

## Electron-Impact Induced Fragmentation of Thiirene and Thiophene Dioxides

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Received May 10, 1974

The electron impact mass spectra of several substituted thiirene and thiophene oxides and dioxides have been investigated using both low and high resolution mass spectrometry. The predominant fragmentation process in the spectra of the thiirene compounds is the elimination of the hetero (SO or SO<sub>2</sub>) function and formation of a substituted acetylene ion. The 5-membered ring thiophene dioxides exhibit mainly elimination of SO rather than SO<sub>2</sub>. Plausible mechanisms leading to the formation of the principal ions are proposed on the basis of metastable transitions.

## Introduction

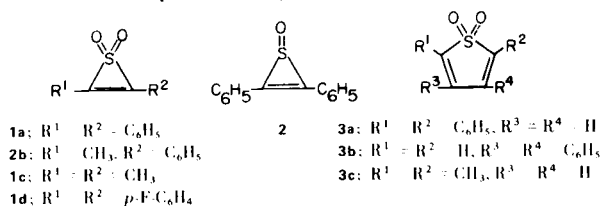
The mass spectrometry of heterocyclic compounds has been the object of considerable study, and numerous papers have been published on the electron-impact induced fragmentation process of saturated cyclopropanes incorporating an oxygen, sulfur or nitrogen heteroatom (2). On the other hand only a few reports have appeared on the mass spectrometry of unsaturated 3-membered ring heterocycles. These include studies on azirines (3) and diazirenes (4). Except for a brief report on the mass spectrum of 1,2,3-triphenylphosphirene oxide (5), no data are available on the especially interesting 3-heterocyclopropenes, compounds in which facile thermal and/ or ionic expulsion of the hetero function is to be expected. For this reason we have undertaken an investigation of the electron impact and chemical ionization mass spectrometric properties of a series of thiirene 1-oxides and thiirene 1,1-dioxides whose syntheses have been reported recently (6). The compounds examined in the present study include 2,3-diphenylthiirene 1,1-dioxide (1a), 2-methyl-3-phenylthiirene 1,1-dioxide (1b), 2,3-dimethylthiirene 1,1-dioxide (1c), 2,3-bis-(*p*-fluorophenyl)thiirene 1,1-dioxide (1d) and 2,3-diphenylthiirene 1-oxide (2) (Figs. 1-5). For comparison purposes we have also examined the electron impact spectra of the related thiophenes, 2,5-diphenylthiophene 1,1-dioxide (3a), 3,4-diphenylthiophene 1,1-dioxide (3b), and 2,5-dimethylthiophene 1,1-dioxide (3c) (Figs. 6-8), using both low and high resolution mass spectrometry.

## Results and Discussion

## Thiirene Compounds.

The mass spectra of compounds 1a, 1b, 1c, 1d and 2 are shown in Figures 1-5 respectively. A common feature in these mass spectra is the high abundance of the substituted acetylene ion, formed by elimination of SO<sub>2</sub> in 1a-1d or SO in 2. This ion constitutes the base peak in the spectra of 1a and 2 (*m/e* 178), 1c (*m/e* 54) and 1d (*m/e* 214) and a major peak in the spectrum of 1b.

Notable is the absence of molecular ions from the spectra of 1a, 1b and 1d while weak, but discernible molecular ion peaks were present in the spectra of 1c and 2. Because of the low thermal stability of thiirene dioxides (6a) it would be reasonable to assume that the absence of a molecular ion from the spectra of 1a, 1b and 1d is due to thermal decomposition during sample vaporization. However, it was possible, under virtually identical sample introduction conditions, to record intense molecular adduct-ion peaks by employing less severe ionization conditions with selective chemical ionization (7). It thus appears that, at least in part, the formation of the disubstituted acetylene ion is due to an ionic process (7). Furthermore elimination of SO<sub>2</sub> is a well established ionic process in the mass spectra of other less strained heterocyclic sulfones (8). Formation of the  $[R^1-C\equiv C-R^2]^+$  ion in the spectra of 1a and 2 is followed by two successive losses of acetylene (*m/e* 152 and *m/e* 126 in 1a and 2) or a combination of HC≡CH and HF losses in 1d. In the case of 1b the aryl-alkyl acetylene ion eliminates a hydrogen atom to give the peak at *m/e* 115  $[C_6H_5=C=C=CH_2]^+$ . The proposed structure for *m/e* 115 depicts elimination of a methyl hydrogen, although in view of recent data (9) and examples from other aromatic systems (10) the hydrogens are probably randomized



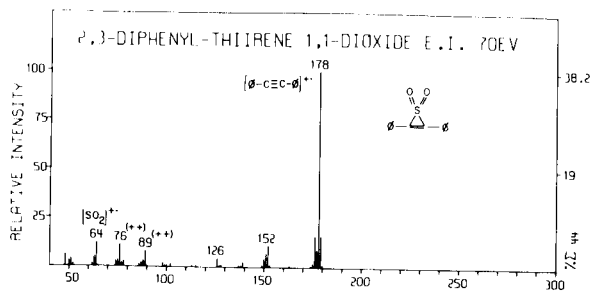


Figure 1. Mass spectrum of 2,3-diphenylthiirene 1,1-dioxide (**1a**).

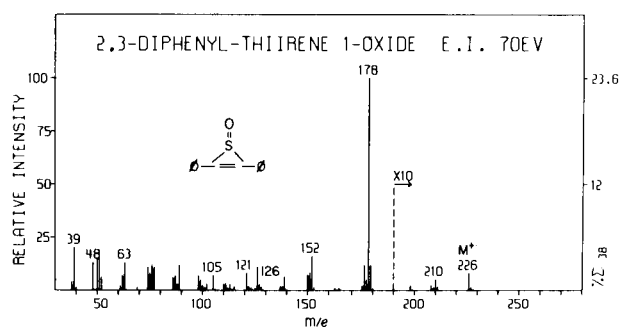


Figure 5. Mass spectrum of 2,3-diphenylthiirene 1-oxide (**2**).

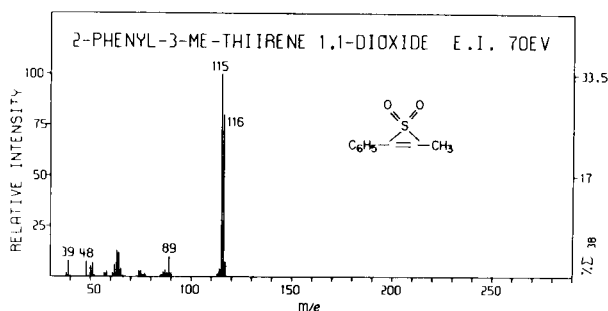


Figure 2. Mass spectrum of 2-methyl-3-phenylthiirene 1,1-dioxide (**1b**).

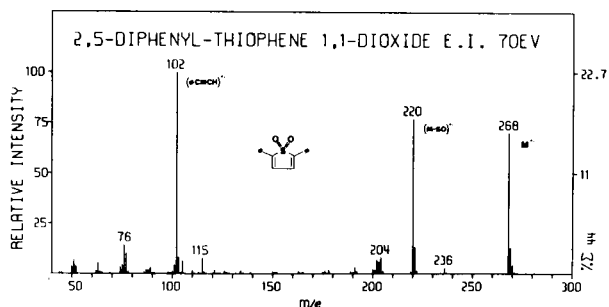


Figure 6. Mass spectrum of 2,5-diphenylthiophene 1,1-dioxide (**3a**).

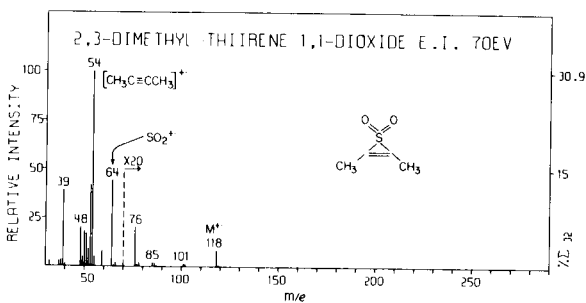


Figure 3. Mass spectrum of 2,3-dimethylthiirene 1,1-dioxide (**1c**).

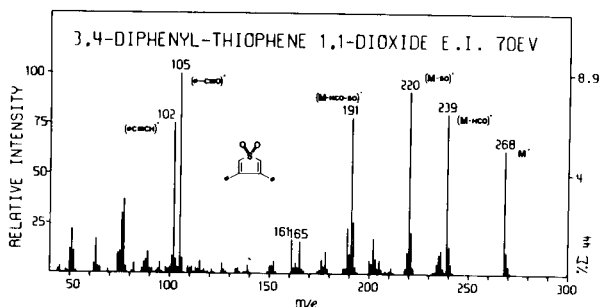


Figure 7. Mass spectrum of 3,4-diphenylthiophene 1,1-dioxide (**3b**).

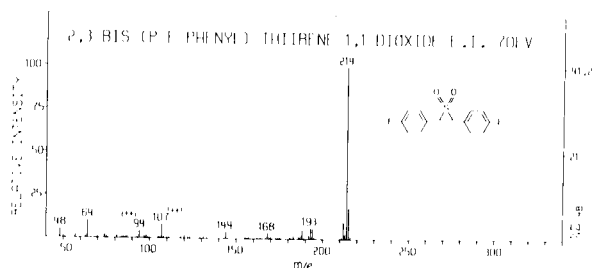


Figure 4. Mass spectrum of 2,3-bis(*p*-fluorophenyl)thiirene 1,1-dioxide (**1d**).

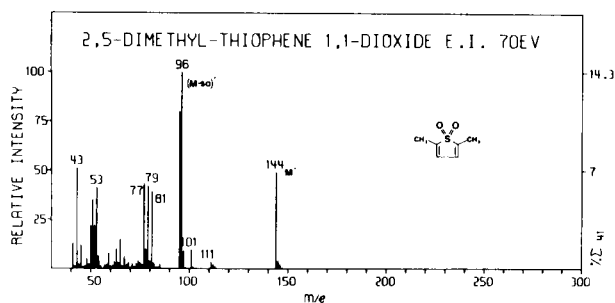


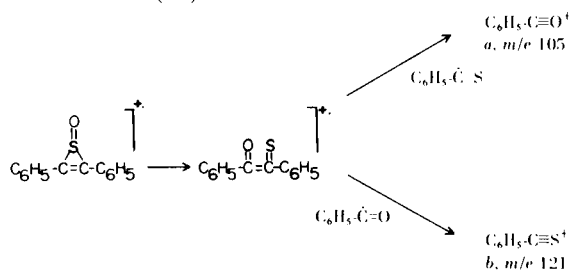
Figure 8. Mass spectrum of 2,5-dimethylthiophene 1,1-dioxide (**3c**).

prior to H<sup>+</sup> elimination.

Other notable features in the spectra of **1a**, **1d** and **2** are the relatively intense doubly charged ion peaks at *m/e* 89 and 76 in the spectra of **1a** and **2** and *m/e* 107 and 94 in the spectrum of **1d**. They correspond respectively to the disubstituted acetylene ion and its doubly charged ion product upon elimination of HC≡CH. Retention of the positive charge with the sulfone function is responsible for the ion at *m/e* 64 (SO<sub>2</sub><sup>+</sup>) and its decomposition product SO<sup>+</sup> (*m/e* 48) in Figs. 1-4.

In comparing the spectra of the diphenyl and dimethyl thiirene dioxides **1a** and **1c** one difference which is immediately apparent is the distinct presence of a molecular ion peak in the spectrum of **1c** as contrasted to its absence in that of **1a**. This difference becomes progressively more evident from the various chemical ionization spectra of these compounds, obtained using methane, isobutane, ammonia and dimethylamine as reagent gases (7). It is apparent that formation of the disubstituted acetylene ion directs the fragmentation of these compounds. Conjugative effects lead to a much more stable product ion from the diphenyl compound **1a** than from the dimethyl counterpart **1c**, and hence to a highly favorable unimolecular decomposition of the molecular ions of **1a**, **1b** and **1d**. Interestingly the spectrum of compound **1c** exhibits a small loss of OH<sup>+</sup> (*m/e* 101) from M<sup>+</sup>, a process frequently observed in aliphatic sulfones (11).

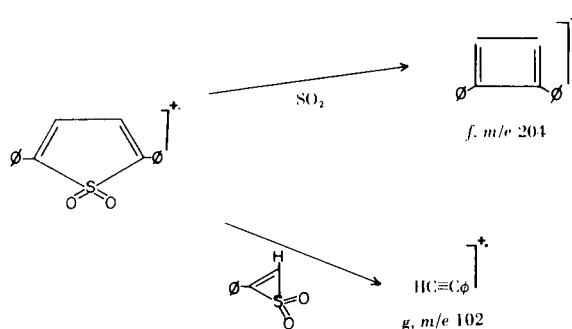
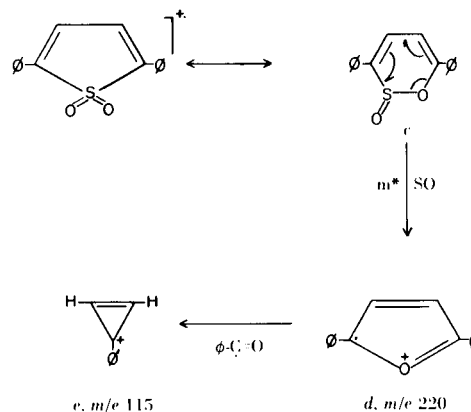
The spectrum of the thiirene sulfoxide **2** generally resembles that of the sulfone **1a** in that the majority of the ions are products of the further decomposition of the diphenylacetylene ion (*m/e* 178). Minor peaks at *m/e* 210 and *m/e* 208 correspond to losses of O and H<sub>2</sub>O, respectively. High resolution mass measurements identified the ions at *m/e* 105 and *m/e* 121 as C<sub>6</sub>H<sub>5</sub>O<sup>+</sup> and C<sub>6</sub>H<sub>5</sub>S<sup>+</sup>, respectively. A plausible mechanism for their formation is depicted in Scheme 1. The ionic intermediate postulated in Scheme 1 is similar to intermediates postulated by Dittmer in his study of the mass spectral fragmentation of monothiobenzil (12).



### Thiophene Dioxides.

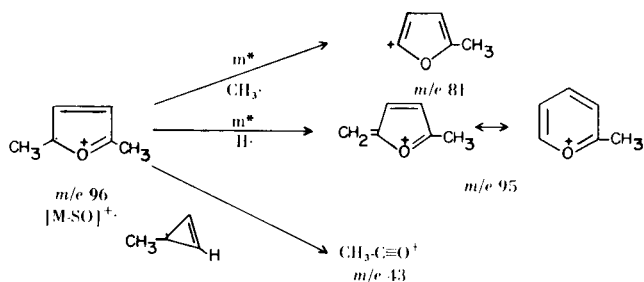
The spectra of compounds **3a-3c** (Figures 6-8) are in-

cluded in this study as less strained homologs of the 3-membered ring compounds. Simple thermal extrusion of sulfur dioxide is not possible in these systems and ionically-induced loss of SO<sub>2</sub> from the molecular ions is less favorable. A common feature in the spectra of the thiophene

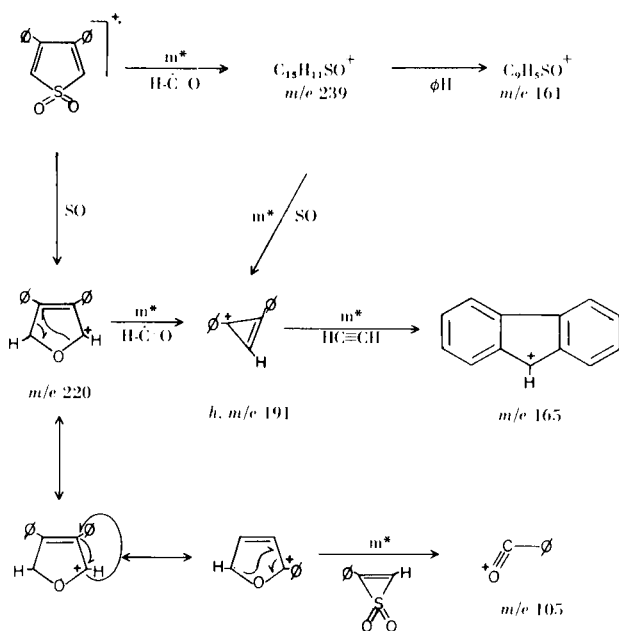


sulfones **3a-3c** is the elimination of SO rather than SO<sub>2</sub>, which gives rise to the peaks at *m/e* 220 in **3a** and **3b** and *m/e* 96 in **3c**. The elimination presumably proceeds *via* an oxathiane intermediate *c* formed by ring expansion as suggested in the mass spectra of other cyclic sulfones (2, 13). The preference for SO rather than SO<sub>2</sub> elimination in the thiophene sulfones is a direct reflection of the stability of the respective fragment ions *d* (*m/e* 220) (Scheme 2) and *f* (Scheme 3). This dependence on product ion stability is in line with the observations of Gamble and Tillett who studied the preference of SO *vs.* SO<sub>2</sub> elimination in cyclic aromatic sulfites (14). The fragmentation sequence for **3a** outlined in Scheme 2 also holds for the dimethyl counterpart **3c**. In addition, the [M-SO]<sup>+</sup> (*m/e* 96) ion in **3c** decomposes further as postulated in Scheme 4. Finally, the ions at *m/e* 77 and *m/e* 79 in the spectrum of **3c** correspond to C<sub>6</sub>H<sub>5</sub><sup>+</sup> and [M-SO<sub>2</sub>H]<sup>+</sup>, respectively.

It is particularly interesting to note the distinct differ-



Scheme 4  
Some characteristic fragmentations of 2,5-dimethyl-  
thiophene 1,1-dioxide (**3c**)



Scheme 5  
Fragmentation of 3,4-diphenylthiophene 1,1-dioxide (**3b**)

ence in the fragmentation patterns of the two isomeric diphenyl thiophene sulfones **3a** and **3b** (Figures 6 and 7). This difference is reflected in the intense peaks at  $m/e$  239, 191, 165, 161 and 105 present in the spectrum of the 3,4-diphenyl isomer in addition to the strong peaks at  $m/e$  102, 220 and 268 also present in the spectrum of **3a**.

Generally the same ionic intermediates utilized to explain the fragmentation of **3a** (Schemes 2 and 3) can also be employed to elucidate the structures of the ions produced upon fragmentation of **3b** (Scheme 5). For example, the loss of  $\text{HCO}^\bullet$  (15) from the molecular ion to give  $m/e$  239 is also preceded by ring expansion, followed by ring opening. (Schemes 2 and 5 respectively). Similarly loss of  $\text{HCO}^\bullet$  from  $m/e$  220 in the spectrum of **3b**, which gives rise to  $m/e$  191 (*h*, Scheme 5), is equivalent to the loss of  $\phi\text{CO}^\bullet$  in the spectrum of **3a** which produces  $m/e$  115 (*e*,

Scheme 2). Surprising is the presence of the base peak at  $m/e$  105 in the spectrum of **3b** (Figure 7). Metastable transitions relate this ion to  $m/e$  220  $[\text{M-SO}]^{\bullet+}$ ; and a phenyl-hydrogen interchange (Scheme 5) is a requirement for its formation. On the other hand it is also possible that this scrambling is a result of a skeletal rearrangement as demonstrated for the case of tetraaryl thiophene-dioxides (16).

## EXPERIMENTAL

Low resolution mass spectra were obtained with an LKB-9000 mass spectrometer. The ionizing energy was 70 eV, accelerating voltage 3.5 kV and the ion source temperature  $250^\circ$ . The mass spectra of the thiirene compounds were also recorded at lower ion source temperatures without any indication of enhancement of the molecular ion abundances. High resolution mass measurements were conducted with a CEC 21-110B high resolution mass spectrometer employing photoplate recording.

## Acknowledgment

The author thanks Dr. L. A. Carpino of the University of Massachusetts at Amherst for helpful comments and for providing the samples of heterocyclic compounds used in this study.

Financial assistance to the Institute for Lipid Research by the National Institutes of Health (GM-13901) is gratefully acknowledged.

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