A Study of the Fragmentation Processes of Some 2-Monoalkyl- and 2,2-Dialkylsubstituted 4,4-Diphenyl-1,3-oxathiolan-5-ones upon Electron Impact

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The mass spectra of seven 2-monoalkyl and 2,2-dialkylsubstituted 4,4-diphenyl-1,3-oxathiolan-5-ones have been recorded. Of the five possible modes of ring cleavage to produce fragments containing two and three ring atoms, only three types have been observed for the monoalkylsubstituted oxathiolanones, while all five modes are operative in the case of the dialkylsubstituted compounds. The predominating fragmentation mode for the monoalkylsubstituted compounds is the expulsion of carbon dioxide. This mode is supressed by the direct formation of a thiobenzophenone ion from the molecular ion in the disubstituted compounds. The difference between the thermal fragmentation of these compounds and their fragmentation upon electron impact, is discussed.

The fragmentation of 1,3-oxathiolane and methylsubstituted 1,3-oxathiolanes upon electron impact has been studied by Pasto.[1] He has found that, of the five possible modes of ring cleavage (type 1 − 5) where fragments containing two and three ring atoms are formed, only two modes are actually observed, *viz.* type 1 and 2.

Type 1   Type 2   Type 3   Type 4   Type 5
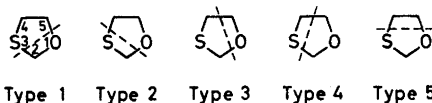
We have studied the fragmentation modes of a series of substituted 1,3-oxathiolan-5-ones I − IV.

I $R^1 = R^2 = H$
II A $R^1 = H, R^2 = CH_3$
II B $R^1 = R^2 = CH_3$
III A $R^1 = H, R^2 = C_2H_5$
III B $R^1 = R^2 = C_2H_5$
IV A $R^1 = H, R^2 = C_3H_7$
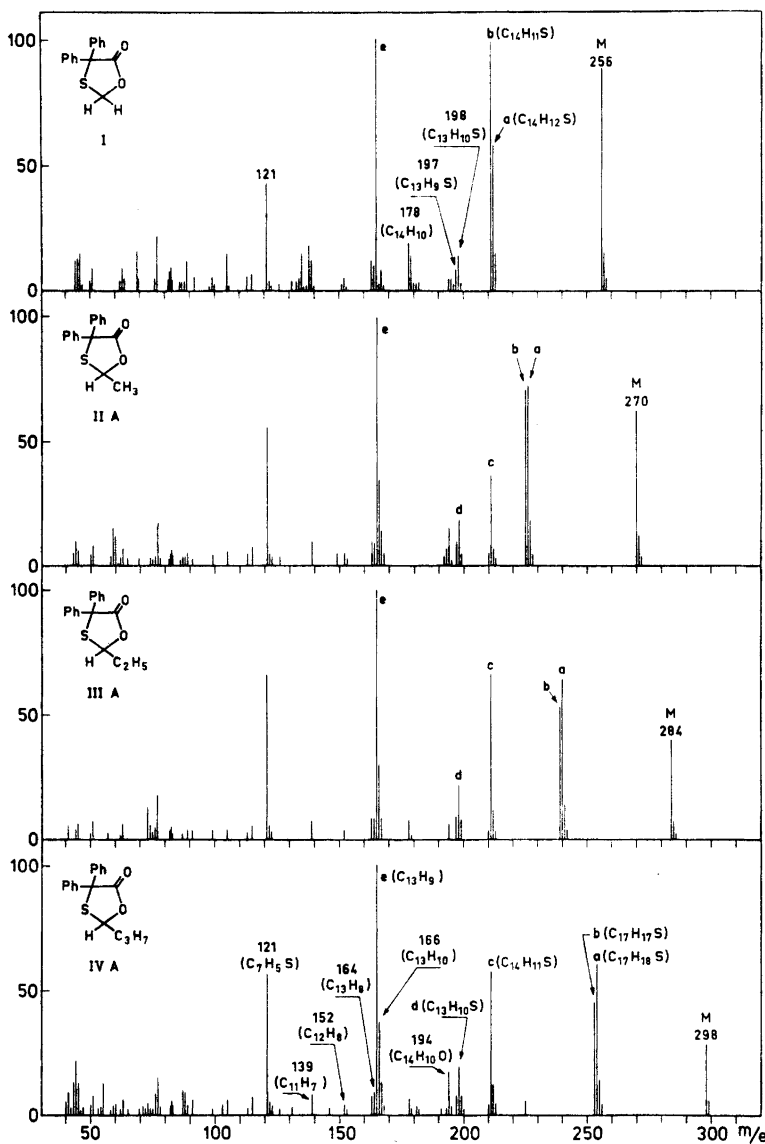IV B $R^1 = R^2 = C_3H_7$

Fig. 1. Mass spectra of unsubstituted or 2-monoalkylsubstituted 4,4-diphenyl-1,3-oxathiolan-5-ones (group A) at 70 eV. Peaks of lower abundance than 2 % are omitted.

The presence of a carbonyl group in the 5-position enhances the possibility of fragmentation of type 3, *i.e.* elimination of carbon dioxide, whereas the presence of two phenyl groups in the 4-position may promote some fragmentations of types 4 and 5.

The mass spectra of (I) and the 2-monoalkylsubstituted oxathiolanones (group A) are shown in Fig. 1; those of the 2,2-disubstituted compounds (group B) are given in Fig. 2.

Where appropriate the elemental compositions of the fragments were determined from high-resolution measurements. These compositions are indicated in the figures by their corresponding elemental formulae.
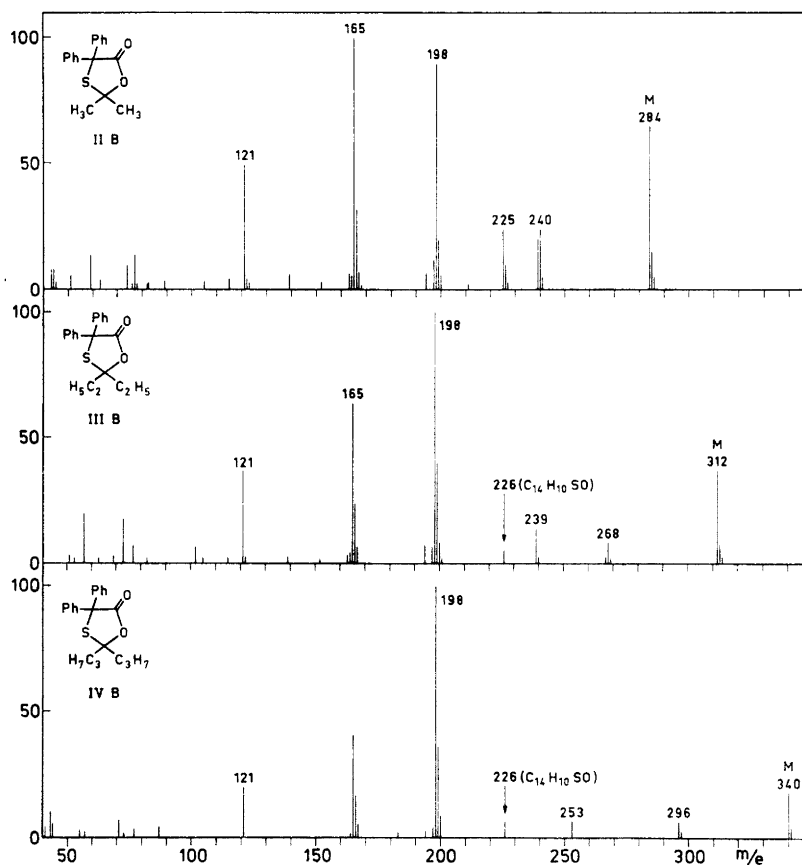

Fig. 2. Mass spectra of 2,2-dialkylsubstituted 4,4-diphenyl-1,3-oxathiolan-5-ones (group B) at 70 eV. Peaks of lower abundance than 2 % are omitted.

The main fragmentation path for group A and group B compounds are given in schemes 1 and 2, respectively.

The transitions marked with asterisks are those in which assignment has been substantiated by the presence of appropriate metastable peaks.
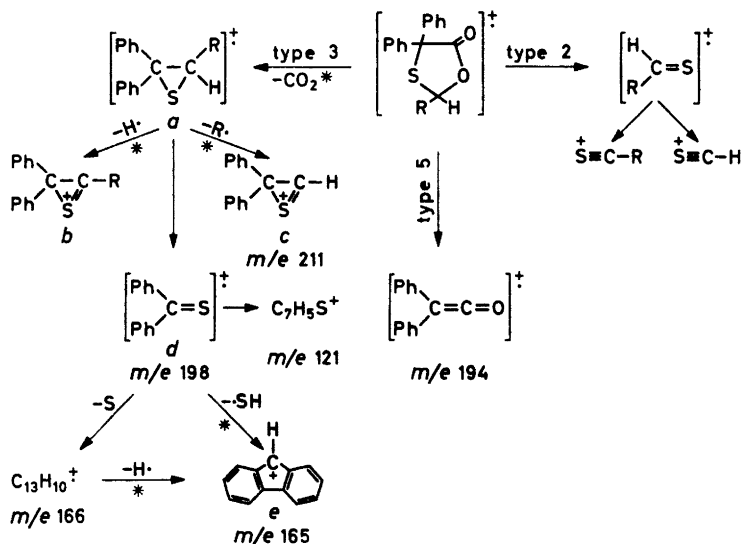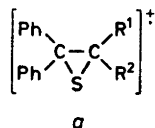
Scheme 1. Main fragmentation pathways for compounds of group A.
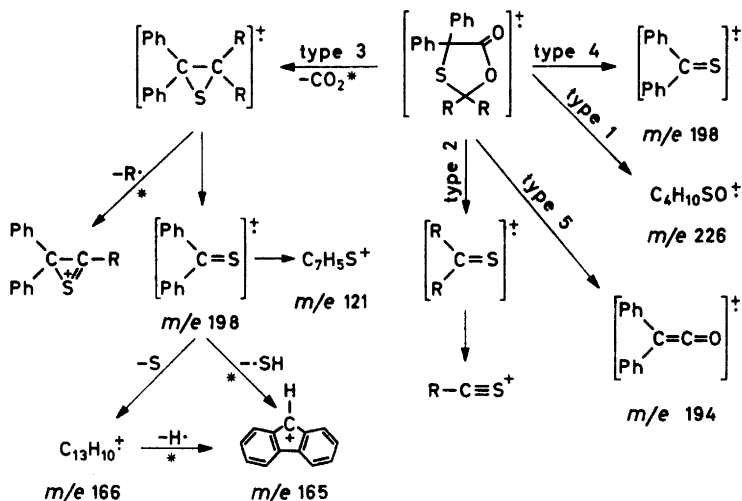
Scheme 2. Main fragmentation pathways for compounds of group B.

Type 3 fragmentation. The most characteristic fragmentation pattern common to all the compounds in group A, and also exhibited by group B compounds, is that of the fragmentation pathway initiated by the expulsion

of CO_2 from the molecular ion. (Schemes 1 and 2). The $M - 44$ ion most probably has the structure a.

$$\left[\begin{array}{c} Ph \\ \diagdown \\ Ph \diagup \end{array} C{-}C{\diagup}{\diagdown} \begin{array}{c} R^1 \\ \\ R^2 \end{array} \right]^{\ddagger}$$

a

This may be compared with the formation of thiiranes by the thermal fragmentation of 2,4,4-triaryl-1,3-oxathiolan-5-ones.[2] Structure a is supported by the elimination of $HS\cdot$ from $a - H$ in the spectrum of (I) yielding an ion at m/e 178 with the elemental composition $C_{14}H_{10}$. A metastable peak indicates that this ion is formed by elimination of $HS\cdot$ from $a - H$. Further decomposition of the primary fragment ion a yields the ion b by loss of $H\cdot$, or the ion c by loss of $R\cdot$.

In the case of group A compounds the m/e 198 ion, d, is also most probably formed from a since, in the low energy spectra recorded at decreasing voltage, the intensity of the latter increases while those of b, c and d are decreased in approximately the same ratio.

However, as is discussed later, the low energy spectra of group B compounds indicate a quite different origin for the m/e 198 ion, although it is possible that the mechanism suggested for the formation of d in group A is also operative in group B.

Metastable peaks in all the spectra support the next step in the degradation scheme as that of the formation of m/e 165, e, which is the base peak in all spectra of the compounds in group A. Pailer et al.[3] have recorded both the mass spectra of (I) and of 2,4,4-triphenyl-1,3-oxathiolan-5-one and have proposed structure e for this ion; cf. the formation of the tribenzotropylium ion from triphenylethylene upon electron impact.[4]

e
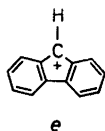
We assume that e can be formed in two ways, either directly, by expulsion of $HS\cdot$ from the rearranged d or, as supported by the low energy spectra, via m/e 166 by successive loss of S and $H\cdot$. Further a rather intense peak m/e 121 is observed, formed from d by loss of a phenyl group.

Apart from the different abundances of m/e 198 in the spectra of the two groups, a comparison of the corresponding peaks formed via the fragmentation pathway initiated by expulsion of CO_2 from the molecular ions shows that they are formed with nearly the same relative intensity.

Also the appearance of the metastable peaks of the two groups, which are associated withs this pathway, shows a high degree of similarity of each

other. The one due to the loss of CO_2 from the molecular ion is, for both groups, of the "flat topped" type.[5,6] The kinetic energy release associated with this process has been calculated for both IV A and IV B from the width of the metastable peaks measured at different accelerating voltages. The values obtained were 0.61 ± 0.01 eV for IV A and 0.59 ± 0.01 eV for IVB *i.e.* there is no significant difference.

Type 4 fragmentation. A comparison of the low-voltage spectra (Fig. 3) of IV A and IV B, which are representative of the two groups, reveals that they are markedly different since, although *a* has become the most important ion in the spectrum of IV A at 13 eV, there is negligible change in the abundance of this ion in the spectrum of IV B at the same voltage.

The fact that *m/e* 198 in IV B still retains its intensity at 13 eV, taken together with the presence of a weak metastable peak in the spectrum of IVB at mass 115 ($198^2/340 = 115.2$), has led to the conclusion that the *m/e* 198 ion can be formed directly from the molecular ion by a ring cleavage of type 4 in group B compounds while, if this type of ring cleavage does occur in group A compounds, it is to a much smaller extent.*

Type 1 fragmentation. A peak at *m/e* 226 is found in all the spectra of the group B compounds; in the case of III B and IV B the elemental composition of the ion corresponding to this peak has been determined as $C_{14}H_{10}SO$. The
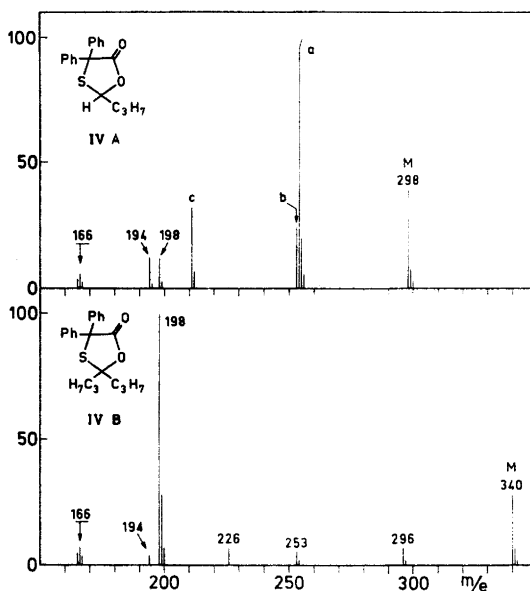

Fig. 3. Mass spectra of 2-propyl-4,4-diphenyl-1,3-oxathiolan-5-one and 2,2-dipropyl-4,4-diphenyl-1,3-oxathiolan-5-one at 13 eV. Peaks of lower abundance than 2 % are omitted.

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* *Note added in proof.* We have later verified this by application of metastable defocussing technique. The molecular ion was found to be a precursor for the *m/e* 198 ion in the case of IV B, while no metastable peaks corresponding to this process were observed in the case of IV A.

ion retains its relative intensity in the low-voltage spectra and is most probably formed by a ring cleavage of type 1.

Type 1 fragmentation can be excluded for the compounds in group A.

Type 2 fragmentation. A ring cleavage of type 2, would result in an ion of the general formula

$$\left[\begin{array}{c} R^1 \\ \diagdown \\ \diagup \\ R^2 \end{array} C{=}S \right]^{+\cdot}$$
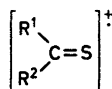
All the spectra, except that of IV B, exhibit a peak with a mass corresponding to this structure. Further degradation of this ion leads to the following fragments

$$\overset{+}{S}{\equiv}C-R^1 \quad \text{and} \quad \overset{+}{S}{\equiv}C-R^2$$
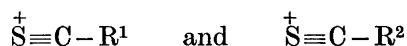
Peaks corresponding to these ions are present in all the spectra, including the spectrum of IV B.

Type 5 fragmentation. A peak at m/e 194, present in all the spectra of both groups, indicates a type 5 fragmentation. A comparison of corresponding A- and B-spectra shows that the abundance of this ion is greater in the group A spectra. This may indicate that the 2-monoalkylsubstituted oxathiolanones have a greater tendency to undergo type 5 fragmentation.

CONCLUSIONS

Of the five possible modes of fragmentation of the oxathiolane ring system, in which the ring is cleaved into fragments of two and three ring-atoms, all are observed for the 2,2-dialkylsubstituted oxathiolanones (group B), while only those of types 3, 5, and 2 are observed in the case of the 2-monoalkyl-substituted oxathiolanones (group A). For group B compounds the predominant fragmentation mode is of type 4, followed by types 3, 1, 2, and 5, in order of decreasing importance, while for group A compounds the most important mode is of type 3, followed by types 5 and 2.

The decomposition pathway initiated by the type 3 fragmentation together with the other 4 types of ring cleavage, taking place without hydrogen transfer, account for nearly all of the important peaks in the mass spectra of both groups. With the ions at m/e 165 and 194 as exceptions, they all contain sulfur.

The marked difference between the spectra of the two groups of compounds can be principally ascribed to the different abundance of the m/e 198 ion, which in turn is due to the different ability of the compounds in the two groups to undergo the same types of ring fragmentation. For all compounds of both groups the m/e 198 ion is the precursor of both the m/e 165 ion, e, and the m/e 121 ion. The ion abundances for the latter two ions are in approximately the same ratio for both group A and group B compounds, whereas the ratio of the ion abundances of each of these peaks to that of the m/e 198 ion is the same only in group A (Table 1).

Table 1. Relative ion abundances of three selected fragments and their ratios with respect to each other.

Compound	*m/e* 198 %	*m/e* 165 %	*m/e* 121 %	$\dfrac{[m/e\ 165]}{[m/e\ 121]}$	$\dfrac{[m/e\ 198]}{[m/e\ 165]}$	$\dfrac{[m/e\ 198]}{[m/e\ 121]}$
I	14	100	43	2.3	0.14	0.46
II A	18	100	55	1.8	0.18	0.33
III A	22	100	66	1.5	0.22	0.32
IV A	19	100	56	1.8	0.19	0.34
II B	90	100	50	2.0	0.9	1.8
III B	100	64	37	1.7	1.6	2.7
IV B	100	41	20	2.0	2.4	5.0

These observations suggest that the *m/e* 198 ion is the precursor of the *m/e* 165 and *m/e* 121 ions (to apparently the same extent for both groups of compounds) only when it is generated via the type 3 fragmentation.

On the other hand these data do not necessarily indicate that the structure of the *m/e* 198 ion generated *via* the type 3 fragmentation is different to that when it is formed directly by the type 4 fragmentation.

In both cases the structure is most probably that of a thiobenzophenone ion, but which is generated with different energy according to the mode of formation. Thiobenzophenone itself forms a fragmentation pattern upon electron impact at 70 eV, in which the dominant fragments are the molecular ion (*m/e* 198) and those at *m/e* 165 and 121, having approximately the same abundances.

THERMOLYSIS OF IV A AND IV B

The thermal fragmentation of 2-monoarylsubstituted 4,4-diphenyl-1,3-oxathiolan-5-ones has been studied in detail.[2] It was found that oxathiolanones of this type decomposed at 100 — 120° with evolution of carbon dioxide. The decomposition further yielded arylsubstituted ethylenes (formed *via* corresponding thiiranes) and elementary sulfur.

In order to determine whether any similarity existed between the thermal fragmentation of mono- and dialkylsubstituted 4,4-diphenyl-1,3-oxathiolan-5-ones, and the fragmentation caused by electron impact, IV A and IV B were thermolysed.

The thermolysis, which is slow below 170°, was followed by thin layer chromatography, as described previously,[2] the compound formed being identified by mass spectrometry. It was found that sulfur and the substituted ethylene, V, were formed from IV A, while IV B yielded VI and sulfur.

<div align="center">

Ph—C(—Ph)=C(—C₃H₇)(—H)

V

Ph—C(—Ph)=C(—C₃H₇)(—C₃H₇)

VI

</div>
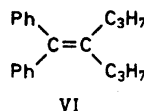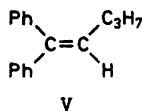
Although it was not possible to detect any thiirane among the pyrolysis products either by thin layer chromatography or by mass spectrometry, it is probable, however, that the formation of the ethylene derivatives proceeds *via* thiiranes but, at the high temperature necessary for the thermolysis, they decompose spontaneously, releasing sulfur. This is not incompatible with the observation that thiirane ions are formed in the fragmentation of the oxathiolanones upon electron impact, since they are stabilised as positive ions.

As no fragments corresponding to the ethylenes are found in the mass spectra of oxathiolanones, any thermal fragmentation taking place before ionisation can be excluded.

EXPERIMENTAL

Mass spectra were obtained on an MS 902 mass spectrometer using the direct sample insertion system and an ion source temperature of approximately 75°C. Unless otherwise stated, 70 eV electrons were used. High resolutions mass measurements were carried out under the same conditions and were accurate to within ± 3 ppm.

Oxathiolanones. These compounds were prepared from aldehydes or ketones and thiobenzilic acid. As the method previously described for the preparation of 2-aryl-substituted oxathiolanones [7] was not found suitable for the preparation of 2-alkyl and 2,2-dialkyl substituted oxathiolanones, the method described below was used.

2-Ethyl-4,4-diphenyl-1,3-oxathiolan-5-one. Propionaldehyde (1 g), thiobenzilic acid (2.4 g) and boron trifluoride diethyl etherate (0.5 ml) were dissolved in 50 ml of dry benzene, and refluxed for 1 h. The mixture was allowed to stand at room temperature for 24 h, after which it was poured onto ice. The benzene layer was washed with water until the water was neutral. The solution was dried over sodium sulfate and evaporated *in vacuo.* The oil obtained in this way crystallised on cooling. Yield 70 %. M.p. 40.0—41.5. Recrystallised from pentane. (Found: C 72.06; H 5.77; S 11.32. Calc. for $C_{17}H_{16}O_2S$: C 71.82; H 5.67; S 11.25).

2,2-Diethyl-4,4-diphenyl-1,3-oxathiolan-5-one. From 3-pentanone. Refluxing time 6 h. Yield 66 %. M.p. 70.5—72.0. Recrystallised from methanol. (Found: C 72.95; H 6.38; S 10.51. Calc. for $C_{19}H_{20}O_2S$: C 73.06; H 6.45; S 10.24).

2-Propyl-4,4-diphenyl-1,3-oxathiolan-5-one. From butyraldehyde. Refluxing time 1 h. Yield 65 %. M.p. 39.5—40.5. Recrystallised from pentane. (Found: C 72.75; H 6.19; S 10.92. Calc. for $C_{18}H_{18}O_2S$: C 72.46; H 6.08; S 10.72).

2,2-Dipropyl-4,4-diphenyl-1,3-oxathiolan-5-one. From 4-heptanone. Refluxing time 6 h. Yield 72 %. M.p. 62.0—63.0. Recrystallised from methanol. (Found: C 74.25; H 7.12; S 9.53. Calc. for $C_{21}H_{24}O_2S$: C 74.09; H 7.11; S 9.40).

Thermolysis. Thermolysis of the 2-alkyl substituted oxathiolanones was carried out in the same manner as that previously described for the thermolysis of 2-aryl substituted oxathiolanones.[2]

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