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Rearrangements in Sulphoxides and Sulphones Induced by Electron Impact

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The survey covers processes involving the isomerisation of molecular ions and the rearrangement of ionic fragments during the initial stages of the dissociative ionisation of sulphoxides and sulphones on electron bombardment. Characteristic ions are formed by skeletal rearrangements, in particular by migration of an alkyl or an aryl group from the sulphur to an oxygen atom. The relative statistical weight of a particular structure of a molecular ion is the main factor determining subsequent competitive decomposition paths of the primary ionic fragments. A list of 82 references is included.

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I. INTRODUCTION

Migrations of groups on electron impact, with the formation of new bonds—so called skeletal rearrangements—make the interpretation of mass spectra substantially more difficult, since they cannot be predicted *a priori* with sufficient certainty. On the other hand, the rearranged ions, whose activation energy of formation is low, often corresponds to the most intense peaks in the mass spectra, and can therefore be most effectively used to identify compounds and establish their structure.

Several reviews have appeared on rearrangements involving aliphatic and aromatic sulphoxides and sulphones[1-5]. They reflect the variety of such processes characterising the behaviour of sulphur-containing organic compounds under electron bombardment—migration of an alkyl or an aryl group from the sulphur atom to an oxygen atom in aliphatic or aromatic sulphoxides and sulphones to form a sulphenic or a sulphinic ester, migration of a hydrogen atom to an oxygen atom in aliphatic sulphoxides and sulphones, and finally reactions involving formation of new bonds accompanied by detachment of neutral molecules, of the type $(ABC)^+ \rightarrow (AC)^+ + B$.

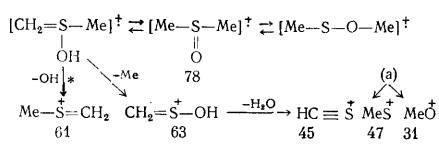
In the present Review we shall summarise the large amount of new work that has appeared on skeletal rearrangements in aliphatic and aromatic sulphoxides and sulphones. Discussion of the mechanisms is based on the application of high-resolution mass spectrometry and isotopic labelling.

II. ALIPHATIC SULPHOXIDES

The breakdown of aliphatic sulphoxides involves the formation of weak peaks of rearranged ions due to loss by the molecular ion of a hydroxy-group or a neutral alkene. These processes are accompanied by migration of hydrogen to the oxygen atom.

Several studies have been made of the behaviour of symmetrical dialkyl sulphoxides[6-11]. The first member of the series—dimethyl sulphoxide—is unable, of course, to eliminate an alkene on electron impact, but its mass spectrum reveals the occurrence of other rearrangements: together with the formation of $[M - OH]^+$ and $[M - CH_3]^+$ ions (where M is the molecular ion), due to successive or simultaneous cleavage of the sulphur–oxygen or a sulphur–carbon bond accompanied by migration of an alkyl hydrogen atom to the oxygen atom, approximately equally intense peaks of CH_3S^+ and CH_3O^+ ions are observed[9] in the mass spectrum of dimethyl sulphoxide. From this it was concluded that the molecular ion isomerised into the structure (a)†, and this was followed by cleavage of the sulphur–oxygen bond (Scheme 1)†. Detachment of a methyl radical leads to formation of the maximum peak (of mass 63) in the spectrum. The high probability of elimination of a hydroxyl from the molecular ion of dimethyl sulphoxide is due to formation of sulphonium ions $R\overset{+}{S}=C\langle$.[10] The spectrum of dimethyl sulphoxide contains also weak peaks corresponding to rearranged hydrocarbon ions $[M - SOH]_n^+$, where $n = 0$–3.

Scheme 1



The dissociative ionisation of higher dialkyl sulphoxides

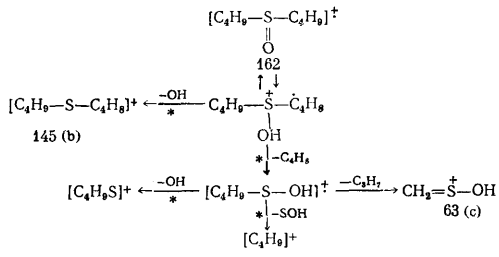


(R = n-C_3H_7, n-C_4H_9, iso-C_4H_9) is accompanied by elimination of R associated with migration of a hydrogen atom to the charged fragment. This process corresponds formally to detachment of a neutral alkene. Detailed study of deuterated di-n-butyl sulphoxide has shown[11] that the migration of hydrogen is non-specific. The location of

†Here and subsequently the numerals accompanying ionic formulae indicate m/e values, and asterisks denote metastable ions.

the migrating hydrogen atom probably determines the probability of successive or simultaneous loss of hydroxyl, cleavage of a carbon–sulphur bond, or other process (e.g. McLafferty rearrangement). Indeed, fission of a carbon–sulphur bond in an aliphatic sulphoxide hardly takes place without migration of hydrogen. Even in dimethyl sulphoxide such migration is probably involved in removal of a methyl group[11]. Formation of the new carbon–hydrogen bond is accompanied by single-stage detachment of a hydroxy-radical with formation of fragment (b) of mass 145 (Scheme 2).

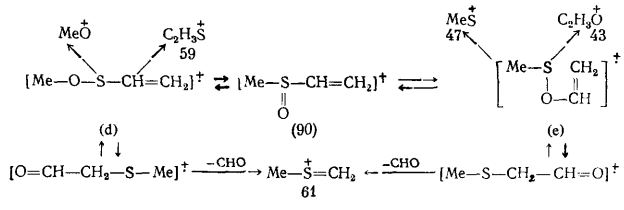
Scheme 2



Another common feature of the mass spectra of these compounds is a characteristic peak due to ions of mass 63 (ion c). Study of deuterated compounds indicates that this fragment contains an α-methylene group and a hydrogen atom that has migrated[11]. The dissociative ionisation of dibutyl sulphoxide exhibits all the characteristic modes of breakdown of dialkyl sulphoxides (Scheme 2). It is interesting that migration to oxygen of a hydrogen atom more remote from the oxygen atom may occur partly also through a McLafferty rearrangement. Randomisation of hydrogen is then completely absent from these compounds[11].

It was suggested[1] that an unsaturated migrating group in an unsymmetrical sulphoxide should facilitate rearrangement, resulting in relatively intense ion peaks due to $[M - SO]^+$, $[M - SOH]^+$ and $[M - SOH_3]^+$.[6] The peaks in the mass spectrum of methyl vinyl sulphoxide[12] due to ionic fragments of masses 31, 43, 47, and 59—$[CH_3O]^+$, $[C_2H_3O]^+$, $[CH_3S]^+$, and $[C_2H_3S]^+$ respectively—also indicate isomerisation of molecular ions of the sulphoxide into the sulphenates (d) and (e) followed by cleavage of the sulphur–oxygen bond. The maximum peak in the spectrum, corresponding to ions of mass 61, however, results from rearrangement of the isomerised molecular ion. This may involve either migration of two methyl hydrogen atoms to the vinyl group of the ion (d) followed by rupture of the sulphur–oxygen bond, or rearrangement of the ion (e) (Scheme 3).

Scheme 3



The spectra of unsymmetrical compounds, such as n-butyl methyl, ethyl, propyl, and isopropyl sulphoxides, show that, when unbranched alkyl groups are present, a small alkyl is eliminated preferentially, with migration of a hydrogen atom to the oxygen; in α-branched systems this effect is ill defined[11].

III. AROMATIC SULPHOXIDES

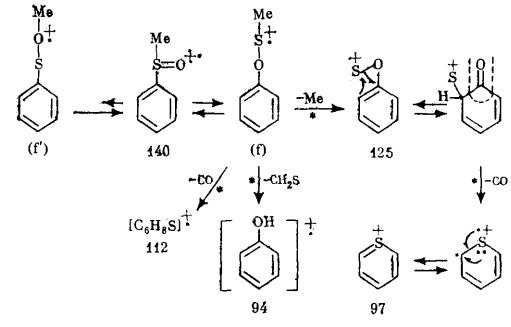
The mass spectra of aromatic sulphoxides, in contrast to those of the aliphatic compounds, containing weak peaks of rearranged ions, are characterised by intense peaks due to ions that may result from isomerisation of the molecular ion. Alternative migration of one of the groups from the sulphur atom to oxygen is observed in the dissociative ionisation of alkyl aryl or unsymmetrical diaryl sulphoxides. This indicates that the molecular ion can exist in at least three forms[1]:



Reversible O → S migration of allyl and benzyl with formation of a sulphoxide has been demonstrated[13] on heat-treatment of the sulphenate. However, phenyl sulphoxides probably do not undergo S → O migration on thermolysis[14].

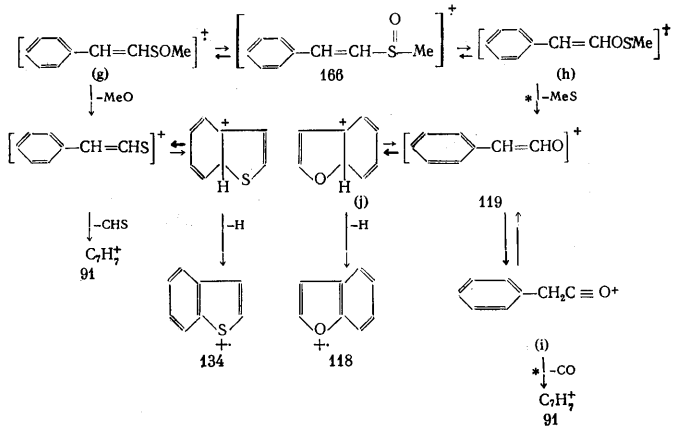
The elimination of carbon monoxide in the dissociative ionisation of aromatic sulphoxides[8] indicates unambiguously formation of a carbon–oxygen bond by isomerisation of the molecular ion or of ionic fragments appearing in the first stage of breakdown. Thus the mass spectrum of methyl phenyl sulphoxide shows that the molecular ion and the ion $[M - CH_3]^+$ of mass 125 lose carbon monoxide. In addition, the molecular ion eliminates a CH_2S group with formation of an ion of mass 94 $[C_6H_6O]^+$ (perhaps having the phenol structure), a process which is confirmed by a metastable peak. The molecular ion of methyl phenyl sulphoxide can be regarded as represented mainly by structure (f) (Scheme 4).

Scheme 4



However, these workers[8] do not detect the CH_3O^+ ion, which would have indicated isomerisation of the molecular ion involving migration of the alkyl group from the sulphur to the oxygen atom (f′). Such isomerisation has been observed with methyl styryl and phenethynyl sulphoxides[15–17], when alternative formation of the intermediate structures (g) and (h) takes place (Scheme 5) with preferential migration of the styryl or the alkyl group from the sulphur to the oxygen atom. Decomposition of these ions (g) and (h) yields the characteristic ionic fragments. Thus the mass spectrum of methyl styryl sulphoxide indicates elimination of a methoxy-group from the former ion, although no metastable ions were observed for this purpose. Study of deuterated derivatives of methyl styryl sulphoxide confirmed the above observation[15].

Scheme 5

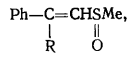


Migration of the styryl group from sulphur to oxygen can be traced by the detachment of a methylthio-radical from the isomerised molecular ion of structure (h) and the appearance of the peak of the corresponding metastable ion. One of the main pathways along which the resulting ion of mass 119 breaks down involves migration of a hydrogen atom to the α-carbon atom relative to the ring with formation of the phenylacylium ion (i) followed by elimination of carbon monoxide (Scheme 5).

Another mode of breakdown of the ion of mass 119 involves [15-17] electrophilic attack on the benzene ring by the positively charged oxygen atom to form the protonated benzofuran ion (j), from which the hydrogen atom splits off to give the pseudomolecular benzofuran ion of mass 118. Electrophilic attack induced by electron impact is made not only by oxygen [18] but also by sulphur [7], as shown by formation of a pseudomolecular benzothiophen ion of mass 134 when structure (g) breaks down.

Appearance of the tropylium ion of mass 91 probably has a lower activation energy [4] than that of the benzofuran ion. With ionising electrons of low energy the process $119^+ \rightarrow 91^+$ still occurs, but the ion of mass 118 disappears.

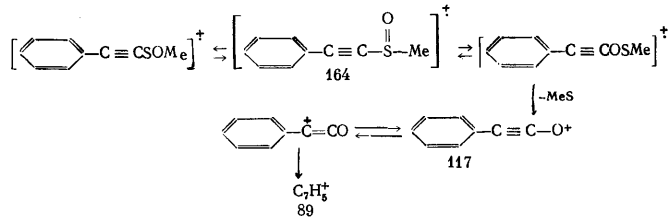
The molecular ion of methyl styryl sulphoxide also loses carbonyl (and/or formyl) and hydroxyl. Examination of deuterium-labelled compounds has established that the carbon atom present in the formyl radical had probably been attached to the sulphinyl group, whereas the hydroxyl hydrogen atom may have belonged either to the phenyl ring or to the alkyl group, which is confirmed by the mass spectra of the compounds



where R = CH_3, C_2H_5, C_6H_5.

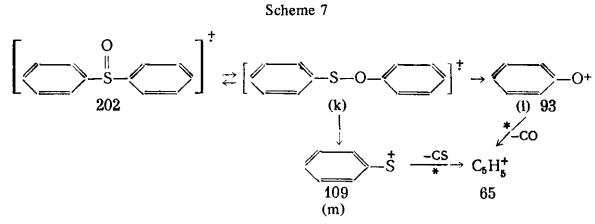
The presence of a second phenyl group in the styryl system greatly facilitates the sulphoxide–sulphenate rearrangement. High-resolution mass-spectrometric data and results for labelled compounds showed that elimination of the sulphinyl group from the molecular ions occurred neither with methyl styryl nor with methyl phenethynyl sulphoxide (Scheme 6), the latter of which is characterised by preferential migration of the acetylenic group with its *sp*-hybridised carbon atom from sulphur to oxygen. Successive detachment of a methylthio-group and of carbonyl gives the $[C_7H_5]^+$ ion of mass 89.

Scheme 6



Formation of a carbon–oxygen bond and elimination of carbon monoxide do not occur on electron bombardment of alkyl aryl sulphoxides having a long alkyl chain [19] and of β-keto-sulphoxides [20], owing to sulphenate isomerisation of the molecular ion. These compounds are characterised not only by rupture of α- and β-bonds relative to the aromatic ring but also by the McLafferty rearrangement, which involves a six-membered transition state. This specific rearrangement occurs even with ionising electrons of very low energy. Elimination of the sulphinyl group from the molecular ion, which takes place with diphenyl [7], dibenzyl [21,22], and di-*p*-tolyl [8] sulphoxides, was not observed.

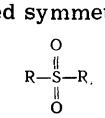
Scheme 7



Some evidence of the isomerisation of molecular ions of diphenyl sulphoxides into sulphenates (k) can be obtained from an examination of the mass spectra of diphenyl sulphoxide. Cleavage of the sulphur–oxygen bond causes the appearance of ions of mass 93 and 109—$[C_6H_5O]^+$ (*l*) and $[C_6H_5S]^+$ (*m*)—(Scheme 7). The metastable peaks indicate that elimination of carbonyl and thiocarbonyl groups leads in each case to an ion of mass 65 $[C_6H_5]^+$. In the mass spectra of higher homologues the fragments (*l*) and (*m*) are formed directly from the molecular ion (Scheme 7). The elementary composition of the fragments is confirmed by the high-resolution spectra [7]. Another feature of the above diaryl sulphoxides is the elimination of carbon monoxide and a hydrogen atom from the molecular ion, as well as the presence of the intense rearranged ion $[M - SO]^+$.

IV. ALIPHATIC SULPHONES

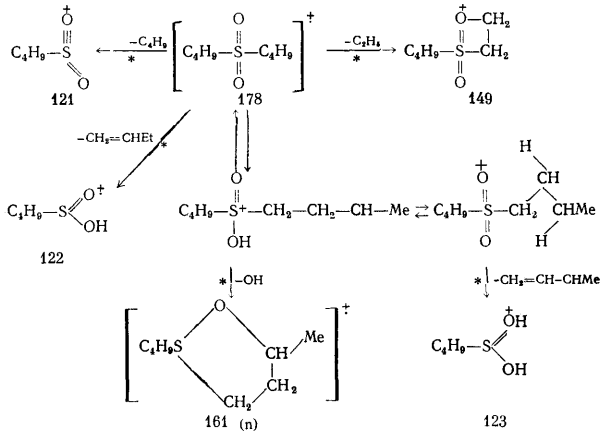
Aliphatic sulphones behave like the sulphoxides towards electrons. With the exception of dimethyl sulphone the mass spectra of saturated symmetrical dialkyl sulphones



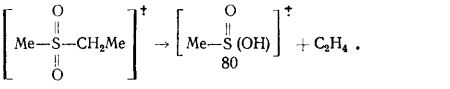
(R = C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}) contain intense peaks of hydrocarbon ions. Formation of rearranged ionic fragments $[RSO_2H_n]^+$, where $n = 0-2$, is characteristic of aliphatic sulphones [7,8,11,23]. The dissociative ionisation of dibutyl sulphone exhibits all the typical features of the breakdown of saturated dialkyl

sulphones due not only to rupture of a carbon–sulphur bond but also to γ-cleavage with migration of one or two hydrogen atoms to the oxygen atoms. The use of deuterium-labelled compounds has shown[11] that oxygen, together with the γ-hydrogen atom migrating to it, is detached from the molecular ion as a result of a McLafferty rearrangement with formation of the cyclic ionic fragment (n) of mass 161 (Scheme 8). It is interesting that the probability that an alkyl group will split off, with double migration of hydrogen to the charged ionic fragment, increases with the length of the alkyl chain[8].

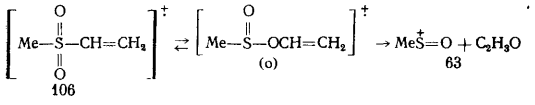
Scheme 8



Study of the mass spectra of unsymmetrical aliphatic sulphones—e.g. ethyl methyl and butyl methyl, ethyl, n-propyl, and isopropyl—shows[11] that the larger group is more easily removed from unbranched compounds, whereas cleavage of the secondary carbon–sulphur bond predominates in α-branched systems. Furthermore, hydrocarbon fragments do not appear from the breakdown of ethyl methyl sulphone, as with dimethyl sulphone. In this case the rearrangement caused by migration of a hydrogen atom to oxygen leads to formation of an ion of mass 80:



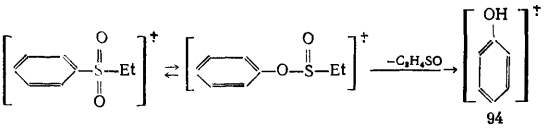
An unsaturated group present in an unsymmetrical sulphone migrates from the sulphur atom to oxygen. Thus the mass spectrum of methyl vinyl sulphone contains an intense peak of the CH_3SO^+ ion formed as a result of S → O migration of the vinyl group followed by fission of the sulphur–oxygen bond in the intermediate structure (o):



V. AROMATIC SULPHONES

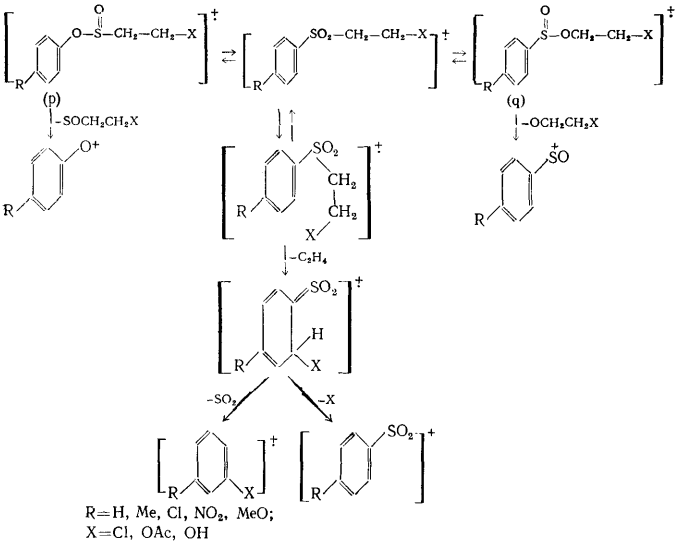
The spectra of mixed alkyl aryl sulphones $C_6H_5.SO_2.R$ (where R = CH_3, C_2H_5, iso-C_3H_7, cyclo-C_3H_7, n-C_4H_9, n-C_6H_{13}) exhibit the S → O migration of phenyl also observed with sulphoxides[8,24–26]. For example, the molecular ion of ethyl phenyl sulphone eliminates C_2H_4SO in a single stage with formation of the $[C_6H_6O]^+$ ion of mass 94. This mode of decomposition has been proved by high-resolution mass spectrometry and by the study of deuterium-labelled specimens (Scheme 9).

Scheme 9



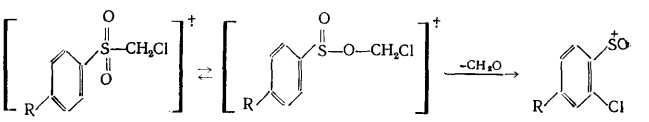
A β-substituent X present in an aryl ethyl sulphone may migrate to the aromatic ring[27–31]. However, the ions $[M - C_2H_4.X]^+$ and $[M - C_2H_4.SO_2]^+$, formed by the McLafferty arrangement, do not represent the chief mode of decomposition. The most intense peaks in the mass spectra of substituted aryl ethyl sulphones correspond to the ions $[M - OCH_2CH_2X]^+$ and $[M - SOCH_2CH_2X]^+$, which can be formed only by isomerisation of the molecular ion followed by rupture of the sulphur–oxygen bond in the intermediate structures (p) and (q) (Scheme 10).

Scheme 10



Furthermore, a substituent in the aromatic ring may influence migration of the aryl group from the sulphur atom to oxygen[25–32]. Thus the electron-accepting *p*-nitro-group hinders S → O migration of the aryl in the dissociative ionisation of 2-chloroethyl *p*-nitrophenyl sulphone, whereas the electron-donating methoxy-group (in 2-chloroethyl *p*-methoxyphenyl sulphone) facilitates such migration.

Although unsaturation in the migrating group is regarded as a factor increasing the probability of rearrangement, investigation of substituted aryl chloromethyl sulphones shows[28] that migration of the alkyl competes successfully with that of the aryl. The appearance of $[RC_6H_4SO]^+$ ions in the mass spectra of these compounds is due to formation of an alkyl–oxygen bond in the transition state with subsequent elimination of the neutral species CH_2O and migration of the chlorine atom to an *ortho*-position relative to the sulphur atom:



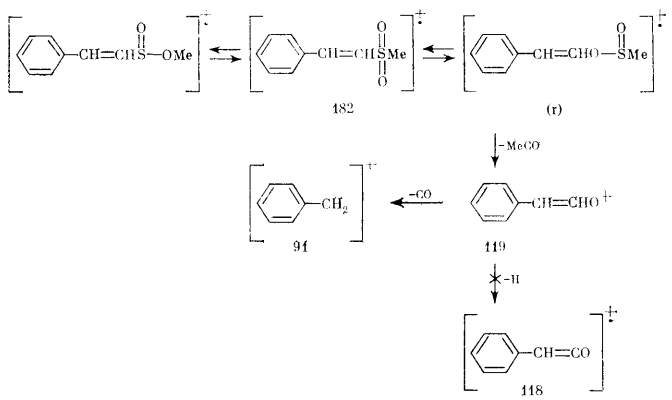
where R = CH_3O, CH_3, H, Cl, Br, NO_2. When the chlorine atom is replaced by hydrogen, such rearrangement is not observed, but an $SOCH_2$ group is eliminated with formation of an ion having the structure of the corresponding phenol.

Evidence of S → O migration of the aryl is lacking for benzenesulphonyl chlorides and their derivatives[27,33,34]. These compounds undergo rearrangement with formation of the $[M - SO_2Cl]^+$ ion. The *ortho*-effect is responsible for the absence of this ion peak in *o*-nitrobenzenesulphonyl chloride, which undergoes initial abstraction of a nitroso-group from the molecular ion followed by elimination of a chlorine radical.

Aryl vinyl sulphones behave similarly to aryl ethyl sulphones. Isomerisation of their molecular ions involves migration of the vinyl in preference to the phenyl group[30]. The peak due to $[M - OCH:CH_2]^+$ ions produced by rupture of the sulphur–oxygen bond is the most intense in the mass spectra of these compounds.

A substituent in the aromatic ring influences not only the migrating power of the phenyl group but also the less significant mode of decomposition involving detachment of a neutral sulphonyl group from the molecular ion. Thus, although the $[M - SO_2]^+$ ion peak is absent from the spectrum of *p*-nitrophenyl vinyl sulphone, it becomes the most intense in the spectrum of the methoxy-derivative, which is evidence of the influence of the electron-donating power of a ring substituent on the probability of elimination.

Scheme 11



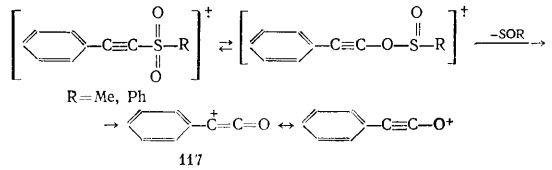
Styryl sulphones show similar competition between the S → O migration of alkyl or styryl[17]. Thus in the decomposition of methyl styryl sulphone on interaction with electrons the preferential migration of styryl from sulphur to oxygen followed by abstraction of a CH_3SO radical from the intermediate structure (r) promotes formation of a carbon–oxygen bond and elimination of carbon monoxide from the fragment of mass 119 (Scheme 11). The loss of hydrogen by the ionic fragment of mass 119 observed with methyl styryl sulphoxides is completely absent from the mass spectrum of the sulphone. The process $119^+ \rightarrow 118^+$ probably requires more energy than does $119^+ \rightarrow 91^+$ (Scheme 11). Elimination of hydrogen from the $[M - CH_3SO]^+$ ion and removal of carbonyl or formyl from the molecular ion are absent also from the mass spectra of higher homologues of methyl styryl sulphone.

In view of the above, the lack of competition between the S → O migration of the groups in phenyl styryl sulphone is extremely curious. The mass spectrum indicates unambiguously migration of the styryl group and absence of migration of phenyl[17].

Loss of the sulphonyl group as a result of a rearrangement of the type $[ABC]^+ \rightarrow [AC]^+ + B$ also exhibits a lower probability than the removal of sulphinyl from methyl styryl sulphoxide.

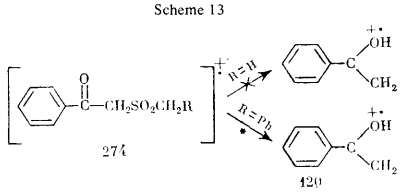
The dissociative ionisation of methyl or phenyl phenethynyl sulphone reveals peculiar behaviour of the acetylenic group, which alone migrates from sulphur to oxygen, while the methyl or phenyl group plays almost no part in the process (Scheme 12).

Scheme 12

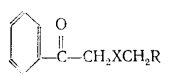


The stability of the neutral species expelled from the molecular ion is responsible for the McLafferty rearrangement[20,22], which has an important role in the formation of the characteristic ions. Indeed, with a keto-sulphone [20] such rearrangement is not followed by elimination of a simple sulphine. In the case of the phenyl derivative, however, such a sulphine may be stabilised, since the spectrum contains a peak at mass 120 corresponding to the $[M - SO_2CHR]^+$ ion, which is confirmed by a metastable transition (Scheme 13).

Scheme 13



Investigation of the series of compounds [20]

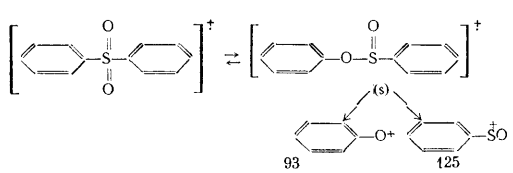


X=O, S, SO, SO_2;
R=H, Ph

revealed that increase in the stability of the neutral fragment XCHR with R = C_6H_5 is accompanied by intensification of the peak of the rearranged ion $[M - XCHR]^+$ in comparison with that obtained with R = H.

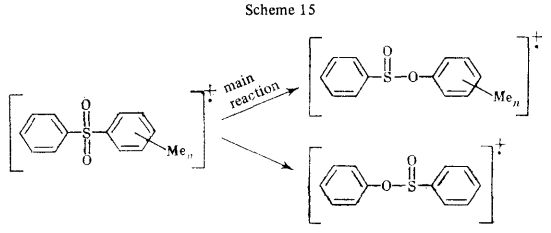
A peculiarity of the dissociative ionisation of diphenyl sulphones is the equally probable S → O migration of aryl with formation of an intermediate aryl arenesulphinate (s). Whereas benzophenone and diphenylmethane are characterised by the formation of ions undergoing rearrangement with detachment of the bridging group, together with one or two hydrogen atoms that have migrated, resulting in formation of an ion of biphenylene structure[35], this process is less strongly developed with diphenyl sulphone, for which the main reaction involves cleavage of the sulphur–oxygen bond in (s) with formation of an intense peak of mass 125 [22] (Scheme 14).

Scheme 14



The introduction of different substituents into the aromatic rings leads to competition in migration of the aryl groups with preferential formation of ionic fragments containing a substituted or an unsubstituted phenyl. The tendency to migrate increases with the number of electron-donating methyl groups [26]. It was suggested [26] that the electron deficit is localised mainly in the non-bonded orbital of the oxygen, so that the phenyl ring better able to function as an electron donor would be more likely to migrate [26,36] (Scheme 15).

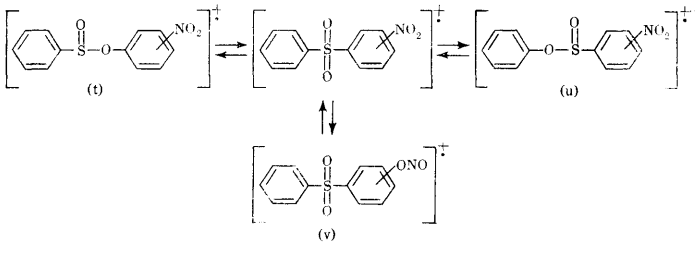
Scheme 15



However, study of a series of *para*-substituted diphenyl sulphones has shown that both electron-donating and electron-accepting substituents are able to increase the migratory power of an aromatic ring [37]. Since an electron-donating group has a considerably stronger stabilising influence on $[ArO]^+$ than on $[ArSO]^+$ ions, the increased migratory power of such a group can be attributed to the stability of the resulting ion. On the other hand, electron-accepting substituents obviously facilitate bond rupture, since they diminish the stability of the positively charged species. If the change in energy of bond rupture exceeds the change in stability of the resulting ion, the migratory power of the aromatic ring containing the electron-accepting group may exhibit an apparent increase [37].

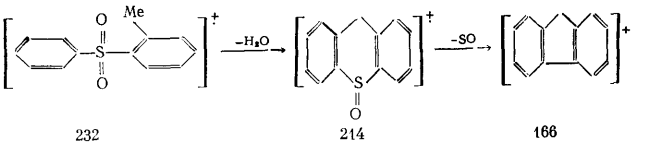
The intensity ratio of the $[ArSO]^+$ and $[ArO]^+$ ion peaks varies within wide limits depending on the type and position of a substituent in the aromatic ring, which indicates competition in formation of intermediate sulphinate structures by migration of a ring from sulphur to oxygen. Thus for the isomeric nitrophenyl phenyl sulphones the probability of formation of the intermediate structure (t) decreases in the sequence *para* > *meta* > *ortho*, whereas the structure (u) is most characteristic of the *ortho*-isomer and less typical of the *para*- and *meta*-compounds [38] (Scheme 16).

Scheme 16



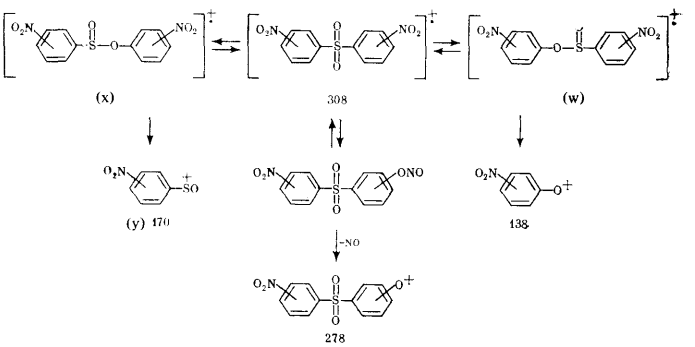
The possibility of nitro-nitrate isomerisation of the molecular ions must be taken into account when considering the dissociative ionisation of nitro-substituted aromatic sulphones [39]. In the case of nitrodiphenyl sulphones it leads to the formation of ions (v) whose subsequent breakdown with elimination of a nitroso-group results in the appearance of characteristic $[M - NO]^+$ ions. The probability of nitro-nitrate isomerisation is doubled in the case of the *ortho*-isomer, owing to the presence of an *ortho*-effect. Such an effect is apparent also in the decomposition of phenyl *o*-tolyl sulphone, where it causes the formation of characteristic $[M - H_2O]^+$ and $[M - OH]^+$ ions, which then eliminate the sulphinyl group [26] (Scheme 17). Elimination of hydrogen atoms from the *o*-methyl group was confirmed by a study of deuterated compounds. The relative intensities of the ion peaks formed by the detachment of SO_2, SO_2H, and SO_2CH_3 from the molecular ion also depend on the position of the substituent in the aromatic ring [26].

Scheme 17



With 2,4-dinitrophenyl phenyl sulphone migration of the unsubstituted aromatic ring from sulphur to oxygen is preferred [38]. The probability of such isomerisation increases with decrease in the energy of the ionising electrons, and the $[ArO]^+$ ion becomes the main peak in the spectrum.

Scheme 18



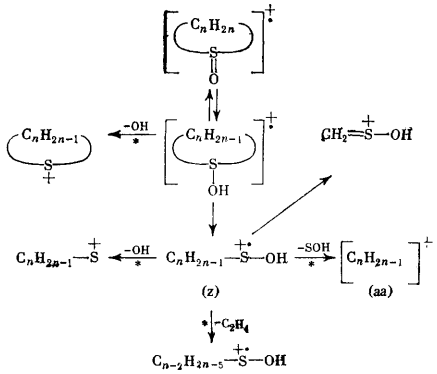
When both rings in a diphenyl sulphone are substituted [40], cleavage of the sulphur–oxygen bond in the ions (w) and (x) formed by migration of either aromatic ring from sulphur to oxygen leads to preferential formation of $[Ar'SO]^+$ ions of mass 170 (y) in relation to $[Ar'O]^+$ ions [40] (Scheme 18). Depending on the positions of substituents in the aromatic ring relative to the sulphonyl group the ion (y), corresponding to the maximum peak in the spectrum of all the isomers other than 2,4'-dinitrodiphenyl sulphone, increases in intensity relative to the total ion current in the sequence of isomers *ortho* < *meta* < *para*.

VI. CYCLIC SULPHOXIDES

The mass spectra of sulphoxides and sulphones containing the sulphur atom in a saturated or partly saturated ring system had not been studied in such great detail as those of the aliphatic and aromatic compounds. The behaviour of saturated cyclic compounds such as thietan, thiolan, thian, and thiepan *S*-oxides is similar to that of aliphatic sulphoxides subjected to electron bombardment [11]. The general pattern is shown in Scheme 19. Migration of a hydrogen atom to the oxygen atom followed by cleavage of a carbon–sulphur bond is responsible for the appearance of the ion $[R-S-OH]^+$ (z). The fact that this bond forms part of the ring impedes direct detection of the migration of hydrogen atoms involved in the process. The character

of the migration can be determined only after loss of the SOH group, i.e. after the process (z) → (aa). Rupture of the carbon–sulphur bond may be followed by removal of ethylene comprising α- and β-methylene groups—process (z) → (ab)—which increases the difficulty of establishing the mechanism of decomposition.

Scheme 19

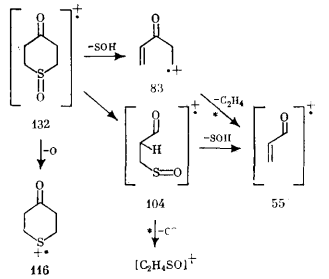


The mass spectra of deuterated sulphoxides [11] indicate that the migration of hydrogen involved in the cleavage of a carbon–sulphur bond (loss of SOH) is effected by a McLafferty rearrangement. The elimination of a hydroxyl is less important than thietan, thiolan, and thian-1-oxides, but leads to intense peaks in the mass spectrum of thiepan 1-oxide, whereas the probability of elimination of the SOH group increases as the ring becomes smaller. This effect is attributed [41] to the difference in the distance of closest approach of the sulphinyl oxygen atom to β- and γ-hydrogen atoms.

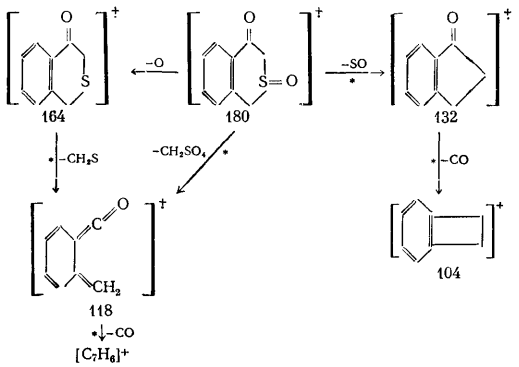
The pattern of decomposition is greatly changed by introduction of a 4-keto-group into thian 1-oxide [42], when it involved mainly loss of ethylene as a result of a retrodiene reaction. This indicates that the presence of an sp^2-hybridised carbon atom attached to sulphur in the cyclic sulphoxides promotes rearrangement, whereas a specifically introduced carbonyl group causes retrodiene decomposition. For example, application of the concept of charge localisation to the dissociative ionisation of 4-oxothian 1-oxide suggests preferential elimination of an alkene from the molecular ion, which is evident in formation of the corresponding metastable ion. Subsequent detachment of the group SOH from the $[M - \text{Alkene}]^+$ ion tends to produce the maximum peak in the spectrum at mass 55 [Scheme 20]. From the low intensity of the $[M - \text{SOH}]^+$ ion peak it may be supposed that this mode of decomposition is less favourable, while the weak ion peak at mass 116, formed as a result of removal of an oxygen atom from the molecular ion, indicates the improbability of this process. The elimination of hydroxyl from the molecular ion, observed with aliphatic and caromatic sulphoxides [8], is found also in the spectrum of the present compound.

Competition between retrodiene decomposition and elimination of a sulphinyl or sulphonyl group has been detected among compounds of the thiachromanone series [43]. Accompanying elimination of an oxygen atom, a hydroxy-group, or a water molecule from the molecular ion, the chief mode of breakdown of 4-oxothiaisochroman 2-oxide involves initial loss with formation of the maximum ion $[M - \text{SO}]^+$. Subsequent detachment of carbon monoxide yields an ion of mass 104 having a benzocyclobutene structure. Scheme 21 is confirmed by the metastable peaks observed in the mass spectrum. Retrodiene decomposition, which is less probable in this case, involves abstraction of a CH_2SO group and is also accompanied by a metastable transition.

Scheme 20

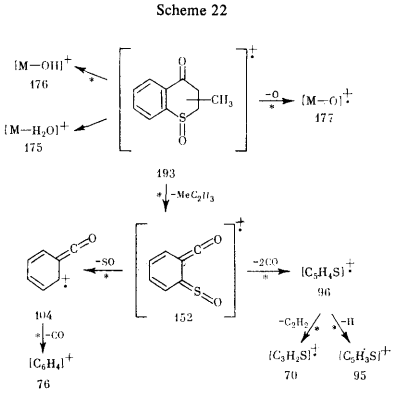


Scheme 21



Thiachromanone and its methyl derivatives undergo breakdown mainly by a retrodiene reaction involving loss of $CH_3C_2H_3$ with formation of a maximum ion peak at mass 152. The ion then loses sulphur monoxide to give an ion peak at mass 104 (Scheme 22). Direct detachment of a sulphinyl group from the molecular ion is secondary in character.

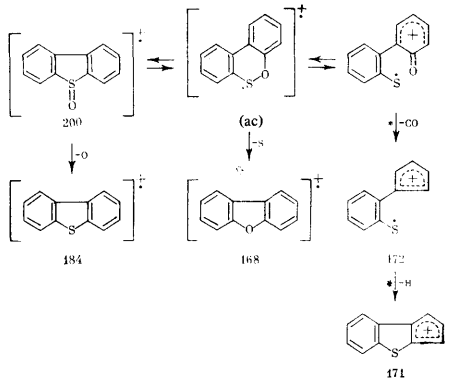
Scheme 22



It is noteworthy that, although sulphur is attached to two sp^2-hybridised carbon atoms in oxothiachroman oxides, rearrangement of the molecular ion into a sulphenate on electron bombardment, which is characteristic of unsaturated cyclic compounds, could not be demonstrated [43]. Thus dibenzothiophen S-oxide breaks down [44] with formation of the dibenzothiophen cation of

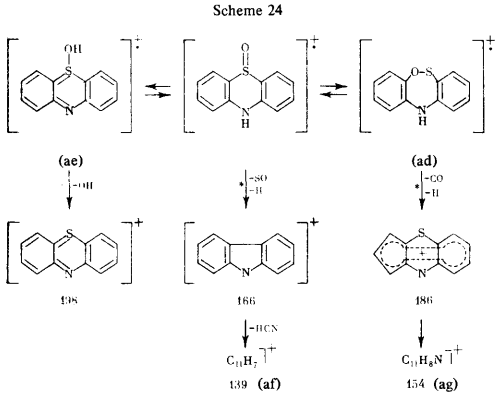
mass 184. This is accompanied by detachment of CO or CO + H from the molecular ion. This can be explained by the rearrangement noted with open-chain sulphoxides[8]. Appearance of the intermediate ion (ac) as a consequence of the rearrangement is confirmed by a weak peak of mass 168, corresponding to the dibenzofuran cation (Scheme 23).

Scheme 23



Detachment of a sulphinyl group in a single stage is not observed with compounds containing two heteroatoms in the middle ring[44], where the sulphoxide oxygen is involved in formation of the $[M - CO - H]^+$ ion, but the ring oxygen atom is involved in a subsequent stage of fragmentation. The dissociative ionisation of phenothiazine 5-oxide is remarkable in a mode of decomposition, accompanying those mentioned above, in which the middle ring expands to seven members (ad).[45] It is also noteworthy that hydroxyl is removed from the molecular ion (ae) following transannular redistribution of hydrogen (Scheme 24). The ions (af) and (ag) are extremely stable: the former is met in almost all mass spectra of dibenzo-derivatives of heterocyclic compounds; and the latter is always present when one or two heteroatoms in a six-membered ring are attached to hydrogen.

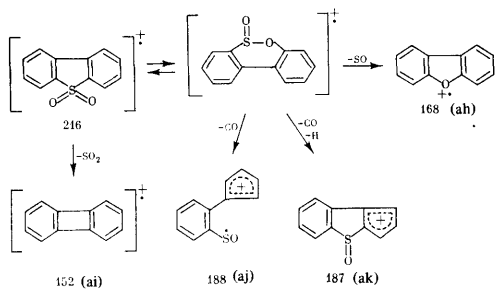
Scheme 24



VII. CYCLIC SULPHONES

Cyclic sulphones are characterised by rearrangements involving isomerisation of the molecular ion. For example, the main processes in the initial breakdown of dibenzothiophen [*S*-dioxide] include the loss of sulphinyl and carbonyl groups[8,46,47], probably as a result of isomerisation of the molecular ion into a sulphinic ester similarly to alkyl aryl and diaryl sulphones[26]. The dibenzofuran ring system (ah) is formed considerably more readily than is the four-membered cyclobutadiene ring of biphenylene (ai). Elimination of carbonyl and formyl groups from the molecular ion produces the ions (aj) and (ak) respectively (Scheme 25).

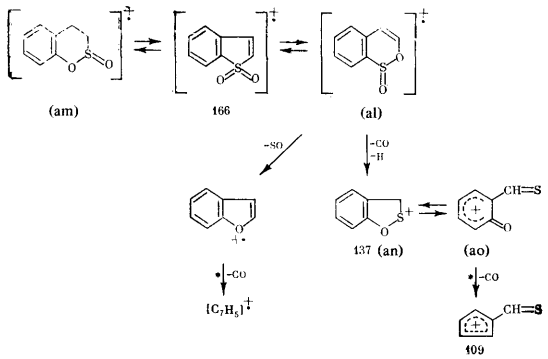
Scheme 25



When a heteroatom has been introduced into the ring—thiaxanthen, oxothiaxanthen, phenothiazine, thianthren, and phenoxathiin *S*-dioxides—decomposition involves preferential elimination of sulphur dioxide[44,45,48]. In the ensuing stages carbon monoxide is removed, which is evidence of formation of a carbon–oxygen bond by isomerisation of the molecular ion into a cyclic sulphinate.

The mode of decomposition is greatly affected by change in the structure of the cyclic sulphone. In this respect the mass spectrum of dihydronaphthobenzothiophen *S*-dioxide is quite remarkable[49], containing an intense peak of $[M - SO_2]^+$ ions but without the elimination of carbonyl and sulphinyl groups resulting from isomerisation of the molecular ion into a sulphinic ester. Yet benzothiophen 1-dioxide[44,50,51] isomerises with preferential formation of the intermediate structure (al), not (am). Subsequent elimination of SO and CO + H groups from the ion (al) leads to the formation of characteristic ions, the latter of which can be represented by the two tautomers (an) and (ao) (Scheme 26). Investigation of deuterated compounds established the initial elimination of CO + D, which was confirmed by the corresponding metastable peak: i.e. the rearrangement involves a hydrogen atom in an α-position with respect to the sulphur atom[50].

Scheme 26

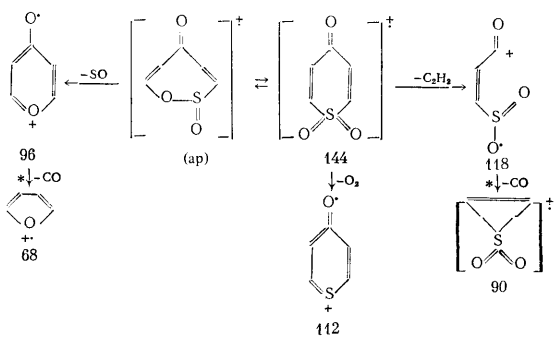


The most probable process with phenylated and chlorinated benzothiophen 1,1-dioxides is the elimination of COC_6H_5 and COCl from the isomerised molecular ion[52]. Nevertheless, dihydrobenzothiophen 1,1-dioxide after isomerisation breaks down in a different way, with elimination of sulphinyl and hydroxymethyl groups from the molecular ion.

The saturated cyclic compounds rearrange and decompose[45] similarly to aliphatic sulphones[8]. The dissociative ionisation of thiolan, thian, and thiepan 1,1-dioxides is accompanied by migration of a hydrogen atom with preferential detachment of sulphonyl and sulphino-groups as a result of rupture of a carbon–sulphur bond[11]. If a carbonyl groups is introduced into the six-membered ring, e.g. at position 4, the pattern of dissociative ionisation changes fundamentally[45], to resemble the scheme of decomposition of substituted five- and six-membered sultams[53]. A characteristic reaction in the decomposition of the above compounds is the detachment of sulphur dioxide not from the molecular ion but from the ionic fragments $[M - C_2H_4]^+$ and $[M - CO]^+$ respectively.

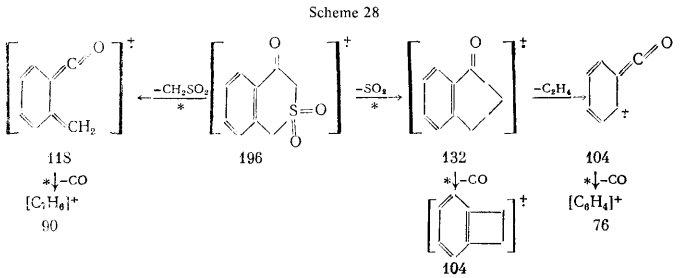
If the ring contains unsaturated bonds, the molecular ions of cyclic sulphones isomerise similarly to aryl sulphones[29]. Thus the dissociative ionisation of thiapyrone 1,1-dioxide [42] involves the intermediate ion (ap), from which sulphinyl is removed. However, the principal mode of decomposition includes preferential elimination of acetylene from the molecular ion. This takes place by a mechanism of retrodiene breakdown with subsequent formation of a carbon–oxygen bond and loss of carbon monoxide (Scheme 27).

Scheme 27



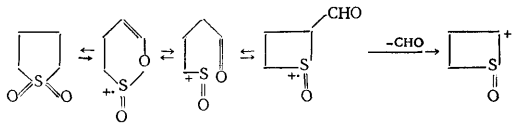
Change in the size of ring in a cyclic sulphone does not affect the mode of decomposition. This was revealed in a study of thiepin 1,1-dioxide and its dihydro-derivative[44,54]. The characteristic $[M - CHO]^+$ ion peak indicates sulphone–sulphinate rearrangement of these compounds.

Scheme 28



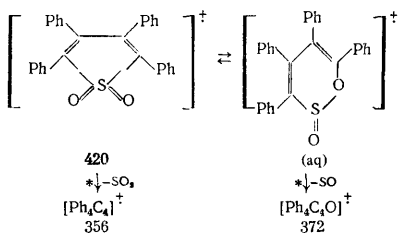
Nevertheless, although sulphur is combined with an sp^2-hybridised carbon atom in such compounds as thiachromanone dioxide, the molecular ion does not isomerise into a sulphinic ester[43] before decomposition begins. For example, 4-oxothiaisochroman 2,2-dioxide breaks down mainly with elimination of sulphur dioxide from the molecular ion. Retrodiene decomposition with the detachment of CH_2SO_2 is of secondary importance (Scheme 28). The most probable process for 4-oxothiachroman 1,1-dioxide, however, involves detachment of ethylene with subsequent elimination of sulphur dioxide. Direct removal of a sulphonyl group from the molecular ion is far less probable. Introduction of a methyl substituent into a thiachromanone does not in principle change the mode of decomposition, which involves a retrodiene reaction resulting in elimination of a C_3H_6 group.

Scheme 29



It is interesting that the mass spectrum of sulpholan contains peaks due to ions formed by direct detachment of SO, HSO_2, and CH_3SO_2 groups from the molecular ion. Cleavage of a carbon–sulphur bond with retention of charge on the carbon fragment is highly probable in the decomposition of this compound[55]. Nevertheless, the presence of unsaturated bonds promotes isomerisation of the molecular ion of sulpholan into a sulphinic ester with subsequent elimination of a COH group (Scheme 29). The molecular ions of mono- and di-substituted sulpholans do not undergo sulphone–sulphite isomerisation on decomposition[55], whereas tetraphenylthiophen 1,1-dioxide readily loses a sulphinyl group from the isomerised molecular ion[56,57] formed as a result of sulphur–oxygen migration of a ring carbon atom (Scheme 30).

Scheme 30



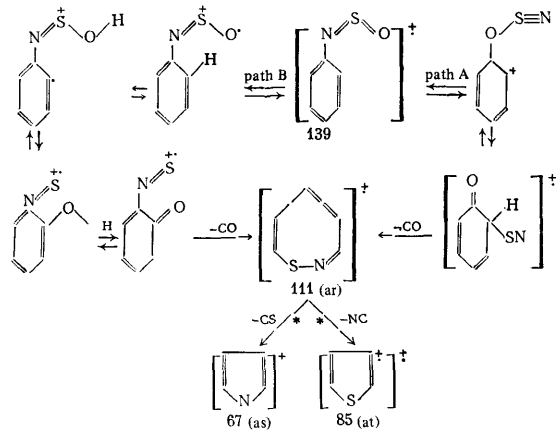
It must be added that complicated cyclic keto-sulphones, which readily lose sulphur dioxide from the molecular ion, do not undergo sulphone–sulphite isomerisation[58,59].

VIII. NITROGEN-CONTAINING SULPHOXIDES AND SULPHONES

Sulphinylanilines

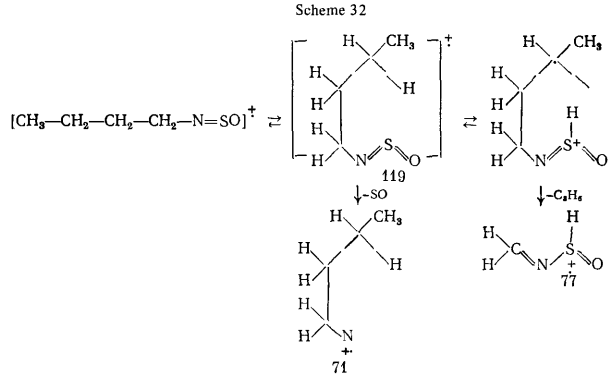
The chief modes of decomposition of arylsulphinylanilines result in formation of a carbon–oxygen bond, and ions are formed even with ionising electrons of low energies. Such rearrangement should take place either with migration of the aromatic ring to the oxygen atom followed by movement of the SN group to position 2 (path A) [60] or with migration of an *ortho*-hydrogen atom from the ring to the oxygen atom followed by regrouping of the hydroxy-group in the aromatic ring (path B)[61]. In the former case the $C_{(1)}$ atom is lost, and the latter case the $C_{(2)}$ atom (Scheme 31). Study of a 1-^{13}C-sulphinylaniline has shown[65] that the $C_{(2)}$ atom, not $C_{(1)}$, is lost when carbon dioxide is eliminated. The $[M - CO]^+$ ion (ar) may be a cyclic ion, which then breaks down with removal of CS and HCN groups to form structures (as) and (at) respectively[62].

Scheme 31

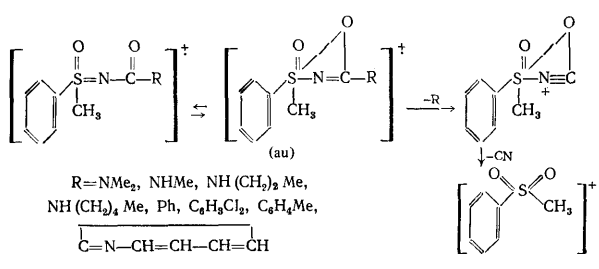


Substituted sulphinylanilines may also undergo rearrangement. The spectrum of *m*-methoxy-sulphinylaniline, for example, reveals well defined rearranged ions, whereas the mass spectra of the *ortho*- and *para*-isomers are devoid of corresponding peaks [63].

Scheme 32



Scheme 33



The decomposition of alkylsulphinylanilines [63-65], however, involves a McLafferty rearrangement, in which the hydrogen atom attached to the γ-carbon atom migrates to the sulphur atom, after which an ionic fragment of mass 77 is formed (Scheme 32). A second important mode of dissociative ionisation is formation of the $[M - SO]^+$ ion. When the α- or β-carbon atom is substituted, however, simple rupture of a carbon–carbon or carbon–nitrogen bond is correspondingly more probable than a McLafferty rearrangement.

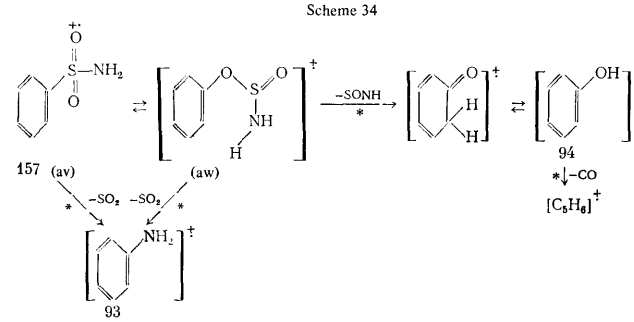
Sulphoximines

The principal decomposition pathway of *N*-substituted sulphoximines is characterised by the appearance of $[M - R]^+$ and $[M - CH_3]^+$ ion peaks. The observed formation of a sulphone ion $[C_6H_5SO_2CH_3]^+$ is due to breakdown of the $[M - R]^+$ ion and is responsible for establishment of a bond between the carbonyl oxygen atoms and the sulphur atom in the transition state [66] (Scheme 33).

Sulphonamides

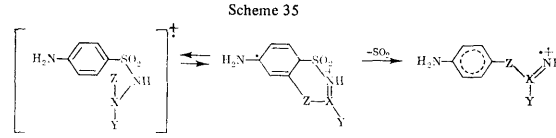
Available data on the decomposition of sulphonamides reveal a tendency to rearrangement with removal of sulphur dioxide. Thus the mass spectrum of benzenesulphonamide and its derivatives shows well defined skeletally rearranged ions resulting from the formation of carbon–oxygen and carbon–nitrogen bonds. Two rearrangements of $(M - SO_2)$ and $(M - SONH)$ take place [36,37,67,68]. The migration of phenyl from the sulphur to an oxygen atom promotes formation of an intermediate structure (aw), from which an ion of phenolic type can then be formed (Scheme 34). The ion of the aniline radical $[M - SO_2]^+$ can probably be formed from (av) or (aw). It is noteworthy that elimination of carbon monoxide from the molecular ion is not observed in the case of sulphonamides [69].

Scheme 34



The nature of the alkyl substituent in secondary sulphonamides affects the behaviour of the compounds on electron impact. The main process is β-rupture relative to the nitrogen atom; skeletally rearranged ions are absent. When alkyl is replaced by amino the main process becomes formation of $[M - NH_2 - O_2]^+$ ions, whereas sulphonamides containing two substituents undergo fission at the nitrogen–sulphur bond with the charge retained on the nitrogen-containing fragment. Skeletally rearranged ions are represented by weak peaks. The mass spectrum contains no ion corresponding to formation of a carbon–oxygen bond.

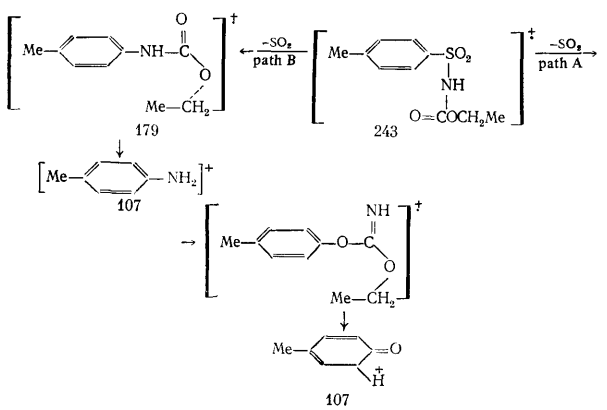
Scheme 35



The probability of the loss of sulphur dioxide increases considerably with the basicity of the substituting group in sulphonamides. With steric factors taken into account, the general direction of decomposition can be represented by Scheme 35. The behaviour of sulphonamide derivatives is explained by the influence of strongly electrophilic substituents, which create a partial positive charge and favour rearrangement with elimination of sulphur dioxide [70,71].

Evident skeletal rearrangements, associated with the appearance of $[M - SO_2]^+$ ions, are in turn characteristic also of sulphonylureas [72,73] and sulphonylcarbamates [74] containing primary, secondary, and tertiary alkyl substituents. The combination of high-resolution mass spectrometry with use of labelled compounds has established the occurrence of two decomposition processes involving rearrangement with elimination of sulphur dioxide from the molecular ion. With both groups of compounds the main process includes preferential formation of an aryl–oxygen bond (path A) and to a lesser extent an aryl–nitrogen bond (path B) followed by breakdown of the $[M - SO_2]^+$ ion with a McLafferty rearrangement. An example is the decomposition of an alkyl *N*-toluenesulphonylcarbamate (Scheme 36). The probability of decomposition of a sulphonylcarbamate by path B can be increased by strengthening the nucleophilic character of the *N*-methylated derivative or by the steric effect of the methyl substituent.

Scheme 36

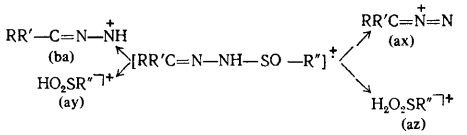


It is interesting that the spectrum of t-butyl *N*-*p*-methoxybenzenesulphonylcarbamate does not contain the $[M - SO_2]^+$ ion. The most probable decomposition involves elimination of carbon dioxide accompanied by a methyl radical. This was explained [74] by the influence on the relative stability of the aryl–sulphur and alkyl–oxygen bonds of the factors responsible for the direction of decomposition. In primary and secondary alkyl derivatives of sulphonylcarbamates the aryl–sulphur bond is weakest, so that decomposition along path B (Scheme 36) predominates. Introduction of a t-alkyl group results in some strengthening of the alkyl–oxygen bond. Yet introduction of an *N*-methyl substituent lowers the strength of the aryl–sulphur bond. This unusual change in stability of the two types of bond on the introduction of a methyl substituent is difficult to interpret in terms of the inductive effect alone, since steric factors cannot be ignored. Interaction of methyl with the sulphonyl group and the aromatic ring lengthens the aryl–sulphur bond sufficiently to neutralise the effect of the t-alkyl on the alkyl–oxygen bond. The relative stability of the former bond can be changed also by introducing various *para*-substituents into the benzene ring: electron-donating substituents will strengthen the aryl–sulphur bond in comparison with unsubstituted rings, whereas electron-accepting substituents will tend to weaken the bond [71].

Sulphonylhydrazones, Sulphonylhydrazines, and Sulphonyl Azides

Elimination of relatively stable neutral species from ions $[ABC]^+ \rightarrow [A-C]^+ + B$ is most characteristic of sulphonylhydrazones [74]. Four ionic species are produced when the molecular ion decomposes with rupture of the nitrogen–sulphur bond. Fragments (ay) and (az) are formed with migration of hydrogen. The ion (az), into which two hydrogen atoms have migrated, is converted into (ay) when the compound contains an alkyl group with hydrogen attached to the α-carbon atom (Scheme 37).

Scheme 37

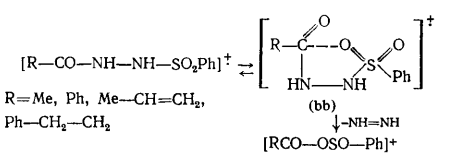


Aromatic sulphonylhydrazones ($R = C_6H_5$, $R' = H$) decompose with elimination of molecular nitrogen from the ion (ax), whereas the ion (ba) rearranges with removal of a nitrile molecule from the middle of the chain.

The mass spectra of aliphatic sulphonylhydrazones indicate formation of (ba) in preference to (ax), (ay), and (az). The decomposition sequence is greatly dependent on the type and size of the aliphatic groups.

The decomposition of *N*-acyl-*N'*-*p*-toluenesulphonylhydrazines [74,75] also involves a rearrangement $[ABC]^+ \rightarrow [AC]^+ \rightarrow B^2$ with elimination of a di-imide molecule from the molecular ion, perhaps via an intermediate cyclic structure (bb) (Scheme 38).

Scheme 38

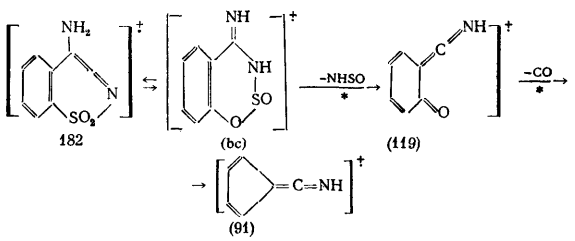


Skeletal rearrangements with elimination of sulphur dioxide from the molecular ion do not occur with sulphonyl azides [76,77]. Detachment of an azide radical is inconsistent with the photochemical behaviour, which involved elimination of nitrogen [75].

Benzisothiazoles and Thiazolidines

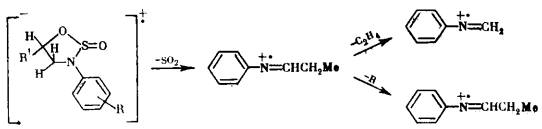
Benzisothiazole derivatives [78] on dissociative ionisation undergo rearrangement with formation of an intermediate structure (bc). For example, an investigation of 3-aminobenzisothiazole 1,1-dioxide labelled with deuterium in the amino-group confirmed the occurrence of decomposition in conformity with Scheme 39.

Scheme 39



ortho-Alkylated derivatives undergo rupture with migration of two hydrogen atoms and loss of an alkyl group followed by elimination of sulphur dioxide from the ionic fragment.

Scheme 40



Higher homologues are characterised by decomposition with McLafferty rearrangement, but *N*-substituted compounds by elimination of an alkylamine from the molecular ion. Direct detachment of sulphur dioxide is improbable. Yet various oxathiazolidines [79,80] undergo rearrangement with removal of sulphur dioxide (Scheme 40). The probability of formation of an $[M - SO_2]^+$ ion varies with the nature and the position of the substituent. Thus with chloro-derivatives this is the most intense peak in the mass spectrum of the *ortho*-isomer, whereas with the methyl derivatives the $[M - SO_2]^+$ ion peak has approximately the same intensity for all the isomers. Its subsequent decomposition can take place in two ways, with elimination of ethylene or of the ring substituent.

The chief mode of decomposition of oxothiazolidine having a t-butyl substituent in the ring [81] involves loss of a methyl radical preceding elimination of sulphur dioxide, whereas introduction of a chloromethyl substituent into the oxathiazolidine ring [82] suppresses the rearrangement associated with the elimination. With such a compound sulphur dioxide and a chlorine radical are detached in a single stage.

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