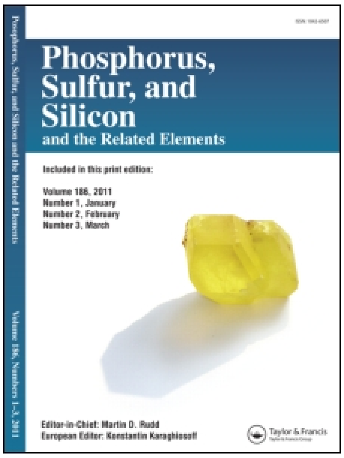

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Photolysis and Thermal Decay of the Sulfur Dioxide Adducts of Benzobenzvalene

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PHOTOLYSIS AND THERMAL DECAY OF THE SULFUR DIOXIDE ADDUCTS OF BENZOBENZVALENE

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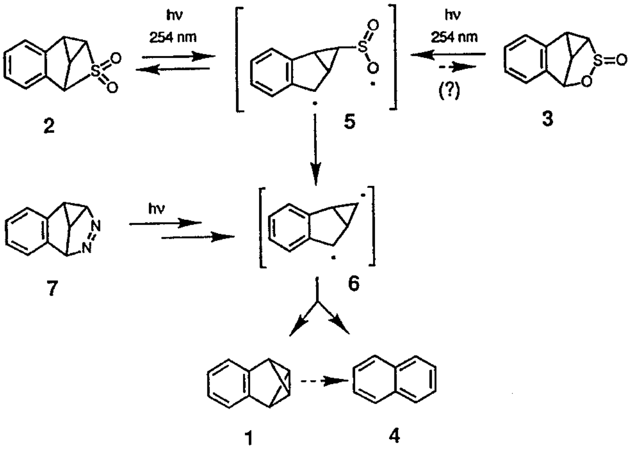
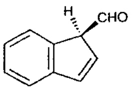
Abstract. Benzobenzvalene **1** is shown to add SO_2 with formation of a strained sulfone **2** and an isomeric γ-sultine **3**. Photochemically (254 nm) the two adducts interconvert. Moreover, SO_2 is extruded during the irradiation of **2** or **3** with regeneration of **1** and formation of naphthalene. This result is interpreted in terms of a reversible homolytic cleavage leading to an intermediate sulfinyloxy biradical **5** and subsequent formation of the benzoprefulvene biradical **6**. The pyrolysis of **2** and **3** gives, in the gas phase (FVP) and in solution, 1H-indene-1-carboxaldehyde **8** and naphthalene. The key step of this thermal reaction is shown to consist of a cycloreversion giving an intermediate sulfene **9**. This can be trapped with N-phenyl maleimide (NPMI). Key structures are ascertained by X-ray analysis.

Condensation of excess SO_2 into a cold ether soln. of benzobenzvalene **1** resulted in smooth addition to give the strained sulfone **2** and its isomeric γ-sultine **3**. These products were formed in a roughly 1:3 ratio and were isolated in 54% total yield. The structure of these adducts was assigned on the basis of their NMR, IR, and electronic spectra. Detailed information, particularly with respect to the configuration at the S-atom of **3**, was obtained from X-ray analysis [1]. When we irradiated a deoxygenated 0.01M soln. of **2** at 254 nm



and at -75° in (D$_8$)-toluene in the presence of 1.5 equiv. of pyridine, we obtained naphthalene **4**, and more interestingly, benzobenzvalene **1**. Monitoring the reaction by ^{1}H-NMR spectroscopy at -75° revealed that these products were formed initially in a 2.8:1 ratio. With increasing irradiation time, the relative concentration of **1** decreased in favour of the amount of **4**. Thus, the known phototransformation of **1** into **4**, though slow, is not negligible under our reaction conditions. The low-temperature photolysis of **3** under the same conditions gave, as above, compounds **1** and **4**, but in addition, it gave **2**. The primary chemical step of the photolysis of **2** and **3** consists, most likely, in the homolytic cleavage of the benzylic C-S and C-O bond, respectively. The presence of the aromatic ring is crucial here, as it provides the necessary chromophore and the benzylic stabilization of the ensuing common intermediate, *i.e.* the sulfinyloxy biradical **5**. The ring opening **2**→**5** is thus obviously reversible. In competition with the ring closure, the sulfinyloxy biradical **5** can lose SO$_2$ to give the C-centered biradical **6** known in the literature as the benzoprefulvene biradical [2]. This intermediate has also been invoked in the photolysis of diazabenzosemibullvalene **7** [2b][3]. The compounds **2** and **3** give 1H-indene-1-carboxaldehyde **8** and naphthalene, upon gas-phase pyrolysis (FVP at 380°) and upon heating in acid free CHCl$_3$ or CH$_2$Cl$_2$ (sealed tube, 120°). To account for the aldehyde formation, ring opening is suggested to give the intermediate sulfene **9** which then could lose SO. The opening **3**→**9**, though not necessarily a concerted process, is reminiscent of 1,3-dipolar cycloreversion reactions. When we heated the γ-sultine **3** in CH$_2$Cl$_2$ with excess N-phenylmaleimide (NPMI) as a trapping agent, a mixture of four stereoisomeric adducts **10(a-d)** was obtained in 82% total yield. The structure of the second most abundant isomer (**10b**) is ascertained by X-ray analysis [4]. Methyl acrylate as the trapping agent gave similar results. This cycloaddition is likely to be a genuine sulfene reaction [4].



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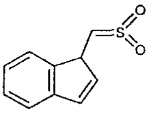

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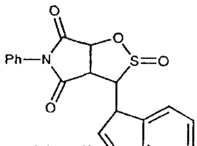

10(a-d)

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