155. The Photoreversible Addition of Sulfur Dioxide to Benzobenzvalene: A New Approach to the Benzoprefulvene Biradical

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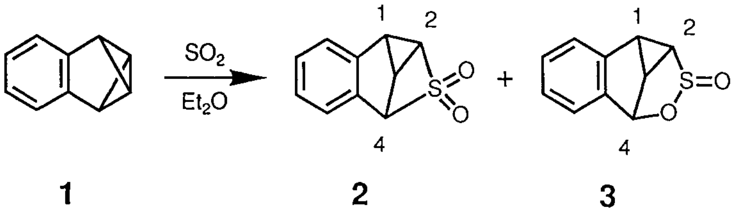
Benzobenzvalene (naphthvalene; **1**) is shown to add SO_2 to a lateral bicyclobutane bond with formation of a sulfone **2** and a 'γ-sultine' **3**. The structure of the latter is unambiguously established by X-ray diffraction. Both adducts extrude SO_2 upon direct photolysis at 254 nm and regenerate **1** accompanied by naphthalene in a 1:3 ratio. This result is interpreted in terms of a reversible homolytic cleavage leading, for both, **2** and **3**, to the same sulfinyloxy biradical **5**, which by loss of SO_2 gives the benzoprefulvene biradical **6**. The latter in its singlet state undergoes ring closure to **1**, or it opens to give naphthalene.

During the last decade, several laboratories have investigated synthetic and mechanistic aspects of the spontaneous addition of SO_2 to strained hydrocarbons, including bridged bicyclo[1.1.0]butane derivatives [1] [2] and quadricyclanes [3]. Interesting cyclic sulfones and sulfinates ('sultines') have been obtained from these reactions. We had reported in a preliminary note [4] that SO_2 reacts smoothly with benzobenzvalene (**1**) to give two isolable crystalline adducts, namely the sulfone **2** and the γ-sultine (= 5-ring sulfinate) **3**. Their nature and basic structure was readily deduced by standard spectroscopic means. More detailed stereochemical information will be given below.

Scheme 1



The adducts **2** and **3** have a heteroatom, S and O, respectively, bound to a benzylic position. This feature combined with the inherent strain is likely to confer on these compounds high photochemical reactivity. Thietane *S,S*-dioxides and 'γ-sultines' with a suitable chromophore have in fact been shown by *Durst et al.* [5] to lose SO_2 upon irradiation. In favourable cases, cyclopropanes were obtained, presumably *via* diradical pathways. The present study deals with the prospect of entering the $C_{10}H_8$ realm by a corresponding route, *i.e.* through light-induced extrusion of SO_2 from **2** and **3**.

Results. – Condensation of excess SO_2 into an Et_2O solution of **1** kept at −50° resulted in smooth addition to give the sulfone **2** and the 'γ-sultine' **3**. These products were formed in a roughly 1:3 ratio and were isolated, after evaporation of volatile material, in 54% total yield by medium-pressure chromatography. The structure of these adducts was assigned on the basis of their NMR, IR, and electronic spectra and by comparison with related compounds [1] [2]. Detailed information, particularly with respect to the configuration at the S-atom of **3**, was obtained by X-ray diffraction. From the *Figure* it is readily seen that SO_2 had added laterally to the former bicyclobutane moiety of **1**. The endocyclic O-atom is bound to the benzylic position and the S-atom to the remaining cyclopropane ring.

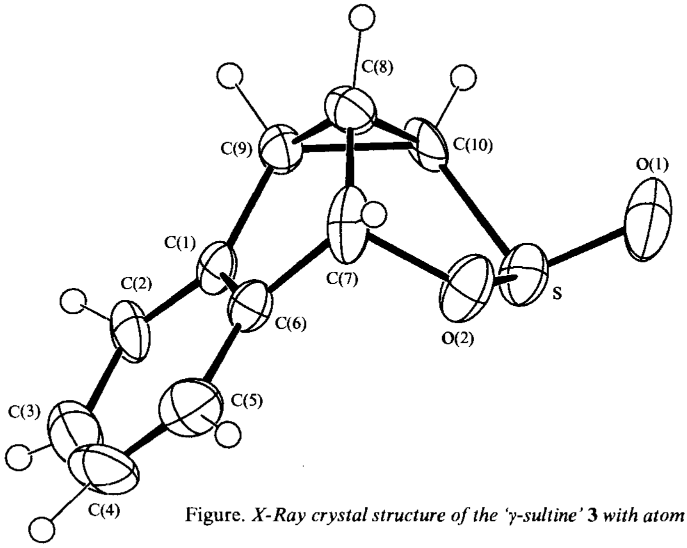


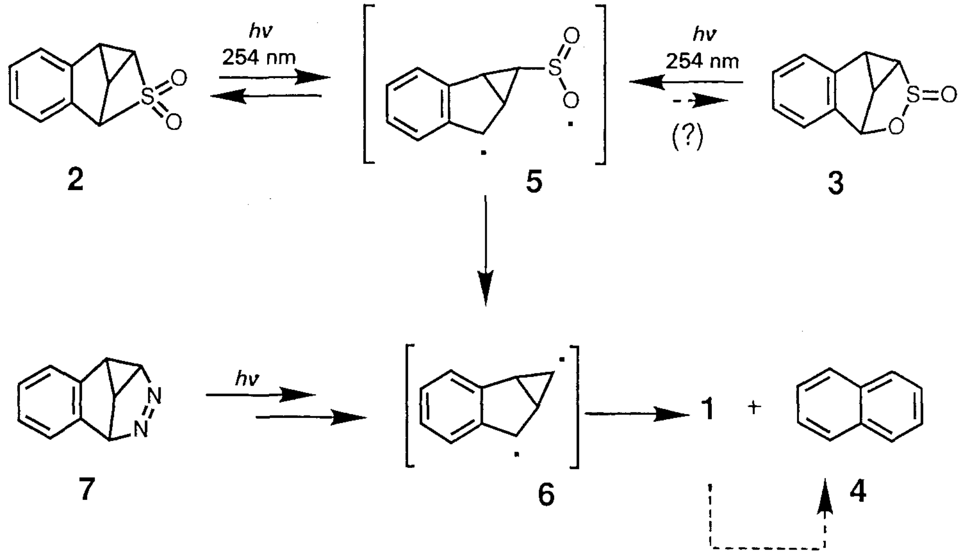
Figure. *X-Ray crystal structure of the 'γ-sultine'* **3** *with atom numbering* (arbitrary)

The exocyclic O-atom points away from the aromatic ring. Similar configurational relations had been found previously for the SO_2 adduct of a bridged tetramethylbicyclo[1.1.0]butane derivative [1]. A summary of crystal data, selected interatomic distances, and bond angles of the 'γ-sultine' **3** is given in the *Exper. Part* (*Tables 1* and *2*).

When we irradiated a deoxygenated 0.01M solution of the sulfone **2** at 254 nm and at −75° in (D_8)toluene in the presence of 1.5 equiv. of pyridine, we obtained two hydrocarbons, namely 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. When irradiated for 60 min, 75% of the starting material **2** was consumed. Integration showed 48% of **4** and 11% of **1** to be present with the material balance being 84%. At still longer irradiation time, the relative concentration of **1** decreased further in favour of an increase in the amount of **4**. Thus, the known phototransformation of **1** into naphthalene [6] is slow, but not negligible under our reaction conditions. The presence of pyridine or of another suitable base was found to be essential in order to protect the labile benzobenzvalene against acid-catalyzed decomposition and readdition of SO_2. The reported reversible electrocylization of pyridine [7] does not seem to affect the outcome of the photolysis of the sulfone **2**. However, the presence of pyridine affects the reaction rate due to its absorption in the spectral range chosen. When Et_3N was used instead, the photoreaction was markedly faster, but it gave, in addition to **1** and **4**, small amounts of unidentified by-products.

The low-temperature photolysis of the γ-sultine **3** in the presence of pyridine under the same conditions as mentioned above, gave, once again, naphthalene and benzobenzvalene (**1**), but in addition, it gave the sulfone **2**. Initially compounds **4**, **1**, and **2** appeared in the ratio 2.7:1:0.4. At 75% conversion, their amounts were 51, 12, and 4%, respectively. When Et_3N was used as the protective base, we obtained a similar result to that above, but the reaction, although faster, was less clean. We note that these experiments can not be performed in MeOH as the 'γ-sultine' **3** underwent a base-catalyzed methanolysis with nucleophilic attack at the S-atom and concomitant ring opening.

Scheme 2



Discussion. – The primary chemical step of the photolysis of **2** and of **3** consists, most likely, in the homolytic cleavage of a 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**. Structurally similar 'γ-sultines' and sulfones without the aromatic grouping have been reported to be photoinert under our reaction conditions [1] [5]. The ring opening **2**→**5** is probably reversible as may be concluded from the formation of **2** during the photolysis of **3**. The corresponding presumably holds for the process **5**→**3**. 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 for historical reasons as the benzoprefulvene biradical [8–10]. It is obvious to invoke the singlet state of this species to account for the formation of benzobenzvalene (**1**). The biradical **6** also provides a rational for the formation of naphthalene. Of course, other pathways, *e.g.* ring opening of **5** with subsequent loss of SO_2, could equally well account for the occurrence of the latter. The mechanism summarized in *Scheme 2* is strongly supported by the investigation of the photochemistry of diazabenzosemibullvalene **7**. *Kjell* and *Sheridan* [9] have shown that the photolysis of this diazene carried out in CD_2Cl_2 at −78°, with a band-pass filter 340–380 nm, gives naphthalene (**4**), benzobenzvalene (**1**), and (diazomethyl)indene in a ratio of 3:1:4. The formation of the hydrocarbons **4** and **1** has been rationalized in terms of the intermediacy of biradical **6**. The (diazomethyl)indene originates from a competing stepwise 1,3-dipolar cycloreversion. It is gratifying to note that the ratio of compounds **4** and **1** of this study is very close to the values found in our experiments, *i.e.* 3:1 *vs.* 2.8:1 and 2.7:1, respectively.

The biradical **6** and its congeners have been a matter of extensive computational studies [10]. The semiempirical UMNDO method [10] predicts the heat of formation of intermediate **6** in the gas-phase to be 96.8 kcal/mol. The activation barrier for its collapse to naphthalene is computed to be $\Delta H^{\neq} = 9.25$ kcal/mol, whereas the barrier of the ring closure of **6** to benzobenzvalene (**1**) is calculated to amount to 22.8 kcal/mol. However, the method obviously overestimates the heat of formation of **1** ($\Delta H = 104.9$ kcal/mol) since it places it above that of the biradical **6**. It is likely, therefore, that the barrier to the ring closure **6**→**1** is equally overestimated. It should, finally, be mentioned that thermochemical investigations in our laboratory suggest that the analogy between the diazene **7** on one hand [11] and the adducts **2** and **3** on the other hand [4] is not limited to the photochemical domain. We will report shortly on that matter.

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Experimental Part

General. Photolyses: *Srinivasan-Griffin* reactor *(Rayonet-RPR-100)* with *RPR* lamps, 2537 Å; quartz vessels. Low-temperature photolyses were run in quartz NMR tubes immerged in a quartz *Dewar* vessel cooled with dry ice/MeOH. UV spectra (λ [nm] ($\log\varepsilon$)): *Kontron-Uvikon-860*. IR spectra [cm^{-1}]: *Polaris-Mattson* FT-IR spectrometer. NMR spectra: *Bruker AMX-400* (9.4 Tesla) or *Varian XL-200* (4.7 Tesla); chemical shifts in δ [ppm] relative to internal TMS; apparent scalar coupling constants J in Hz; multiplicities for ^{13}C according to DEPT editing or to attached-proton test (APT); explicit ^{13}C assignment is based on heteronuclear-shift correlation. MS (m/z (% rel. to base peak)): *Finnigan-4023* with INCOS data system; electron impact.

*1,1a,6,6a-Tetrahydro-1,6-epithiocycloprop[*a*]indene 7,7-Dioxide (= 1a,1b,5b,5c-Tetrahydrocyclopropa[1′,2′-*c*;1′,3′:2,3]indeno[1,2-*b*]thiete 1,1-Dioxide*; **2**) *and 2a,2b,6b,6c-Tetrahydro-1-oxa-2-thiabenzo[*a*]cyclopropa[*cd*]-pentalene 2-Oxide (= 2a,2b,6b,6c-Tetrahydrocyclopropa[1′,2′-*c*;2′,3′:2,3]indeno[2,1-*d*][1,2]oxathiole 2-Oxide*; **3**) *from* **1**. A soln. of 332 mg (2.5 mmol) of **1** [12] in 25 ml of dry Et_2O was placed in a three-necked vessel equipped with an inplet pipe for gaseous SO_2, a dry-ice condenser, and an outlet pipe connected to an absorption flask charged with 10M NaOH. The soln. was cooled to −50°, whereupon *ca.* 8 g (125 mmol) of SO_2, dried over P_2O_5, was condensed into the vessel. The mixture was allowed to warm up slowly and to reach r.t. after *ca.* 20 h. Residual volatile material including the solvent was removed at 12 Torr. The remaining dark green oil was purified by medium-pressure chromatography (silica gel, petroleum ether/AcOEt 2:3) to give **2** (67.2 mg, 13.5%) and **3** (202 mg, 40.5%).

Compound **2**: Colourless crystals. R_f 0.38. M.p. 113–114.5°. IR (CCl_4): 1330*s*, 1260*m*, 1220*m*, 1158*s*, 1138*s*. ^{1}H-NMR (numbering as in *Scheme 1*; 200 MHz, $CDCl_3$): 3.22 (*t*, *J* = 5.9, H–C(1)); 3.68 (*ddd*, *J* = 5.9, 5.7, 3.9, H–C(3)); 3.81 (*ddd*, *J* = 5.9, 5.7, 3.2, H–C(2)); 5.13 (*dd*, *J* = 3.9, 3.2, H–C(4)); 7.2–7.5 (*m*, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 32.4; 36.5; 53.9 (C(2)); 83.0 (C(4)); 123.9; 124.8; 128.0, 129.7; 137.6, 138.7. MS (20 eV): no M^+ at 192, 167 (10), 149 (9), 144 (36), 129 (11), 128 (100). Anal. calc. for $C_{10}H_8O_2S$ (192.24): C 62.48, H 4.20, S 16.68; found: C 62.32, H 4.31, S 16.38.

Compound **3**: Colourless crystals. R_f 0.30. M.p. 134–135° (dec.). IR (CCl_4): 1605*w*, 1480*w*, 1460*w*, 1150*s*, 1070*m*, 910*m*, 890*m*. ^{1}H-NMR (numbering as in *Scheme 1*; 360 MHz, C_6D_6): 2.03 (*dd*, *J* = 6.0, 5.8, H–C(1)); 2.55 (*ddd*, *J* = 6.0, 5.8, 5.0, H–C(3)); 2.85 (*t*, *J* = 6.0, H–C(2)); 5.62 (*d*, *J* = 5.0, H–C(4)); 6.80–6.94 (*m*, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 34.5 (C(1)); 36.3 (C(3)); 66.6 (C(2)); 91.8 (C(4)); 124.1; 124.8; 127.8, 129.9, 138.0, 142.0. MS (20 eV): 192 (2, M^+, $C_{10}H_8O_2S$), 167 (18), 149 (18), 144 (20), 129 (11), 128 (100).

Crystallographic Data for **3**. Cell parameters and reflection intensities were measured at r.t. on a *Nonius-CAD4* diffractometer with graphite monochromated MoK_α radiation. Crystal data, intensity measurements, and structure refinements are summarized in *Table 1*, selected interatomic distances and bond angles in *Table 2*. The structure was solved by direct methods (MULTAN-80) [13] and refined by least-square analysis with the XTAL [14] programme. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

Table 1. *Crystal Data, Intensity Measurement, and Structure Refinement for 'γ-Sultine'* **3**

Formula	$C_{10}H_8O_2S$	μ [mm^{-1}]	0.319
Molecular weight	192.2	$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.60
Crystal system	orthorhombic	No. measured reflections	1832
Space group	*Pbca*	No. observed reflections	833
Crystal size [mm]	0.03 × 0.30 × 0.33	Criterion for observed	$\lvert F_0\rvert > 4\sigma(F_0)$
a [Å]	6.649(1)	Refinement (on *F*)	full-matrix
b [Å]	10.540(2)	H-atoms	observed and refined
c [Å]	24.512(5)	No. of parameters	142
V [Å^3]	1717.8(7)	Weighting scheme	$\omega = 1/\sigma^2(F_0)$
Z	8	Max. and average Δ/σ	0.154, 0.011
F_{000}	800	Max. and min. $\Delta\rho$ [e·Å^{-3}]	0.95, −1.16
D_c [gr·cm^{-3}]	1.49	*R*, ωR	0.098, 0.067

Table 2. *Selected Interatomic Distances* [Å] *and Bond Angles* [°] *with e.s.d.'s in Parentheses for 'γ-Sultine'* **3**

S–O(1)	1.475(8)	C(6)–C(7)	1.49(2)
S–O(2)	1.659(7)	C(7)–C(8)	1.535(15)
S–C(10)	1.800(11)	C(7)–O(2)	1.455(12)
C(1)–C(6)	1.375(14)	C(8)–C(9)	1.502(15)
C(1)–C(9)	1.496(14)	C(8)–C(10)	1.521(14)
O(1)–S–O(2)	105.6(4)	C(9)–C(8)–C(10)	62.3(7)
O(1)–S–C(10)	103.5(5)	C(1)–C(9)–C(8)	107.4(8)
O(2)–S–C(10)	94.1(4)	C(1)–C(9)–C(10)	119.4(9)
C(6)–C(7)–C(8)	105.9(8)	C(8)–C(9)–C(10)	59.5(7)
C(6)–C(7)–O(2)	106.9(9)	C(8)–C(10)–S	108.2(7)
C(8)–C(7)–O(2)	107.2(8)	C(9)–C(10)–S	123.6(7)
C(7)–C(8)–C(9)	104.2(8)	C(8)–C(10)–C(9)	58.2(6)
C(7)–C(8)–C(10)	106.7(8)		

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