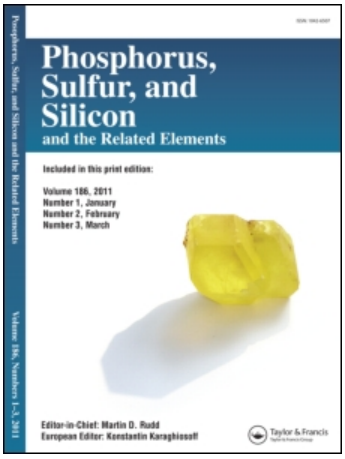


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# STUDIES IN THE HETEROCYCLIC COMPOUNDS: II. THE MASS SPECTRA OF SOME THIOPHENE-SULFONYL DERIVATIVES

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# STUDIES IN THE HETEROCYCLIC COMPOUNDS: II. THE MASS SPECTRA OF SOME THIOPHENE-SULFONYL DERIVATIVES

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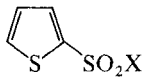
Mass spectra of five 2-thiophenesulfonyl derivatives are determined and the interpretations given are based on mechanistic analogy and supported in most cases by metastable peaks.



(**1**): X = Cl
(**2**): X = $NH_2$
(**3**): X = $N_3$
(**4**): X = NH—$C_6H_{11}$
(**5**): X = N(CH$_3$)(Ph)

FIGURE 1 Compounds studied



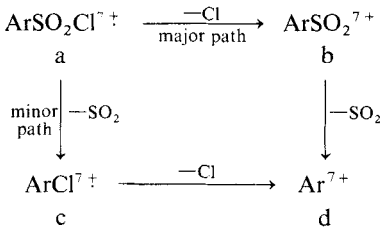
There are reports in the literature of the effect of electron-impact on thiophene,[1] alkylthiophenes,[2] 2-acyl, 2-aroyl and nitroaroylthiophenes.[3–5] However, there has been no report on the mass spectra of 2-thiophenesulfonyl derivatives. The present paper reports an examination of the mass spectra of five 2-thiophenesulfonyl compounds (1–5), figure 1, in order to assess the similarity between the fragmentation pattern of these compounds and those of other reported arysulfonyl derivatives.

## RESULTS AND DISCUSSION

The five 2-thiophensulfonyl compounds were prepared according to the procedure in part I[6] of this series. The most important ions in the mass spectra of the five compounds, at electron energies 70 eV and 20 eV, are given in Table I.

The mass spectra of the five compounds exhibit parent peaks varying in intensity from 48.4% in the sulfonamide (**2**) to 11% in the azide (**3**). Furthermore, the mass spectra of compounds 1–4 appears to be dominated by cleavage of the S—X bond (X = Cl, $NH_2$, $N_3$, $NHC_6H_{11}$) and their base peaks (at 70 eV) all occurring at m/e 39.

The spectrum of the sulfonyl chloride (**1**) showed a fragmentation pattern similar to those reported for other arylsulfonyl chlorides[7,8,9] (Scheme 1). The ion corresponding to b (m/e 147) in the spectra of 1 has a relative intensity of 95.7% at 70 eV while the ion corresponding to C (m/e 118) is only 4.3% (rel. int.).




SCHEME 1 General fragmentation pathway, upon electron-impact, of aromatic-sulfonyl derivatives.

However, in addition to these "major" and "minor" processes, a new fragmentation pathway

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TABLE I[a]

The mass spectra of 2-thiophenesulfonyl derivatives

| m/e | X = Cl (Rel. int.) 20 eV | 70 eV | $NH_2$ 20 eV | 70 eV | $N_3$ 20 eV | 70 eV | $NH\text{-}C_6H_{11}$ 20 eV | 70 eV | $N(CH_3)Ph$ 20 eV | 70 eV |
|---|---|---|---|---|---|---|---|---|---|---|
| 39 | 81.1 | 100 | 86 | 100 | 80.1 | 100 | 18.6 | 100 | 6.2 | 65.2 |
| 41 | | | | | | | | 42 | | |
| 42 | | | | | | | | 12 | | |
| 43 | | | | | | | | 19 | | |
| 45 | 16.2 | 42.6 | 16.3 | 35.5 | 21.2 | 45.6 | | 21.5 | | |
| 48 | | 17 | | | 11.1 | 18.8 | | | | |
| 51 | | | | | | | | | | 29 |
| 54 | | | | | | | | 16 | | |
| 55 | 11.3 | 10 | 17.7 | 13.2 | 12 | 10 | 16.8 | 25 | | |
| 56 | | | | | | | 14.2 | 13.5 | | |
| 57 | 13.5 | 37.2 | 10 | 32.3 | | 30 | | 15 | | |
| 64 | 16.8 | 24 | 24.2 | 21 | 19.5 | 20 | | | | |
| 67 | | | | | | | | 10 | | |
| 71 | 10 | 10 | 11.6 | 11.3 | 8.1 | 12.5 | 5.3 | 6 | | |
| 77 | | | | | | | | | 27.6 | 87 |
| 78 | | | | | | | | | 14.6 | |
| 82 | | | | | | 10 | | 12 | | |
| 83 | 24.3 | 27 | 23.2 | 17.4 | 25.7 | 21.9 | | 17.5 | | |
| 84 | | | | | | | 13.3 | 12.0 | | |
| 98 | | | | | | | | 24.5 | | |
| 99 | 27.0 | 34.4 | 60.5 | 42.9 | 35.8 | 27.5 | | 27 | | |
| 106 | | | | | | | | | 100 | 100 |
| 125 | | | | | | | 28.3 | 12.5 | | |
| 147 | 100 | 95.7 | 86 | 54.8 | 100 | 59.4 | 86.7 | 74 | | |
| 148 | | | | | | | | | 15.4 | 16.7 |
| 163 | | | 100 $[M]^+$ | 48.4 | | | | | | |
| 182 | 35.1$[M]^+$ | 28.4 | | | | | | | | |
| 184 | 13.5 | 10.6 | | | | | | | | |
| 189 | | | | | 15.3$[M]^+$ | 11 | | | 49.6 | 38.4 |
| 202 | | | | | | | 100 | 59.4 | | |
| 245 | | | | | | | 43 $[M]^+$ | 20 | | |
| 253 | | | | | | | | | 12.2$[M]^+$ | 11.6 |

[a] Parent peak is denoted by $[M]^+$. All peaks $\geq 10\%$ of base peak included.

*List of Metastable Peaks*

In Compound 1: 119 (m/e 182 → 147); 66–67 (m/e 147 → 99); 51 (m/e 99 → 71); 30–31 (m/e 99 → 55).

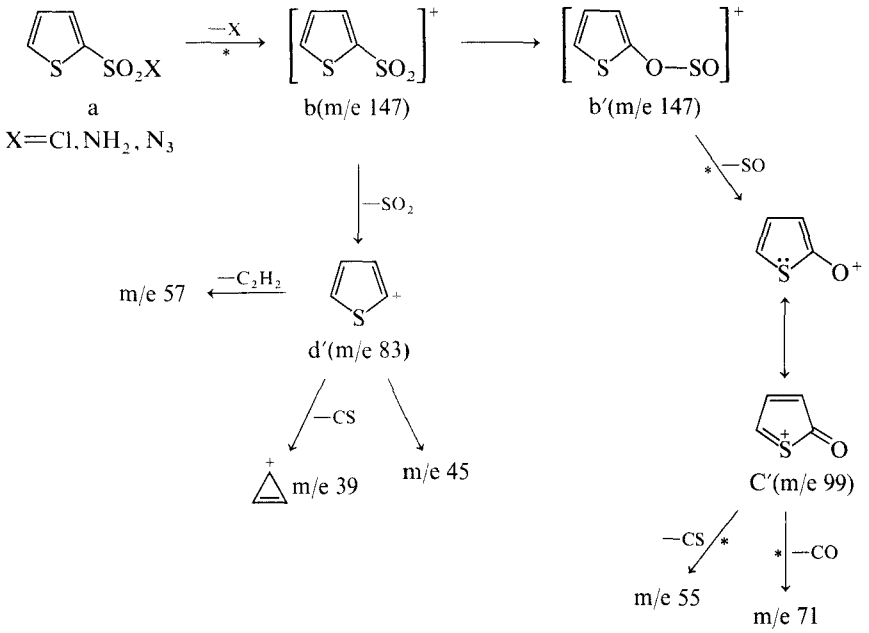
In Compound 2: 66–67; 51; 30–31 (as in 1).

In Compound 3: 114 (m/e 189 → 147); 66–67; 51; and 30–31 (as in 1).

In Compound 4: 190–191 (m/e 245 → 216); 166–167 (m/e 245 → 202); 107 (m/e 202 → 147); 36–37 (m/e 83 → 55).

In Compound 5: 141–142 (m/e 253 → 189); 59 (m/e 189 → 106); 56 (m/e 106–77); 33–34 (m/e 77 → 51).

is exhibited probably involving the migration of the thiophene ring from sulfur to oxygen, in a manner similar to aryl sulfone rearrangement.[10] This can be rationalized as involving formation of thiophenesulfonyl cation b (m/e 147) by loss of X group, then probably undergoing a C-S → C-O rearrangement to give $b^1$, followed by loss of sulfur monoxide to afford ion $C^1$ (m/e 99) in a one-step process. That this is a one-step process is supported by a metastable peak lying between m/e 66 and 67. This process is most probably a consequence of the presence of the sulfur atom in the thiophene ring whose lone pair of electrons can conjugate with the double bonds of the ring to afford the stable, fully conjugated 2-keto-sulfonium ion $C^1$ (m/e 99) (Scheme 2).



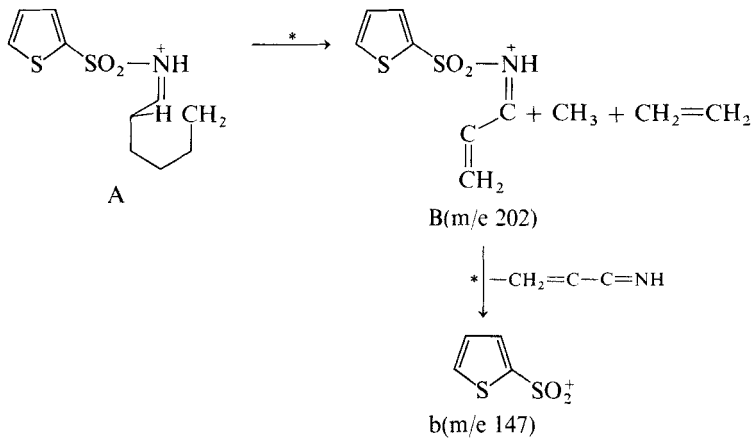

SCHEME 2 Fragmentation route of 2-thiophene Sulfonyl Chloride (**1**), amide (**2**) and the azide (**3**).

This is followed by loss of either CS or CO from C' to give ions at m/e 55 and m/e 71 respectively. Loss of these molecules from ion C' is established by metastable peaks. The relative intensities of the ions at m/e 99, 55 and 71 are included in Table 1. Interestingly, the above fragmentation pathway (Scheme 2) occurs not only in the sulfonyl chloride but also in the sulfonamide (**2**), azide (**3**) and the N-cyclohexylsulfonamide (**4**). Metastable peaks occur between m/e 30 and 31 for loss of CS and another one at m/e 51 for loss of CO (except in 4).

In the sulfonyl azide (**3**), the spectrum is dominated by the M-$N_3$ ion (59.4%, int.) and in fact becomes the base peak at lower electron energy, 20 eV. There was no peak corresponding to the loss of nitrogen molecule to give the sulfonyl nitrene (as is observed in the thermal decomposition of this azide in cyclohexene).[11] This is in line with the fragmentation pathway observed in the mass spectra of other sulfonyl azides.[12] Similarly in the sulfonamides (**2**), loss of the $NH_2$ is the main pathway as can be seen from Table I. In N-cyclohexylsulfonamide (**4**), a different mode of fragmentation probably takes place because of the intense peak at m/e 202 (57.5% rel. int. at 70 eV which becomes the base peak at 20 eV) corresponding to M–43. This can be attributed to the presence of the cyclohexyl group on nitrogen. This M–43 ion has been observed to be the most intense ion in the mass spectrum of *N*-ethylcyclohexylamine.[13] The loss of mass 43 has been attributed to the loss of either a methyl radical and ethylene or a propyl radical.[13] Hence, the fragmentation of compound 4 could probably be rationalized as in Scheme 3.

The ion B (m/e 202) then eliminates the vinylimine to give the thiophenesulfonyl cation b (m/e 147). This is supported by a metastable peak at m/e 107. The thiophenesulfonyl cation then fragments f rther by the two routes shown in Scheme 2. Another peak which appeared in the mass spectrum of 4 is the one corresponding to the parent amine $C_6H_{11}NH$ (m/e 98) with a relative intensity of 24.5%. Fragment ions corresponding to the intact amine have been observed in the fragmentation of some *p*-toluenesulfonamides.[14]

In the mass spectrum of compound 5, the base peak corresponds to the amine moiety, PhMeN (m/e 106) and the phenyl ion (m/e 77) resulting from the fragmentation of this amine showed up as the second most important peak (rel. int. 87%) at 70 eV. An abundant ion also occurs at m/e 189 $[M-64]^+$ corresponding to the loss of $SO_2$. At 20 eV, the ion at m/e 106 is still the base peak but the $[M-64]^+$ ion is now the second most




SCHEME 3 Fragmentation route of N-Cyclohexyl-2-thiophenesulfonamide (**4**).

abundant peak. This fragmentation pattern is similar to that observed for N-substituted-*p*-toluenesulfonamides,[14] but in that case, the ions corresponding to the tosyl group are abundant, unlike in compound 5, where ions corresponding to the thiophenesulfonyl cation or those resulting from it (m/e 147, 83, 45) do not appear or are negligible.

## SUMMARY

The low resolution mass spectra of five 2-thiophenesulfonyl derivatives were recorded and the major fragmentation modes were elucidated with the aid of metastable ions and mechanistic analogy. It was found that in all the five compounds, the parent peaks are observed with varying intensities. In compounds 1–3, cleavage of the sulfur-X ($X = Cl, NH_2, N_3$) bond is the main fragmentation route. In 4 however, this cleavage ($S—NHC_6H_{11}$) takes places in two steps due to the presence of the cyclohexyl substituent on nitrogen. In compound 5, the sulfur-substituent type of cleavage becomes unimportant. Due to the presence of sulfur in the aromatic ring, further fragmentation of the thiophenesulfonyl cation b, (m/e 147), formed by the initial loss of X, takes place by two routes: (i) by loss of $SO_2$ and subsequent fragmentations of the thiophene ring giving rise to ions at m/e 83, 57, 45 and 39. (ii) By loss of SO to afford the sulfonium ion C′ (m/e 99) and subsequent fragmentations giving rise to ions at m/e 55 and 71. This second process (ii) is more important than process (i) judging from the relative intensities of the respective ions.

## EXPERIMENTAL

The thiophenesulfonyl derivatives, 1-5, were prepared according to the procedures given in part I of this series.[6] The low resolution mass spectra were recorded on a model AEL-MS-12 spectrometer with ion source 200° using the direct insertion probe at an ionizing voltage of 70 and 20 eV. All peaks whose relative intensity equals or exceeds 10% of the base peak are listed in table 1 except for compound 4 at m/e 71.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. Ref. 13. p. 231–235.
2. M. Srinivasan and J. B. Rampal, *Tetrahedron Lett.*, 2883 (1974).
3. T. Nishiwaki, *Tetrahedron*, **23**, 2979 (1967).
4. J. H. Bowie, R. G. Cooks, S. O. Lawesson, and C. Nolde, *J. Chem. Soc. B*, 616 (1967).
5. M. Srinivasan, J. B. Rampal, and S. Thiagerajan, *Phosphorus and Sulfur*, **3**, 221 (1977).
6. Submitted for publication in this journal.
7. E. Dynesen, S. O. Lawesson, G. Schroll, J. H. Bowie, and R. G. Cooks, *J. Chem. Soc. B*, 15 (1968).
8. R. J. Soothill and L. R. Williams, *Org. Mass Spectrom.*, **6**, 141 (1972).
9. P. P. Davis, J. S. Grossert, R. F. Langler, and W. S. Mantle, *Org. Mass Spectrum*, **12**, 659 (1977).
10. A. I. Khodair, A. A. Swelim, and A. A. Abdel-Wahab, *Phosphorus and Sulfur*, **2**, 173 (1976) and references therein.
11. Part 1 of this series, Ref. 6.
12. M. M. Campbell and A. D. Dunn: *Org. Mass. Spectrum*, **6**, 599 (1972).
13. H. Budzikiewicz, C. Djerassi, and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden-Day, Inc., California (1967), p. 307.
14. G. M. Singer, W. Lijinsky, and W. T. Rainey, Jr., *Org. Mass Spectrom*, **10**, 473 (1975).