Mass Spectrometric Studies of α-(1,3-Dithiol-2-ylidene)-thioketones and Thioaldehydes

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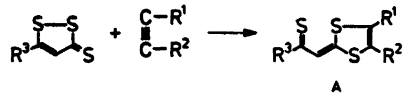
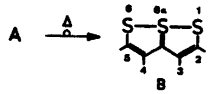
The reactions of 1,2-dithiol-3-thiones with activated acetylenes such as phenylacetylene, benzoylacetylene, acetylene dicarboxylic acid ester, and phenylacetylene carboxylic acid esters result in compounds which can be formulated as α-(1,3-dithiol-2-ylidene)thioketones and thiolaldehydes (A).[1-3]



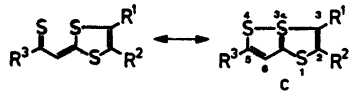
A

The compounds readily rearrange at high temperature in the presence of sulfur containing compounds such as phosphorus pentasulfide, thioacetamide and sulfur to the isomeric 1,6,6aλ^4-trithiapentalenes (B).[1,4,5]



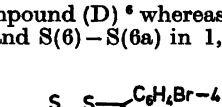
B

The close relationship to the 1,6,6aλ^4-trithiapentalenes has resulted in the formulation of analogous bicyclic canonical forms such as (C) for these compounds, (C) is a 1,3aλ^4,4-trithiapentalene. However, X-ray investigations



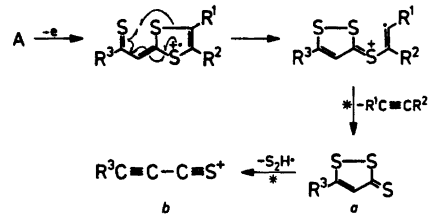
C

have shown, that the distance S(3a)–S(4) is 2.91 Å in compound (D) [6] whereas the distances S(1)–S(6a) and S(6)–S(6a) in 1,6,6aλ^4-trithiapentalene fall in the range 2.23–2.51 Å.[7] This seems to indicate that these compounds are most correctly described by structure (A); this assumptions is in accordance with the electron impact induced fragmentation of the compounds. The loss of a hydrogen atom from the aromatic bicyclic 1,6,6aλ^4-trithiapentalenes and loss of substituents from the aryl substituted 1,6,6aλ^4-trithiapentalenes were found to be a characteristic feature in the mass spectra of the latter,[8] whereas the corresponding processes are insignificant here.



D

The mass spectra of VI and IX have recently been published by one of us.[9] In both cases the predominant fragmentation was loss of phenylacetylene from the molecular ions probably under formation of 5-substituted-1,2-dithiol-3-thiones. We now report this fragmentation to be a general process for compounds of this type *cf.* Table 1. A probable mechanism is suggested in scheme 1.



Scheme 1.

This fragmentation mode accounts for most of the significant ions. One exception is the $[C_6H_5CO]^+$ ion found in the spectra of IX to XII (this ion gives rise to the base peak in XII). Another ion which was found in some abundance when both R^1 and R^2 are aromatic substituents is the $[R^1C{\equiv}CR^2]^{+\cdot}$ ion. The peak corresponding to $[R^3CS]^+$ is remarkably small when compared with $[C_6H_5CS]^+$ in the mass spectra of 5-phenyl substituted 1,6,6aλ^4-trithiapentalenes.[8] The same ion is present in the mass spectra of phenyl substituted 1,2-dithiol-3-thiones [10] in which case it appears in approximately the same abundance as in I to XII. However, it cannot be excluded that the $[R^3CS]^+$ ion in these cases also is formed directly from the molecular ion. The mass spectrum of VIII (Fig. 1) indicates that also a $[R^1CS]^+$ ion is formed (*m/e* 121) (in this case in the same abundance as $[R^3CS]^+$, *m/e* 151). The ion at *m/e* 132 corresponds to $[R^3C{\equiv}CH]^{+\cdot}$ which is a typical fragment in the spectra of 1,2-dithiol-3-thiones.[10]

Small peaks from doubly-charged ions corresponding to M^{2+} are present in all cases and to $[M-CS]^{2+}$ in the spectra of II to VIII. In the spectra of III and VIII the latter ion appears in relatively high abundance (*cf.* Fig. 1). If R^3 is a *p*-methoxy-phenyl group the methoxy

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Table 1.

Compound A										
	R^1	R^2	R^3	M^+ %	$[M-R^1C{\equiv}CR^2]$ a	$[a-S_2H]$ b	R^3CS	COPh 105	$R^1C{\equiv}CR^2$	C_6H_5 77
I	$COOCH_3$	H	H	54	100	18	8	—	—	—
II	$COOCH_3$	H	C_6H_5	55	100	47	14	—	—	8
III	$COOCH_3$	H	4-$C_6H_4OCH_3$	68	100	49	9	—	—	—
IV	$COOCH_3$	$COOCH_3$	C_6H_5	36	100	43	17	—	—	14
V	$COOCH_3$	C_6H_5	C_6H_5	35	100	44	11	—	—	6
VI	C_6H_5	H	CH_3	48	100	38	10	—	9	4
VII	C_6H_5	H	C_6H_5	61	100	48	14	—	13	6
VIII	C_6H_5	H	4-$C_6H_4OCH_3$	28	100	58	8	—	4	17
IX	COC_6H_5	H	C_6H_5	40	100	41	10	11	1	22
X	COC_6H_5	H	4-$C_6H_4OCH_3$	43	100	40	6	11	6	17
XI	C_6H_5	COC_6H_5	C_6H_5	23	100	95	35	18	1	58
XII	COC_6H_5	COC_6H_5	C_6H_5	18	62	25	8	100	1	52

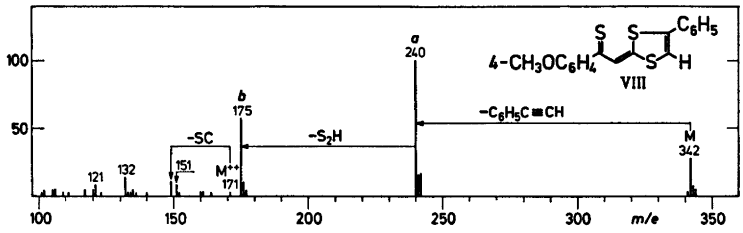

Fig. 1.

group may allow further stabilization of $[M-CS]^{2+}$ as important factors for stabilization of doubly charged ions are separation of charges and a possible formation of a conjugated system in the ion.[11] Loss of CS from the singly charged molecular ions in no cases gave rise to discernible ions.

Experimental. Mass spectra were obtained on a MS 902 spectrometer using the direct sample insertion system and the lowest feasible ion source temperature. 70 eV electrons were used. Peaks corresponding to doubly-charged ions appearing at half mass numbers and peaks of abundance lower than 2 % were omitted. When necessary the elemental composition of an ion was determined by accurate mass measurements (± 10 ppm).

α-(1,3-Dithiol-2-ylidene)thioketones and thioaldehydes were prepared by reacting the appropriate 1,2-dithiole-3-thiones with acetylenes.[12]

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