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PYROLYSIS OF CYCLIC AROMATIC SULFITES AND CARBONATES

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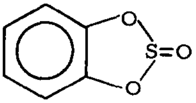
The gas-phase pyrolysis of o-phenylene sulfite (1) proceeds via loss of SO followed by CO.[1,2] Cyclopentadienone, which results from this path, dimerizes; 1,8-diketo-4,7-methano-3a,4,7,7a-tetrahydroindane (2) is isolated in 30-80% yield, depending on the conditions of pyrolysis.[1,2] The major products from the gas-phase pyrolyses of o-phenylene carbonate (3) are indene and naphthalene.[3] When 3 is pyrolyzed with CH_3OH in the stream, dimer 2 (14%) and dimers of cyclopentadiene-1-carboxylate (4, 34-44%) are isolated.[3] Thus, upon pyrolysis, 3 eliminates CO_2 forming ketene 5, which is trapped with methanol; in a competing path, 2CO are lost resulting in the formation of 2. Tetrachloro-o-phenylene carbonate and tetrachloro-o-benzoquinone have also been pyrolyzed in the gas phase.[4]



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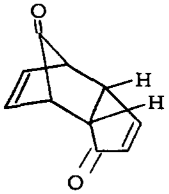

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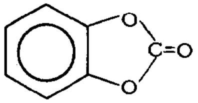

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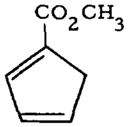

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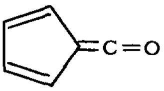

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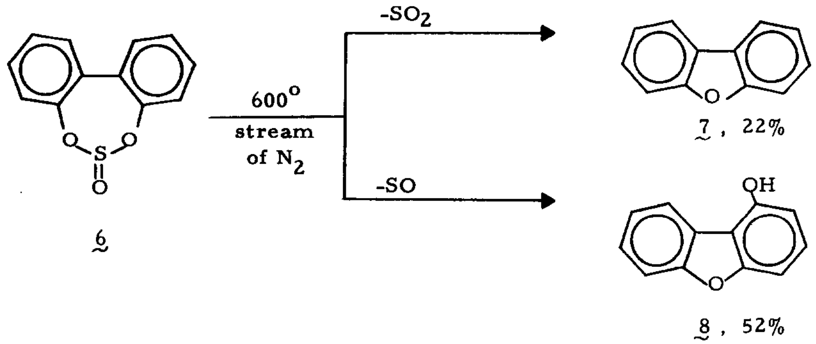
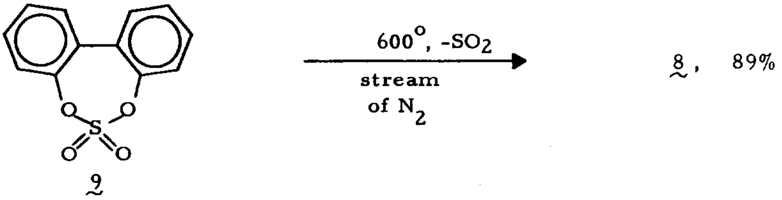
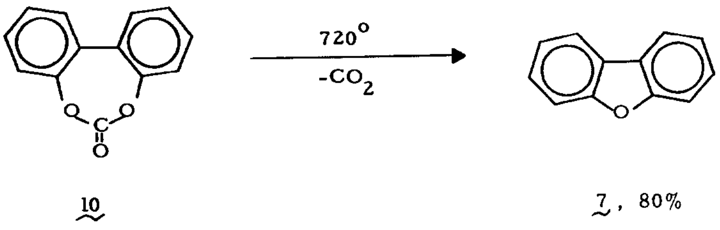
We have pyrolyzed biphenylylene-2,2'-sulfite (6) in the gas phase, using a previously reported[2,4] system. Dibenzofuran (7) is obtained in 22% yield via loss of SO_2. 1-Hydroxydibenzofuran (8) is obtained in 52% yield via loss of SO: mp 141-142° (lit.,[5] 140-140.5°);





bromo derivative, mp 180° (lit.,[5] 178°); mol. weight 184 (mass spectrometry). Pyrolysis of biphenylylene-2, 2'-sulfate (9) at 600° gives 8 via loss of SO_2, in 89% yield. Pyrolysis of dibenzofuran (7) at 600° results in its recovery (98%); pyrolysis of 1-hydroxydibenzofuran (8) at 600° results in 97% recovery.

In comparison, biphenylylene-2, 2'-carbonate (10) was pyrolyzed in the gas phase using a previously reported[6] system. Dibenzofuran (7) was obtained as the major product, in 80% yield.



The mass spectra of these compounds give an interesting comparison with the pyrolysis results. Sulfite 1 eliminates SO upon pyrolysis and loss of SO is the major fragmentation of its molecular ion.[1,2] In contrast, carbonate 3 eliminates CO_2 upon electron impact and the major product from pyrolysis forms upon CO_2 loss.

The mass spectrum of 6 has been reported;[2,7] the molecular ion fragments by competitive losses of SO and SO_2. Both paths exhibit metastable peaks which identify ions belonging to the separate but parallel paths. We added the relative intensities of the ions belonging to each path in order to get a rough estimate of the importance of each path. At 15 eV, we find the sum of the ions formed *via* the path involving initial loss of SO is 0.9 times as large as the sum of the ions formed *via* the path involving initial loss of SO_2. The product (8) from pyrolytic loss of SO is obtained in 2.4 times higher yield than the product (7) from the pyrolytic loss of SO_2. Thus, both SO and SO_2 loss are important in each process. Biphenylylene-2,2'-sulfate (9) eliminates SO_2 upon both electron impact and pyrolysis. On the other hand, carbonate 10 shows loss of CO_2 upon pyrolysis and from its molecular ion.

Naphthylene-1,8-sulfite eliminates SO_2 almost exclusively from its molecular ion at 70 eV.[7] We find that the corresponding 2,3-sulfite eliminates SO and SO_2 with nearly equal ease at 70 eV. We are studying the pyrolysis of the latter compound, as well as the pyrolyses of various substituted cyclic aromatic sulfites. We hope to develop an understanding of the relationships between the two processes and to explain the reasons for the SO *vs* SO_2 and the CO *vs* CO_2 results discussed above.

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