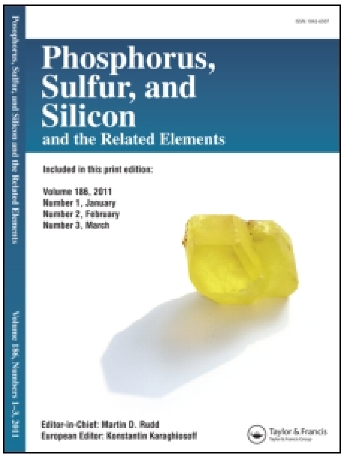

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# MASS SPECTRA OF SELECTED SULFONES SULFONE-SULFINATE REARRANGEMENT

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# MASS SPECTRA OF SELECTED SULFONES SULFONE-SULFINATE REARRANGEMENT

by

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## ABSTRACT

Mass spectra of three sulfones selected to reveal certain structural features were obtained and interpreted. The mass spectra of the two isomeric sulfones, benzyl methyl sulfone and methyl *p*-tolyl sulfone, were quite different. The spectra showed that rearrangement of sulfones to the isomeric sulfinates occurs under the influence of the electron impact and that the migration of the aryl group is preferred over migration of the alkyl group.

Recent studies on the mass spectra of sulfones revealed that sulfone-sulfinate rearrangement with the formation of a C–O bond is one of the main processes which may occur under the influence of the electron beam. Kutz and Weinger[1] and Weinberg and Stafford[2] reported that one of the most abundant ions in the spectra of unsaturated cyclic sulfones can be rationalized by postulation of a pathway involving sulfone-sulfinate rearrangement. Soothill and Williams[3] reported the occurrence of similar rearrangement in the mass spectra of 2-hydroxy and 2-chloroethyl aryl sulfones and noted that both alkyl and aryl migration took place. The same authors concluded that in the mass spectra of vinyl aryl sulfones migration of the vinyl group was more preferable than migration of the aryl group.

In this work, we have examined the mass spectra of three simple sulfones, namely benzyl methyl sulfone, methyl *p*-tolyl sulfone and phenyl *p*-tolyl sulfone, in an endeavour to determine the migratory aptitude of alkyl *vs.* aryl migration in the sulfone-sulfinate rearrangement.

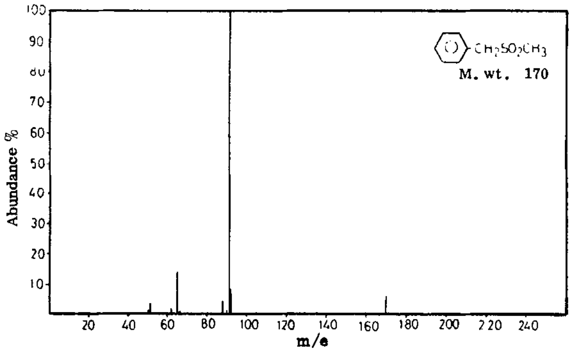
### Results and Discussion

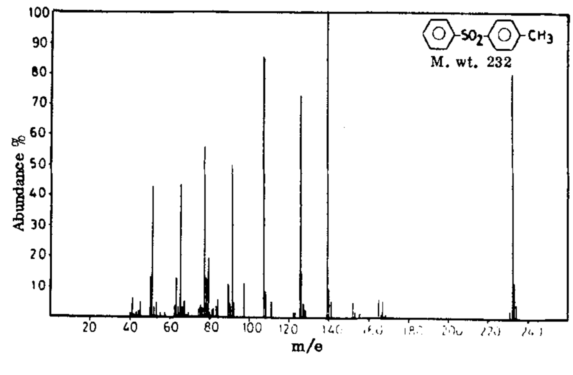
The most important ions in the mass spectra of three sulfones, benzyl methyl sulfone (**1**), methyl *p*-tolyl sulfone (**2**), and phenyl *p*-tolyl sulfone (**3**), are given in Table I and full mass spectra are shown in the figures. Of particular interest is the big difference between the spectra of the two isomeric sulfones **1** and **2**. While the tropylium ion (m/e 91) is the most abundant ion in both spectra, the abundance of the molecular ion in the spectrum of **2** is about 15 times as much as that of **1**. This suggests that simple cleavage of phenyl-sulfur bond is harder than cleavage of alkyl-sulfur bond. This is supported further by the presence of an intense peak in the spectrum of **2** at M – 15.

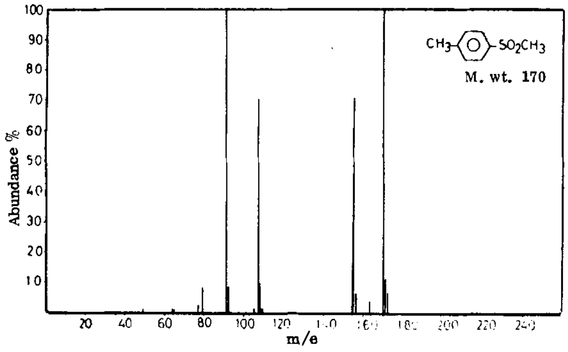
**TABLE I**

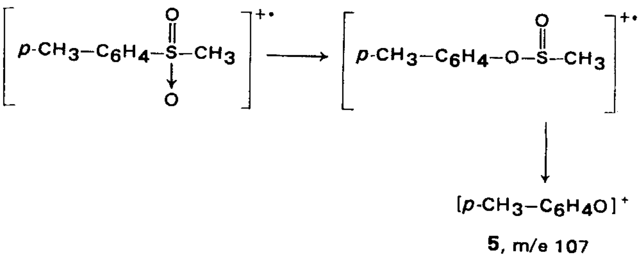
**Partial Mass Spectra of the Sulfones 1, 2, and 3**

| | | % Abundance | | |
|---|---|---|---|---|
| Ion | m/e | 1 | 2 | 3 |
| | 50 | 1.7 | | 13.8 |
| | 51 | 3.5 | | 51 |
| $C_5H_5$ | 65 | 14 | 1.2 | 43 |
| $C_6H_5$ | 77 | | 2.5 | 56 |
| $C_6H_7$ | 79 | | 9 | 20.5 |
| $C_7H_7$ | 91 | 100 | 100 | 47.5 |
| $C_7H_7O$ | 107 | | 63 | 87 |
| $C_6H_5SO$ | 125 | | | 74 |
| $C_7H_7SO$ | 139 | | | 100 |
| $C_7H_7SO_2$ | 155 | | 63 | 2 |
| $C_8H_{10}SO_2$ | 170 | 6 ($M^+$) | 99 ($M^+$) | |
| $C_{13}H_{12}SO_2$ | 232 | | | 80 ($M^+$) |







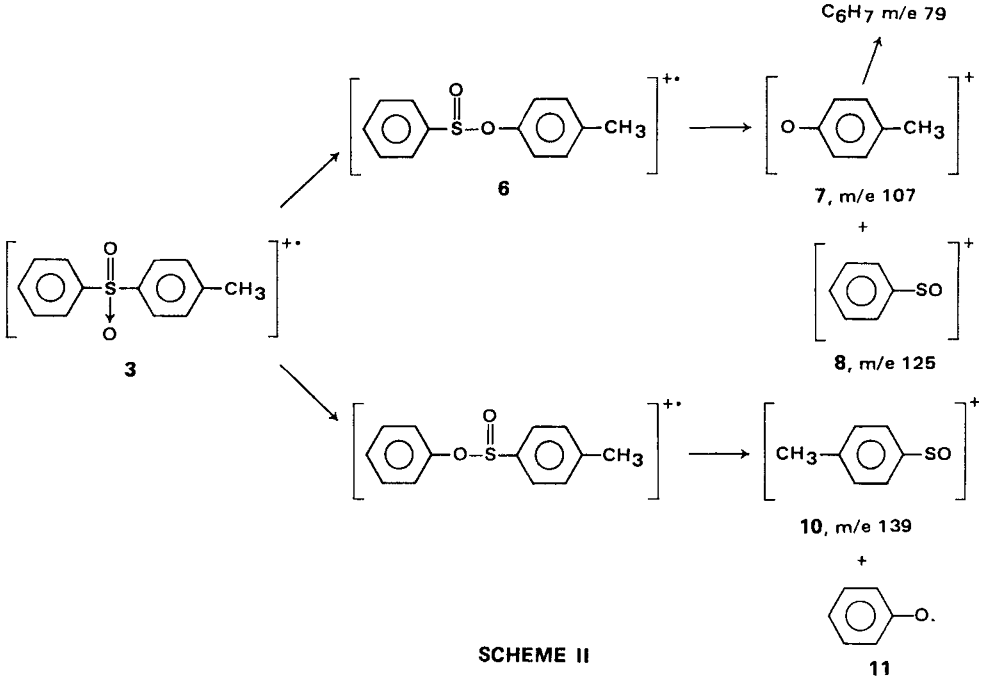


SCHEME I

The abundant peak at m/e 107 may be attributed to ion **5** which may be formed by migration of the aryl group from sulfur to oxygen followed by simple cleavage of the S–O bond as shown in Scheme I.

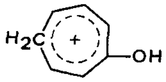
The absence of M–$CH_3O$ in the spectra of both **1** and **2** suggests that migration of the methyl group from sulfur to oxygen does not occur. These results clearly indicate that, unlike vinyl group, simple saturated alkyl group of alkyl aryl sulfones is not involved in the sulfone-sulfinate rearrangement and migration of the aryl group is more preferable.

Sulfone **3** gave a very abundant molecular ion and a base peak at m/e 139. Beside the base peak, intense peaks were observed at m/e 107 and 125. The presence of these peaks suggests that migration of both phenyl and tolyl groups from sulfur to oxygen takes place.



SCHEME II

It is of interest to note that while the charge was almost equally distributed between ions **7** and **8**, ion **10** retained almost all the charge (no significant peak was observed at m/e 93). Since the only difference between fragments **7** and **11** is the presence of the *p*-methyl group in the former fragment, it seems reasonable to assume that ion **7** exists in the equivalent tropylium ion form



From the results presented above together with the earlier data it may be concluded that sulfones rearrange to the isomeric sulfinates under the influence of the electron impact and the migratory aptitude decreases in the following order: vinyl ≥ phenyl > *β*-substituted ethyl > methyl.

## Experimental

Phenyl *p*-tolyl sulfone and methyl *p*-tolyl sulfone were prepared from the reaction of di-*p*-tolylcadmium with benzene- or methane-sulfonyl chloride, respectively.[4] Benzyl methyl sulfone was prepared according to the published procedure[5] by dissolving methanesulfinic acid and benzyl chloride in alcoholic potassium hydroxide solution (1.8 g in 50 ml alcohol) and heating under reflux for 1.5 hr.

Mass spectra were obtained on a Hitachi Perkin-Elmer RMV-6E mass spectrometer, the ionizing voltage was maintained at 70 eV.

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