Tetrahedron, 1966, Vol. 22, pp. 3515 to 3525. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES IN MASS SPECTROMETRY—XV[1]

MASS SPECTRA OF SULPHOXIDES AND SULPHONES. THE FORMATION OF C—C AND C—O BONDS UPON ELECTRON IMPACT

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(*Received* 8 *April* 1966)

Abstract—Although dialkyl sulphoxides and sulphones behave relatively simply upon electron impact, aromatic sulphoxides and sulphones show a pronounced tendency to undergo C—O bond formation, as evidence by a number of decomposition pathways which involve the elimination of carbon monoxide. For example, dibenzothiophene dioxide (XV) decomposes from its molecular ion by successive eliminations of carbon monoxide.

Details of the behaviour of sulphoxides upon electron impact have not been reported, except for our preliminary communication[2] which noted the loss of SO from dibenzyl sulphoxide (V). With respect to sulphones, the spectra of methyl vinyl sulphone and methyl ethyl sulphone have been reported by Quayle,[3] and those of isopropyl and cyclopropyl phenyl sulphones discussed by Meyerson and McCollum.[4] The only detailed study deals with diphenyl sulphone and a number of derivatives alkylated in the phenyl rings.[5] Molecular weight determinations by mass spectrometry have recently been recorded for two bridged naphthalene sulphones,[6] while interesting rearrangements occur in some sulphonylhydrazones[7] upon electron impact. The present paper gives details of the spectra of a variety of sulphoxides and sulphones, including a number of reactions of the type ABC → AC + B and examples of C—O bond formation occurring to an important extent upon electron impact.

The mass spectra of the aliphatic sulphoxides I–IV which have been determined are relatively simple. In the spectrum (Fig. 1) of dimethyl sulphoxide (I), the base peak (*m/e* 63) arises from the loss of a methyl group, but the formation of *m/e* 61 by the elimination of OH from the molecular ion in a one-step process is somewhat unexpected.[8] The decomposition of the M—CH_3 ion by loss of water in a one-step

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[1] Part XIV, J. H. Bowie, S.-O. Lawesson, J. Ø. Madsen, G. Schroll and D. H. Williams, *J. Chem. Soc.* in press.

[2] J. Ø. Madsen, C. Nolde, S.-O. Lawesson, G. Schroll, J. H. Bowie and D. H. Williams, *Tetrahedron Letters*, 4377 (1965).

[3] A. Quayle, *Chimia. (Aarau), Colliquium Spectroscopium Internationale* VIII, p. 259 (1959).

[4] S. Meyerson and J. D. McCollum, Division of Physical Chemistry 136th Meeting, ACS, Atlantic City, N.J., September, 1959.

[5] S. Meyerson, H. Drews and E. K. Fields, *Analyt. Chem.* **36**, 1294 (1964).

[6] R. W. Hoffmann and W. Sieber, *Angew Chem.* (Int. Ed.) **4**, 786 (1965).

[7] A. Bhati, R. A. W. Johnstone and B. J. Millard, *J. Chem. Soc.* 358 (1966).

[8] Transitions indicated by an asterisk (*) either in the figures or in the text are supported by the presence of an appropriate metastable peak.

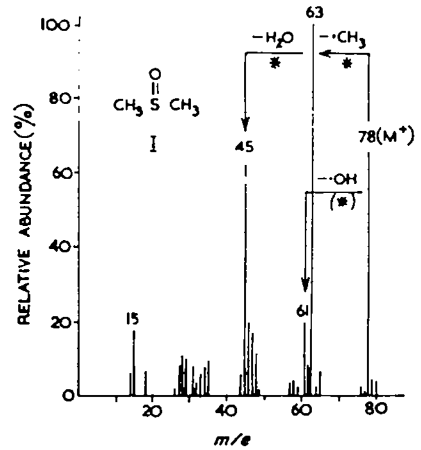
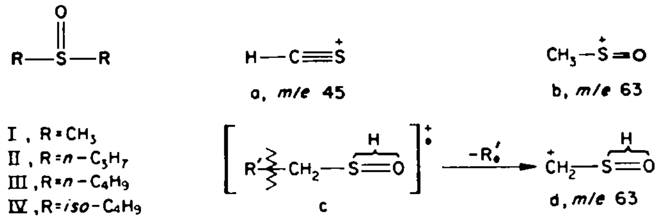


FIG. 1

process to *m/e* 45 (probably the thioformyl cation *a*) does not favour its representation solely as the simple cation *b*.



In general, the spectra of the sulphoxides II–IV containing larger alkyl groups contain prominent peaks due to loss of R with an associated hydrogen rearrangement to the charged fragment. Formally, this process corresponds to the elimination of a neutral olefin, e.g., to the elimination of propylene from dipropyl sulphoxide (II) to give *m/e* 92 (see Fig. 2). No metastable peaks are present in the spectra to confirm that

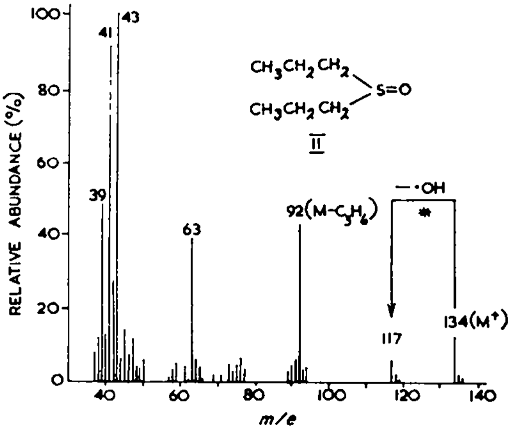


FIG. 2

the olefin elimination is induced by electron impact, and indeed the reaction is almost certainly in part thermally induced since dialkyl sulphoxides can undergo olefin elimination at 250° in the injection port of a GLC instrument,[9] or upon refluxing in dimethyl sulphoxide solution.[10] However, we believe the olefin elimination to be largely an electron impact phenomenon, since the spectrum (Fig. 2) of II is very similar whether obtained by introduction of the sample through a heated inlet system (at approximately 150°) or obtained by the direct inlet procedure at a source temperature of approximately 60°. Another feature common to the spectra of II–IV is the occurrence of prominent peaks at *m/e* 63 (CH_3SO^+, high resolution, see Fig. 2). Ions of this composition may arise via allylic cleavage in the M–olefin species *c* to give *d* (*m/e* 63), but no metastable peaks are evident to substantiate this possibility. In all three spectra the most intense peaks are associated with fragments derived from one of the alkyl chains [e.g., *m/e* 43 ($C_3H_7^+$), *m/e* 41 ($C_3H_5^+$) and *m/e* 39 ($C_3H_3^+$) in Fig. 2].

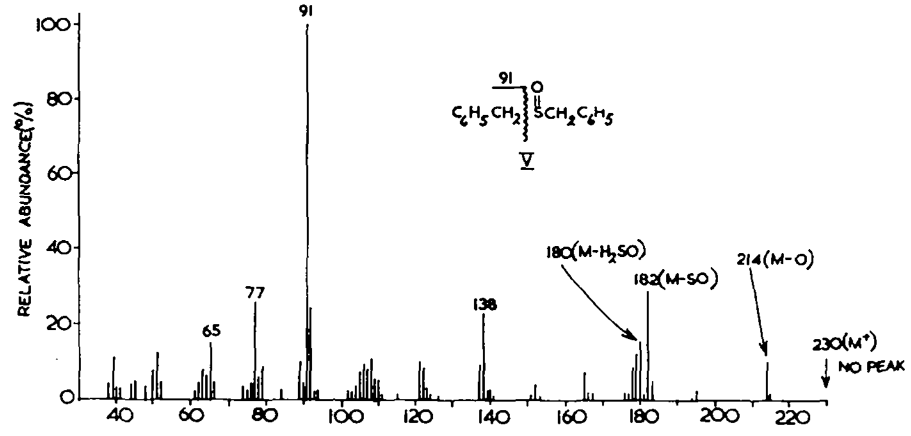
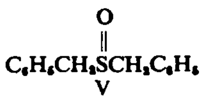
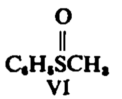


Fig. 3

Although the spectra of the purely aliphatic sulphoxides are devoid of abundant skeletal rearrangement fragments, this is not the case in the presence of the phenyl groups of dibenzyl sulphoxide (V); the spectrum (Fig. 3) contains abundant ions at *m/e* 182 ($C_{14}H_{14}^+$, M—SO, h.r.) and *m/e* 180 ($C_{14}H_{12}^+$, h.r.). In agreement with our earlier conclusions for disulphides[11] and aromatic thioethers,[1] the $[ABC]^+ \rightarrow [AC]^+$ reaction seems to be facilitated by sites of unsaturation in the vicinity of the bond cleavage.


$$\overset{\displaystyle O}{\overset{\|}{C_6H_5CH_2SCH_2C_6H_5}}$$
V


$$C_6H_5\overset{\overset{\displaystyle O}{\|}}{S}CH_3$$
VI


$$R—\overset{\overset{\displaystyle O}{\|}}{S}—R$$
VII, R = C_6H_5
VIII, R = p-$CH_3C_6H_4$

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[9] S. I. Goldberg and M. S. Sahli, *Tetrahedron Letters* 4441 (1965).

[10] I. D. Entwistle and R. A. W. Johnstone, *Chem. Comm.*, 29 (1965); see also C. Walling and L. Bollyky, *J. Org. Chem.* **29**, 2699 (1964) and W. Z. Herdt, *Ibid.* **30**, 3897 (1965).

[11] J. H. Bowie, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, G. Schroll and D. H. Williams, *J. Chem. Soc.* in press.

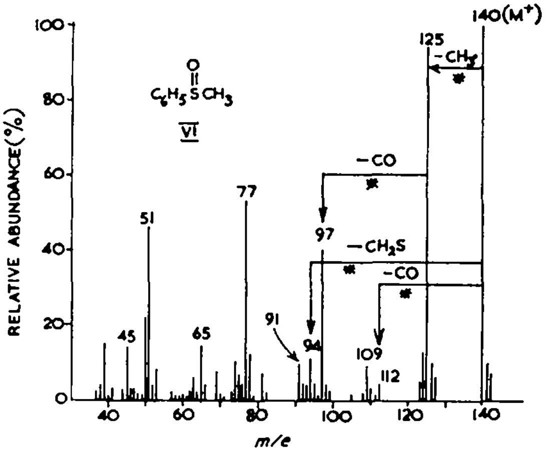

Fig. 4

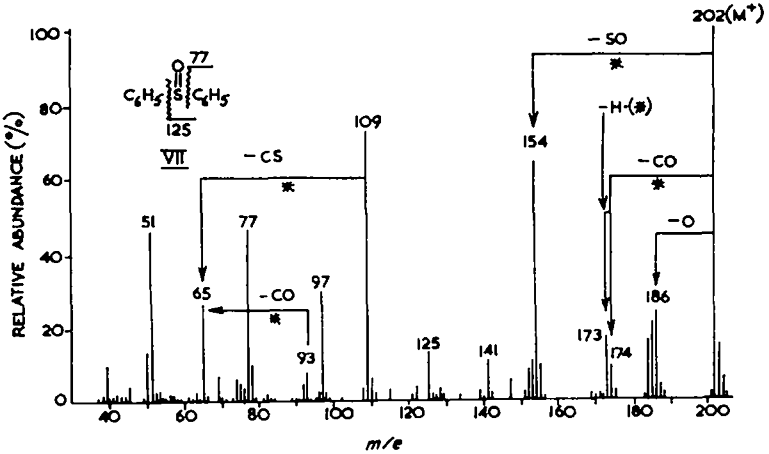

Fig. 5

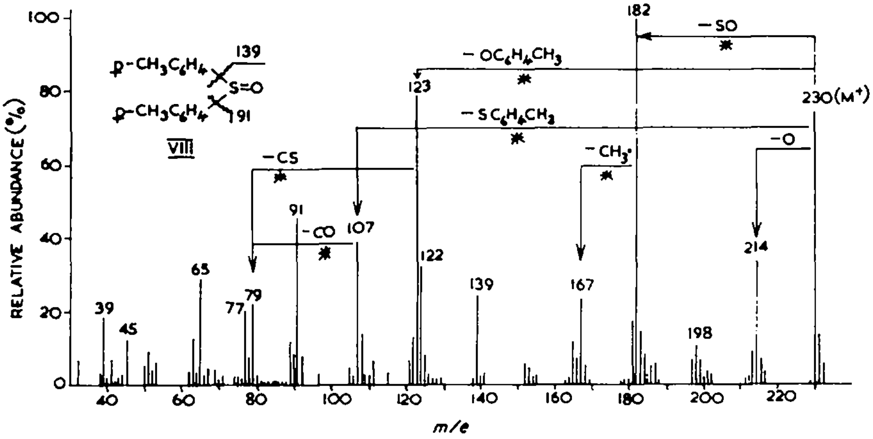

Fig. 6

The spectra (Figs. 4–6) of methyl phenyl sulphoxide (VI), diphenyl sulphoxide (VII) and di-*p*-tolyl sulphoxide (VIII) are remarkable for the abundance and diversity of the rearrangement ions which they contain. Only when both groups attached to the sulphoxide moiety are aromatic does the loss of SO give a very abundant ion (64% of the base peak in Fig. 5 and base peak in Fig. 6). Most noteworthy are the decomposition pathways which involve elimination of carbon monoxide (see Figs. 4–6); the transitions supported by appropriate metastable ions are indicated in the figures and pertinent high resolution data for VI and VII are given in Table 1.

TABLE 1. HIGH RESOLUTION DATA FOR THE SPECTRA OF VI AND VII

Compd	Peak	Composition
VI	97	C_5H_5S
	94	C_6H_6O
	91	C_7H_7
VII	186	$C_{12}H_{10}S$
	174	$C_{11}H_{10}S$
	173	$C_{11}H_9S$
	154	$C_{12}H_{10}$
	141	$C_{11}H_9$
	125	C_6H_5SO
	109	C_6H_5S
	97	C_5H_5S

In all three compounds (VI–VIII) which contain the structural unit $C_6H_4{-}\overset{|}{S}{=}O$, reactions involving the formation of C—O bonds are induced by electron impact. For example, in the spectrum (Fig. 4) of methyl phenyl sulphoxide (VI), both the molecular ion and the M—CH_3 ion eliminate CO, and in addition the molecular ion loses CH_2S in a one-step process. The C—O bond formation may occur via a 1,2-migration of the phenyl group from sulphur to oxygen (VI → e); the loss of carbon monoxide from the rearranged molecular ion is then no more unusual than the elimination of the same neutral fragment from diphenyl ether.[12] The formation of *m/e* 94 ($C_6H_6O^+$, perhaps ionized phenol, f) then follows simply. A plausible mechanism for the formation of *m/e* 97 by the loss of CO from the M—CH_3 ion is indicated by the sequence g → h → i ($C_5H_5S^+$). Routes may also be visualized in which the C-2 carbon atom of the aromatic ring is eliminated as CO. The formulation of *m/e* 97 ($C_5H_5S^+$) as the thiopyrylium cation i is reasonable in the light of the large delocalization energy of this ion as calculated using a simple molecular orbital method.[13] A 1,2-migration analogous to VI → e has previously been postulated to occur in some diaryl sulphones upon electron impact.[5]

Similarly, a number of transitions which are evident from the spectra (Figs. 5 and 6) of the diaryl sulphoxides VII and VIII support a 1,2-phenyl migration from sulphur to oxygen (see j). Simple S—O bond cleavage in j would then furnish *m/e* 109 and

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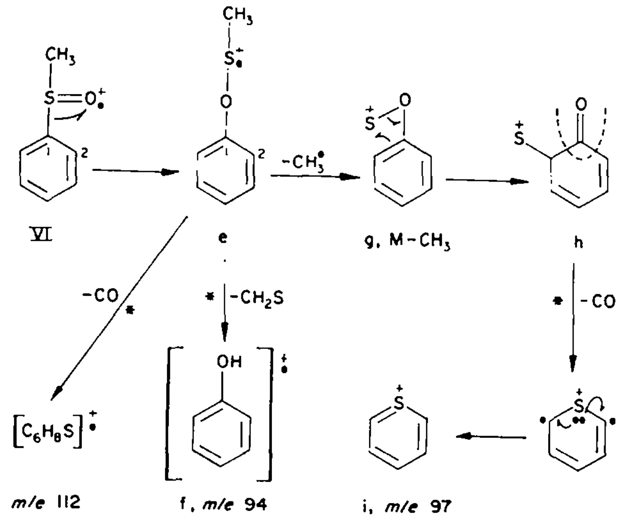
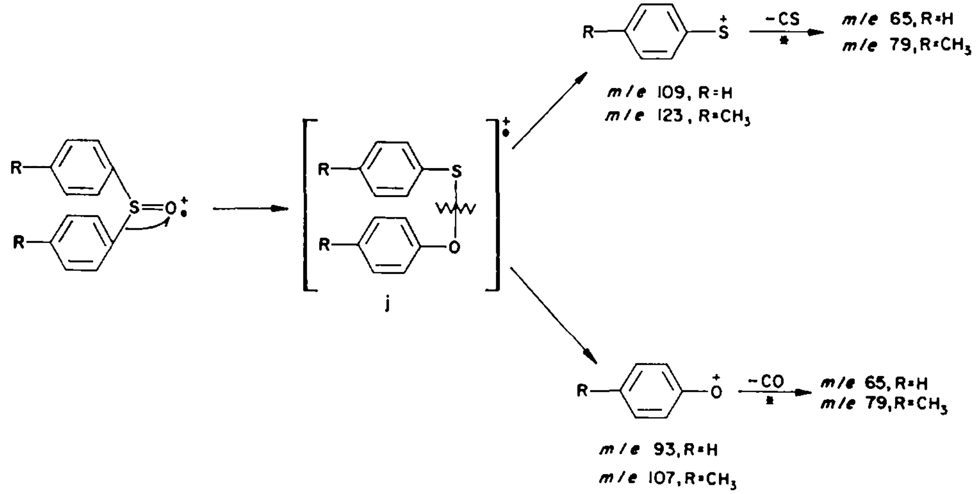
[12] J. H. Beynon, G. R. Lester and A. E. Williams, *J. Chem. Phys.* **63**, 1861 (1959).

[13] J. Koutecky, *Coll. Czech. Chem. Comm.* **24**, 1609 (1959).



m/e 93 when R = H and m/e 123 and m/e 107 when R = CH_3 (see Figs. 5 and 6). The further decompositions of m/e 109 (Fig. 5) and m/e 123 (Fig. 6), by elimination of CS, and of m/e 93 (Fig. 5) and m/e 107 (Fig. 6) by elimination of CO are in good accord with this hypothesis.



Of the spectra of aliphatic sulphones (IX–XII) which have been determined, only that (Fig. 7) of dimethyl sulphone (IX) is not dominated by purely hydrocarbon fragment ions; in this case the base peak (m/e 79) corresponds to the loss of a methyl radical. High resolution measurements establish the composition of ions of lower abundance: m/e 45 (CHS), m/e 48 (5% of CH_4S and 95% of SO), m/e 63 (CH_3SO), m/e 64 (SO_2) and m/e 65 (HSO_2). In the spectra of diethyl sulphone (X), dipropyl sulphone (XI) and di-isobutyl sulphone (XII, Fig. 8), the base peaks occur at m/e 29 ($C_2H_5^+$), m/e 43 ($C_3H_7^+$) and m/e 57 ($C_4H_9^+$), respectively. It is interesting to note that whereas diethyl sulphone (X) gives a peak (10%) due to loss of C_2H_4 [but does not appreciably (<1%) eliminate C_2H_3], dipropyl sulphone (XI) loses both C_3H_6 and

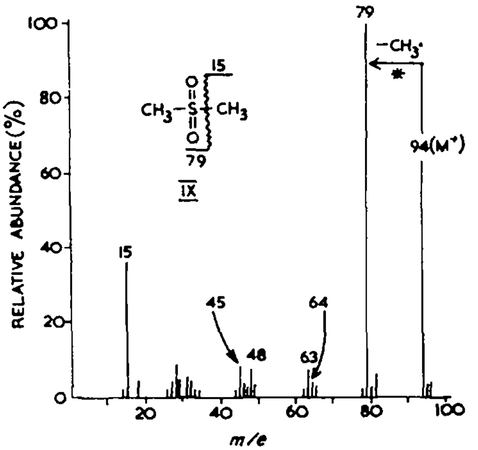


FIG. 7

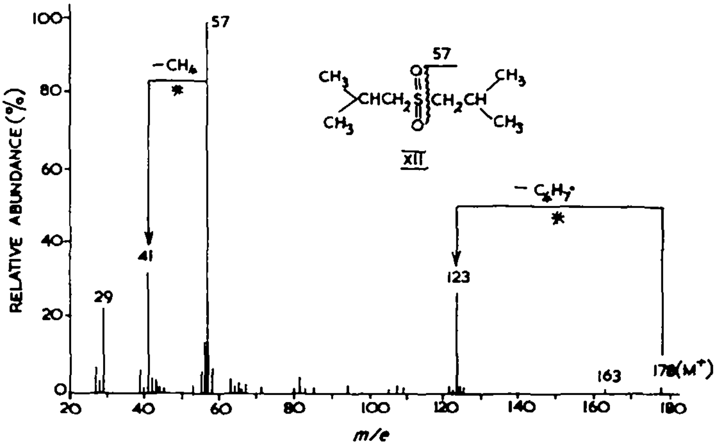
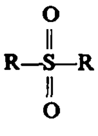


FIG. 8

C_3H_5 (peaks of relative abundance 11% and 8%, respectively) and di-isobutyl sulphone (XII) almost exclusively eliminates C_4H_7 (see Fig. 8), i.e., the tendency to eliminate the alkyl group with associated double hydrogen rearrangement to the charged fragment increases with increasing size of the alkyl group.



$$R-\overset{\overset{\large O}{\|}}{\underset{\underset{\large O}{\|}}{S}}-R$$

IX, R = CH_3 XI, R = n-C_3H_7

X, R = C_2H_5 XII, R = iso-C_4H_9

As in the case of sulphoxides, the complexities of skeletal rearrangement are evident in the spectra of sulphones (XIII–XV) containing a phenyl moiety directly attached to the functional group. The most unusual features of the spectra (Figs. 9 and 10) of methyl phenyl sulphone (XIII) and ethyl phenyl sulphone (XIV) are the decompositions of the molecular ions by losses of CH_2SO and C_2H_4SO, respectively, in one-step processes (high resolution data for XIII–XV are summarized in Table 2). The processes

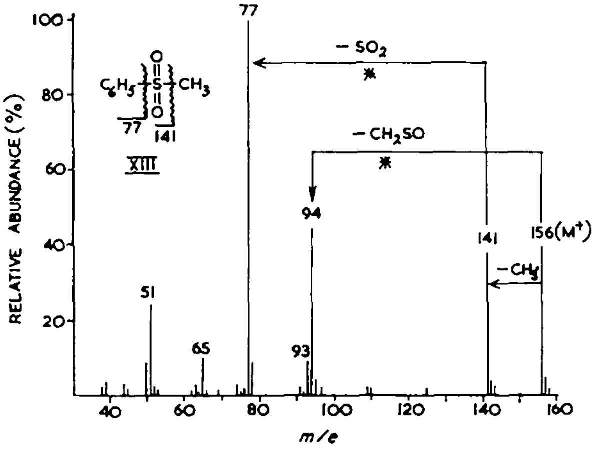


Fig. 9

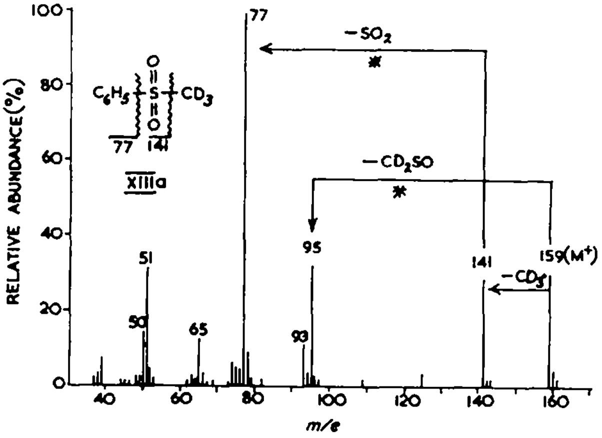


Fig. 9a

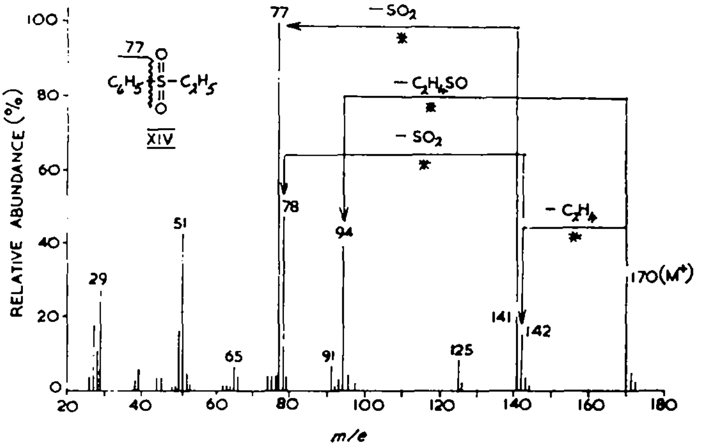


Fig. 10

are interpreted in terms of a 1,2-phenyl migration (XIII and XIV → k), as in the case of sulphoxides and of the diaryl sulphones of Meyerson, Drews and Fields.[5] In the spectrum (Fig. 9a) of trideuteromethyl phenyl sulphone (XIIIa), the *m/e* 94 ion ($C_6H_6O^+$) of Fig. 9 is almost quantitatively shifted to *m/e* 95 ($C_6H_5DO^+$), whereas *m/e* 93 ($C_6H_5O^+$) is not shifted. The rearrangement which leads to C—O bond formation does not appear to be a particularly high energy process, since the total ion current carried by the *m/e* 94 ions from XIII and XIV is increased slightly at lower energies (e.g., 15 eV spectra vs. 70 eV spectra).

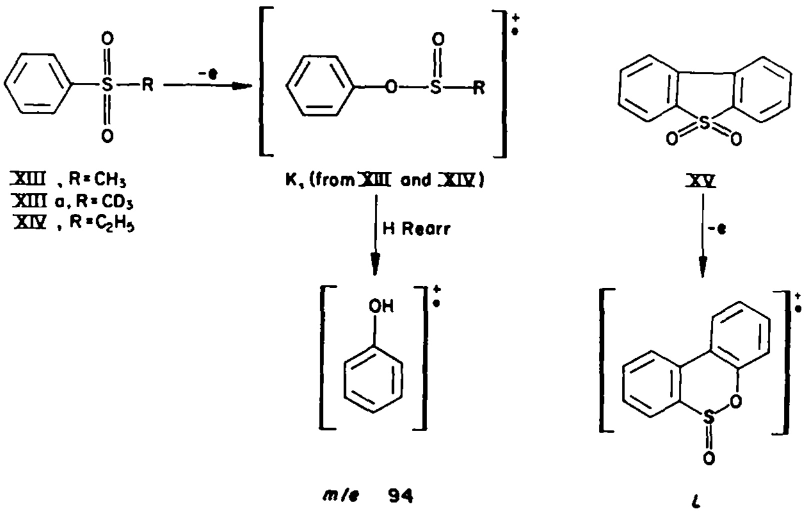


TABLE 2. HIGH RESOLUTION DATA FOR THE SPECTRA OF XIII–XV

Compd	Peak	Composition
XIII	94	C_6H_6O
XIV	141	$C_6H_5SO_2$
	125	C_6H_5SO
	94	C_6H_6O
	91	C_7H_7
XV	188	$C_{11}H_8SO$
	187	$C_{11}H_7SO$
	168	$C_{12}H_8O$
	160	$C_{10}H_8S$
	152	$C_{12}H_8$

The behaviour of simple diaryl sulphones has been so thoroughly documented by Meyerson *et al.*,[5] that it does not merit additional discussion here. However, it is noteworthy that dibenzothiophene dioxide (XV) not only decomposes by elimination of SO, but also by successive losses of carbon monoxide from the molecular ion (see Fig. 11) as established by high resolution measurements (Table 2). A C—O bond in

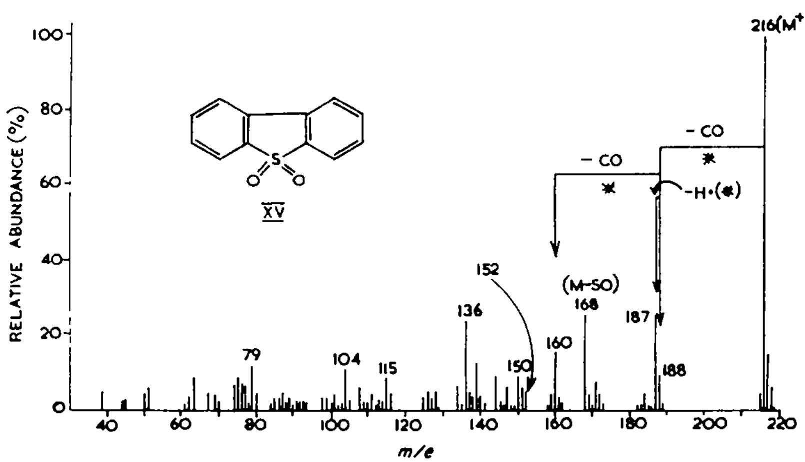
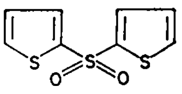
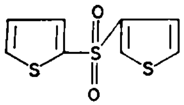


Fig. 11

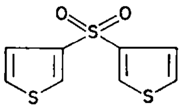
the molecular ion of XV may be formed by a 1,2-shift (XV → I) and the process can obviously be repeated (either prior to or after the elimination of the first molecule of carbon monoxide) for the formation of the second necessary C—O bond.[13a]



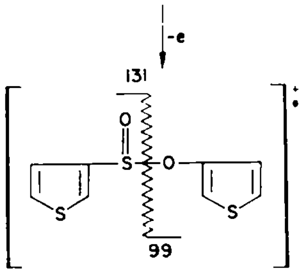
XVI



XVII



XVIII



m

The spectra of the dithienyl sulphones XVI–XVIII suggest that the 1,2-migration of a thienyl group from sulphur to oxygen upon electron impact occurs in a similar manner to the corresponding phenyl migration. All three spectra (see, for example, Fig. 12) contain abundant ions at *m/e* 131 and *m/e* 99 which can rise by S—O bond cleavage in the rearranged molecular ion m.

The results presented in this paper illustrate that although aliphatic sulphoxides and sulphones behave relatively simply upon electron impact, the corresponding aromatic compounds undergo well-defined skeletal reorganization. The nature of the

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[13a] *Note added in proof*—This rearrangement has concurrently been observed by E. K. Fields and S. Meyerson [*J. Amer. Chem. Soc*, **88**, 2836 (1966)]. The authors wish to thank Dr. Meyerson for sending a copy of the manuscript to them prior to publication.

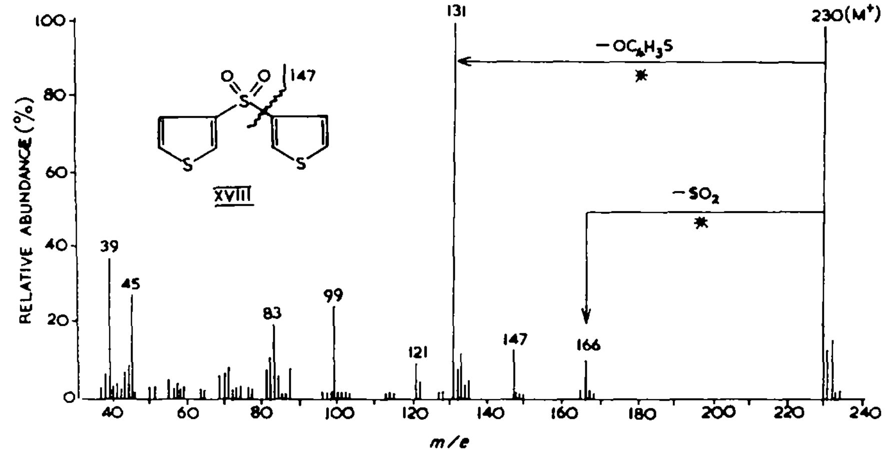

FIG. 12

reorganization is not only of mechanistic interest, but also a knowledge of the rearrangements is important to permit a secure interpretation of the spectra for analytical purposes.

EXPERIMENTAL

All mass spectra were determined on an AEI MS9 double focussing mass spectrometer operating at 70 eV and a source pressure of $(1\cdot0–5\cdot0) \times 10^{-7}$ mm Hg. Unless otherwise stated, samples were introduced into the source through a heated inlet system at a temperature of approximately 150°.

Dimethyl sulphoxide (I), di-*p*-tolyl sulphoxide (VIII) and dibenzothiophene dioxide (XV) were purified commercial samples. Previously published procedures were used for the preparation of di-n-propyl sulphoxide (II),[14] di-n-butyl sulphoxide (III),[14] di-isobutyl sulphoxide (IV),[15] dibenzyl sulphoxide (V),[16] diphenyl sulphoxide (VII),[17] dimethyl sulphone (IX),[14] diethyl sulphone (X),[14] di-n-propyl sulphone (XI),[14] and the dithienyl sulphones (XVI–XVIII).[18]

Di-isobutyl sulphone (XII) was prepared by the oxidation of di-isobutyl sulphoxide (IV) with H_2O_2 in AcOH. H_2O_2 in AcOH was also employed for the oxidation of thioanisole and d_3-thioanisole to methyl phenyl sulphoxide (VI), methyl phenyl sulphone (XIII) and trideuteromethyl phenyl sulphone (XIIIa). The same reagent furnished ethyl phenyl sulphone (XIV) from ethyl phenyl sulphide.

Acknowledgements—One of us (J. H. B.) is grateful for the award of an I.C.I. Fellowship. Thanks are expressed for a grant (to Aarhus University) from "Thomas B. Thriges fond" and to Dr. E. Jones for compounds XVI–XVIII.

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[14] C. W. N. Cumper, J. F. Read and A. J. Vogel, *J. Chem. Soc.* 5323 (1965).

[15] D. Ll. Hammick and R. B. Williams, *J. Chem. Soc.* 211 (1938).

[16] A. J. Vogel and D. M. Cowan, *J. Chem. Soc.* 16 (1943).

[17] A. Schönberg, *Ber. Dtsch. Chem. Ges.* **56**, 2275 (1923).

[18] E. Jones and J. M. Moodie, *Tetrahedron* **21**, 2413 (1965).