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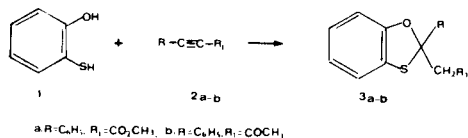
The electron impact mass spectrometric behaviour of 2-(methoxycarbonylmethyl)-2-phenyl-1,3-benzoxathiole **3a** and 2-acetyl-2-phenyl-1,3-benzoxathiole **3b** has been studied in detail. The structures of the more interesting fragment ions have been confirmed with the aid of accurate mass measurements, 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 carboxy-containing 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-acetyl-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-acetyl-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 2-hydroxybenzenethiol, 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-

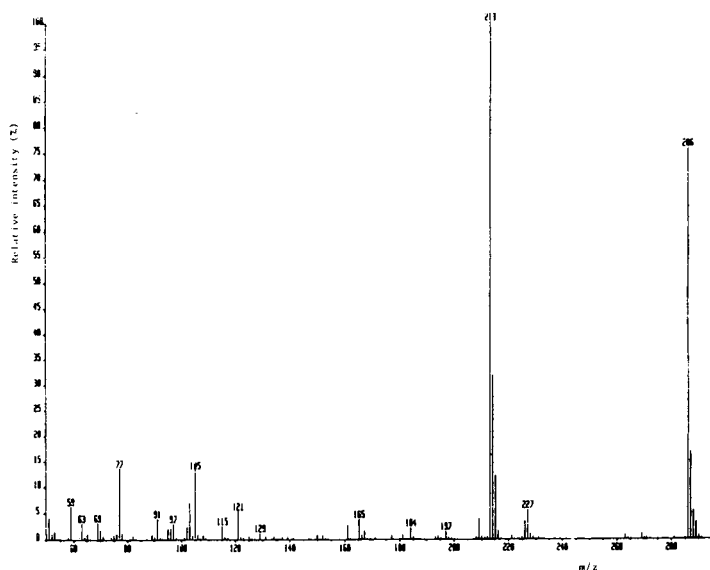


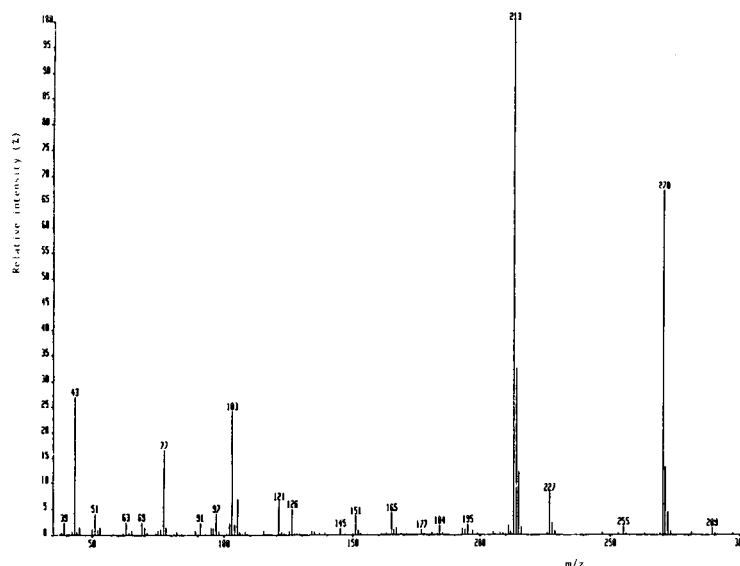
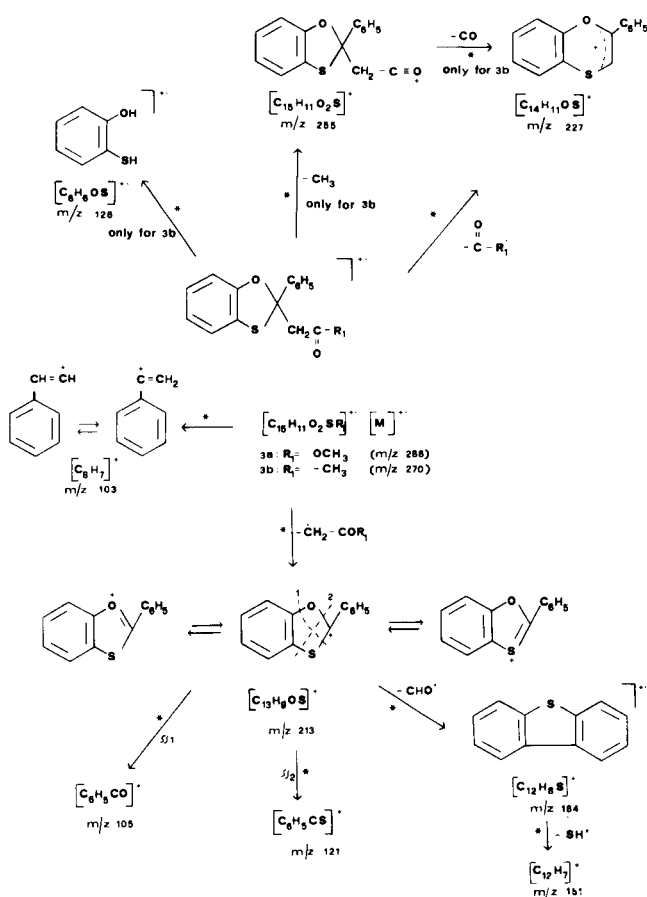
Figure 1. 70 eV EI mass spectrum of compound **3a**.

investigate 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  $-\text{CH}_2\text{CO}-\text{R}$  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**.

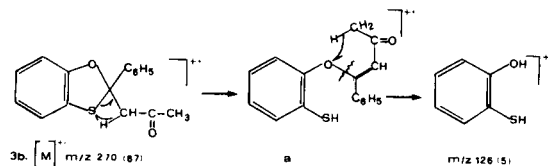
are not present for compound **3a**, showing that the methoxy loss, usually observed in methyl ester mass spectrometry, is in this case not favoured. The cleavage in an

$\alpha$ -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*-hydroxybenzenethiol: 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

