Mass Spectra and Pyrolyses of *o*-Phenylene Sulfite and Related Compounds[1a,b]

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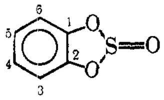
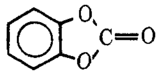
The mass spectra of *o*-phenylene sulfite (**1**) and its 3-methyl (**7**), 4-methyl (**8**), 4-*tert*-butyl (**9**), 3,5-di-*tert*-butyl (**10**), 4,5-dichloro (**11**), and 4-nitro derivatives are discussed. The predominant fragmentation of the molecular ions of **1**, **7**, **8**, and **11** is loss of SO. The molecular ions of **9** and **10** lose $CH_3\cdot$ from the *tert*-butyl substituents; the 4-nitro derivative eliminates $NO\cdot$. The molecular ions of biphenylylene-2,2′ sulfite (**2**) and its 3,5,3′,5′-tetrachloro derivative and of benzophenone-2,2′ sulfite (**12**) and its 4,4′-dimethoxy derivative lose SO and SO_2 competitively. *o*-Phenylene sulfate and biphenylylene-2,2′ sulfate fragment in the mass spectrometer exclusively *via* initial loss of SO_2. The gas-phase pyrolyses of **1**, **7**, **9**, **10**, and **11** give high yields of the dimers of the corresponding cyclopentadienones, which form upon SO loss. Dibenzofuran, from loss of SO_2, and 1-hydroxydibenzofuran, from loss of SO, form upon pyrolysis of **2**. Dibenzofuran, xanthone, and 3,4-dibenzocoumarin are the major products from the pyrolysis of **12**, arising from initial loss of SO_2. These results from pyrolyses are compared to the fragmentations in the mass spectrometer with the emphasis on using mass spectra to predict pyrolysis products.

In preliminary publications, we have reported the mass spectra and the results of pyrolysis of *o*-phenylene sulfite (**1**)[2,3] and of biphenylylene-2,2′ sulfite (**2**).[3] These data have been compared with the mass spectra and pyrolyses of *o*-phenylene carbonate (**3**),[4] tetrachloro-*o*-phenylene carbonate,[5] and related compounds. Similarities and differences have been noted. For example, in the mass spectrum of **1**, minor loss of SO_2 competes with the major loss of SO from the molecular ions, and in the mass spectrum of **3**, minor loss of CO competes with the major loss of CO_2. As can be seen in Scheme I, the fragment ions are the same with regard to elemental composition from each compound. However, the major path in the 70 eV mass spectrum of **1** is the minor path in the 70 eV mass spectrum of **3**, and vice versa. Relatively intense metastable peaks, indicated by asterisks, are found for the major paths, but not for the minor paths.



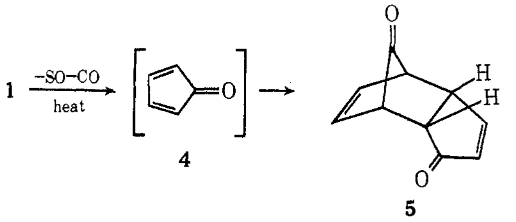
1



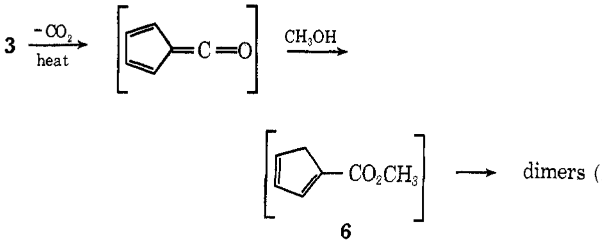
3

The gas-phase pyrolysis of **1**, in a stream of nitrogen, proceeds *via* loss of SO followed by CO, giving cyclopentadienone (**4**), which dimerizes to 1,8-diketo-4,7-methano-3a,4,7,7a-tetrahydroindene (**5**) (eq 1).[2] In contrast, gas-phase pyrolysis of **3**, with methanol in the stream, yields dimers of methyl cyclopentadiene-1-carboxylate (**6**) as the major product (eq 2).[4] Thus, there are similarities between the electron-impact and pyrolytic reactions of **1**; *i.e.*, SO rather than SO_2 is initially lost. The same is true of the corresponding reactions of **3**, *i.e.*, CO_2 rather than CO is initially lost.

The intermediacy of dienone **4** (eq 1) has been proven recently.[6] When **1** was pyrolyzed in a furnace attached to a low-temperature ir cell, **4** was deposited directly on a NaCl plate at −196°, and its ir spectrum was obtained. A ketene was obtained from **3**, but it was not identified.



(1)



(2)

We have been studying the differences between the behavior of cyclic aromatic sulfites and the corresponding carbonates upon electron impact and pyrolysis. In this article we expand our preliminary publications,[2,3] reporting in detail on the mass spectra and pyrolyses of *o*-phenylene sulfite and related compounds.

Mass Spectra.—The mass spectra of a few cyclic aromatic sulfites,[2,3,7] alicyclic sulfites,[8,9] and dialkyl sulfites[10] have been reported. For example, the mass spectra of *meso*- and *dl*-hydrobenzoin cyclic sulfites do not contain molecular ions; the consequence of ioniza-

SCHEME I

$$\begin{tikzcd}
\substack{\text{M}\cdot^{+},\ \text{from } \mathbf{1}\\ 80.0\%} \arrow[r, "-\text{SO}", "*"'] \arrow[dr, "-\text{SO}_2"'] & \substack{\text{C}_6\text{H}_4\text{O}_2\cdot^{+}\\ 35.0\%} \arrow[r, "-\text{CO}", "*"'] & \substack{\text{C}_5\text{H}_4\text{O}\cdot^{+}\\ 100.0\%} \arrow[r, "-\text{CO}", "*"'] & \substack{\text{C}_4\text{H}_4\cdot^{+}\\ 80.0\%} & \\
& \substack{\text{C}_6\text{H}_4\text{O}\cdot^{+}\\ 3.7\%} \arrow[r, "-\text{CO}", "*"'] & \substack{\text{C}_5\text{H}_4\cdot^{+}\\ 15.4\%} & & (3)
\end{tikzcd}$$

$$\begin{tikzcd}
\substack{\text{M}\cdot^{+},\ \text{from } \mathbf{3}\\ 80.0\%} \arrow[r, "-\text{CO}"] \arrow[dr, "-\text{CO}_2", "*"'] & \substack{\text{C}_6\text{H}_4\text{O}_2\cdot^{+}\\ 0.3\%} \arrow[r, "-\text{CO}"] & \substack{\text{C}_5\text{H}_4\text{O}\cdot^{+}\\ 1.8\%} \arrow[r, "-\text{CO}"] & \substack{\text{C}_4\text{H}_4\cdot^{+}\\ 14.3\%} & \\
& \substack{\text{C}_6\text{H}_4\text{O}\cdot^{+}\\ 58.5\%} \arrow[r, "-\text{CO}", "*"'] & \substack{\text{C}_5\text{H}_4\cdot^{+}\\ 100.0\%} & & (4)
\end{tikzcd}$$

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[2] D. C. DeJongh, R. Y. Van Fossen, and C. F. Bourgeois, *Tetrahedron Lett.*, 271 (1967).

[3] D. C. DeJongh, R. Y. Van Fossen, and A. Dekovich, *ibid.*, 5045 (1970).

[4] D. C. DeJongh and D. A. Brent, *J. Org. Chem.*, **35**, 4204 (1970).

[5] D. C. DeJongh, D. A. Brent, and R. Y. Van Fossen, *ibid.*, **36**, 1469 (1971).

[6] O. L. Chapman and C. L. McIntosh, *Chem. Commun.*, 770 (1971).

[7] A. A. Gamble and J. G. Tillett, *Tetrahedron Lett.*, 3625 (1970).

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[9] J. G. Pritchard and P. T. Funke, *J. Heterocycl. Chem.*, **3**, 209 (1966).

[10] A. A. Gamble, J. R. Gilbert, J. G. Tillett, R. E. Coombs, and A. J. Wilkinson, *J. Chem. Soc. B*, 655 (1969).

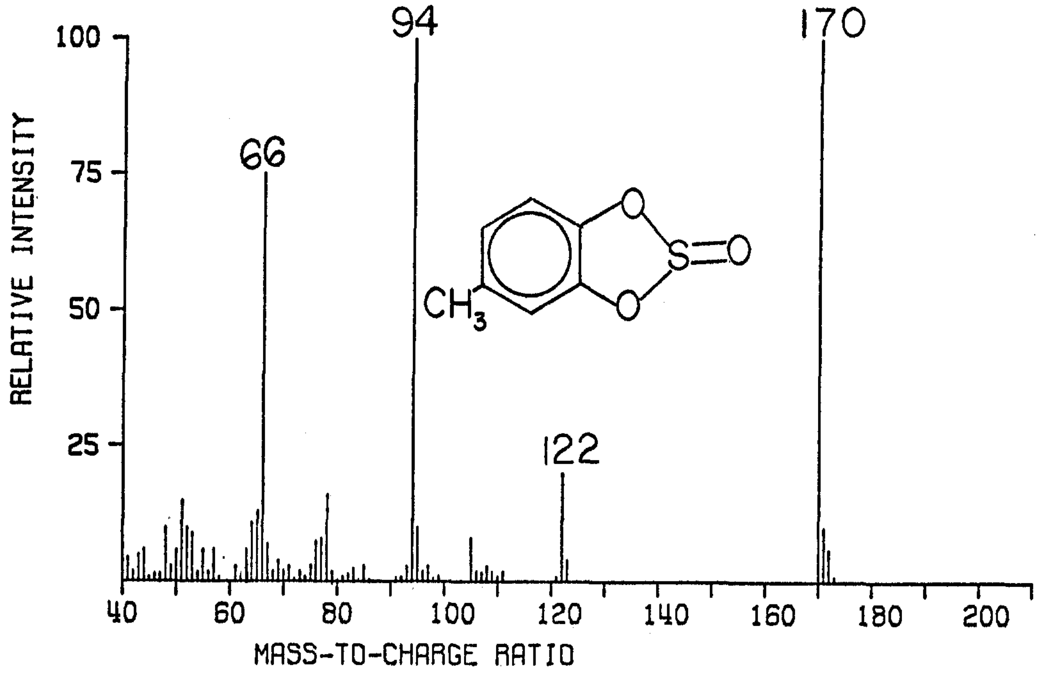


Figure 1.—Mass spectrum (70 eV) of 4-methyl-*o*-phenylene sulfite.

tion is loss of benzaldehyde followed by rearrangement and further fragmentation.[9] On the other hand, the mass spectra of cyclic sulfites of acyclic 1,2-diols show loss of SO_2 from the molecular ions, but this competes with loss of $C_nH_{2n}O$ and HSO_2.[8] In contrast, cyclic aromatic sulfites fragment *via* the major M − SO path illustrated in Scheme I for sulfite **1**.[2,3,7]

The major peaks in the mass spectra of 3-methyl (**7**), 4-methyl (**8**), 4-*tert*-butyl (**9**), 3,5-di-*tert*-butyl (**10**), 4,5-dichloro (**11**), and 4-nitro derivatives of *o*-phenylene sulfite (**1**) are given in the Experimental Section. The mass spectra of **8** and **9** are illustrated in Figures 1 and 2. Mass spectral data from biphenylylene-2,2′ sulfite (**2**) and its 3,5,3′,5′-tetrachloro derivative, from benzophenone-2,2′ sulfite (**12**), and from 4,4′-dimethoxybenzophenone-2,2′ sulfite are also given in the Experimental Section. In addition to data from these sulfites, data from two sulfates, *o*-phenylene sulfate and biphenylylene-2,2′ sulfate, are included.

If the relative intensities at 20 eV of the ions belonging to the M − SO path in the mass spectrum of **1** are added together, and those belonging to the M − SO_2 path are added together, the sum of the former is 14.7 times larger than the sum of the latter. The ratio is 11.3 at 70 eV. This summation of paths, $\Sigma SO/\Sigma SO_2$, can be used to get a rough estimate of the importance of each path. Relatively intense metastable peaks are present for the M − SO path but not for the M − SO_2 path. At 15 eV, the M − SO path remains, but the M − SO_2 path has been eliminated.

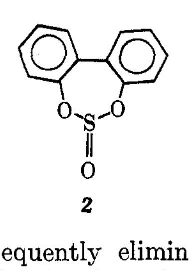
The mass spectra of 3-methyl- and 4-methyl-*o*-phenylene sulfite (**7** and **8**, respectively) are very similar and differ only in relative intensities (see the Experimental Section). In both cases the mode of fragmentation that predominates is the loss of SO. At 70 eV, $\Sigma SO/\Sigma SO_2$ for **7** is 10.8 and for **8** is 6.0. Metastable peaks are found only for the M − SO route. Loss of H· from the methyl substituent to form a benzylic or tropylium ion at M − H is not observed.

In the mass spectra of 4-*tert*-butyl- and 3,5-di-*tert*-butyl-*o*-phenylene sulfite (**9** and **10**, respectively), the molecular ion fragments almost exclusively *via* loss of CH_3·, giving the base peak in the spectra. The resultant ion then decomposes further to a small extent by competitive losses of SO, SO_2, and CO. In the 70 eV mass spectrum of **9**, the peak for the loss of SO is 0.7% and the peak for the loss of SO_2 is 0.8% relative intensity. Below 15 eV, the only fragmentation observed is loss of CH_3· from the molecular ion.

In the 70 eV mass spectrum of 4,5-dichloro-*o*-phenylene sulfite (**11**), the ratio of paths $\Sigma SO/\Sigma SO_2 = 13.7$, with metastable peaks present for the M − SO path only. Fragment ions decompose further by loss of Cl·. The molecular ions of 4-nitro-*o*-phenylene sulfite fragment exclusively by loss of NO· to give an ion which eliminates SO and SO_2 competitively.

Biphenylylene-2,2′ sulfite (**2**) also fragments by competitive losses of SO and SO_2.[3,7] At 70 eV the loss of SO_2 is twice as prominent as the loss of SO ($\Sigma SO/\Sigma SO_2 = 0.5$), whereas at 15 eV they are approaching the same importance.[3] Metastable peaks are found for both paths. The 3,5,3′,5′-tetrachloro derivative gives the same results, except that Cl· is lost from fragment ions.

In the 70 eV mass spectrum of benzophenone-2,2′ sulfite (**12**), the base peak results from loss of SO; this ion subsequently eliminates three molecules of CO. The molecular ion also fragments *via* loss of SO_2 followed by losses of 2 CO. The $\Sigma SO/\Sigma SO_2$ ratio is 1.1 at 70 eV and 3.6 at 14 eV. Both paths show corresponding metastable peaks. The mass spectrum of the 4,4′-dimethoxy derivative is similar, although additional fragmentation of the M − SO and M − SO_2



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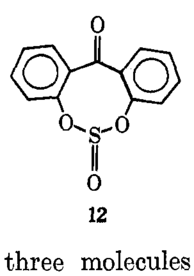

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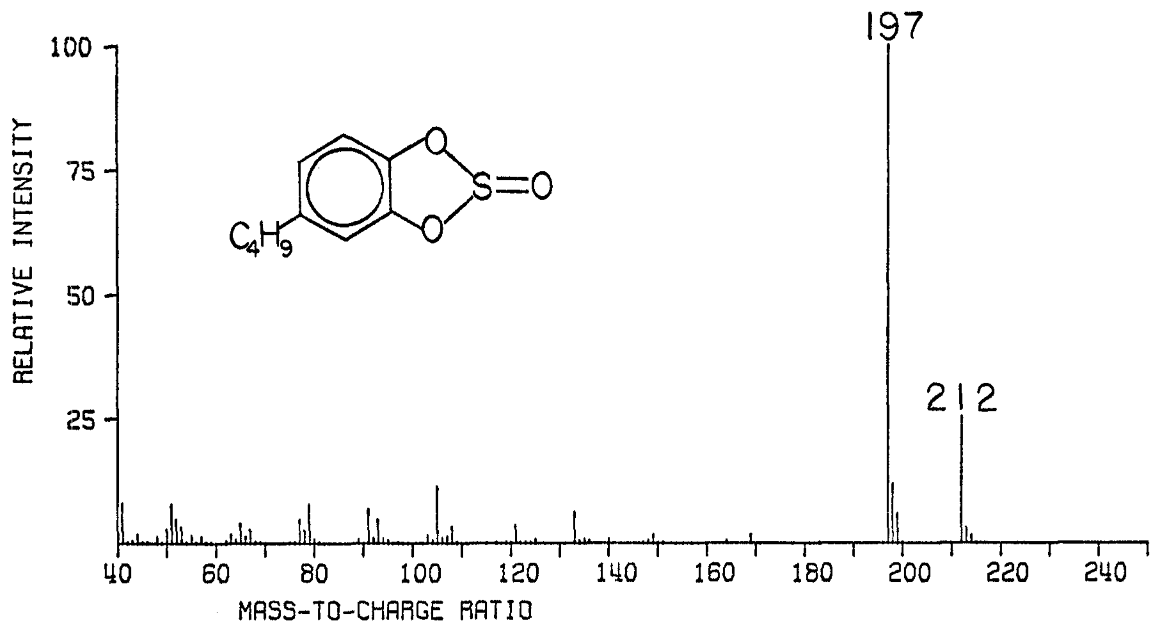
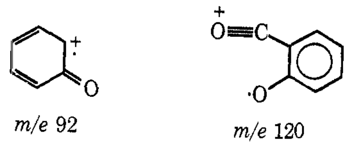


Figure 2.—Mass spectrum (70 eV) of 4-*tert*-butyl-o-phenylene sulfite.

ions involves losses of $CH_3O\cdot$ and $CH_3\cdot + CO$. The $M - SO$ ion from these compounds also fragments to give two ions which formally correspond to *m/e* 92 and 120.



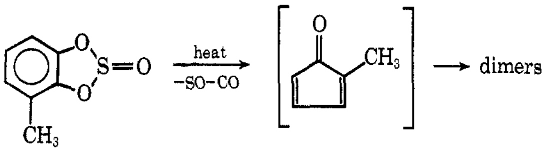
(5)

o-Phenylene sulfate and biphenylylene-2,2′ sulfate fragment exclusively by one pathway, the loss of SO_2. This path corresponds to the loss of SO from **1** and **2**; the loss of SO_3, corresponding to loss of SO_2 from the sulfites, is not observed. From comparison of the mass spectra of the sulfites with those of the corresponding sulfates, it is possible to determine exactly which peaks in the mass spectra of **1** and **2** are associated with the $M - SO$ path.

Pyrolyses of *o*-Phenylene Sulfites.—Parallel reactions induced by heat and by electron impact have attracted much interest in the last few years. Two examples relevant to this work are *o*-sulfobenzoic anhydride[11] and dibenzothiophene 5,5-dioxide.[12] In these cases, mass spectra were used to guide exploratory studies of pyrolytic reactions.

The results of the pyrolysis of *o*-phenylene sulfite (**1**) are summarized in the Experimental Section. The major product is the dimer (**5**) of cyclopentadienone and yields range up to 80%, depending on the conditions. Small amounts of 3a,7a-dihydroindenone result from decarbonylation of **5**; a black, polymeric material is also obtained. The optimum conditions for high yields of **5** are pyrolysis over a nichrome wire heated to 500°, a nitrogen flow rate of 0.1 l./min, and a system pressure of 10–15 mm. Four grams or less of starting material was used with our apparatus.[5] Lower temperatures and higher flow rates result in large amounts of recovered starting material. Higher temperatures and lower flow rates give complex mixtures of products.

Pyrolysis of 3-methyl-*o*-phenylene sulfite (**7**) gave 37.1% of a yellow oil which had ir, uv, and mass spectra characteristic of cyclopentadienone dimers. These data indicate that the oil is a mixture of dimers of 2-methylcyclopentadienone (eq 6). Likewise, the pyrolysis of 4-*tert*-butyl-*o*-phenylene sulfite (**9**) gave 39.6% of the dimers of 3-*tert*-butylcyclopentadienone (eq 7). Garbisch and Sprecher have reported that 1,8-diketo-3,6-di-*tert*-butyl-4,7-methano-3a,4,7,7a-tetrahydroindene (**13**) is probably the major dimer.[13] A trace amount of 3,6-di-*tert*-butyl-1-indanone (**14**) was also isolated.



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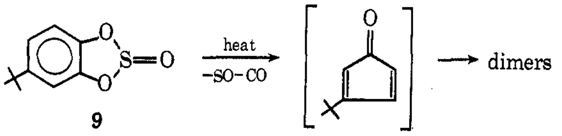

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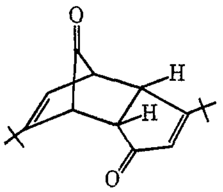

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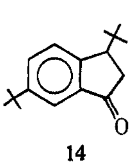
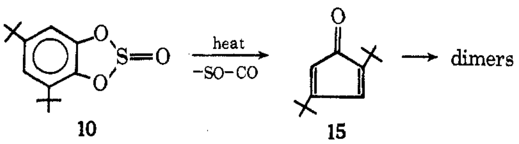


14

A 16.5% yield of 2,4-di-*tert*-butylcyclopentadienone (**15**) and a 63.8% yield of the dimer were obtained from pyrolyses of 3,5-di-*tert*-butyl-*o*-phenylene sulfite (**10**) (eq 8). Of the dimers of **15** prepared by another route,



10 15 (8)

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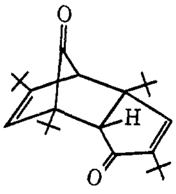
[11] S. Meyerson and E. K. Fields, *Chem. Commun.*, 275 (1966).

[12] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 2836 (1966).

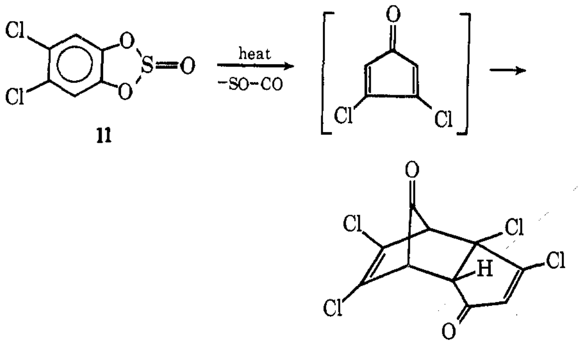
[13] E. W. Garbisch, Jr., and R. F. Sprecher, *J. Amer. Chem. Soc.*, **91**, 6785 (1969).

Garbisch and Sprecher chose **16** as the most likely structure.[13]



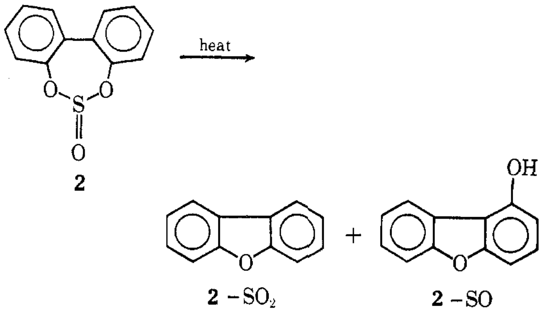
16

The pyrolysis of 4,5-dichloro-*o*-phenylene sulfite (**11**) gave a 14.7% yield of the dimer of 3,4-dichlorocyclopentadienone (eq 9).



(9)

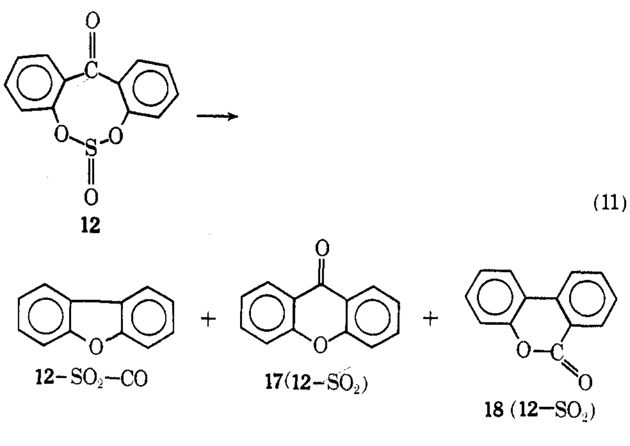
In the Experimental Section, the results of pyrolyses of biphenylylene-2,2′ sulfite (**2**) are reported. In a typical run, 980 mg was pyrolyzed over a nichrome wire at 600°, with a nitrogen flow rate of 0.2 l./min and a system pressure of 5 mm. A 21.9% yield of dibenzofuran and a 52.3% yield of 1-hydroxydibenzofuran were obtained (eq 10). The dibenzofuran results from loss of SO_2 and the 1-hydroxydibenzofuran results from loss of SO. 1-Hydroxydibenzofuran and dibenzofuran do not pyrolyze under these conditions. Pyrolysis of biphenylylene-2,2′ sulfate (**2**, $-OSO_2O-$ instead of $-OSOO-$) under these conditions gave 89% of 1-hydroxydibenzofuran upon loss of SO_2.



(10)

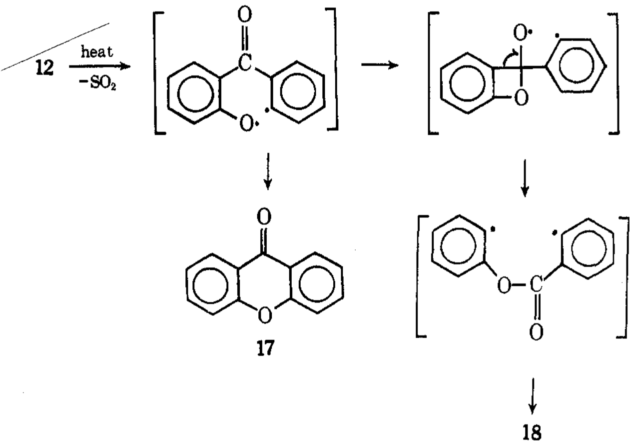
Pyrolysis of benzophenone-2,2′ sulfite (**12**) under various conditions gave a mixture of products, arising mainly from the loss of SO_2. The three major products are dibenzofuran (32.2%), xanthone (**17**, 11.6%), and 3,4-benzocoumarin (**18**, 19%) (eq 11). Pyrolyses of dibenzofuran and of xanthone under the conditions used for pyrolyses of **12** resulted in recovered starting material. Pyrolysis of **12** in an eutectic mixture containing 26.5% of biphenyl and 73.5% of diphenyl ether for 20 hr at 258° gave a 40.3% yield of xanthone (**17**) upon loss of SO_2.

The formation of 3,4-benzocoumarin (**18**) was an interesting and unexpected result. It does not form from **17**. A possible route to **18** is given in Scheme II.



(11)

SCHEME II



Discussion

Gas-phase pyrolyses of *o*-phenylene sulfite (**1**), 3-methyl-*o*-phenylene sulfite (**7**), and 4,5-dichloro-*o*-phenylene sulfite (**11**) give rise to products resulting from loss of SO. For these compounds, the pyrolyses are consistent with the fragmentations in the mass spectrometer, which proceed with initial loss of SO from the molecular ions. On the other hand, the 3-*tert*-butyl- (**9**) and 3,5-di-*tert*-butyl- (**10**) substituted *o*-phenylene sulfites fragment differently under electron-impact and pyrolytic conditions. Electron impact leads to loss of a methyl radical from a *tert*-butyl group, presumably forming a very stable tertiary benzylic cation or a ring-expanded analog. The molecules SO and SO_2 are lost at nearly the same extent from these $M - CH_3\cdot$ ions. Upon pyrolyses of **9** and **10**, products resulting from SO loss are observed, similar to the pyrolytic behavior of **1**, **7**, and **11**.

In the *tert*-butyl cases, the reaction centers differ between the two processes owing to the greater importance of stabilization of charge upon electron impact than upon pyrolysis. We have generally observed that there is less similarity between the two processes as the molecules become increasingly aliphatic.

Striking similarity has also been observed in the case of biphenylylene cyclic sulfites. Electron-impact fragmentation of biphenylylene-2,2′ sulfite leads to competitive losses of SO and SO_2. The importance of the loss of SO increases as the electron voltage is lowered, until the two losses are nearly equal in importance. Products related to competitive SO and SO_2 losses in the pyrolysis were isolated in the ratio 2.4:1. On the other hand, major products from the pyrolysis of benzophenone-2,2′ sulfite are due to the loss of SO_2, whereas SO and SO_2 are lost competitively from the molecular ions with almost the same importance at 70 eV.

On the basis of these data, it seems that the mass spectra of aromatic cyclic sulfites can be used to predict the most probable products of pyrolysis. However, it cannot be used to predict quantitatively the ratio of product formation. As aliphatic substituents are added which can lead to very stable cations, the mass spectra are dominated by cleavage to stable ions, whereas the pyrolysis results resemble those of the unsubstituted analogs.

Experimental Section

Melting points were determined by the open capillary method and are reported uncorrected. Boiling points are also uncorrected. For the ir spectra, 10% solutions in methylene chloride were used in sodium chloride cells. Ultraviolet spectra were recorded in ethanol solutions. The solvents used for obtaining nmr spectra were $CDCl_3$ or CD_3COCD_3; TMS was used as an internal standard. Mass spectra were obtained from an Atlas CH4 (heated inlet, 90–150°) or an AEI MS-902 (direct probe, 100–150°) mass spectrometer.

Pyrolyses were performed on an apparatus described previously.[5] The mixture of pyrolysis products was dissolved in methylene chloride and treated as described below. Silica gel was used for tlc. The gc analyses used a thermal conductivity detector. Analyses were obtained from Midwest Microlabs, Inc., Indianapolis, Ind.

Some of the ions could conceivably arise from pyrolysis in the ion source, followed by ionization. However, metastable ions suggest that this is not happening. Also, the mass spectra are the same from different instruments and at different ion source temperatures.

Except where indicated, the diols used in the syntheses of the sulfites were obtained commercially from Aldrich or from Matheson Coleman and Bell.

***o*-Phenylene Sulfite.**—*o*-Phenylene sulfite and its ring-substituted analogs were prepared by a procedure based on one described by Green.[14] The modified procedure is given below for preparation of *o*-phenylene sulfite. The data from the substituted sulfites are given in Table I. Characteristic ir absorptions were observed at 1200–1220 cm^{-1}.

A solution of 30 g of catechol in 150 ml of dry carbon disulfide and 43 ml of pyridine was cooled to 10° by means of an ice–water bath. Thionyl chloride (20.3 ml) in 80 ml of carbon disulfide was then added. The mixture was stirred at room temperature for 1 hr and then heated at reflux for several hours. An additional 2 ml of thionyl chloride was added after cooling to room temperature, followed by stirring for 1 hr. The mixture was filtered to remove the pyridinium hydrochloride. The solution was concentrated and then distilled under reduced pressure in a nitrogen atmosphere. *o*-Phenylene sulfite had bp 58° (1.5 mm); ir (neat) 1220, 1240, 1460 cm^{-1}; uv (pentane) λ_{max} (absorbance) 273 (0.51), 269 (0.575), 265 nm (sh) (0.450); yield, 72%. *o*-Phenylene sulfite is a strong lachrymator which hydrolyzes to catechol readily. For this reason, it was distilled before use and checked by glpc.

TABLE I

PREPARATION OF THE AROMATIC CYCLIC SULFITES

A. Substituted *o*-Phenylene Sulfites

Compd	Diol, g	Solvent	Yield, %	Bp, °C (mm)
3-Methyl (**7**)	10.0	C_6H_6	77	61 (0.5)
4-Methyl (**8**)	0.6	CS_2	85	82 (3.4)
4-*tert*-Butyl (**9**)	10.0	C_6H_6	84	75 (0.1)
3,5-Di-*tert*-butyl (**10**)	7.6	C_6H_6	78.5	110 (0.5)
4,5-Dichloro (**11**)	1.8	CS_2	31.5	96 (2.0)
4-Nitro	0.5	C_6H_6	10	

B. Biphenylylene-2,2 Sulfite (**2**)

Compd	Diol, g	Solvent	Yield, %	Mp, °C	Calcd, %		Found, %	
					C	H	C	H
2	10.0	C_6H_6	95	74–75[a]	62.07	3.45	61.96	3.31

C. Benzophenone-2,2 Sulfite (**12**)

Compd	Diol, g	Solvent	Yield, %	Mp., °C	Calcd, %		Found, %	
					C	H	C	H
12	10.0	C_6H_6	80	116–117	59.99	3.10	60.07	3.25
4,4′-Dimethoxy	10.0	C_6H_6	70	165–166	56.24	3.78	56.12	3.76

[a] Lit. mp 72.5–74°: P. B. de la Mare, J. G. Tillett, and H. F. van Woerden, *J. Chem. Soc.*, 4888 (1962).

3,5,3′5′-Tetrachlorobiphenylylene-2,2′ Sulfite.—3,5,3′,5′-Tetrachloro-2,2′-biphenol was prepared from 2,2′-biphenol. To a solution of 2.5 g of sodium in 100 ml of absolute ether was added dropwise a solution of 10 g of 2,2′-biphenol in 100 ml of ether. Stirring was maintained, and the temperature was kept at 0°. Then a solution of 10.8 g of SO_2Cl_2 in 10 ml of ether was added dropwise over a period of 1 hr. The reaction mixture was stirred at 0° for an additional hour and then at room temperature for 3 hr. The ether was distilled and 50 ml of ethyl acetate was added to the residue. The ethyl acetate layer was extracted with water, dried, and evaporated. The oily residue was dissolved in hexane. The tetrachlorobiphenol was obtained from an alumina column and recrystallized from hexane: mp 174–175° (lit.[15] mp 178°); yield 57%; blue $FeCl_3$ test; ir (KBr) 3505 cm^{-1}; ir (CH_2Cl_2) 3080, 3030 cm^{-1}; uv (EtOH) λ_{max} 218, 315 (sh), 350 nm (sh); nmr (CD_3COCD_3, TMS) δ 8.3 (2 H, s), 7.25 (4 H, AB quartet); mass spectrum *m/e* 322, 324, 326, 328 (molecular ions with relative intensities characteristic of four chlorines).

The corresponding cyclic sulfite was prepared as described above for *o*-phenylene sulfite: 0.8 g of diol; solvent, C_6H_6; yield 7.2%; mp 220°.

***o*-Phenylene Sulfate.**—The procedure of Denivelle[16] was modified as follows. Catechol (16.5) was dissolved in 25 ml of pyridine in a nitrogen atmosphere and held at 0°. Sulfuryl chloride (12 ml) in 25 ml of petroleum ether (bp 30–60°) was added over a period of 1 hr. Then 5 ml of additional pyridine in 10 ml of petroleum ether was added. The petroleum ether layer was washed with dilute HCl and evaporated. The sulfate was recrystallized from petroleum ether, mp 34–35° (lit.[17] mp 34–35°), yield 4%.

Biphenylylene-2,2′ Sulfate.—To 25 g of 2,2′-biphenol in 75 ml of absolute ether and 13.6 g of triethylamine was added 11 ml of SO_2Cl_2 in 40 ml of absolute ether, dropwise at 0°. Stirring was maintained throughout the addition. The reaction mixture was stirred for 2 hr at room temperature and filtered, and the solvent was evaporated. The sulfate was recrystallized from ethanol: mp 120–121°; yield 30%; ir (CH_2Cl_2) 1410, 1220, 870 cm^{-1}.

Anal. Calcd for $C_{12}H_8O_4S$: C, 58.06; H, 3.23. Found: C, 58.19; H, 3.35.

Mass Spectra.—*o*-Phenylene sulfite (**1**): *m/e* (rel intensity) 156 (80), 108 (35), 92 (4), 80 (100), 64 (15.5), 63 (16), 52 (80), 51 (31), 50 (25), 48 (14), 39 (14.5), and 38 (11.5). Biphenylylene-2,2′ sulfite (**2**): *m/e* (rel intensity) 232 (100), 184 (45), 168 (100), 156 (13), 155 (8.0), 140 (6.5), 139 (26.5), 128 (8), 127 (11.5) 102 (12.5), 84 (16.5), 63 (12), 51 (15.5), and 39 (11). 3-Methyl-*o*-phenylene sulfite (**7**): *m/e* (rel intensity) 170 (58), 122 (6), 106 (4), 105 (12), 94 (100), 78(30), 77 (14), 66 (96), 65 (22), 63 (12.5), 52 (16), 51 (24), 50 (11), 48 (12), 40 (24), 39 (54), and 38 (14). 4-Methyl-*o*-phenylene sulfite (**8**): *m/e* (rel intensity) 170 (100), 122 (20), 106 (2), 105 (8), 94 (100), 78 (16), 77 (8), 66 (75), 65 (13), 64 (11), 52 (10), 51 (15), 48 (10), 40 (17), and 39 (37). 4-*tert*-Butyl-*o*-phenylene sulfite (**9**): *m/e* (rel intensity) 212 (25.5), 197 (100), 169 (2), 149 (2), 133 (6.5), 121 (4), 105 (11.5), 93 (5), 91 (7), 79 (8), 78 (3), 77 (5), 65 (4), 53 (4), 52 (5), 51 (8), 41 (8), and 39 (8.5). 3,5-Di-*tert*-butyl-*o*-phenylene sulfite (**10**): *m/e* (rel intensity) 268 (26), 253 (100), 189 (6.5), 149 (8), 119 (9), 105 (9), 91 (8), 75 (28), and 41 (17). 4,5-Di-

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(15) W. S. Gump, U. S. Patent 2,487,799 (1950); *Chem. Abstr.*, **44**, 9702*b* (1950).

(16) L. Denivelle, *C. R. Acad. Sci.*, **203**, 194 (1936).

(17) E. T. Kaiser, I. R. Katz, and T. F. Wulfers, *J. Amer. Chem. Soc.*, **87**, 3781 (1965).

chloro-*o*-phenylene sulfite (**11**): *m/e* (rel intensity) 224 (100), 176 (14), 148 (91), 132 (7.5), 120 (23), 113 (63), 97 (15), 85 (21), 63 (15), 60 (13.5), 50 (46), 49 (15.5), and 48 (11.5). 4-Nitro-*o*-phenylene sulfite: *m/e* (rel intensity) 201 (100), 171 (3), 123 (2.5), 107 (18), 79 (60), 78 (12), 63 (10), 51 (10), and 50 (17). 3,5,3′,5′-Tetrachlorobiphenylylene-2,2′ sulfite: *m/e* (rel intensity) 368 (53), 320 (22), and 304 (70); the chlorine isotope peak at *m/e* 306 is the base peak. Benzophenone-2,2′ sulfite (**12**): *m/e* (rel intensity) 260 (76), 259 (9.5), 212 (100), 196 (21.5), 184 (18), 168 (50), 140 (9.5), 139 (32), 128 (11), 120 (26), 92 (52), 84 (10), 76 (18), 64 (19), and 63 (28). 4,4′-Dimethoxybenzophenone-2,2′ sulfite: *m/e* (rel intensity) 320 (100), 319 (49), 272 (81), 257 (13.5), 256 (25), 255 (13), 244 (10), 241 (13), 229 (16), 213 (26), 201 (16.5), 185 (12.5), 170 (11), 151 (22), 150 (50), 122 (68), 114 (14.5), 107 (25), 106 (12.5), and 79 (31). *o*-Phenylene sulfate: *m/e* (rel intensity) 172 (63), 108 (8), 80 (85), 79 (10.5), 64 (29), 52 (100), 51 (29), 50 (21), and 48 (16). Biphenylylene-2,2′ sulfate: *m/e* (rel intensity) 248 (100), 184 (38.5), 156 (69), 155 (14), 128 (45), 127 (15), 102 (21), 78 (14), 64 (21), 63 (16), and 51 (25).

Pyrolyses of *o*-Phenylene Sulfite (**1**).—Examples of pyrolyses of **1** under various conditions are given in Table II. The pyrolysate was worked up in one of three ways: preparative tlc with CH_2Cl_2 as solvent; sublimation and recrystallization of the sublimate from hexane; glpc, 10% SE-30 on 60–80 Chromosorb W or 15% Carbowax 20M on 60–80 Chromosorb W, 60–200° at 8°/min, injection port at 170°, detector at 238°. 1,8-Diketo-4,7-methano-3a,4,7,7a-tetrahydroindene (**5**) was obtained: mp 102–102.5° (lit.[18] mp 101–101.5°); ir 1710, 1780 cm^{-1} (lit.[18] 1710, 1780 cm^{-1}); nmr δ 7.4 (1 H, m), 6.3 (3 H, m), 3.45 (2 H, m), 3.2 (1 H, m), and 2.9 (1 H, t).

TABLE II

DATA FROM PYROLYSES OF *o*-PHENYLENE SULFITE (1)

Pyrolysis no.	a	b	c	d	e	f
Amount of **1**, g	3.9	0.74	0.68	1.7	0.83	3.7
Temp, °C	500	550	450	550	450	500
N_2 flow, l./min	0.2	0.1	0.08	0.8	0.06	0.1
Pressure, mm	27	11	10	25	13	16
Time, min	120	180	60	60	230	200
Recovered **1**, g	0.33	0.05	0	1.3	0.28	0
Amount of **5**, g	1.03	0.14	0.11	0	0.20	1.50
Yield of **5**, %[a]	54.5	38.6	30.7	0	69.2	77.1

[a] Based on unrecovered starting material.

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 75.09; H, 5.17.

In pyrolysis e, 88 mg of 1-indanone was isolated. 1-Indanone was identified by comparison of melting point, ir, uv, and mass spectrum with those of an authentic sample.

Pyrolysis of 3-Methyl-*o*-phenylene Sulfite (**7**).—The pyrolysis of 0.64 g of **7** at 540–550° (17 mm) and a N_2 flow rate of 0.6 l./min for 1 hr gave a crude yellow pyrolysate. The pyrolysate was distilled at 0.1 mm and 0.13 g (37.1%) of material was obtained: ir (CH_2Cl_2) 1815, 1700 cm^{-1}; uv (EtOH) λ_{max} 205, 243, 280 nm. These data indicate the product is a mixture of the dimers of 2-methylcyclopentadienone. The mass spectrum contains major peaks at *m/e* 160 (dimer − CO, 60%), 159 (dimer − HCO, 20%), 132 (dimer − 2 CO, 12.5%), and 145 (dimer − CO − CH_3, 100%). Attempts to separate the mixture of dimers were unsuccessful.

Pyrolysis of 4-*tert*-Butyl-*o*-phenylene Sulfite (**9**).—The pyrolysis of 1.16 g of **9** was carried out at 550° (10 mm) and a N_2 flow rate of 0.2 l./min. Crude pyrolysate weighed 0.33 g. The major band from tlc was eluted with benzene and the material in it was recrystallized from hexane. The product was the dimer of 3-*tert*-butylcyclopentadienone: 0.295 g (39.6%); mp 68–70° (lit.[13] mp 70–72°); ir (CH_2Cl_2) 1800, 1710 cm^{-1} (lit.[13] 1790, 1710 cm^{-1}); mass spectrum, *m/e* 244 (dimer − CO).

Another band on tlc contained material which was eluted with methanol and recrystallized from hexane to give 7 mg of product. This product appears to be 3,6-di-*tert*-butyl-1-indanone, formed by loss of CO from the dimer: mp 70–73° (lit.[13] mp 75–77°); ir (CH_2Cl_2) 1710 cm^{-1} (lit.[13] 1705 cm^{-1}); mass spectrum, *m/e* 244 (molecular ion).

Pyrolysis of 3,5-Di-*tert*-butyl-*o*-phenylene Sulfite (**10**).—In a typical run, 1.20 g of **10** was pyrolyzed at 10 mm, 500°, and a N_2 flow rate of 0.7 1/min. A yellow oil (0.94 g) was obtained. Three fractions were collected from an alumina column eluted with benzene. The first fraction contained 0.14 g (16.5%) of 2,4-di-*tert*-butylcyclopentadienone: ir (CH_2Cl_2) 1710 cm^{-1} (lit.[13] 1708 cm^{-1}); mass spectrum, *m/e* 192 (molecular ion). When allowed to stand overnight, this product dimerized: mp 145–150° dec (lit.[13] mp 151–153°); ir (CH_2Cl_2) 1765, 1700 cm^{-1} (lit.[13] 1765, 1700 cm^{-1}); mass spectrum, *m/e* 356 (dimer − CO).

The second fraction contained 0.55 g (63.8%) of a white solid which was purified by sublimation. This product is the dimers of 2,4-di-*tert*-butylcyclopentadienone: mp 148–151° (lit.[13] mp 151–153°); ir (CH_2Cl_2) 1765, 1700 cm^{-1} (lit.[13] 1765, 1700 cm^{-1}); mass spectrum, *m/e* 356 (dimer − CO).

The third fraction was 30 mg of starting material.

Pyrolysis of 4,5-Dichloro-*o*-phenylene Sulfite (**11**).—The pyrolysis of 0.72 g of **11** was carried out at 500° (9 mm) and a N_2 flow rate of 0.6 l./min. A colorless solid, 0.07 g (14.7%), recrystallized from hexane, was obtained: mp 134–136° dec; ir (KBr) 1820, 1725 cm^{-1}; uv (EtOH) 205, 222 nm (sh); mass spectrum *m/e* 232, 234, 236, 238 (dimer − CO − HCl and isotopes for 3 Cl). These data are consistent with the formation of the dimer of 3,4-dichlorocyclopentadienone.

Pyrolysis of Biphenylylene-2,2′ Sulfite (**2**).—The pyrolysis of **2** was carried out under 11 sets of conditions. For example, 0.98 g was pyrolyzed at 600°, a system pressure of 5 mm, and a N_2 flow rate of 0.2 1/min, which took 5 hr. Two fractions were isolated from a silica gel column eluted with benzene. The first fraction, after recrystallization from hexane, contained 21.9% of dibenzofuran, identified by comparison of ir, uv, and mass spectra with those of authentic spectra and by mixture melting point.

The second fraction was recrystallized from hexane. A 52.3% yield of 1-hydroxydibenzofuran was obtained: mp 141–142° (lit.[19] mp 140–140.5°); ir (KBr) 3220, 1440, 1025 cm^{-1}; uv (EtOH) λ_{max} 214, 226, 260, 271, 277, 300 (sh), 310 nm; nmr (CD_3COCD_3) δ 7.0–7.6 (6 H, m), 8.3 (1 H, m), 9.3 (1 H, s); mass spectrum *m/e* 184 (molecular ion). 1-Hydroxydibenzofuran was brominated in acetic acid, mp 180° (lit.[19] mp 178°). Reduction of 1-hydroxydibenzofuran with zinc gave 2,2′-biphenol, identified by comparison with an authentic sample.

Pyrolyses of 0.14 g of 1-hydroxydibenzofuran at 600° (8 mm) and a N_2 flow rate of 0.2 l./min resulted in 97.1% recovery of starting material; no dibenzofuran was isolated. Pyrolysis of 0.90 g of dibenzofuran under the same conditions gave a 98% yield of recovered starting material.

Pyrolysis of Biphenylylene-2,2′ Sulfate.—At 600° (8 mm) and a N_2 flow rate of 0.2 l./min, 0.62 g of biphenylylene-2,2′ sulfate was pyrolyzed. 1-Hydroxydibenzofuran was isolated in 89% yield. Starting material (7.7%) was also recovered.

Pyrolysis of Benzophenone-2,2′ Sulfite (**12**).—The pyrolysis of **12** was run under five sets of conditions. When 0.56 g was pyrolyzed at 600° (8 mm) and 0.2 l./min N_2 flow rate, crude pyrolysate was obtained, which was eluted through a column of silica gel with hexane–benzene mixtures (10:1, progressing to 1:1 to 0:1), giving three fractions. The first fraction (32.3% yield) was identified as dibenzofuran. The second fraction (11.6% yield) was identical with an authentic sample of 9-xanthenone: mp 174–175° (lit.[20] mp 174°); mixture melting point undepressed. The third fraction was 3,4-benzocoumarin: mp 90–91° (lit.[21] mp 90–91°); ir (CH_2Cl_2) 1740 cm^{-1}; mass spectrum *m/e* 196 (molecular ion); yield, 19.0%.

Several other minor components were present on tlc but could not be obtained in sufficient amount for identification. Pyrolysis of 9-xanthenone at 600° (8 mm) and a N_2 flow rate of 0.2 l./min resulted in 97.5% recovery.

When 0.34 g of **12** was pyrolyzed in refluxing Dowtherm A for 20 hr, 0.10 g (40.3%) of 9-xanthenone was isolated.

Registry No.—**1,** 6255-58-9; **2,** 4425-34-7; **5,** 826-65-3; **7,** 33482-96-1; **8,** 33482-97-2; **9,** 33537-36-9; **10,** 33482-98-3; **11,** 17138-92-0; **12,** 33537-37-0; 3,5,3′,5′-

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tetrachlorobiphenylene-2,2′ sulfite, 33483-00-0; *o*-phenylene sulfate, 4074-55-9; biphenylylene-2,2′ sulfate, 31268-08-3; 4-nitro-*o*-phenylene sulfite, 33483-03-3; 4,4′-dimethoxybenzophenone-2,2′ sulfite, 33483-04-4; 3,4-dichlorocyclopentadienone dimer, 33483-05-5; 1-hydroxydibenzofuran, 33483-06-6.

A Semiempirical Molecular Orbital Study of *o*-Phenylene Carbonate and *o*-Phenylene Sulfite[1]

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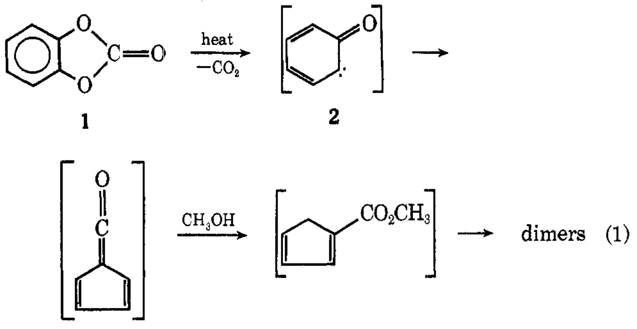
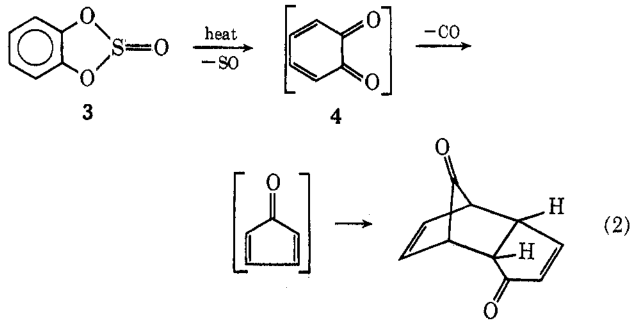
A molecular orbital approach to the rationalization of the preferential loss of CO_2 upon pyrolysis of *o*-phenylene carbonate and from its molecular ions and of the preferential loss of SO from the corresponding species of *o*-phenylene sulfite is reported. Overlap populations obtained from a CNDO/2 program are used as indications of total bond strengths. Also, minimum energies of the species produced by competing fragmentation pathways are compared.

The mass spectrum and gas-phase pyrolysis of *o*-phenylene carbonate (**1**)[3] have been reported. The molecular ion of **1** forms an ion C_6H_4O of major intensity upon loss of CO_2, at *m/e* 92, along with a metastable ion; it also loses CO to a minor extent, forming an ion $C_6H_4O_2$ at *m/e* 108. If **1** is pyrolyzed in a stream of nitrogen with CH_3OH in the stream, the major products are the dimers of methyl cyclopentadiene-1-carboxylate (44%) (eq 1). Thus, CO_2, rather than CO, is preferentially lost from **1** pyrolytically as well as from the molecular ions.



On the other hand, *o*-phenylene sulfite (**3**)[4,5] and substituted analogs[6] preferentially lose SO rather than SO_2. The major loss from the molecular ion of **3** is SO to form a $C_6H_4O_2$ ion at *m/e* 108 along with the corresponding metastable ion. A minor loss of SO_2 occurs without a metastable ion to form an ion C_6H_4O at *m/e* 92. When **3** is pyrolyzed in a stream of nitrogen, SO, followed by CO, is lost and cyclopentadienone forms, which dimerizes (80%) (eq 2).

In summary, the major path from **1** corresponds to the minor path from **3**, and vice versa. In this article we report a molecular orbital approach toward the rationalization of the preferential loss of CO_2 from **1** and the preferential loss of SO from **3**.



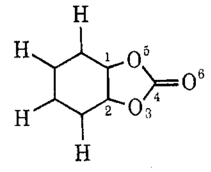
Experimental Section

Mass spectra, pyrolysis results, and syntheses of **1** and **3** have been reported elsewhere.[3-5] Calculations were obtained on an IBM 360/67 computer at the Wayne State University Computing and Data Processing Center.

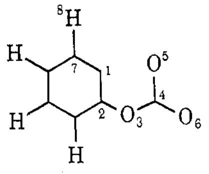
Pople and Beveridge's CNDO/2 program[7] was used to calculate Mulliken overlap populations and total energies.[8] The overlap populations were used as an indication of total bond strengths.[9] There has been a substantial amount of controversy as to whether 3d orbitals should be included to represent third-

Table I

Overlap Populations from Calculations Made on 1



1



1a

Structure	Charge	Overlap population for bond 1–5, 2–3	3–4, 4–5	2–3	3–4
1	0	0.817	0.914		
1	+1	0.822	0.941		
1a[a]	0			0.932	0.891
1a[a]	+1			0.922	0.911
1a[b]	0			1.026	0.893
1a[b]	+1			0.994	0.898

[a] A planar benzenoid-type geometry was used for the ring. [b] A carbenoid-type geometry was used for the ring.

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[7] J. A. Pople and D. L. Beveridge, "CINDO," Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, No. 141.

[8] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955).

[9] Previously, π-bond orders have been used as indication of bond strengths; see R. C. Dougherty, R. L. Foltz, and L. B. Kier, *Tetrahedron*, **26**, 1989 (1970).