

Electron Impact Induced Fragmentation of 3-(5'-Aryl-1',2'-dithiol-3'-ylidene)-6-methyl-2H-pyran-2,4-diones and 3-(5'-Aryl-1',2'-dithiol-3'-ylidene)-3H-benzo[*b*]pyran-2,4-diones

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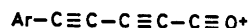
α -(1',2'-Dithiol-3'-ylidene)ketones and -aldehydes cannot be considered normal carbonyl compounds as it has been shown that a rather strong oxygen-sulfur interaction is present.^{1,2} Therefore, it is necessary to consider 3-(5'-aryl-1',2'-dithiol-3'-ylidene)-6-methyl-2H-pyran-2,4-diones (*1*) and 3-(5'-aryl-1',2'-dithiol-3'-ylidene)-2H-benzo[*b*]pyran-2,4-diones (*2*) as resonance hybrids of structures such as *x*, *y* and *z*.³ ¹⁹F NMR and ¹³C NMR studies³ indicate that *1* and *2* are relatively polar substances, whose structures are best represented by *z*. In contrast, the structure of simple alkyl and aryl substituted α -(1',2'-dithiol-3'-ylidene)-ketones and -aldehydes is best described by the non-polar form corresponding to *x*.

The mass spectra of these compounds were studied previously⁴ in connection with the systematic studies of the physico-chemical

properties of 1,2-dithioles performed in this laboratory.³ We found it of interest to examine whether the greater polarity of *1* and *2* is reflected in their fragmentation on electron impact. Representative mass spectra are shown in Fig. 1. The molecular ions generally give rise to the base peaks.

3-(1',2'-Dithiol-3'-ylidene)-6-methyl-2H-pyran-2,4-diones (*1*). The predominant fragmentation mode is loss of ketene from the molecular ions giving rise to ion *a*, which decomposes by extrusion of carbon monoxide or ketene forming ions *b* and *c*, respectively. Using metastable defocusing technique, it was shown that *c* is likewise formed directly from the molecular ions.

The decomposition of *c* depends on the substitution pattern of the dithiole ring. If the ring bears no substituent in position 4' (*1a-1c*), *c* eliminates CO or HS₂ giving rise to ions *d* and *e*, respectively. A mechanism for the extrusion of HS₂ observed in the fragmentation of related compounds has been proposed.⁴ Accordingly, 4'-substituted compounds should be incapable of losing HS₂ and ion *e* was not observed in the decomposition of these compounds (*1d-1f*). The structure of *e* is probably *3*.⁵

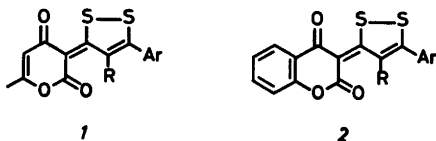


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Loss of a methyl group and carbon monoxide have been found in the fragmentation of some 2-pyrones.⁵ Extrusion of these fragments from the molecular ions of *1* is found in most cases, but the intensities of the corresponding peaks are generally low (< 10%). The structures of the resulting ions *f* and *g*, respectively, may be formulated in analogy to those proposed for the fragment ions derived from the 2-pyrones.⁵ Ion *f* decomposes by extrusion of CO yielding ion *h*.

Elimination of a hydrogen atom is a possible process, but only for compounds *1d* (63%) and *1f* (16%) the abundance exceeds 5%. In these cases the structural requirements for formation of a six-membered ring are present.

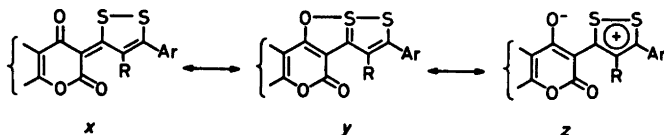
* The elemental composition was shown by accurate mass measurements to be in accordance with the proposed structure.



Compounds Ar

<i>1a,2a</i>	C ₆ H ₅	H
<i>1b,2b</i>	<i>p</i> -CH ₃ OC ₆ H ₄	H
<i>1c,2c</i>	<i>p</i> -FC ₆ H ₄	H
<i>1d,2d</i>	C ₆ H ₅	CH ₃
<i>1e,2e</i>	C ₆ H ₅	C ₆ H ₅
<i>1f,2f</i>	-CH=CH-CH=CH-	

* We shall for the sake of consistency and brevity refer to all compounds by the dithiole name corresponding to form *x*.



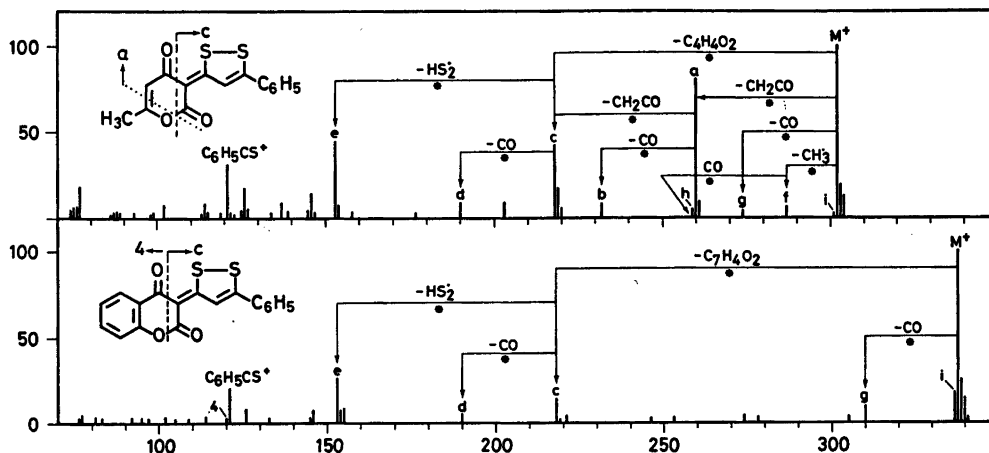
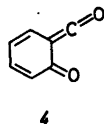


Fig. 1. Mass spectra of 3-(5'-phenyl-1',2'-dithiol-3'-ylidene)-6-methyl-2H-pyran-2,4-dione (1a) and 3-(5'-phenyl-1',2'-dithiol-3'-ylidene)-2H-benzo[b]pyran-2,4-dione (1b).

3-(1',2'-Dithiol-3'-ylidene)-2H-benzo[b]pyran-2,4-diones (2). The important decomposition modes are principally the same as described for 1 (cf. Fig. 1). However, the intensities of the resulting peaks are generally lower.

Ions *c* are formed from the molecular ions by loss of the fragment 4. The reversed charge distribution gives rise to a peak at m/e 120 ($C_7H_4O_2$), but only in the spectrum of 2f the intensity (54%) exceeds 6%. The further fragmentation of *c* is in accordance with the decomposition modes described for 1.

Loss of carbon monoxide and hydrogen from the molecular ions are possible processes. The abundance of the $[M-H]^+$ ions are greatly increased [10% (2b) to 94% (2d)], whereas elimination of CO also in this series gives rise to peaks of low intensities.



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In both series of compounds, the primary decomposition modes are related to the pyrone part of the molecules. Analogously, the fragmentations of simple α -(1,2-dithiol-3-ylidene) ketones are reported to be connected with the carbonyl group. Thus, the incorporation of the carbonyl group in the quasiaromatic ring and the resulting change in charge distribution do not in principle change the decomposition modes, reflecting the high stability of the 1,2-dithiole ring upon electron impact.

Experimental. The mass spectra were recorded on an AEI MS-902 mass spectrometer by Mrs. E. Wolff-Jensen, The H. C. Ørsted

Institute, University of Copenhagen, or on a Varian MAT 311A by Mr. C. Jøpsen, Department of Chemistry, Odense University. The ion source temperature was typically 130 °C (70 eV, direct sample insertion). The preparation of the compounds is reported elsewhere.³

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