Mass Spectra of Saturated and Unsaturated Derivatives of Thiacyclohexane and 4-Thiacyclohexanone

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In the series 4-thiacyclohexanone, its oxide, and its dioxide, the fragmention patterns indicate that less and less ionization takes place at sulfur upon electron impact as its oxidation state increases. The primary processes in the mass spectral decomposition of 4-thiapyrone 4,4-dioxide appear to be sulfone-sulfinate rearrangement, loss of O_2, and ring-cleavage reactions analogous to those found for 4-thiapyrone. 3-Phenyl-2H-thiapyran 1,1-dioxide decomposes principally to stabilized hydrocarbon ions. The behavior of these and similar compounds is discussed in terms of charge localization upon electron impact.

The concept of charge localization has proven very useful in the interpretation of the mass spectra of heteroatomic organic molecules.[1] It holds, essentially, that ionization can be represented as the net removal of an electron of low ionization potential; these are frequently localized in the nonbonding orbitals associated with the heteroatoms. Recent studies of the ionization potentials of polyheteroatomic molecules support this view.[2] Much attention has been devoted of late to mass spectrometric rearrangements,[3] and many of these may be rationalized by invoking charge localization. We cite as examples the rearrangement of aromatic nitro compounds to nitrite molecular ions;[4] the rearrangement of aromatic sulfoxides[5] and sulfones[5,6] to sulfenate and sulfinate ester molecular ions; and the loss of C_6F_5O from $(C_6F_5)_3PO$,[7] presumably by way of the phosphinite ester, all upon electron impact. Each of these rearrangements involves a reduction in oxidation state of the least electronegative heteroatom (N, S, or P), making that atom a better site for charge localization. A change from higher to lower metal valence states has been shown to be an important determinant of the mass spectral cracking patterns of organometallic compounds.[8]

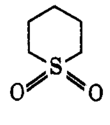
With these concepts in mind we undertook a study of various cyclic sulfones and some related compounds. The fragmentation patterns of aromatic and acyclic aliphatic sulfones and sulfoxides are well documented. The aromatic derivatives tend to lose SO_2[5,6] and SO,[5] respectively, as well as undergoing the rearrangements noted above. There is no evidence of appreciable rearrangement of aliphatic sulfoxides[5] or sulfones[5,9] upon electron impact. Carbon–sulfur bond cleavage seems to be the dominant process, accompanied by hydrogen transfer from the alkyl group to the sulfur oxide portion of the molecule. Most of the ion current arises from hydrocarbon fragments. Alkyl alkanesulfonates behave very similarly to sulfones upon electron impact,[10] and their spectral patterns are compatible with those predicted from charge localization considerations.

Saturated Compounds.—Our reference compound was pentamethylene sulfone (1). Its mass spectrum (Table I)[11] was unexceptional, consisting in the main of peaks due to hydrocarbon ions. Loss of SO_2 and HSO_2 are important processes, with the latter predominating. In fact, the spectrum strongly resembled that of cyclopentane and/or 1-pentene,[12] except for the unusually intense peaks at *m/e* 69, 43, and 28. A small peak at M − 28 indicates that loss of C_2H_4 is a minor process.

TABLE I

PARTIAL MASS SPECTRUM OF PENTAMETHYLENE SULFONE

m/e	Probable composition	%Σ_{26}
134	M	4.3
106	M − C_2H_4	0.70
70	M − SO_2	3.2
69	M − SO_2H	11.
55	$C_4H_7^+$	8.3
43	$C_3H_7^+$	4.1
42	$C_3H_6^+$	15.
41	$C_3H_5^+$	12.
39	$C_3H_3^+$	5.4



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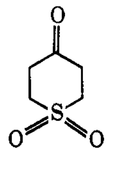

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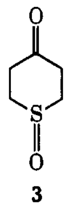

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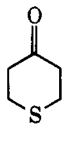

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Introduction of a carbonyl group at C-4 of the sulfone (4-thiacyclohexanone 4,4-dioxide, 2) radically alters the fragmentation pattern (Figure 1). Peaks corresponding to M − SO_2 and M − SO_2H are no longer discernible. The relative abundance of M − 28 rises sharply, reflecting the ease of α cleavage at both the carbonyl and sulfonyl groups. Sulfur dioxide is apparently lost next, giving rise to the base peak at *m/e* 56. A large peak is also found at *m/e* 55, which may arise by expulsion of SO_2H from the M − 28

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(1) (a) F. W. McLafferty, *Chem. Commun.*, 78 (1966); (b) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Molecules," Holden-Day, Inc., San Francisco, Calif., 1967, p 9.

(2) M. Baldwin, A. Kirkien-Konasiewicz, A. G. Loudon, A. Maccoll, and D. Smith, *Chem. Commun.*, 574 (1966); H. J. Svec and G. A. Junk, *J. Amer. Chem. Soc.*, **89**, 790 (1967).

(3) P. Brown and C. Djerassi, *Angew. Chem. Intern. Ed. Engl.*, **6**, 477 (1967).

(4) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964); S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, **88**, 4974 (1966).

(5) J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, **22**, 3515 (1966).

(6) S. Meyerson, H. Drews, and E. K. Fields, *Anal. Chem.*, **36**, 1294 (1964).

(7) H. J. Emeléus and J. M. Miller, *J. Inorg. Nucl. Chem.*, **28**, 662 (1966); J. M. Miller, *J. Chem. Soc.*, *A*, 828 (1967).

(8) J. S. Shannon and J. M. Swann, *Chem. Commun.*, 33 (1965).

(9) R. T. Aplin and K. Baily, *J. Chem. Soc.*, *B*, 513 (1967).

(10) W. E. Truce, R. W. Campbell, and G. D. Manning, *J. Org. Chem.*, **32**, 308 (1967).

(11) Mass spectrum was determined with a Varian M-66 mass spectrometer.

(12) B. J. Millard and D. F. Shaw, *J. Chem. Soc.*, *B*, 664 (1966).

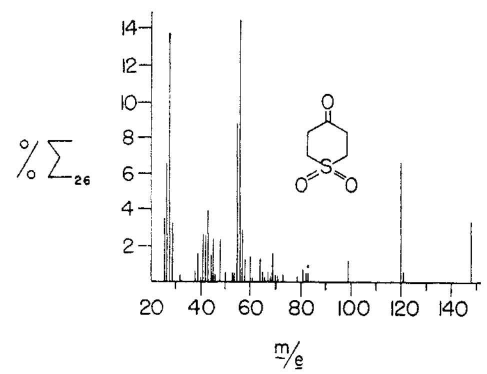
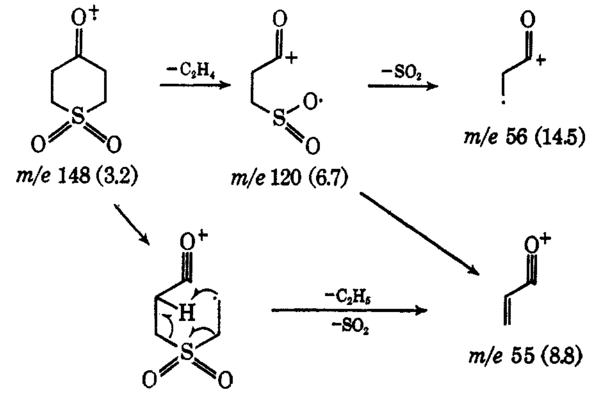


Figure 1.—Mass spectrum of 4-thiacyclohexanone 4,4-dioxide, Varian M-66.

species; alternatively, the molecular ion may lose C_2H_5 and SO_2. The latter pathway is similar to one found for cyclohexanone, in the spectrum of which *m/e* 55 is the base peak.[13]

Scheme I indicates the proposed fragmentation paths for **2**[14] (asterisks denote processes for which metastables were observed). They may be adequately accounted for by assuming initial ionization at the carbonyl group. A small peak at *m/e* 99 gives the only indication that some ionization may take place at the sulfone group. This peak most likely corresponds to M − HSO, which would be in line with our detection of a peak at *m/e* 48 (SO^+). The occurrence of these peaks implies some C–O bond formation.

SCHEME I



4-Thiacyclohexanone 4-oxide (**3**) decomposes somewhat similarly to the corresponding sulfone,[11,15] but significant differences are observed (Figure 2). The M − 28 peak is now the second most intense one, its stability possibly reflecting the lower valence state of sulfur. A greater over-all percentage of the ion current in the sulfoxide spectrum is carried by sulfur-containing ions.

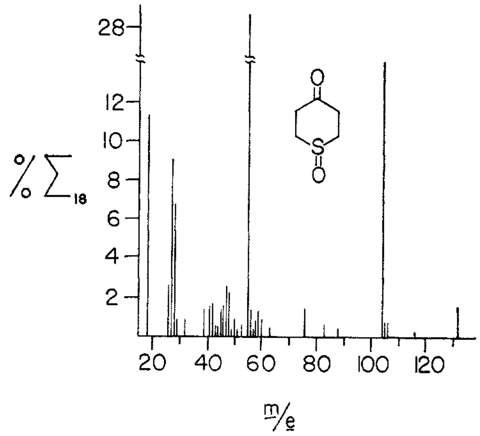
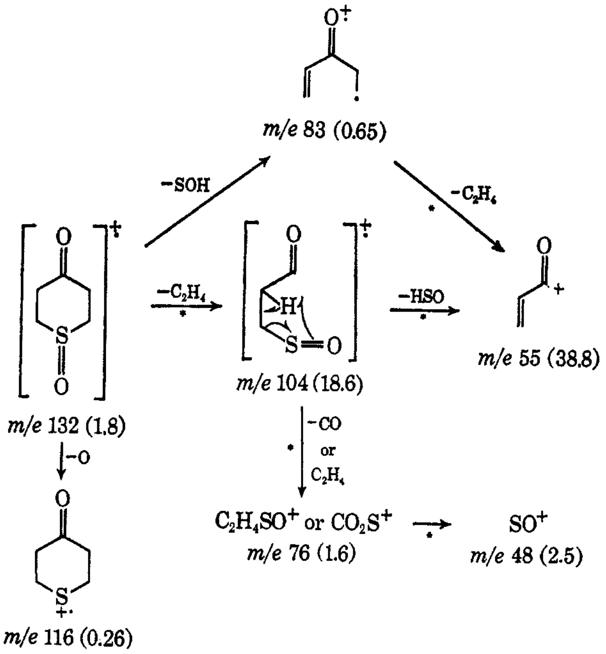


Figure 2.—Mass spectrum of 4-thiacyclohexanone 4-oxide, AEI MS9.

SCHEME II



The base peak of the spectrum is located at *m/e* 55, indicating that the sulfur is lost as HSO (Scheme II); sulfoxide groups are known to abstract hydrogen pyrolytically[16] and under electron impact.[5,16] An alternative route to *m/e* 55 involves loss of HSO first and subsequent loss of C_2H_4; the low abundance of *m/e* 83 ions (M − HSO) might indicate that this path is less favorable.

A very weak peak at *m/e* 116 corresponds to the molecular ion of 4-thiacyclohexanone (**4**). Loss of O and OH radicals from aromatic and aliphatic sulfoxide molecular ions has been observed;[5] the same fragments are also expelled by the molecular ions of aromatic N oxides.[17] Interestingly, loss of O or OH from sulfones upon electron impact has rarely been reported.

The mass spectrum (Table II)[11] of **4** itself might readily have been predicted from the spectra of **2** and **3**. While M − 28 is still prominent, *m/e* 55 is relatively weak and *m/e* 56 barely discernable. Groups of intense peaks are found at *m/e* 45, 46, 58, 59, and 60, a pattern characteristic of the mass spectra of cyclic sulfides.[18] Most of the ion current from fragmentation of **4** is carried by sulfur-containing ions, and it seems

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(13) Reference 1b, p 143.

(14) In our discussion of the mass spectra of **2–4**, it is assumed that M − 28 corresponds mainly to M − C_2H_4, rather than M − CO. Retention of the carbonyl group would most reasonably rationalize the fragmentation patterns, and it is to be expected from the behavior of related compounds.

(15) Mass spectrum was obtained with an AEI MS9 mass spectrometer.

(16) I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc.*, *C*, 302 (1967).

(17) T. A. Bryce and J. R. Maxwell, *Chem. Commun.*, 206 (1965); A. Tatematsu, H. Yoshizumi, E. Hayashi, and H. Nakata, *Tetrahedron Lett.*, 2985 (1967).

(18) Reference 1b, p 284.

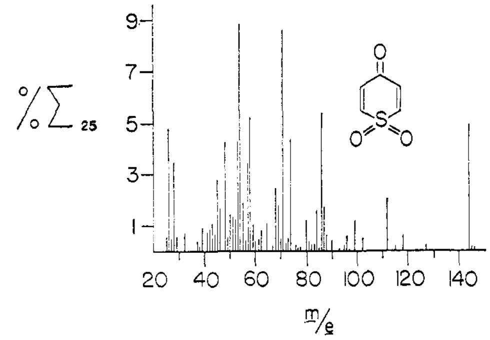


Figure 3.—Mass spectrum of 4-thiapyrone 4,4-dioxide, Varian M-66.

clear from the fragmentation patterns that a larger portion of the ionization takes place at sulfur as one goes from **2** to **3** to **4** (see Schemes I and II, and Table II).

TABLE II

PARTIAL MASS SPECTRUM OF 4-THIACYCLOHEXANONE

m/e	Probable composition	$\%\Sigma_{26}$
116	M	17.1
88	M − C_2H_4	10.5
60	$C_2H_4S^+$	12.4
59	$C_2H_3S^+$	5.8
58	$C_2H_2S^+$	3.3
55	M − C_2H_5S	2.4
47	CH_3S^+	0.92
46	CH_2S^+	12.0
45	CHS^+	9.2

Very recently a report on some cage keto sulfones has appeared in the literature, including their mass spectra.[19] These molecules tend to lose SO_2 and CO readily upon electron impact; as the authors observe, however, there are very strong compressional forces present.

Unsaturated Compounds.—Marked changes occur in the mass spectra of cyclic sulfones upon introduction of unsaturation into the ring. Sulfone–sulfinate rearrangement might be expected, by analogy with the aryl sulfones, and evidence for such rearrangements has been uncovered. The mass spectrum[11,20] of 4-thiapyrone 4,4-dioxide (**5**) exhibits its second most intense peak at *m/e* 71, which can only correspond to the ions $C_3H_3O_2^+$ and/or $C_3H_3S^+$. The former, which seems more likely on mechanistic grounds (*vide infra*), requires a rearrangement involving C–O bond formation. Noteworthy in this regard is a substantial peak corresponding to SO^+.

Loss of acetylene from the molecular ion by a "retro Diels–Alder" process (*m/e* 118) was to be expected on the basis of the mass spectrometric behavior of 4-pyrone[21] (**6**) and 4-thiapyrone[22] (**7**). Most remarkable, however, and perhaps not to be expected by analogy with other systems, is a peak at *m/e* 112, M − 32 (Figure 3),[23] corresponding most probably to $C_5H_4OS^+$ or $C_5H_4O_3^+$. Close examination of an MS12 spectrum revealed that *m/e* 112 consisted of an unresolved doublet, in which the component of smaller mass predominated. This would tend to eliminate $C_5H_4O_3^+$, since the low intensity of *m/e* 110 and 111 precludes any substantial contribution to *m/e* 112 from ions containing heavy isotopes. The molecular ion thus loses O_2,[24] the driving force no doubt being the formation of an aromatic cation having a large fraction of the charge localized on sulfur. We infer that the oxygen atoms are lost as molecular oxygen, since M − 16 or M − 17 peaks are not observed.

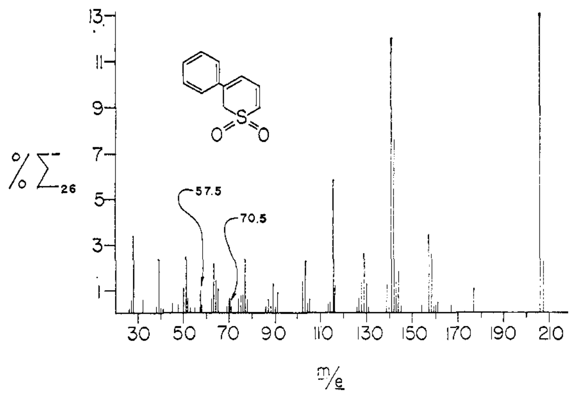
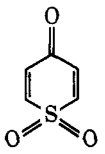


Figure 4.—Mass spectrum of 3-phenyl-2H-thiapyran 1,1-dioxide, AEI MS12.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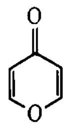
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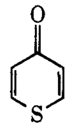
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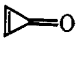
The M − O_2 ion from **5** is the molecular ion of **7**. Decomposition of **7** by a "retro Diels–Alder" cleavage is well established,[22] and the spectrum of **5** contains an intense peak at *m/e* 86 identical with this fragment ion. Furthermore, metastable peaks establish the conversion of *m/e* 86 into 58 and 54, ions which are prominent in the spectrum of **7**.

The low intensity peak at *m/e* 96 may be formulated as the molecular ion of **6**. Loss of CO from this ion, which is a prominent decomposition mode of **6**,[21] is suggested by a metastable at *m/e* 48.2; the fact that other transitions could give rise to a metastable in this region prevents our making this assignment with certainty. The odd-electron ions at *m/e* 112 (**7**), 96 (**6**), and 54 [cyclopropenone (**8**), base peak] are similar in that they may be depicted with the positive charge delocalized in an aromatic ring, and the odd spin localized on an exocyclic oxygen.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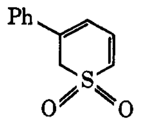
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[19] L. A. Paquette and L. D. Wise, *J. Amer. Chem. Soc.*, **89**, 6659 (1967).

[20] Mass spectrum was obtained with an AEI MS12 mass spectrometer.

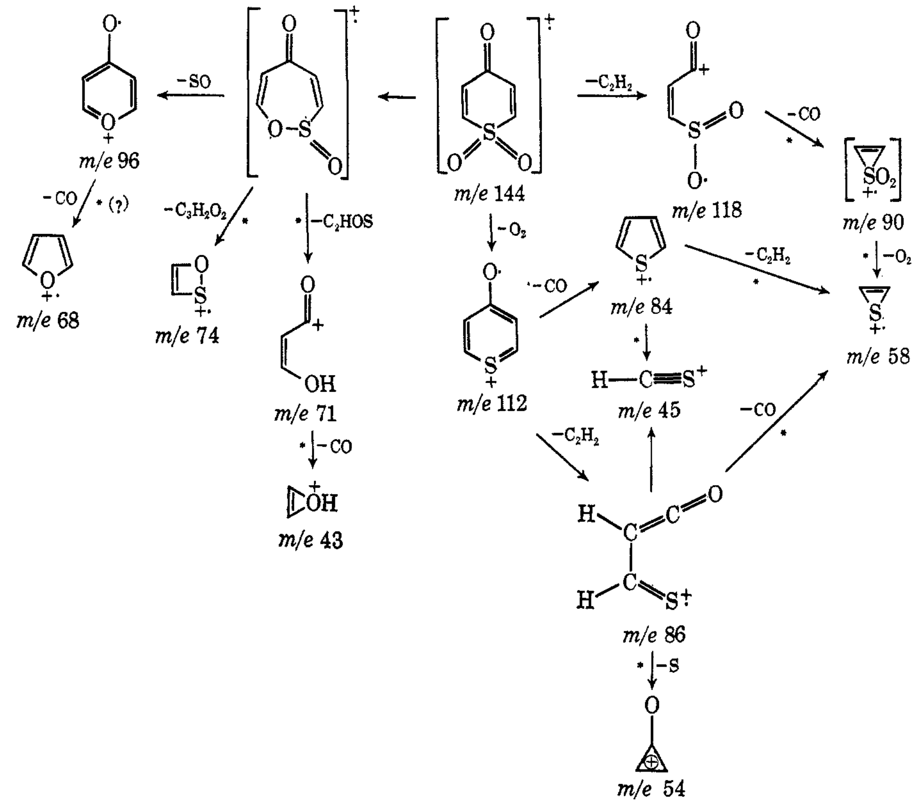
[21] P. Beak, T. H. Kinstle, and G. Carls, *J. Amer. Chem. Soc.*, **86**, 3833 (1964).

[22] J. Bonham, E. McLeister, and P. Beak, *J. Org. Chem.*, **32**, 639 (1967).

[23] This peak, which had an intensity about 23% that of the base peak on the M − 66 spectrum, was very weak on the MS12 spectrum (1% relative intensity). In general, peaks at *m/e* > 54 were much less intense in the MS12 spectra. The dependence of cracking pattern on instrument design has been noted many times before; for an opposite example, see ref 1b, p 8. Further discussion may be found in the Experimental Section.

[24] Dibenzothiophene 5,5-dioxide loses O_2 upon pyrolysis or electron impact [E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 2836 (1966)]; in the mass spectrum, M − O_2 has a relative intensity of 4%. This seems to be the only other reported case of O_2 loss from a sulfone.

SCHEME III



There may be one more instance of O_2 loss in the fragmentation of **5**. A weak metastable at *m/e* 37.4 could correspond to the transition $90^+ \rightarrow 58^+ + 32$ (calculated m* 37.5). Once again, a sulfone would be reduced to a sulfide in the process. Also of interest is the presence of an $M - SO_2$ peak, in view of the absence of an M − CO peak; CO loss from **6** and **7** was very prominent. The highly electronegative sulfone unit may be a better "leaving group" than carbon monoxide. Scheme III depicts the proposed fragmentation scheme for 4-thiapyrone 4,4-dioxide.

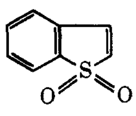
Loss of oxygen from the molecular ion of **5** is presumably favored by the relative stability of the product. We sought to ascertain the effect of a keto group on the various decomposition modes by measuring the mass spectrum of 3-phenyl-2H-thiapyran 1,1-dioxide (**9**).[20] While our own work was in progress we learned that Molenaar and Strating had prepared the parent compound, 2H-thiapyran 1,1-dioxide.[25] Their results and ours are in qualitative agreement as far as the mass spectrometric behavior of these compounds is concerned. We will amplify a bit more on their similarities and differences below.

Loss of HO_2 from the molecular ion of **9** would be necessary to achieve a thiapyrylium structure; a low intensity peak at *m/e* 173 (M − 33) would seem to indicate that this is not a major process. A metastable peak corresponding to the loss of S from the fragment ion has been detected, but that assignment would not be unique. The expected sulfone–sulfinate rearrangement apparently also occurs, as evidenced by the peaks at *m/e* 144 ($M - CH_2SO$), 157 (M − HSO), 158 (M − SO), and 177 (M − CHO). The dominant fragmentation pathways involve loss of SO_2 and SO_2H. We have deduced a fairly detailed decomposition scheme for the molecular ion of **9**, aided by the abundance of metastable peaks in the mass spectrum (Figure 4 and Scheme IV).

Many product ions are depicted as phenyl-substituted stable cyclic cations. The presence of peaks corresponding to the ions at *m/e* 173^{2+}, 167^{2+}, 157^{2+}, 144^{2+}, 142^{2+}, 141^{2+}, 129^{2+}, and 115^{2+} is certainly compatible with these formulations. The peaks arising from 141^{2+} and 115^{2+} are particularly intense, and a metastable peak at *m/e* 46.9 may correspond to the transition $141^{2+} \rightarrow 115^{2+} + 26$ (calculated m* 46.9).

Unsubstituted 2H-thiapyran 1,1-dioxide[25] has the base peak of its mass spectrum at *m/e* 66 ($M - SO_2$), while the molecular ion is the base peak in the spectrum of the phenyl derivative. Peaks corresponding to the unsubstituted thiapyrylium (*m/e* 97) and pyrylium (*m/e* 81) ions are observed, with intensities relative to the base peak of 3.5 and 26%, respectively.

In light of the analyses presented it might be expected that loss of O_2 from the cyclic unsaturated sulfones would show a dependency on ring size; there is some evidence in favor of this interpretation. The mass spectrum of benzo[*b*]thiophen 1,1-dioxide[26] (**10**) contains no $M - O_2$ peak, although a low intensity M − O peak was observed. No indication of O_2 expulsion was obtained either from the mass spectrum of



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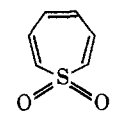

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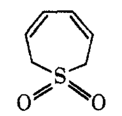

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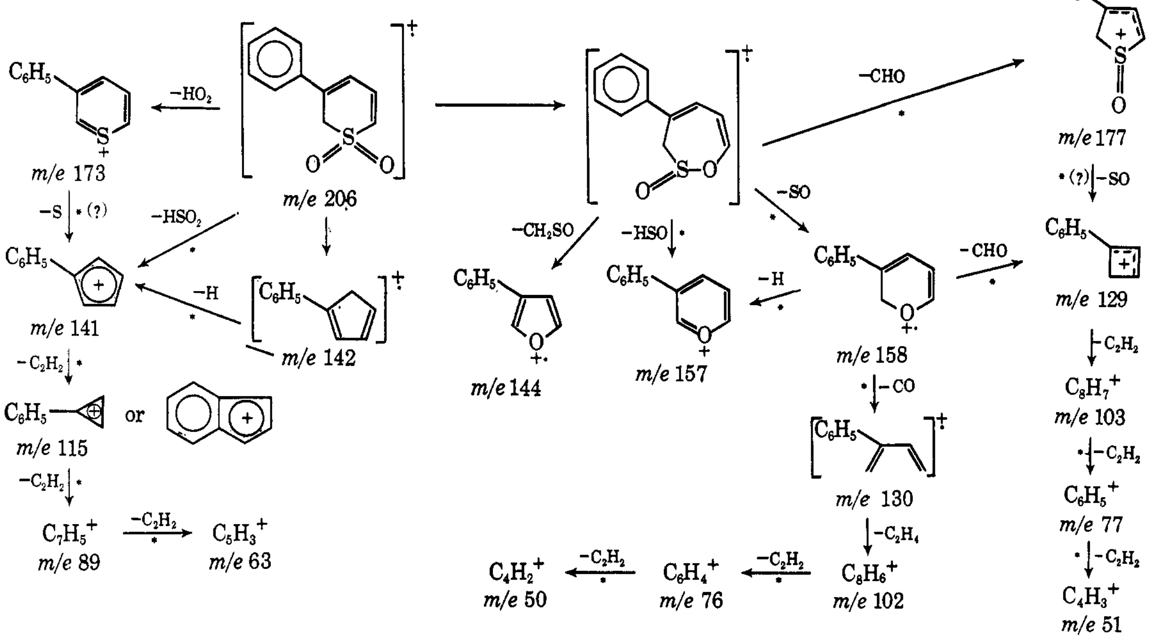
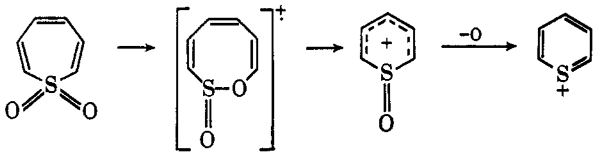
(25) Professor J. Strating, personal communication; E. Molenaar and J. Strating, *Rec. Trav. Chim.*, **86**, 1047 (1967).

(26) Q. N. Porter, *Aust. J. Chem.*, **20**, 103 (1967).

Scheme IV



thiepin 1,1-dioxide (**11**).[27] A characteristic M − CHO peak signaled the occurrence of the sulfone–sulfinate rearrangement. The formation of thiapyrylium ion may be inferred from the presence in the spectrum of a low intensity peak at *m/e* 97. Its formation is easily rationalized on the basis of the preceding discussions. 2,7-Dihydrothiepin 1,1-dioxide (**12**) loses neither O_2 nor HO_2 upon electron impact. In common with **11**, its principal modes of decomposition involve loss of SO_2 and HSO_2.



Experimental Section[28]

Pentamethylene Sulfone (1).—Pentamethylene sulfide was prepared by the reaction of 1,5-dibromopentane with excess sodium sulfide.[29] The corresponding sulfone was obtained by oxidation of the sulfide with 35% hydrogen peroxide in acetic acid. The sulfone was best recrystallized from carbon tetrachloride, mp 98.5–99.5° (lit.[30] mp 97–98°). Its mass spectra were obtained with the probe at 30° and the analyzer at 100°.

4-Thiacyclohexanone (4).—This compound was prepared essentially by the method of Fehnel and Carmack.[31] Condensation of 2 mol of methyl acrylate with 1 mol of hydrogen sulfide in the presence of a catalytic amount of Triton B led to methyl-β-thiodipropionate. The diester underwent cyclic Claisen condensation when treated with 1 mol of sodium hydride (mineral oil suspension, Metal Hydrides, Inc.) and a small quantity of dry methanol in absolute ether. We found this method to be superior to that employing 1 mol of sodium methoxide. Hydrolysis of the keto ester in refluxing 10% sulfuric acid gave 4-thiacyclohexanone, recrystallized from hexane, mp 59–60° (lit.[31] mp 59–60°). Its mass spectrum was determined with the probe at room temperature and the analyzer at 120°.

4-Thiacyclohexanone 4-Oxide (3).—The sulfoxide was prepared by oxidation of **4** with 35% hydrogen peroxide in acetic acid. It was recrystallized from hexane, mp 111–112° (lit.[32] mp 109–110°).

The mass spectrum of **3** seemed to be critically dependent in certain ways on the operating conditions. In the M-66 (probe 45°, analyzer 110°) the sulfoxide yielded no molecular ion; in addition, peaks of low–medium intensity were present at *m/e* 76, 77, and 78, with the latter the most intense. Spectra obtained with the MS9 (ion source 90°) contained a molecular ion of 26% relative intensity and no peaks at *m/e* 77 and 78. The spectrum of this compound obtained at 100° was essentially identical, but a spectrum obtained at 140° was substantially different, with no observable molecular ion. Spectra obtained with both spectrometers had reasonably intense peaks at *m/e* 18.

4-Thiacyclohexanone 4,4-Dioxide (2).—This sulfone was obtained by oxidation of **4** with excess 35% hydrogen peroxide in acetic acid, mp 173–174° (lit.[31] mp 170°). Its mass spectrum was measured with the probe at 75° and the analyzer at 100°.

4-Thiapyrone 4,4-Dioxide (5).—Bromination of **2** with 2 mol of bromine in acetic acid, followed by dehydrobromination of the product with sodium acetate in acetone, led to **5**.[31] The crude product was recrystallized from acetic acid and further purified by sublimation *in vacuo*, mp 176–177.5° (lit.[31] mp 173–174°). Its ir spectrum agreed with one published in the literature.[33]

The M-66 mass spectra were obtained with the probe at 50° and the analyzer at 110°; the MS12 spectra were obtained with a source temperature of 50–60° and a slightly warmer probe.

The mass spectrum of **5** not only varies from instrument to instrument, it is also dependent on the length of time that the sample spends in the spectrometer. If a moderate amount of time elapses after sample introduction, before the scan is started, the resultant M-66 spectrum resembles the MS12 spectra. As time increases, *m/e* 26 increases in intensity at the expense of other peaks. The material used for this study was a mixture of freshly prepared compound and original compound, purified together. The likelihood that *m/e* 112 arises from an impurity of 4-thiapyrone in the sample is rendered unlikely because (1) there is no evidence of any **4** in the sample of **2** used to prepare 4-thiapyrone 4,4-dioxide and (2) there are profound changes in

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[27] Dr. W. L. Mock, private communication of data to be published; *J. Amer. Chem. Soc.*, **89**, 1281 (1967).

[28] Melting points are uncorrected. All samples were introduced directly into the ionizing regions of the various mass spectrometers by means of probes, and all spectra were obtained with a nominal ionizing voltage of 70 V. The complete mass spectra will be submitted to the Mass Spectrometry Data Centre, Atomic Weapons Research Establishment, Aldermaston, Berks, England. They are also tabulated in the M.S. thesis of A. A. Kutz, Worcester Polytechnic Institute, 1968.

[29] W. E. Haines, R. V. Helm, G. L. Cook, and J. S. Ball, *J. Phys. Chem.*, **60**, 550 (1956).

[30] L. Bateman, J. I. Cunneen, and J. Ford, *J. Chem. Soc.*, 1539 (1957).

[31] E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **70**, 1813 (1948).

[32] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

[33] D. S. Tarbell and P. Hoffman, *J. Amer. Chem. Soc.*, **76**, 2451 (1954).

the entire spectrum, such as the great variation in intensity of *m/e* 71, which could not possibly be laid to this source.

3-Phenyl-2H-thiapyran 1,1-Dioxide (9).—The preparation of this compound has recently been reported.[34] Mercapotacetone, prepared from chloroacetone, was treated with phenacyl bromide in the presence of triethylamine. The diketo sulfide was oxidized to the corresponding sulfone with acidic potassium permanganate, and the sulfone underwent internal aldol condensation in the presence of acetic acid–sodium acetate.

The cyclic keto sulfone was reduced to an alcohol with sodium borohydride, and the alcohol dehydrated with 85% phosphoric acid to yield the desired product. The latter material was taken up in a small volume of methanol, and approximately twice the volume of water was added. After standing overnight in the refrigerator the mixture deposited clear needles, mp 99–101.5° (lit.[34] mp 99–100°). The mass spectrum of this compound was obtained with an ion source temperature of approximately 100° and a slightly warmer probe.

Registry No.—**1**, 4988-33-4; **2**, 17396-35-9; **3**, 17396-36-0; **4**, 1072-72-6; **5**, 17396-38-2; **9**, 6581-28-8.

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[34] S. Rossi and G. Pagani, *Tetrahedron Lett.*, 2129 (1966).

Addition of Bromotrichloromethane and Carbon Tetrachloride to Dibenzobicyclo[2.2.2]octatriene

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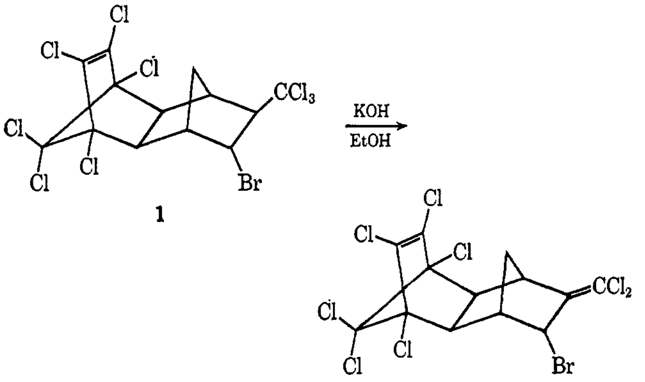
Bromotrichloromethane reacts with dibenzobicyclo[2.2.2]octatriene (**5**) at 105° to give a 1:1 adduct in high yield, whereas the reaction between carbon tetrachloride and **5** at 125–130° (sealed tube) gives a 1:1 adduct in low yield (*ca.* 5%). Both additions occur stereospecifically *trans* and are not accompanied by rearrangement. Upon treatment with base, the 1:1 adduct of bromotrichloromethane and **5** loses both hydrogen chloride (75%) and hydrogen bromide (25%). The 1:1 adduct of **5** and carbon tetrachloride upon treatment with base gives only the exocyclic olefin **8**. Some free-radical and solvolytic reactions of these olefins are discussed.

Additions of carbon tetrahalides to bridged cyclic compounds have been investigated by a number of workers.[1] Bromotrichloromethane reacts readily under free-radical conditions to give 1:1 adducts with norborene,[2,3] bicyclo[2.2.2]octene,[2] norbornadiene,[4,5] aldrin,[6] and hexachloronorbornadiene.[7] The reaction of these compounds with carbon tetrachloride was significantly slower, and in one case[7] the addition reaction failed to take place. Strong evidence has been presented to indicate that these additions to norbornene[3] and aldrin[6] were the result of stereospecific *trans* additions.

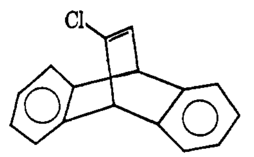
The resulting adducts of bromotrichloromethane with norbornene and bicyclo[2.2.2]octene were inert to 0.7 *N* potassium hydroxide in ethanol at 50° for 6 hr.[2] However, later it was shown that the 1:1 adducts of both carbon tetrachloride and bromotrichloromethane with norbornene lost hydrogen chloride in alcoholic potassium hydroxide to give 2-dichloromethylene-*endo*-3-chloro(bromo)norbornane. Also, the 1:1 adduct (**1**) of bromotrichloromethane and aldrin underwent dehydrohalogenation under similar conditions to give as the only observable product the exocyclic olefin **2**, the result of dehydrochlorination.[6]



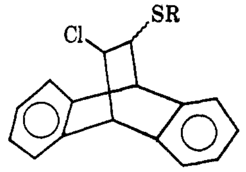
1

2

In the free-radical addition of thiols to 7-chlorodibenzobicyclo[2.2.2]octatriene (**3**) the stereochemistry of the products depended on the mercaptans used. Both *p*-thiocresol[8] and methyl mercaptan[9] gave mixtures of *cis* and *trans* adducts **4**.



3



4

Results and Discussion

The addition of bromotrichloromethane to dibenzobicyclo[2.2.2]octatriene (**5**) went smoothly in neat

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[1] For reviews in this area, see (a) D. I. Davies and S. J. Cristol in "Advances in Free-Radical Chemistry," Vol. 1, G. H. Williams, Ed., Logas Press, London, 1965, p 155; (b) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, Chapter 2.

[2] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

[3] E. Tobler and D. J. Foster, *ibid.*, **29**, 2839 (1964).

[4] D. J. Trecker and J. P. Henry, *J. Amer. Chem. Soc.*, **85**, 3204 (1963).

[5] D. I. Davies, *J. Chem. Soc., C*, 2691 (1967).

[6] D. I. Davies, *ibid.*, 3669 (1960).

[7] J. A. Clasisse, D. I. Davies, and C. K. Alden, *ibid.*, 1498 (1966).

[8] S. J. Cristol and R. P. Arganbright, *J. Amer. Chem. Soc.*, **79**, 6039 (1957).

[9] S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *ibid.*, **87**, 5679 (1965).