Mass Spectrometric Studies of α-(1,2-Dithiole-3-ylidene) ketones and α-(1,2-Dithiole-3-ylidene)aldehydes

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The mass spectra of seventeen α-(1,2-dithiole-3-ylidene)ketones and α-(1,2-dithiole-3-ylidene)aldehydes are reported and discussed together with those of appropriate deuterated analogues. Some analogies with 1,6,6a^{IV}S-trithiapentalenes are observed in the formation of M − OH and M − SH ions. α-Cleavage with respect to the carbonyl group is observed and the two possible modes of cleavage are discussed. A $C_{16}H_{10}$ ion, proposed as a 1,4-diphenyl-1,3-butadiyne ion, is formed in all possible cases. The generation of this ion is discussed in detail on the basis of the application of metastable defocusing technique on different compounds together with a deuterium labeled compound. In some cases the $C_{16}H_{10}$ ion is formed through elimination of HS_2·. The similarity between the precursor from which the $C_{16}H_{10}$ ion is formed *via* expulsion of HS_2· and 1,2-dithiole-3-thiones and 1,2-dithiole-3-ones is discussed. In addition the possibility of sulfur-oxygen interaction is discussed.

1,2-Dithiole-3-thiones, 1,2-dithiole-3-ones and 1,6,6a^{IV}S-trithiapentalenes are the only 1,2-dithiole derivatives whose fragmentation upon electron impact has been studied in detail so far.[1,2] As α-(1,2-dithiole-3-ylidene)ketones and aldehydes are structurally and synthetically closely related to the previously studied compound, it was found desirable to make a study of the mass spectra of these ketones and aldehydes.

The compounds studied in this work cannot be considered normal carbonyl compounds as it has been shown that a rather strong oxygen-sulfur interaction is present. The infrared spectra of these compounds do not exhibit a normal carbonyl vibration [3-5] and dipole moment measurements indicate that polar

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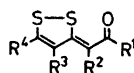* Postgraduate research fellow at Chemical Laboratory II, 1970/71.

forms must contribute to the structure.[6] It is therefore necessary to consider the compounds as resonance hybrids of structures such as a, b, and c.
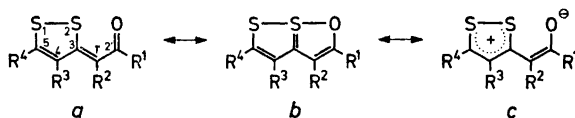
For the sake of consistency and brevity, however, we shall refer to all compounds and molecular ions only by the dithiolylidene name corresponding to the form a.

We have recorded the mass spectra of the compounds shown in Table 1 and with exception of the deuterated compounds the mass spectra are given in Figs. 1, 2, and 3.

Table 1.

|	R^1	R^2	R^3	R^4
I A	H	H	H	H
II A	H	H	H	C_6H_5
II B	H	H	C_6H_5	H
III A	C_6H_5	H	H	C_6H_5
III B	C_6H_5	H	C_6H_5	H
III C	H	C_6H_5	H	C_6H_5
III D	H	H	C_6H_5	C_6H_5
III E	C_6D_5	H	C_6H_5	H
III F	C_6H_5	H	C_6D_5	H
III G	C_6D_5	H	C_6D_5	H
III H	C_6H_5	D	H	C_6H_5
III I	C_6H_5	H	D	C_6H_5
III J	H	C_6D_5	H	C_6H_5
III K	CH_3	H	H	CH_3
III L	CH_3	H	H	C_6H_5
IV A	C_6H_5	C_6H_5	C_6H_5	H
IV B	C_6H_5	C_6H_5	H	C_6H_5
IV C	C_6H_5	H	C_6H_5	C_6H_5
IV D	H	C_6H_5	C_6H_5	C_6H_5
IV E	C_6H_5	C_6H_5	C_6D_5	H
IV F	H	C_6D_5	C_6H_5	C_6H_5
IV G	C_6H_5	H	CH_3	CH_3
IV H	CH_3	C_6H_5	H	C_6H_5
V A	C_6H_5	C_6H_5	C_6H_5	C_6H_5
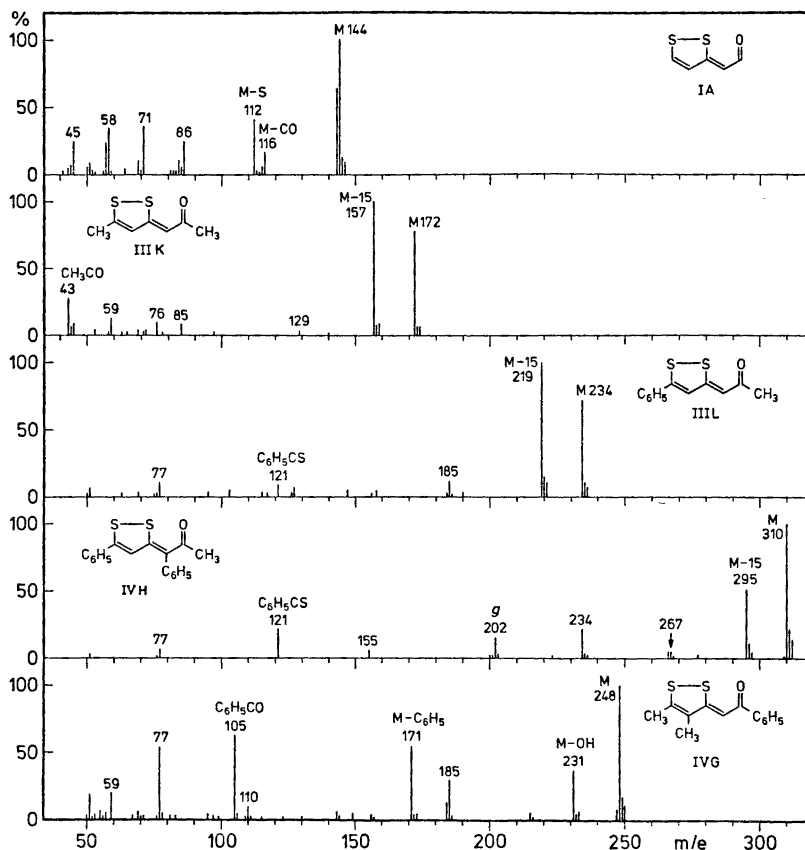
Fig. 1. Mass spectra of α-(1,2-dithiole-3-ylidene)acetaldehyde and α-(1,2-dithiole-3-ylidene) ketones with methyl groups.

As was observed in the case of 1,6,6a^{IV}S-trithiapentalenes[2] the mass spectra of 1,2-dithiolylidene ketones and 1,2-dithiolylidene aldehydes were to some extent dependent on the ion source temperature. Increasing ion source temperature resulted mainly in decreasing intensity of the molecular ion peak and also gave rise to more intense M – S peaks, which seemed to be due to a catalytic effect as the increase in the intensity of the M – S peak was particularly pronounced when the ion source was contaminated with previous samples.

The mass spectra of 1,2-dithiole-3-ylidene ketones and aldehydes all exhibit intense molecular ion peaks which, with few exceptions, are the base peaks.

In the parent compound I A the base peak, due to the molecular ion, and prominent peaks corresponding to M – H, M – CO, M – S, $C_3H_2SO^+$, $C_3H_3S^+$, and $C_2H_2S^+$ are present.

Fig. 2. Mass spectra of α-(1,2-dithiole-3-ylidene)aldehydes and ketones with one or two phenyl groups.

The ion at m/e 86 ($C_3H_2SO^+$) is probably formed by the following ring cleavage:

III K which only bears aliphatic substitutents gives a mass spectrum, which is dominated by the loss of a methyl radical from the molecular ion. The M − S peak has an intensity of only 2 %. No peak corresponding to M − CO
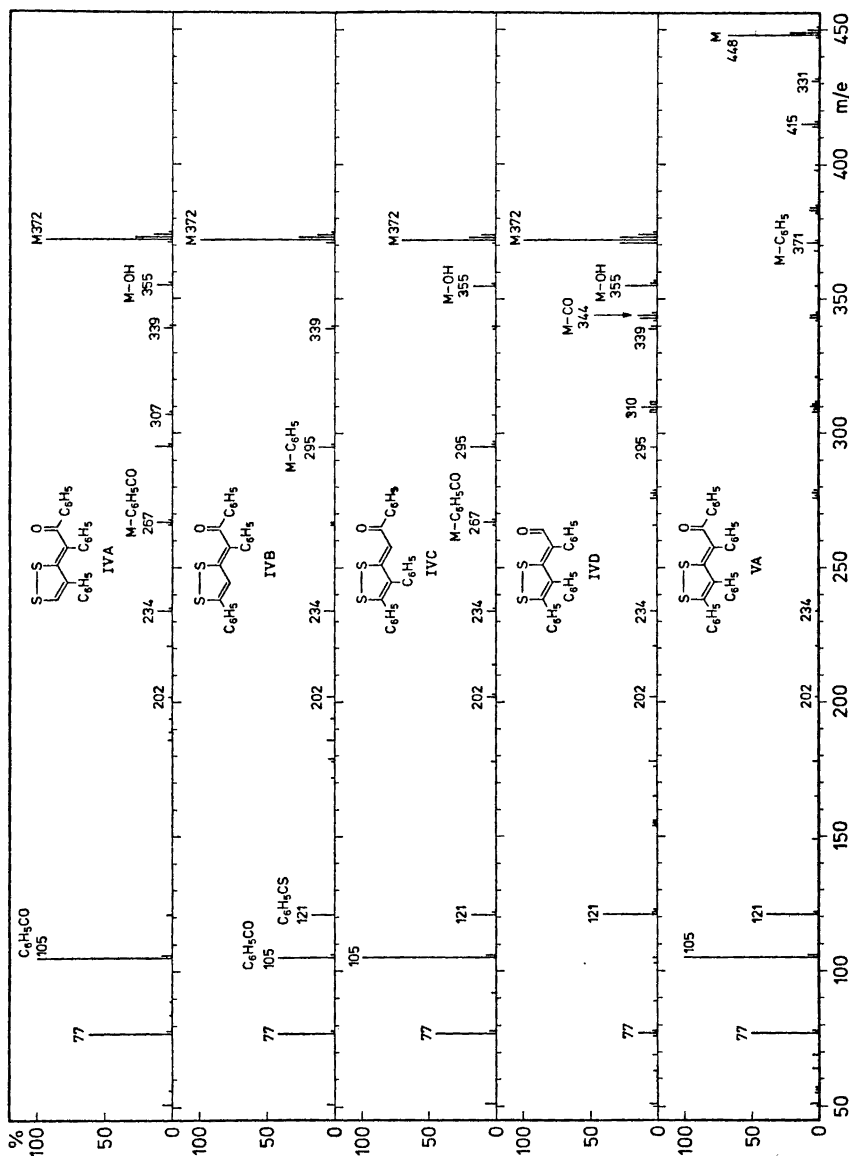
Fig. 3. Mass spectra of α-(1,2-dithiole-3-ylidene)aldehydes and ketones with three or four phenyl groups.

is present, instead CO is expelled from the M − 15 ion giving rise to a peak at m/e 129 (3.9 %).

The ring cleavage depicted above for the parent compound is not operative in the case of III K as the analogous ion at m/e 100 is not observed. A peak at m/e 85 corresponds to C_4H_5S.

α - C l e a v a g e

α-Cleavage with respect to a carbonyl group, being a favourable process for most carbonyl compounds, results in the two types of cleavage depicted above. For all compounds fragmentation according to type B gives rise to prominent peaks, whereas type A is only important in compounds where $R^1 = C_6H_5$.

In all compounds with $R^1 = CH_3$ type B gives rise to important peaks corresponding to $M - 15$ while CH_3CO^+ (m/e 43) formed via type A cleavage gives rise to a prominent peak only in the spectrum of III K (28 %).

Charge retention on the other fragment leads to ions corresponding to $M - R^1CO$. Peaks corresponding to these ions are often present in the spectra, and are sometimes due to direct loss of R^1CO in a one step process.

In the case of IV A and IV C the m/e 267 ion is formed by loss of C_5H_5CO from the molecular ion in a one step process shown by the application of the metastable defocusing technique (MDT). In III D where two phenyl groups are present in the dithiole ring it is shown that the $M - HCO$ ion (m/e 267) is formed directly from the molecular ion as well as from the $M - CO$ ion (MDT). In the case of III C this ion is not found to have the molecular ion as the precursor (MDT).

For compounds with $R^1 = C_6H_5$ an important fragmentation proceeds via an α-cleavage of type A leading to intense peaks corresponding to $C_6H_5CO^+$ (m/e 105). In cases where $R^1 = R^3 = C_6H_5$ this peak is the base peak. In other compounds the abundance is $40 - 60$ %. Peaks corresponding to $M - C_6H_5$ are due to fragmentation type B as these peaks are only important when $R^1 = C_6H_5$ and are practically absent in the diphenyl compounds where $R^1 = H$. The deuterium labeled compounds III E and III F show that the expulsion of a phenyl radical from the molecular ion in these compounds takes place exclusively as an α-cleavage (type B).

Elimination of ·OH and ·SH

In compounds where R^2 or R^3 are phenyl, elimination of ·OH from the molecular ions gives rise to peaks with relative high abundance in all other cases than IV B. The hydrogen involved in this process is shown to originate from the phenyl groups in 1′ or 4 position by labeling experiments (III F and III J), and, if both R^2 and R^3 are phenyl groups, from both of them (IV F). In the spectrum of IV F the ratio between the $M - OH$ and $M - OD$ peaks is found to be 3 : 2.

The loss of a hydroxy radical involving the abstraction of a hydrogen from a phenyl group in the 4-position of the dithiole nucleus has parallel in the loss of ·SH from 1,6,6a[IV]S-trithiapentalenes [2] in which case the hydrogen involved in the abstraction was also shown to originate from the phenyl group in the equivalent position. The mechanism for the formation of the M − OH ion is probably similar to the mechanism for the formation on the M − SH ion in the trithiapentalenes [2] and the structure of the ion (d) formed is probably also the same as that proposed for the M − SH ion.

$$
\begin{array}{c}
\overset{+}{S}-S \\
R^4 \diagdown \diagup R^2 \\
\diagup R^1
\end{array}
$$

d
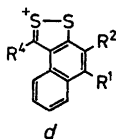
Due to the symmetrical structure of the trithiapentalene nucleus a parallel to the loss of ·OH involving a hydrogen atom from the phenyl group in the 1′ position does not exist. The expulsion of ·OH must, in this case, involve the rearrangement of a phenyl proton.

Loss of ·OH from the molecular ion is also observed in the case of IV G, the corresponding M − OH ion can in this case be formulated as *e*.

$$
\begin{array}{c}
\overset{+}{S}-S \\
H_3C \diagdown \diagup H \\
C_6H_5
\end{array}
$$

e
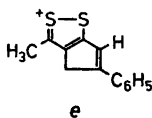
In addition to the loss of an OH group the elimination of an SH radical was often observed, but to a much smaller extent. For the phenyl substituted compounds it is obvious that the intensity of the M − SH peak is dependent on the substituent R^2. If $R^2 = C_6H_5$ the intensity of this ion is 6 − 13 % but if $R^2 = H$ it is only 2 − 3 % with III A as the only exception. This suggests that the hydrogen involved in the process originates from R^2 when this is phenyl by analogy with the elimination of ·SH from the trithiapentalenes mentioned above. This suggestion is further supported by the mass spectrum of III J which exhibits an M − SD peak. In the case of 1,2-dithiolylidene ketones the resulting ion might be formulated as *f*.

$$
\begin{array}{c}
S-\overset{+}{O} \\
R^3 \diagdown \diagup R^1 \\
R^4 \diagup
\end{array}
$$

f
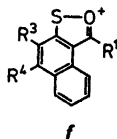
III A also exhibits a peak corresponding to the loss of ·SH but as III A has no phenyls in the 1′ and 4 positions the expulsion must occur *via* another mechanism. This is also shown by the fact that both III H and III I exhibit peaks corresponding to the loss of both ·SD and ·SH *i.e.* when only hydrogen is present in the 1′ and 4 positions these hydrogens can be eliminated together with sulfur.

Formation of $C_6H_5CS^+$ *(m/e* 121)

It has been observed that a peak corresponding to $C_6H_5CS^+$ occurs in the mass spectra of 2 and 5 substituted 1,6,6a^{IV}S-trithiapentalenes with characteristic substituent dependent abundances.[2] In 1,2-dithiole-3-ylidene ketones and aldehydes with $R^4 = C_6H_5$ the abundance of this ion is lower than that observed for the trithiapentalenes. It is found to be $16-24$ % in all compounds with the exceptions of IV D and V A where it is 40 %.

Formation of a 1,4-diphenyl-1,3-butadiyne ion

In the mass spectra of III C and III D important ions corresponding to *m/e* 234 and *m/e* 202 are present. By high resolution mass measurements their elemental compositions have been determined to be $C_{16}H_{10}S$ and $C_{16}H_{10}$ respectively.

By application of metastable defocusing technique the ions at *m/e* 234 and *m/e* 267 for both compounds have been found to be precursors for the *m/e* 202 ion and this ion can most probably be formulated as *g*.

$$C_6H_5-C\equiv C-C\equiv C-C_6H_5\rceil^+$$

g
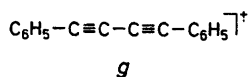
The mechanism for the formation of this ion is, however, rather complicated. In III D it requires a phenyl migration and in the case of III C it was shown by means of the mass spectrum of the deuterated analogue III J that a hydrogen from the phenyl group in the 1′ position was also eliminated to the extent of *ca.* 50 %.

In order to solve the problems concerning the formation of these ions the metastable defocusing technique was applied to III J and the fragmentation pattern shown in Scheme 1 can thus be proposed for this compound.

According to Scheme 1 the *m/e* 271 and *m/e* 272 are both able to eliminate ·HS under the formation of *m/e* 239 and *m/e* 238, respectively. We have no evidence for the origin of the hydrogen involved in these processes. The next step in these fragmentations is the elimination of S with formation of *m/e* 207 and *m/e* 206, respectively.
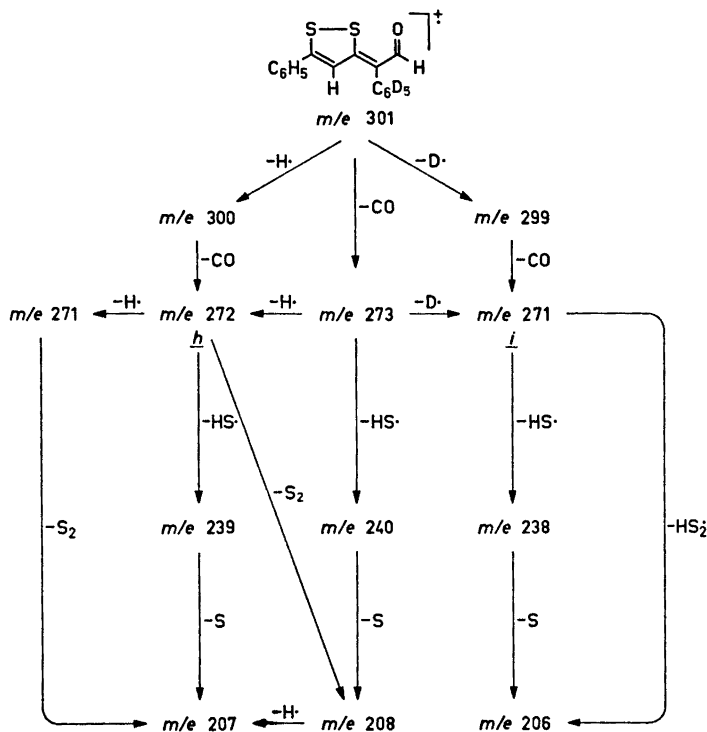
Scheme 1. Fragmentation pattern for III J. All transitions shown in the scheme are supported by metastable peaks.

The m/e 271 and m/e 272 ions, however, must be ascribed different structures, as the m/e 271 ion eliminates $HS_2\cdot$ in a one step reaction while this is not the case for the m/e 272 ion.

The structures h and i are proposed for these two ions.
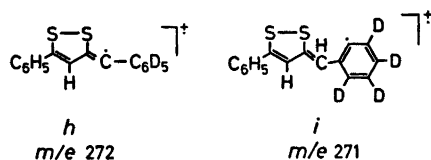
It is known from studies of the fragmentation of 1,2-dithiole-3-ones and 1,2-dithiole-3-thiones upon electron impact[1] that abstraction of $HS_2\cdot$ in a one step process is a possible fragmentation mode provided the dithiole ring is monosubstituted in the 5-position. The following mechanism was proposed for the expulsion of $HS_2\cdot$.

An explanation for the differing ability of the m/e 272 and m/e 271 ions to eliminate $HS_2 \cdot$ could be that m/e 272 had the structure h' rather than h.

h'

This ion should not be able to eliminate $HS_2 \cdot$ after the mechanism shown above, as no hydrogen is present in the 4 position. As shown (Scheme 2) IV H also gives rise to an ion at m/e 267 to which the structure h rather than h' must be ascribed, as it is formed by loss of CO from the M − 15 ion. No

Scheme 2. Fragmentation pattern for IV H. All transitions are supported by peaks detected by metastable defocusing technique. The heavy lines indicate fragmentations also associated by normal metastable peaks detectable in the spectrum.

direct loss of $HS_2\cdot$ from this ion could be observed and its further fragmentation mode is the same as that found for h. We will therefore conclude that the ions m/e 272 and m/e 267 have the same structure $i.e.$ the structure h.

As $HS_2\cdot$ loss only occurs from i and not from h one may conclude that i is more "like" a 1,2-dithiole-3-one or 1,2-dithiole-3-thione than h is.

The formation of the m/e 202 ion from III D may be rationalized by the fragmentation shown in Scheme 3.
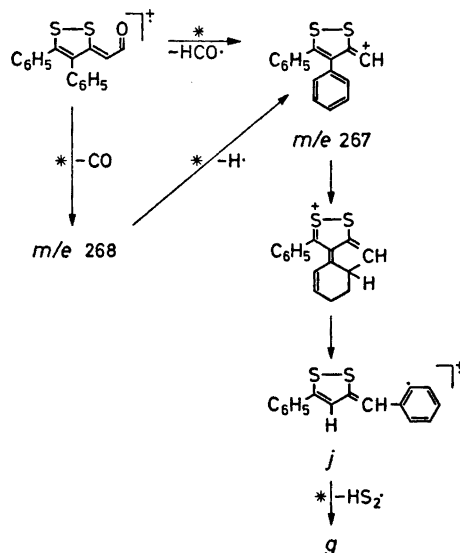
Scheme 3. Formation of the 1,4-diphenyl-1,3-butadiyne ion from IV H via a phenyl migration with subsequent loss of $HS_2\cdot$.

According to this fragmentation mode m/e 267 rearranges to the ion j which is analogous to i, and able to eliminate $HS_2\cdot$ in the same way as i.

Also in the case of III D the fragmentation of j proceeds via the m/e 234 ion to form the ion m/e 202.

The peak at m/e 202 and its precursors m/e 234 and m/e 267 are present also in the spectra of the triphenyl substituted compounds with intensities varying with the substituent pattern. In the case of V A only m/e 202 and m/e 234 are present and only with abundance of 2.4 % and 2.2 %, respectively.

Mass spectrometry has recently been used to show sulfur oxygen interaction in monothiobenzil [7] as it was claimed that the loss of SO upon electron impact was favoured in the oxathiet structure.
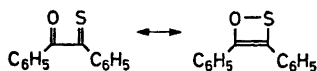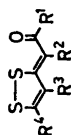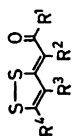
Table 2.

No.	R¹	R²	R³	R⁴	Formula	M⁺ found	M⁺ calc.	¹H NMR spectrum
III G	C_6D_5	H	C_6D_5	H	$C_{17}H_2D_{10}OS_2$	306.0948	306.0957	7.30s(1H); 7.78s(1H)
III E	C_6D_5	H	C_6H_5	H	$C_{17}H_7D_5OS_2$	301.0656	301.0643	7.30s(1H); 7.38s(5H); 7.78s(1H)
III F	C_6H_5	H	C_6D_5	H	$C_{17}H_7D_5OS_2$	301.0641	301.0643	7.30s(1H); 7.2−7.4m(3H); 7.78s(1H) 7.7−7.9m(2H)
III J	H	C_6D_5	H	C_6H_5	$C_{17}H_7D_5OS_2$	301.0654	301.0643	7.1−7.7m(6H); 9.27s(1H)
IV E	C_6H_5	C_6D_5	C_6D_5	H	$C_{23}H_{11}D_5OS_2$	377.0954	377.0956	6.66s(5H); 7.05s(5H); 7.91s(1H)
IV F	H	C_6D_5	C_6H_5	C_6H_5	$C_{23}H_{11}D_5OS_2$	377.0955	377.0956	6.50−6.85m(5H); 6.90−7.50m(5H); 9.20s(1H)

Table 3.

No.	R¹	R²	R³	R⁴	Formula	Analysis						M.p. °C	¹H NMR spectrum
						C		H		S			
						found	calc.	found	calc.	found	calc.		
IV G	C_6H_5	H	CH_3	CH_3	$C_{13}H_{12}OS_2$	62.90	62.85	4.87	4.93	25.78	25.54	147−148[b]	2.02s(3H); 2.40s(3H); 5.25− 7.6m(4H); 7.8−8.1m(2H)
III D	H	H	C_6H_5	C_6H_5	$C_{17}H_{12}OS_2$	68.85	68.91	4.17	4.08	21.49	21.60	160−161[a]	6.39d(1H) J=2Hz; 6.9− 7.5m (10H); 9.25d(1H) J=2Hz
IV H	CH_3	C_6H_5	H	C_6H_5	$C_{18}H_{14}OS_2$	69.50	69.67	4.55	4.70	20.40	20.62	114−115[b]	2.13s(3H); 7.0−7.8m(11H)
IV B	C_6H_5	C_6H_5	H	C_6H_5	$C_{23}H_{16}OS_2$	74.40	74.18	4.40	4.33	17.30	17.18	177−178[a]	6.9−7.6m
IV C	C_6H_5	H	C_6H_5	C_6H_5	$C_{23}H_{16}OS_2$	74.15	74.18	4.43	4.33	17.01	17.18	191−192[a]	7.02s(1H); 7.1−7.5m(13H); 7.6−8.0m(2H)
	4-$CH_3C_6H_4$	H	C_6H_5	C_6H_5	$C_{24}H_{18}OS_2$	74.40	74.60	4.74	4.70	16.33	16.67	188−189[a]	2.33s(3H); 6.9−7.8m(15H)

Recrystallized from [a] 2-methoxy ethanol, [b] ethanol.

In the mass spectrum of IV H (*cf.* Scheme 2) fragment ions corresponding to the one step loss of COS and ·COSH (MDT) from the M − 15 ion is observed. The expulsion of these fragments is analogous to the loss of SO from monothiobenzil and may then be taken as an indication of a contribution of the oxathiapentalene structure *b*, as proposed by some authors.[6],[8] It can, however, not be excluded that we are dealing with the simultaneous loss of CO and S or CO and ·SH, respectively.

EXPERIMENTAL

Mass spectra were obtained on an MS 902 mass spectrometer using the direct sample insertion system and the lowest feasible ion source temperature, *e.g. ca.* 120°C for monophenyl substituted compounds. Unless otherwise stated 70 eV electrons were used. High resolution mass measurements were carried out under the same conditions and were accurate to within ± 3 ppm. Peaks corresponding to doubly charged ions appearing at half mass numbers, and peaks of abundance lower than 2 % were omitted.

It was observed that the thermal catalytic loss of S and SH was augmented when the ion source was not clean. Therefore the spectra were recorded with the same precautions as was taken when spectra of 1,6,6a^{IV}S-trithiapentalenes were recorded.[2]

^{1}H NMR spectra were recorded on a Varian A 60A spectrometer from *ca.* 5 % solutions in CDCl$_3$ with TMS as internal standard. The chemical shifts are given as δ values.

1,2-Dithiolylium perchlorates. These salts were prepared from the corresponding 1,2-dithiole-3-thiones by oxidation with 30 % hydrogen peroxide in glacial acetic acid.[9]

1,2-Dithiolylium hydrogensulfates. The hydrogensulfates were prepared by the method of Klingsberg [10] with the modification that *m*-chloro perbenzoic acid was used for the oxidation instead of peracetic acid.

4-Pentadeuteriophenyl-1,2-dithiolylium hydrogensulfate. From 4-pentadeuteriophenyl-1,2-dithiole-3-thione.[1] Recrystallized from ethanol yield 75 %, m.p. 233 − 34°C. ^{1}H NMR spectrum in D$_2$O: 10.46 S, deuteration grade 90 %. (Found: C 38.25; H 2.84; S 34.00. Calc. for C$_9$H$_3$D$_5$O$_4$S$_3$: C 38.44; H 2.84; S 34.14.)

α-(1,2-Dithiole-3-ylidene)acetaldehyde. Prepared by decomposition of the mercury chloride complex of 4*H*-thiapyran-4-thione.[11]

α-(1,2-Dithiole-3-ylidene)ketones and α-(1,2-dithiole-3-ylidene)aldehydes. These compounds were prepared by one of the methods A-E. For new compounds *cf.* Tables 2 and 3.

Method A. Reaction of 1,2-dithiolylium salts with appropriate ketones.[6],[12] This method was used for the preparation of the following compounds: III B, III A, III E, III G, IV A, IV B, IV C, IV E, IV H, V A.

Method B. Reaction of 1,2-dithiolylium salts with ethyl vinyl ether.[13] This method was used for the preparation of the following compounds: II B, III D.

Method C. Desulfuration of corresponding 1,6,6a^{IV}S-trithiapentalenes.[14],[15] This method was used for the preparation of the following compounds: III C, III J, III K, III L, IV D, IV F.

Method D. Reaction of substituted 1,2-dithiole-3-thiones with phenacyl halides.[16],[17] This method was used for the preparation of the following compounds: III F, IV G.

Method E. Hydrolysis of α-(1,2-dithiole-3-ylidene)alkyliminium salts with sodium hydroxide in dimethyl formamide.[18] This method was used for the preparation of the following compounds:

II A

1'-Deuterio-1'-(5-phenyl-1,2-dithiole-3-ylidene)acetophenone.[19]

4-Deuterio-1'-(5-phenyl-1,2-dithiole-3-ylidene)acetophenone.[19]

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