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COMPARATIVE STUDIES OF ELECTRON-IMPACT AND THERMOLYTIC FRAGMENTATION. II. o-PHENYLENE SULFITE.[1a]

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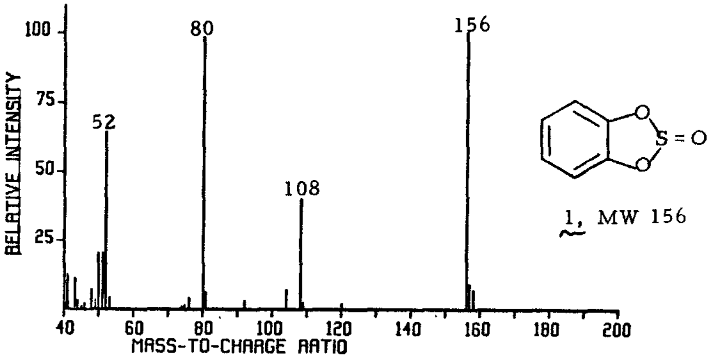
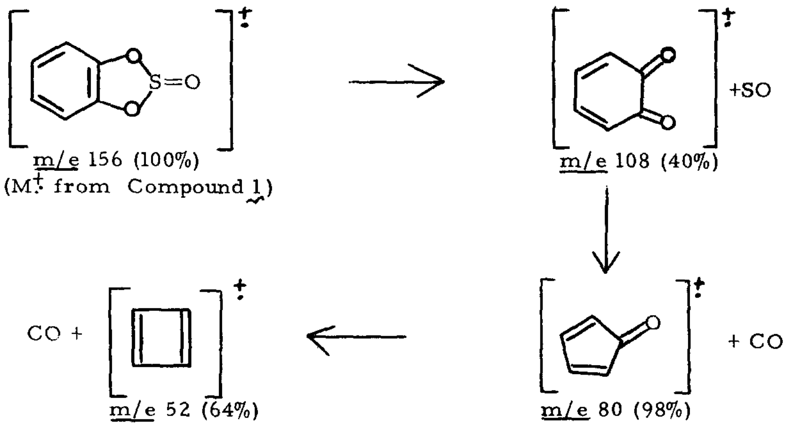
It has been shown that correlations exist between the electron-impact-induced fragmentation of a molecule and its thermolysis products.[1,2] For example, the ion of 95.5% relative intensity at m/e 76 in the mass spectrum[1] of phthalic anhydride corresponds to $C_6H_4^{+\cdot}$, which might be related to ionized benzyne. Thermolysis of this anhydride produced a substantial yield of biphenylene, presumably from the dimerization of benzyne.[1,2a,k] In order to explore further the potentiality of using the mass spectrum of a compound as a basis for predicting its thermolysis products, we have undertaken a comparative study using o-phenylene sulfites, carbonates, and sulfates.

The 70 ev mass spectrum[3] (Fig. 1) of o-phenylene sulfite[4] (1) shows an initial loss of sulfur monoxide followed by successive losses of two molecules of carbon monoxide. The mass spectrum does not provide information on the structures of ions formed. However, Scheme I outlines a possible fragmentation path for sulfite 1, which suggests that its thermolysis might provide a synthetic route to o-benzoquinone, cyclopentadienone, and/or cyclobutadiene.

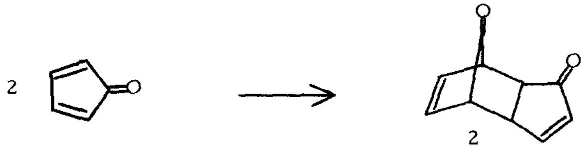
FIG. 1



Scheme I



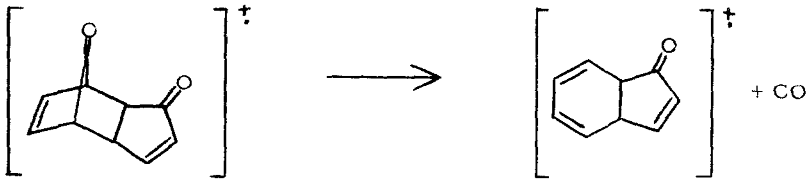
o-Phenylene sulfite in the gas phase in a stream of nitrogen at 10 mm was passed over a glowing Nichrome coil, ca. 800°, and the thermolysate was trapped on a cold finger at -78°. Sublimation at 65° (3 mm) gave a crude product from which was obtained a colorless compound after crystallization from hexane and resublimation. The product, obtained in 30% yield, was identified as 1, 8-diketo-4, 7-methano-3a, 4, 7, 7a-tetrahydroindene (2), the dimer of cyclopentadienone (Equation 1): mp 102-102.5° (lit.[5] 101-101.5°); infrared bands, 5.6 and 5.85μ (lit.[5] 5.6 and 5.85μ). No products attributable to cyclobutadiene were isolated.


2

(1)

o-Benzoquinone[7] was also thermolyzed under the same conditions used for sulfite 1. A mixture was obtained, which mass-spectral analysis showed to consist of dimer 2 as the major product. This indicates that *o*-benzoquinone is an intermediate in the formation of cyclopentadienone from compound 1, and that it loses carbon monoxide too readily to be isolated as a thermolysis product.

The mass spectrum of dimer 2 exhibits a relatively small molecular-ion peak which disappears with time. The base peak at *m/e* 132 arises from the elimination of carbon monoxide from the molecular ion and, most likely, by a competing thermal process. In Equation 2, 3a,7a-dihydroindenone (3) is suggested as a possible structure for this ion. In



(2)

m/e 160 (<1%)
(M$^{+\cdot}$ from Compound 2)

m/e 132 (100%)

fact, thermolysis of sulfite **1** also produced, in very low yield, compound **3** which was isolated as its maleic anhydride adduct; mp 241-242° (lit.[6] 241°).

The electron-impact-induced fragmentation of meso- and *dl*-hydrobenzoin sulfites proceeds by entirely different routes.[2j] Ring opening occurs and no sulfur monoxide is eliminated from the molecular ion. The thermolysis products of these cyclic sulfites have also been examined.[2j]

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