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FRAGMENTATION OF ORGANIC COMPOUNDS ON ELECTRON IMPACT—IV[1]

CYCLIC SULFONES

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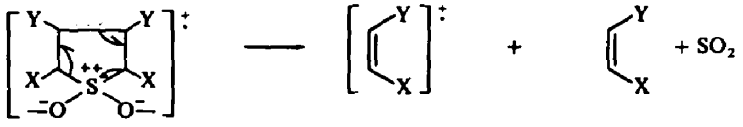
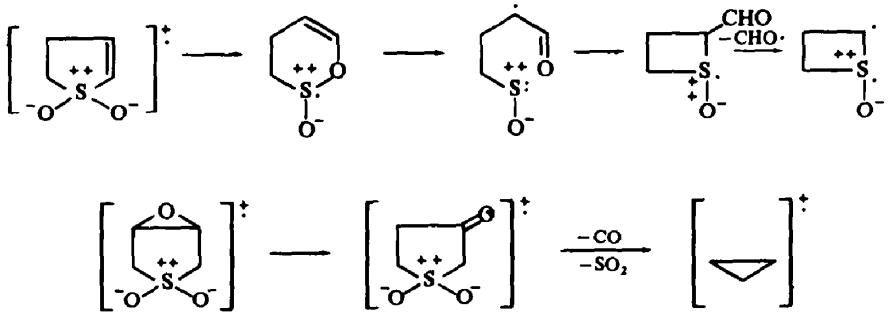
Abstract—The mass spectra of nineteen cyclic sulfones are reported and fragmentation patterns are interpreted with the aid of high resolution mass measurements and deuterium labeling techniques.

Sulfolane, monosubstituted sulfolanes, and disubstituted sulfolanes all undergo a characteristic cyclic decomposition reaction which is represented as follows:



This fragmentation produces abundant ions when strong fragmentation-directing groups (—NH_2, —OH, OMe, OEt) are present in the molecule, but assumes lesser importance when all of the substituents are weak directing groups (—H, —OAc, —Cl, —Br). The latter compounds fragment preferentially with elimination of the substituent. The most abundant ions produced by 2-sulfolene and 3,4-epoxysulfolane are generated by deep-seated molecular rearrangements which are rationalized as follows:



RECENTLY, several workers have published brief discussions of the behavior of sulfones on electron impact.[2–7] In general, they observed that both acyclic and cyclic sulfones eliminate sulfur dioxide and that one compound, dibenzothiophene-5,5-dioxide, eliminates carbon monoxide and a H atom as well.[5,6] The peaks representing the various rearranged ions have intensities which vary from a few per cent to 40% of the intensity of the base peak. We have studied several substituted sulfolanes in order to determine the generality of rearrangements in this system and our results are reported here.

DISCUSSION OF MASS SPECTRA

The mass spectra of all of the cyclic sulfones discussed in this paper were recorded on a Consolidated Electrodynamics Corporation 21–110 high resolution mass spectrometer and the partial mass spectra are listed in Table 1. The elemental compositions of all ions discussed in this paper were calculated from high resolution mass

TABLE 1. PARTIAL* MASS SPECTRA OF SELECTED COMPOUNDS

Compound	*m/e* (Intensity)
Sulfolane	27(17), 28(50), 29(10), 41(100), 55(68), 56(82), 120(35)
2-Sulfolene	27(20), 28(33), 39(54), 41(17), 53(43), 54(25), 61(11), 62(10), 64(16), 69(10), 70(13), 89(100), 118(37)
3-Methyl-2-sulfolene	27(17), 28(18), 29(10), 39(50), 41(41), 42(12), 43(32), 55(33), 57(15), 64(15), 67(45), 68(18), 84(13), 89(10), 103(100), 132(46)
3-Aminosulfolane	28(10), 42(20), 43(100), 56(29)
3-Hydroxysulfolane	27(12), 28(12), 29(11), 43(13), 44(100), 53(10), 57(10), 64(10), 89(17)
3-Methoxysulfolane	58(100), 71(24), 120(14)
3-Ethoxysulfolane	29(11), 43(14), 44(53), 55(26), 57(13), 72(100), 85(13), 119(10)
3-Bromosulfolane	55(100), 119(13)
3-Acetoxysulfolane	43(100), 53(13)
3,4-Epoxysulfolane	41(23), 42(100), 43(54), 44(35), 48(17), 53(18), 54(27), 64(35), 70(30)
trans-3,4-Dihydroxysulfolane	31(15), 43(33), 44(100), 45(33), 58(22)
trans-3-Amino-4-hydroxysulfolane	28(12), 41(12), 42(30), 43(100), 54(10), 64(10), 69(35)
3-Hydroxy-4-methoxysulfolane	43(15), 58(100)
trans-3-Chloro-4-hydroxysulfolane	27(10), 43(19), 44(100)
trans-2-Chloro-3-hydroxysulfolane	27(20), 28(11), 41(11), 42(10), 43(11), 45(14), 55(25), 57(53), 78(100), 80(32), 114(24), 152(12)
trans-3-Bromo-4-hydroxysulfolane	27(12), 43(24), 44(100), 71(10)
trans-3,4-Dibromosulfolane	39(15), 41(19), 51(14), 53(100), 54(22), 64(11), 80(15), 82(15), 106(10), 108(10), 118(10), 133(81), 135(83)
trans-3,4-Dichlorosulfolane	27(22), 28(42), 39(11), 41(13), 51(10), 53(30), 62(100), 64(34), 75(29), 77(10), 88(15), 89(13)
trans-2,3-Dichlorosulfolane	27(25), 28(10), 39(16), 41(30), 50(14), 51(10), 53(90), 54(10), 55(10), 62(60), 64(20), 75(46), 77(16), 88(28), 89(70), 90(13), 91(16), 96(100), 98(63), 100(10), 123(18), 124(10), 125(12), 152(10)

* Only peaks with intensities greater than or equal to 10% of the base peak are listed.

spectral data or from the distribution of isotope peaks. Important deuterium shifts are depicted in Tables 2–4 while the abundance of selected ions expressed as per cent of Σ_{27} produced by the different compounds is shown in Tables 5–6.

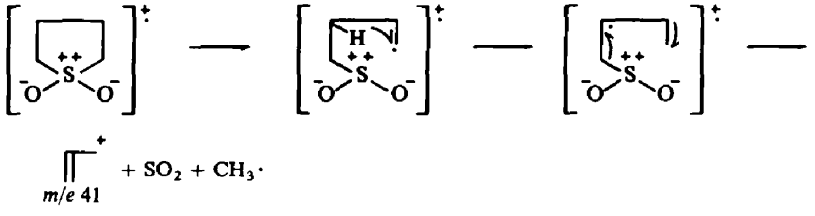
Sulfolane. The major peaks in the mass spectrum of sulfolane **1** appear at *m/e* 120 (molecular ion), *m/e* 56 (M-SO_2), *m/e* 55 (M-HSO_2), *m/e* 41 (M-CH_3SO_2), *m/e* 29 (C_2H_5), *m/e* 28 (C_2H_4), and *m/e* 27 (C_2H_3). All other peaks have intensities which are less than 10% of the base peak.

The hydrocarbon ion at *m/e* 56 represents 12·2% of Σ_{27} and is formed by the elimination of SO_2 from the molecule. Since the molecular ion of SO_2 (*m/e* 64) represents only 1·0% of Σ_{27}, cleavage of the C—S bonds of sulfolane with charge retention on the hydrocarbon fragment is a very favorable process. The result is consistent with the

low ionization potential of hydrocarbons, such as the butenes (9·24–10·8 ev)[8] relative to that of SO_2 (12·05–13·4 ev)[9] and indicates that the sulfone functional group is a poor fragmentation directing group.

The ion at *m/e* 55 is also a hydrocarbon ion; the H atom ejected along with SO_2 originates from both C-2, C-5 and C-3, C-4 since the peak at *m/e* 55 shifts to *m/e* 59, 77% of the time and to *m/e* 58, 23% of the time in the spectrum of sulfolane $-2,2,5,5\text{-}d_4$ **2**. The primary deuterium isotope effect has been found by Djerassi *et al.* to vary from 0·50 to 0·98[10] when defined as "atoms of deuterium per atom of hydrogen transferred for the hypothetical case in which equal numbers of deuterium and hydrogen are available for transfer",[11] If we assume the isotope effect in our system falls in the same range observed by Djerassi, elimination of an H atom from C-2 and C-5 in **1** would occur 23 to 37% of the time; a larger effect would suggest a still higher frequency of elimination of an H atom from C-2 and C-5 in the nondeuterated compound and hence it is apparent that the elimination does not represent a very specific process.

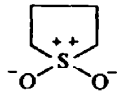
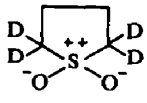
The formation of the hydrocarbon ion at *m/e* 41 also appears to occur by a non-specific process. On the basis of energetic considerations,[12] we would expect the elimination to occur by the loss of a Me radical and a neutral SO_2 molecule, perhaps to some extent as shown in Eq. 1.



$$\underset{m/e\ 41}{\text{[C}_3\text{H}_5\text{]}^+} + SO_2 + CH_3\cdot \qquad (1)$$

The mass spectrum of **2** suggests that C-2 and C-5 are ejected preferentially, as this mechanism requires, since *m/e* 41 shifts to *m/e* 43 49% of the time. However, the peak also shifts to *m/e* 42 8% of the time, *m/e* 44 37% of the time, and to *m/e* 45 6% of the time. Hence, considerable scrambling of H atoms occurs before loss of C-2

TABLE 2. PRINCIPAL MASS SPECTRAL PEAKS OF SULFOLANE AND DEUTERATED ANALOG

Compound	Isotopic purity, % C_4H_8	*m/e* (% Shift)						
		C_4H_8	C_4H_7	C_3H_5	C_2H_5	C_2H_4	C_2H_3	C_2H_2
		56	55	41	29*	28*	27*	26*
	7 d_3 93 d_4	60(q)	59(71) 58(23)	45(6) 44(37) 43(49) 42(8)	32(61) 31(39)	31(6) 30(77) 29(16) 28(1)	29(56) 28(37) 27(7)	28(28) 27(48) 26(24)

* The peak shifts were not corrected for the presence of 7% d_3, but represent directly measured values.

TABLE 3. PRINCIPAL MASS SPECTRAL PEAKS OF 2-SULFOLENE AND DEUTERATED ANALOG

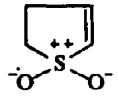
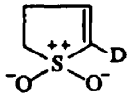
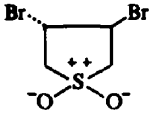
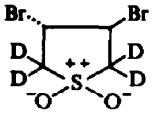
Compound	Isotopic purity, %	m/e (% Shift)				
		C_4H_5SO	C_3H_6O	C_3H_5O	C_4H_6	C_4H_5
		89	70	69	54	53
	84 d_1 16 d_0	89(q)	70(q)	70(50) 69(50)	55(q)	54(80) 53(20)

TABLE 4. PRINCIPAL MASS SPECTRAL PEAKS OF trans-3,4-DIBROMOSULFOLANE AND DEUTERATED ANALOG

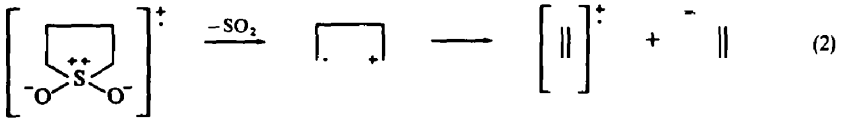
Compound	Isotopic purity, %	m/e (% Shift)				
		$C_4H_6SO_2Br$	C_4H_6Br	C_2H_2Br	C_4H_6	C_4H_5
		197	133	106	54	53
	98 d_4 2 d_3	201(q)	137(q)	108(q)	58(q)	57(38) 56(62)

and C-5 or scrambling occurs along with loss of C-3 and C-4 as well. This result suggests that to some extent SO_2 may be eliminated before the Me radical since hydrocarbons are known to undergo extensive rearrangements on electron impact.[13]

We examined in some detail the hydrocarbon ions at *m/e* 26 to *m/e*32 produced from **1** and **2**. With the resolution of the mass spectrometer set at 19,300, we were able to detect and to estimate the abundance of ions which differ in mass by only 0·00155 mass units (i.e., the mass difference of the D-H_2 doublet). Our results appear in Table 2.

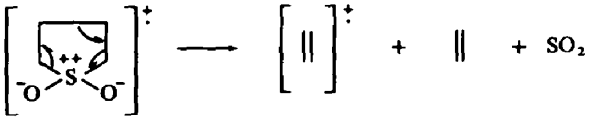
The peak at *m/e* 28 is the most interesting peak produced by **1**. It represents a singly charged ion since the corresponding carbon-13 isotope ion appears at *m/e* 29 (Table 1) and no ions appear at non-integral values between *m/e* 28 and *m/e* 29.

The peak shifts to *m/e* 30 77% of the time in the spectrum of **2** (the shift occurs 83% of the time if a correction for the isotopic impurity of **2** is made); consequently, the ion must be created by a rather specific cyclic decomposition fragmentation which may be represented by Mechanism A or Mechanism B.



(2)

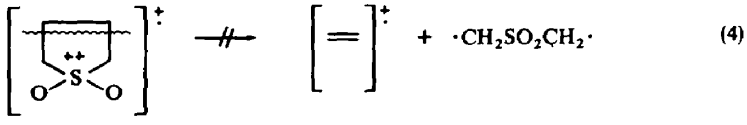
Mechanism A (Stepwise fragmentation)



(3)

Mechanism B (Concerted fragmentation)

We could not detect metastable peaks in support of either mechanism with our instrument, but we favor Mechanism B in view of the small degree of deuterium scrambling which occurs.[13] Since very few of the ions at *m/e* 28 produced by **2** contain no deuterium, the mechanism depicted by Eq. 4 does not occur to any significant extent.



(4)

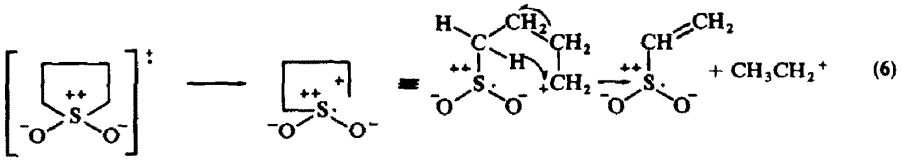
In addition, the absence of ions containing four atoms of deuterium suggests that recombination of the molecule after ejection of SO_2 and subsequent fragmentation does not occur.

(5)

The driving force for the fragmentation is probably the production of two small, neutral molecules and the molecular ion of ethylene.[14] Other less specific mechanisms are also operative to some extent, since *m/e* 28 shifts to *m/e* 29 and *m/e* 31 part of the time, but the dominant reaction seems to be simple cleavage of the molecule with retention of C-2 and C-3 by the positive ion.

The peak at *m/e* 29 shifts to *m/e* 32 61% of the time and to *m/e* 31 39% of the time. This observation is interesting since it means that a D atom is transferred more readily than an H atom in the formation of the product ion in spite of an adverse isotope effect. This may be explained by assuming that cleavage of the weak C—S

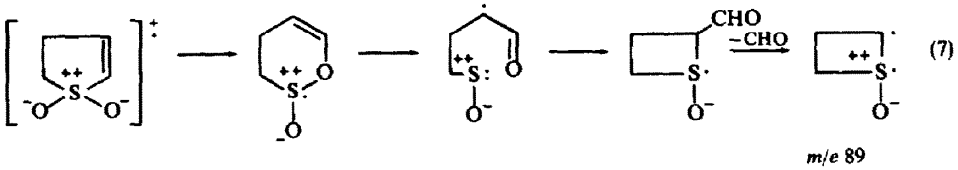
bond is followed by the transfer of the H atom by means of a 5-membered transition state.



(6)

The peaks at *m/e* 26 and 27 shift preferentially to *m/e* 28 and 29, respectively. This indicates that the corresponding ions contain C-2 and C-3, primarily, but in view of the numerous modes of formation possible, further discussion is not warranted.

2-*Sulfolene*. The most abundant ion in the mass spectrum of 2-sulfolene **3** has the composition C_3H_5SO and represents 20·6% of Σ_{27}. It is derived from the molecular ion by the elimination of the elements C, H and O; since the peak at *m/e* 89 remains at *m/e* 89 in the spectrum of 2-deutero-2-sulfolene **4** and the same peak shifts to *m/e* 113 in the spectrum of 3-methyl-2-sulfolene **5**, it appears that the fragmentation is quite specific and proceeds exclusively by the elimination of an O atom, C-2, and its associated H atom as CHO in a concerted process. A plausible mechanism for this fragmentation is given in Eqn 7.



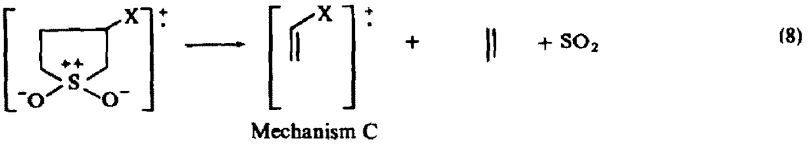
(7)

m/e 89

The behavior of **3** is somewhat different from that of dibenzothiophene-5,5-dioxide studied recently by Meyerson and Field[6] and by Bowie *et al.*[5] They found that the elimination of "CHO" is not the most favored fragmentation process and moreover that the process occurs in two steps, with an H atom and CO being ejected separately. It would be interesting to determine the specificity of the hydrogen elimination in their system.

Additional ions of interest occur at *m/e* 70 and *m/e* 69. High resolution measurements indicate that the ions are generated by the loss of SO and SOH. The loss of hydrogen is not as specific as in the formation of the ion at *m/e* 89 since fifty per cent of *m/e* 69 shifts to *m/e* 70 in the spectrum of **4**. The peaks at *m/e* 54 and *m/e* 53 correspond to the loss of SO_2 and SO_2H; in this case, the loss of hydrogen appears to be almost random since 80% of *m/e* 53 shifts to *m/e* 54.

Monosubstituted sulfolanes. The mass spectra of the monosubstituted sulfolanes we examined exhibited very few peaks. The most abundant ions produced from 3-aminosulfolane **6**, 3-hydroxysulfolane **7**, 3-methoxysulfolane **8**, and 3-ethoxysulfolane **9**, all appear to arise by the same cyclic decomposition process postulated earlier for sulfolane (Mechanism B).

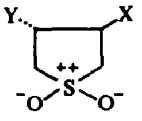


(8)

Mechanism C

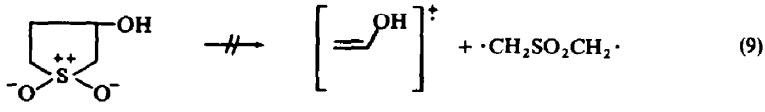
As in the case of sulfolane, the reaction may be stepwise instead of concerted (Eqns 2 and 3), but we prefer the above representation since the abundance of the ($M-SO_2$) ion is small. The composition of the ions (C_2H_3X) were confirmed by high resolution measurements. Small peaks corresponding to the molecular ions of ethylene (*m/e* 28) and SO_2 (*m/e* 64) can be detected in the spectrum of each compound, but most of the charge is carried by the monosubstituted ethylene molecule. The importance of this fragmentation for monosubstituted sulfolanes containing strong fragmentation directing groups can be seen in Table 5 which lists the per cent of Σ_{27} represented by $C_2H_3X^{+\cdot}$, $C_2H_4^{+\cdot}$, and $SO_2^{+\cdot}$.

TABLE 5. PER CENT OF Σ_{27} REPRESENTED BY SELECTED IONS*

Compound Number		Per cent of Σ_{27}		
		$(C_2H_3X)^{+\cdot}$	$(C_2H_3Y)^{+\cdot}$	$(SO_2)^{+\cdot}$
1	X = Y = H	6·1	6·1	1·0
6	X = NH_2, Y = H	61·0	0·6	0·1
7	X = OH, Y = H	34·5	4·2	0·3
8	X = OCH_3, Y = H	54·5	1·6	1·2
9	X = OCH_2CH_3, Y = H	34·8	0·7	0·4
10	X = Br, Y = H	2·2	6·6	2·2
11	X = $OCOCH_3$, Y = H	0·6	1·2	trace
13	X = Y = OH	21·1	21·1	0·8
14	X = OH, Y = NH_2	0·7	37·0	3·7
15	X = OH, Y = OCH_3	3·4	69·0	0·7
16	X = OH, Y = Cl	61·3	1·6	1·2
18	X = OH, Y = Br	46·5	1·0	0·5
19	X = Y = Br	3·5	3·5	3·9
20	X = Y = Cl	17·6	17·6	1·7

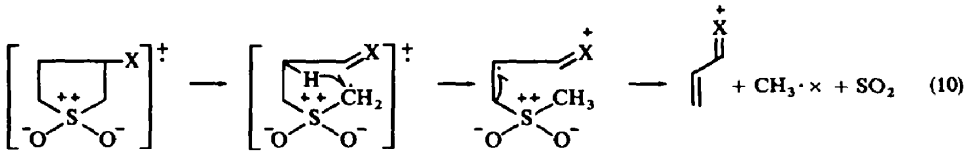
* Isotope corrections applied only to ions containing halogen atoms.

An alternative process may occur producing a monosubstituted ethylene ion incorporating C-3 and C-4 instead of C-2 and C-3, but we believe this process to be of minor importance because less stable neutral products would be produced and because the process is of very little importance in the fragmentation of sulfolane itself or in the fragmentation of 2,3- and 3,4-disubstituted sulfolanes.



(9)

The only other moderately abundant ion produced by all four compounds has the composition C_3H_4X and probably arises to some extent in the same manner as the corresponding ion generated from monosubstituted cyclopentanes.[15]

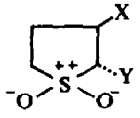


(10)

The small peak at *m/e* 89 in the spectra of **7**, **8** and **9** probably arises by the elimination of HX followed by the rearrangement described earlier for **3**.

The two important ions produced from 3-bromosulfolane **10** arise by the elimination of an atom of Br and an atom of Br plus a molecule of SO_2 This behavior exemplifies the poor fragmentation-directing ability of the bromine and sulfone groups. Only one abundant ion is produced by 3-acetoxysulfolane **11** on electron impact and it is the acetyl fragment formed by cleavage of the C—O bond. Elimination of acetic acid to form a low abundant ion at *m/e* 54 also occurs to a small extent.

TABLE 6. PER CENT OF Σ_{27} REPRESENTED BY SELECTED IONS*

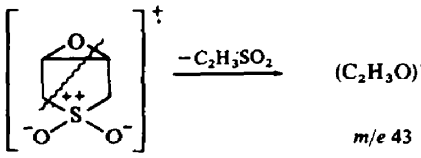
Compound number		Per cent of Σ_{27}		
		$(C_2H_2XY)^+$	$(C_2H_4)^+$	$(SO_2)^+$
17	X = OH, Y = Cl	38·8	2·4	0·9
22	X = Y = Cl	23·5	1·3	2·6

* Isotope corrections applied only to ions containing halogen atoms.

3,4-*Epoxysulfolane.* The most abundant ion produced by 3,4-epoxysulfolane **12** has the composition C_3H_6. This fragment is extremely interesting because it must be generated by the elimination of the elements of SO_2 and CO from the molecular ion with the cleavage of at least five bonds. We postulate that the epoxide rearranges to the corresponding ketone[16] and that the ketone eliminates SO_2 and CO. The abundance of the three ions parallels their relative ionization potentials: C_3H_6, 25·1% Σ_{27} (I.P. = 9·7–10·1 ev),[17] SO_2, 8·8% Σ_{27} (I.P. = 12·05–13·4 ev)[18] and CO, 1·5% Σ_{27} (I.P. = 14·0–14·1 ev).[19]

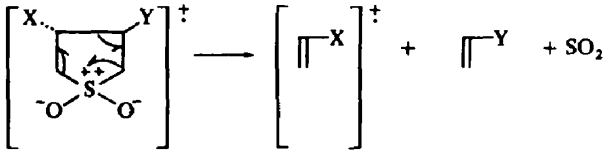
C-13 labeling would be required to determine which C atom is lost in the fragmentation since all of the H atoms present in **12** appear in the product ion (*m/e* 42).

The ion at *m/e* 70 is generated by the elimination of a molecule of SO_2 while the ion at *m/e* 54 is a hydrocarbon ion which arises by the elimination of a molecule of SO_2 and an atom of O. The ejection of an atom of O from epoxides has been observed earlier by Djerassi and Reusch,[20] but the abundance of the ion was low. Evidently, the formation of an ion formally equivalent to the molecular ion of butadiene must provide sufficient driving force to permit an ordinarily unfavorable process to assume substantial importance. The ion at *m/e* 43 has the composition C_2H_3O and could form by simple cleavage of the molecule.



(11)

Disubstituted sulfolanes. The most abundant ion produced from *trans*-3,4-dihydroxysulfolane **13** occurs at *m/e* 44. We postulate that the ion is generated by Mechanism D (Eq. 12) where X = Y = OH.



(12)

Mechanism D

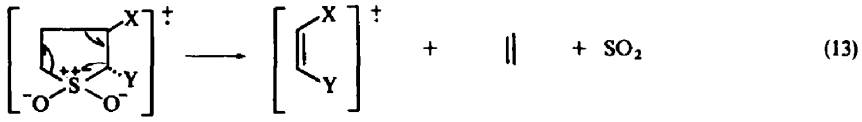
The hydroxyethylene ion (*m/e* 44) represents 42·3% of Σ_{27} while the analogous ion produced from **7** represents 34·5% of Σ_{27}. If the alternative mode of fragmentation suggested for **7** occurs for **13** (Eq. 9), then the ion produced must decompose completely since no peak at *m/e* 60 is present. The ions at *m/e* 45 and *m/e* 58 have the compositions C_2H_5O and C_3H_6O, respectively, and must represent rearrangement products. The ion at *m/e* 43 may arise by loss of an H atom from the *m/e* 44 ion or an OH group from the *m/e* 60 ion.

The inability of the OH group to compete effectively with the NH_2 group in directing fragmentation is illustrated clearly by the mass spectrum of *trans*-3-amino-4-hydroxysulfolane **14**. The aminoethylene ion at *m/e* 43 is the most abundant ion and arises by Mechanism D where X = NH_2 and Y = OH. It represents 61·0% of Σ_{27} while the hydroxyethylene ion represents only 0·6% of Σ_{27}. Analogous behavior has been observed for the fragmentation of 1-amino-2-hydroxysulfolane, which produces nineteen times as much $CH_2NH_2^+$ (*m/e* 30) as CH_2OH^+ (*m/e* 31).[21] The $C_4H_5NH_2$ ion at *m/e* 69 in the spectrum of **14** forms upon the elimination of SO_2 and water from the molecule.

The mass spectrum of 3-hydroxy-4-methoxysulfolane **15** is dominated by a peak at *m/e* 58. It represents the methoxyethylene ion and contributes 69·1% of Σ_{27}. Surprisingly, the OH group does not compete effectively with the OMe group since the hydroxyethylene ion contributes only 3·4% of Σ_{27}. It is unlikely that thermal elimination of water occurs before electron impact since the conditions employed in the mass spectrometer were identical to those used to obtain the spectrum of 3-hydroxysulfolane and very little 2- or 3-sulfolene was generated from this material.

The fragmentation of *trans*-3-chloro-4-hydroxysulfolane **16** is directed by the OH group. The most intense peak in the spectrum occurs at *m/e* 44 and represents the ion $C_2H_3OH^{+\cdot}$, which is generated by Mechanism D where X = OH and Y = Cl. This ion represents 61·3% of Σ_{27}, while the ion at *m/e* 62 ($C_2H_3Cl^{+\cdot}$) represents only 1·2% of Σ_{27}.

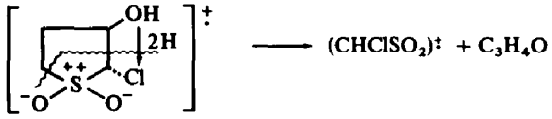
The mass spectrum of the isomeric compound *trans*-2-chloro-3-hydroxysulfolane **17** is very informative. The most abundant ion occurs at *m/e* 78 and has the composition C_2H_2ClOH and is probably generated as shown in Eq. 13, where X = OH, Y = Cl.



(13)

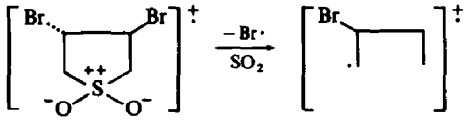
Mechanism E

Hence, the absence of this type of ion in the spectrum of 3,4-disubstituted sulfolane is not due to its inherent instability but to its unfavorable mechanism of formation. Since highly substituted C—C single bonds cleave more readily than less substituted ones, cleavage of the C-2 and C-3 bond would be expected to be more favorable in **17** than in the compounds discussed up to this point and an abundant ion apparently resulting in part from such a cleavage does appear at *m/e* 114.



The mass spectrum of *trans*-3-bromo-4-hydroxysulfolane **18** is similar to that of **16**. The primary difference is the appearance of ions representing bromine and hydrogen bromide in the *m/e* 79 to 82 region; a weak ion at *m/e* 106 represents the product formed by Mechanism D, where X = Y = Br, but it contributes only 0·5% Σ_{27}.

The mass spectrum of *trans*-3,4-dibromosulfolane **19** exhibits a peak at *m/e* 133 which represents an ion with the composition C_4H_6Br and which shifts to *m/e* 137 in the spectrum of *trans*-3,4-dibromosulfolane-2,2,5,5-d_4 **20**. It arises by the elimination of an atom of Br and a molecule of SO_2 from the molecular ion.

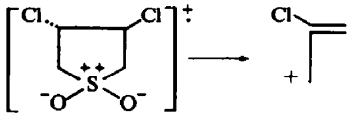


(14)

Concurrent or subsequent loss of a molecule of HBr produces a peak at *m/e* 53, which shifts to *m/e* 56 62% of the time and to *m/e* 57 38% of the time in the spectrum of **20**. This means that the elimination of an H atom from the C-2 and C-5 positions of **19** must occur preferentially. The peak at *m/e* 106 represents the product formed by Mechanism D, since it has the composition C_2H_2Br and shifts to *m/e* 108 in the spectrum of **20**. Its low abundance testifies to the weak fragmentation-directing ability of the bromine functional group.

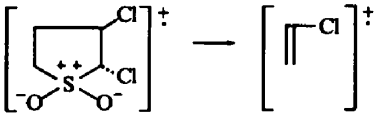
In contrast to the behavior of **19**, *trans*-3,4-dichlorosulfolane **21** does fragment primarily through the operation of Mechanism D, where X = Y = Cl, since the

most abundant ion occurs at *m/e* 62 and has the composition $C_2H_2Cl_2$. The ion at *m/e* 53 results upon the elimination of Cl, HCl, and SO_2 from the molecule while the ion at *m/e* 64 represents the molecular ion of SO_2. It is more difficult to explain the formation of the ion at *m/e* 75. It has the composition C_3H_4Cl and can be rationalized in the following manner, although its presence is unexpected.



$$+ SO_2 + HCl + CH_3 \qquad (15)$$

The mass spectrum of *trans*-2,3-dichlorosulfolane **22** is more complex than that of **21** just as the mass spectrum of **17** is more complex than that of **16**. The most abundant ion (*m/e* 96) arises from the operation of Mechanism E, where X = Y = Cl. The abundant ion at *m/e* 62 probably is formed as shown in Eq. 16.



$$+ SO_2 + \cdot CH_2SO_2CHCl\cdot \qquad (16)$$

This observation is surprising in view of the absence of an analogous ion in the spectrum of **17**.

EXPERIMENTAL

All mass spectra were recorded using a Consolidated Electrodynamics Corporation 21–110 high resolution mass spectrometer at 70 ev. Samples were introduced through a heated inlet system at 200° into the ion source which also was maintained at 200°. All of the compounds except **2**, **4**, **15** and **20** were obtained from commercial sources or were prepared by techniques described in the literature and gave satisfactory elemental analyses, mol wts, m.ps or b.ps and NMR spectra.

3-*Hydroxy*-4-*methoxysulfolane* **15**. 3,4-Epoxysulfolane was treated with a threefold excess of NaOMe in MeOH at room temp for 2 days. The mixture was neutralized, filtered and concentrated. The concentrate was extracted with $CHCl_3$, dried, filtered and fractionally distilled. A fraction, b.p. 144–147° (10^{-3}mm) was collected. It solifidied on standing and was recrystallized from EtOH to give the product, m.p. 98·6–99·5°. (Found: C, 36·2; H, 6·0; MW, 158. Calc. for $C_4H_{10}SO_4$: C, 36·14; H, 6·06%; MW, 166).

Sulfolane-2,2,5,5-d_4 **2**. 3-Sulfolene was dissolved in a soln of D_2O, THF and K_2CO_3 and the homogeneous soln was allowed to stand at room temp for 2 days. The solvent was removed and the process was repeated. The residue was hydrogenated using triphenylphosphinerhodium chloride[22] and the product distilled, b.p. 83° (0·5 mm). The mass spectrum indicated the compound contained 93% d_4 and 7% d_3; the NMR spectrum indicated that all of the deuterium was at C-2 and C-5.

2-*Sulfolene*-2-d **4***. 2-Sulfolene was exchanged with D_2O using a KOD catalyst. After purification, the compound exhibited a m.p. of 49·5–50·5° (2-sulfolene, m.p. 49·5–50·5°). The mass spectrum indicated the compound contained 92% d_1 and 8% d_0; the NMR spectrum[23] and mass spectral fragmentation pattern (see Discussion) indicated all of the deuterium was attached to C-2.

trans-3,4-*Dibromosulfolane*-2,2,5,5-d_4 **20**. A sample of 3-sulfolene-2,2,5,5-d_4 (see above) was treated with Br_2 to give the desired product, m.p. 144·0–144·8° (non-deuterated *trans*-3,4-dibromosulfolane, m.p. 141·0–141·8°). The mass spectrum indicated that the compound contained 98% d_4 and 2% d_3.

* Prepared by H. Dunn.

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