

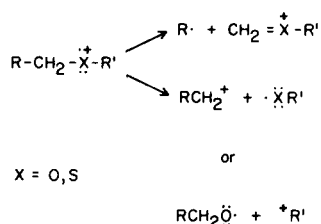
Electron Bombardment Induced Fragmentation of Substituted Oxathiolanes

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The mass spectral fragmentation patterns of 1,3-oxathiolane and 2-, 4-, and 5-substituted oxathiolanes have been recorded. The various fragments have been identified by high-resolution mass spectrometry when appropriate. Of the five possible modes of ring cleavage to produce two- and three-atom fragments only two modes are actually observed. The mode of fragmentation of the 1,3-oxathiolane ring differs from that proposed for 1,3-dioxalane and in all probability occurs in multistep processes.

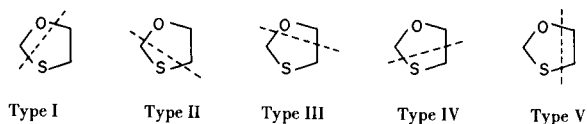
The molecular radical cations of ethers and sulfides formed in the mass spectrometer undergo two predominant modes of fragmentation outlined in the following equation.



The interpretation of the mass spectral fragmentation patterns of ethylene ketals and thioketals has received considerable attention with respect to structure elucidation in the steroid series (2). However, little attention has been devoted to the fragmentation of the dioxalane or dithiolane ring systems. Friedel and Sharkey (3) have recorded the mass spectra of several "acetal-type" compounds including 1,3-dioxalane. Friedel and Sharkey (3) propose that 1,3-dioxalane fragmentation may be considered as occurring by "two bonds simultaneously" as illustrated in 1.



The 1,3-oxathiolane system (2) provides a rather interesting system for study in view of the number of possible "two-bond" fragmentations as illustrated below.

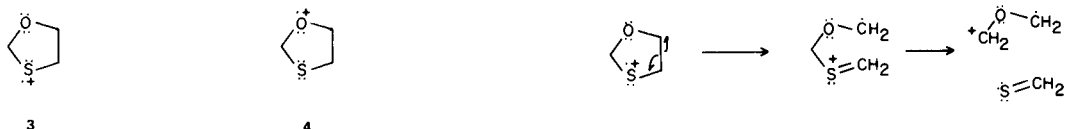


As a number of substituted oxathiolanes were available from a previous study (4) the mode(s) of fragmentation of the 1,3-oxathiolane system on electron bombardment were subjected to study. The m/e data, and high-resolution m/e data when appropriate, and elemental compositions of the fragments are provided in Table 1.

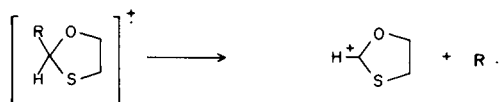
Prior to the consideration of possible modes of fragmentation of the 1,3-oxathiolane ring system, consideration should be given to the probable electronic structure(s) of the molecular ion formed on electron bombardment. The ionization potentials of 2-methyl-2-ethyl- and 4-methyl-1,3-oxathiolane were determined to be 8.6 and 8.7 ± 0.2 eV, respectively. The lowest ionization energy is most consistent with the loss of a non-bonded electron (5) from sulfur giving 3 as indicated by comparison with the ionization potentials of dimethylsulfide (8.69 eV) and diethyl sulfide (8.43 eV) (6). Exclusive ionization at sulfur is not probable, owing to the only slightly higher ionization potentials for removal of a non-bonded electron from oxygen [dimethyl ether (10.5 eV) and diethyl ether (9.55 eV) (7)] and the relatively broad energy range for the exciting electron beam. Hence, 4 is also probably formed to a considerable extent.

Fragmentation with Loss of Alkyl Substituents.

Comparison of the data for the parent system (2), the

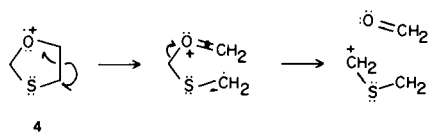


2,2-disubstituted-1,3-oxathiolanes, and the 4- and 5-methyl-1,3-oxathiolanes shows that alkyl groups are lost by β -carbon-carbon bond scission, as illustrated below, from the 2-position much more readily than alkyl groups in the 4- and 5-positions. Loss of a hydrogen atom from the 2-, 4-, or 5-positions is not a relatively favorable reaction. Loss of the largest alkyl group from the 2,2-disubstituted-1,3-oxathiolanes is readily apparent and is consistent with the observations of Djerassi and coworkers (2).



Type III Fragmentation.

Type III fragmentation involving the cleavage of the C_4-C_5 bond could conceivably be initiated by C_4-C_5 bond scission in 4 as illustrated (8). This pathway would produce



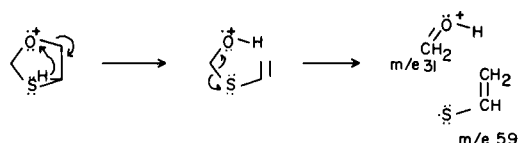
a C_2H_4S (m/e 60) fragment from 1,3-oxathiolane; the second most intense peak in the mass spectrum of 2. However, this process would lead directly to the formation of C_4H_8S (m/e 88), $C_5H_{10}S$ (m/e 102), and C_2H_4O (m/e 44) fragments from 2,2-dimethyl, 2-methyl-2-ethyl-, and 5-methyl-1,3-oxathiolane, respectively. Inspection of the data in the table reveals that these fragments are not formed (9), and hence, type III fragmentation is not a detectable mode of fragmentation of the 1,3-oxathiolane ring system.

Type IV Fragmentation.

Type IV fragmentation, similar to the type III fragmentation involving C_4-C_5 bond cleavage as outlined below, does not occur to any substantial extent as evidenced by the absence of $C_4H_8O^+$ and $C_5H_{10}O^+$ fragments in the mass spectra of 2,2-dimethyl- and 2-methyl-2-ethyl-oxathiolane.

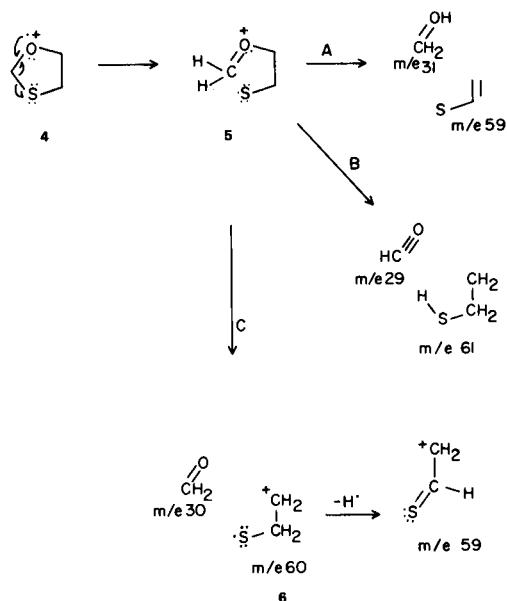
Type I Fragmentation.

Type I fragmentations can conceivably occur by two basically different processes, only one of which appears to occur. Cleavage of the C_5-O bond of 1,3-oxathiolane by β -hydrogen abstraction as illustrated below followed by C_2-S bond cleavage would produce CH_3O (m/e 31) and C_2H_3S (m/e 59) fragments. The m/e 31 peak is barely



detectable whereas the m/e 59 peak is one of the more prominent peaks in the mass spectrum of 2. However, the m/e 59 peak of 2 is apparently formed by loss of a hydrogen atom from the $C_2H_4S^+$ (m/e 60) fragment as evidenced by a metastable peak at 58.05 (calcd. 58.05). No metastable peak corresponding to the $M \rightarrow 59$ fragmentation is evident. The cyclic nature of the oxathiolane system apparently does not allow for the formation of a suitable transition state for the β -hydrogen atom abstraction and elimination reaction.

Type I cleavage does occur *via* intermediate 5 formed by C_2-S bond cleavage in 4 as is illustrated below. Decomposition of 5 *via* path A does not occur to any significant extent (see above discussion). Path B decomposition with



hydrogen atom rearrangement occurs to some extent giving HCO^+ (m/e 29) and $\text{C}_2\text{H}_5\text{S}^+$ (m/e 61) from **2**. The HCO^+ and $\text{C}_n\text{H}_{2n+1}\text{S}^+$ fragments are not observed in the mass spectra of the 2,2-dialkyloxathiolanes.

Path C decomposition of **5** is the predominant fragmentation process for **5** giving the $\text{C}_2\text{H}_4\text{S}^+$ fragment (m/e 60), metastable peak at 39.95 (calcd. 39.95), as the second most intense peak in the mass spectrum of **2**. Intense peaks corresponding to $\text{C}_3\text{H}_6\text{S}^+$ (m/e 74) appear in the mass spectra of the 4- and 5-methyloxathiolanes. The $\text{C}_2\text{H}_4\text{S}^+$ fragment is the most abundant ion formed in the fragmentation of the 2,2-dialkyloxathiolane molecular ions. The introduction of alkyl groups in the 4- and 5-positions of the oxathiolane ring leads to an even greater favoring of decomposition of **5** via path C relative to path B.

Fragment **6** undergoes loss of a hydrogen atom to give $\text{C}_2\text{H}_3\text{S}^+$ (m/e 59) as indicated by a metastable peak at 58.05 (calcd. 58.05). This type of ion is not very abundant in the mass spectrum of 4-methyloxathiolane, but is quite abundant in the mass spectra of the 5-methyl and 2,2-dialkyloxathiolanes.

The decomposition of **6** to a sulfur atom and olefin will be discussed further under Type V fragmentation.

Although the Type I fragmentation is depicted as a two step process involving initial C₂-S bond cleavage, Type I fragmentation may also occur by a simultaneous two-bond fragmentation process. However, the involvement of **5** as an intermediate in the Type I fragmentation process has the virtue of providing mechanisms for the formation of other ions observed in the mass spectra of the substituted oxathiolanes.

Type II Fragmentation.

Type II fragmentation is very similar to the type I fragmentation; only one pathway of the two possible

occurring as is illustrated above. Products formed via initial transannular β -hydrogen atom abstraction with olefin formation are not present.

As with **5**, intermediate **7** may fragment in one of several pathways (designated A', B', and C' which are analogous with fragmentation pathways A, B and C for **5** as described above).

Fragmentation of **7** via path A' occurs to a limited extent to give CH_3S^+ (m/e 47). The analogous pathway for fragmentation of **5** was not observed. Fragmentation of **7** via path B' would appear to be the most favorable mode of decomposition of **7** giving CHS^+ (m/e 45) and $\text{C}_2\text{H}_5\text{O}^+$ (m/e 45), the former fragment being by far the more abundant. Neither of these fragments appear in the mass spectra of 2,2-dialkyloxathiolanes. However, the CH_2S^+ fragment derived from **7** via path C' may well undergo the loss of a hydrogen to give CHS^+ . Unfortunately, no metastable peaks are observed which would help clarify this matter.

Fragment **8** undergoes the loss of hydrogen, but only to a relatively minor extent relative to **6**. Again, as with **6**, the presence of a methyl group on the carbon from which the hydrogen is lost disfavors the reaction. Loss of olefin from **8** will be discussed under type V fragmentation.

Again one cannot distinguish between a two-step process and a simultaneous two-bond fragmentation process although the two-step process readily provides a consistent rationalization for the formation of many other ions in the mass spectra of the oxathiolanes.

Type V Fragmentation.

Type V fragmentation in **2** and the 2,2-dialkyloxathiolanes is best represented as occurring by the decomposition of intermediates of the type **6** and **8** formed by Type I and II fragmentation of the molecular ion as illustrated below. A direct fragmentation of the molecular ion of **2** to produce olefin cation in a two-bond cleavage process would also lead to the formation of a OCH_2S^+ (m/e 62) fragment, a fragment which is not found in the mass spectra of **2** and the 2,2-dialkyloxathiolanes.

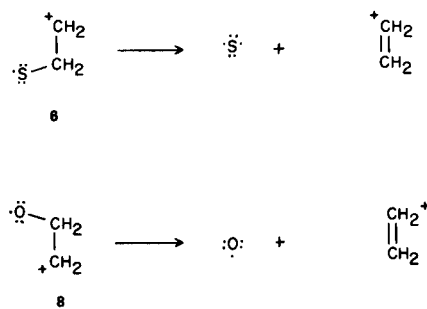
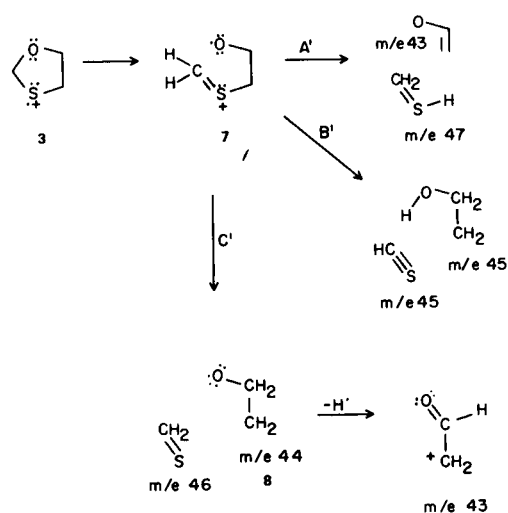

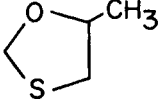
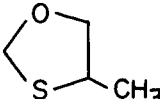
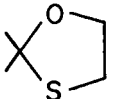
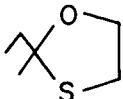


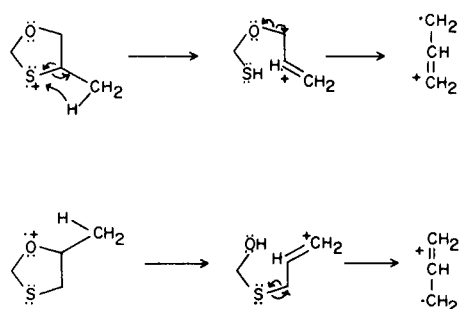
TABLE I

 Tabulation of Mass Spectral Data (a)
 Relative Intensities

m/e (b)	Identity (c)					
132	C ₆ H ₁₂ OS					69
118	C ₅ H ₁₀ OS				60.8	
117	C ₅ H ₉ OS					5.9
104	C ₄ H ₈ OS		100	73		
103	C ₄ H ₇ OS				13.0	100
90	C ₄ H ₆ OS	100				
89	C ₄ H ₉ S	17				1.0
88	C ₄ H ₈ S				<2	2.2
74 (74.017)	C ₃ H ₆ S(74.019)		57	100	<3	
73 (73.065)	C ₃ H ₉ O(73.067)					11.4
(73.011)	C ₃ H ₅ S(73.013)			5.0		0.5
72	C ₃ H ₈ O					5.3
61	C ₂ H ₅ S	20				
60	C ₂ H ₄ S	78	84		100	100
59	C ₂ H ₃ S	37	30		30	14.6
58	C ₃ H ₆ O			8.0		
57(57.034)	C ₃ H ₅ O(57.033)					6.0
(56.980)	C ₂ HS(56.978)					5.3
55	C ₃ H ₃ O					5.9
47(46.996)	CH ₃ S(46.999)	8				
46(45.991)	CH ₂ S(45.986)	8	23	14		
45(45.037)	C ₂ H ₅ O(45.034)	v.w.			15	9.1
(44.984)	CHS(44.980)	38	37	58		
44(44.026)	C ₂ H ₄ O(44.025)	5				1.4
(43.972)	CS(43.972)	2	2	12		1.0
43	C ₂ H ₃ O	4	18		31	62
42	C ₃ H ₆	4	12	8		
41(41.040)	C ₃ H ₅ (44.039)		73	27		
39	C ₃ H ₃		25	30		
30	CH ₂ O		<1	12		
29(29.039)	C ₂ H ₅ (29.039)	v.w.				2.1
(29.003)	CHO(29.003)	15	20	8		5.0
28(28.031)	C ₂ H ₄ (28.031)	11			7	5.9

(a) Recorded on an Associated Electronics Ltd., MS902 Spectrometer. Peaks arising from ¹³C and ³⁴S containing fragments have not been included in the tabulation. (b) Values in parentheses are observed high resolution m/e values using perfluoro-tri-butylamine as standard. (c) Values in parentheses are the calculated m/e values.

The introduction of a methyl group in the 4- and 5-positions enhances the Type V fragmentation. However, one does not form a C_nH_{2n} cation as expected for this process. Intense peaks appear for C_nH_{2n-1} fragments which cannot be readily visualized as arising from initial Type I or II fragmentation processes. Modified Type I and II processes in which the C_4-S and C_5-O bonds are cleaved in β -hydrogen atom abstraction-elimination reactions followed by C_2-O and C_2-S bond cleavages and loss of O and S respectively, do give rise to the $C_3H_5^+$ fragments (illustrated below). These pathways for type V fragmentation are considerably more important than the pathways for formation of the C_nH_{2n} fragments from intermediates of Type 6 and 8.



Summary

Of the five possible modes of fragmentation of the oxathiolane ring system to give two- and three-atom fragments, only Types I and II occur to a significant extent. The formation of the various fragments observed in the mass spectra of **2** and the substituted oxathiolanes can be readily rationalized in terms of a two-step fragmentation of the oxathiolane ring; some of the intermediates thus formed undergoing several modes of further fragmentation.

The ratios of Type I: Type II fragmentation vary with

the position of alkyl substitution on the oxathiolane ring system. The approximate ratios are 2.6:1 for **2**, 1:1 for 4-methyloxathiolane, 2.5:1 for 5-methyloxathiolane, and 2.3-2.5:1 for the 2,2-dialkyloxathiolanes. The predominant mode of fragmentation (Type I) occurs *via* loss of an electron from oxygen despite the fact that the non-bonded electrons on sulfur possess the lower ionization potential.

Acknowledgment.

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- (8) The structures of fragments employed in this article are used only to illustrate the origin of the atoms appearing in the two- and three-atom fragments and are not intended to represent possible structures of the fragments. In later schemes an $A-B^+$ radical cation may produce two sets of fragments, $A^+ + B^+$ and $A^+ + B^-$. In such cases the electrons and charges will not be illustrated.
- (9) Other fragmentation pathways are conceivably possible, however, the end results and conclusions are the same.

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