving diagnostic pathways.

#### **EXPERIMENTAL**

All mass spectrometric measurements were performed on a VG-ZAB-2F instrument coupled with a VG 11/250 data system and operating in the electron impact (EI) mode (70 eV, 200  $\mu$ A).

Samples were introduced via the direct inlet system without any probe heating and with an ion source temperature of 200°. Metastable transitions were detected by B/E and B²/E linked scans [6]. Accurate mass measurements were performed with the peak matching technique at 10,000 resolving power (10% valley definition). Collisionally activated decomposition (CAD) mass analyzed ion kinetic energy (MIKE) spectra [7] were obtained by 8 KeV ions colliding with air in the second field-free region. The pressure in the collision cell was such to reduce the main beam intensity to 60% of its usual value.

Compounds 3a and 3b were analytically pure samples synthesized and purified according to the literature [1].

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