

Photolysis of Benzo[*c*]-1,2,5-thiadiazole 2-Oxide. Spectroscopic Evidence for the Reversible Formation of 2-Thionitroso-nitrosobenzene

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Photolysis at room temperature of benzo[*c*]-1,2,5-thiadiazole 2-oxide in ethanol produces benzo[*c*]-1,2,5-thiadiazoline 1,1-dioxide. This product was shown, by flash photolysis, to be formed *via* benzo[*c*]-1,2,5-thiadiazole 1-oxide. Independent of this reaction 2-thionitrosobenzene is formed reversibly as a short-lived intermediate ($k = 100 - 200 \text{ s}^{-1}$) absorbing near 500 nm. In cyclohexane, the same primary products, in the approximate ratio of 3:1, were identified spectroscopically in degassed solution, but only polymeric material was isolated after photolysis in non-protic solvents. The activation parameters for the thermal reversion of 2-thionitrosobenzene at room temperature are tabulated. At 20 K in solid argon and at 85 K in EPA and PVC the same two products are formed ($\sim 1:2$ in PVC) as shown by spectroscopy. Under these conditions 2-thionitrosobenzene can also be photochemically reverted to starting material.

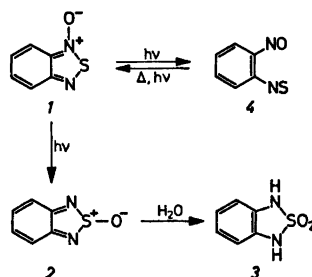
1,2,5-Oxadiazole 2-oxides (furoxans) can isomerize both thermally and photochemically *via* intermediates assumed to be 1,2-dinitroso compounds¹ and the properties of benzo[*c*]-1,2,5-selenadiazole 2-oxide indicate that a selenonitroso species exists as a short-lived intermediate.² It was therefore found of interest to examine the photochemistry of benzo[*c*]-1,2,5-thiadiazole 2-oxide.

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RESULTS

*Irradiation of benzo[*c*]-1,2,5-thiadiazole 2-oxide (1) at room temperature.* Compound 1, $4 \times 10^{-3} \text{ M}$ in aerated 96 % ethanol, produced benzo[*c*]-1,2,5-thiadiazoline 1,1-dioxide (3, Chart 1) in 90 % yield at 350 nm. The product was identified by comparison with an authentic sample.³ Photolysis at 350 and 400 nm of $2 \times 10^{-4} \text{ M}$ solutions in aerated 96 % ethanol followed by UV analysis showed that compound 3 was formed without any long-lived intermediates. The quantum yield at 400 nm for disappearance of compound 1 in aerated 96 % ethanol was measured to 0.014 ± 0.002 . In degassed solution the quantum yield was only slightly greater (*ca.* 20 %).

Irradiation at 400 nm of an aerated 10^{-4} M solution in cyclohexane led to a new absorption at 463 nm. On addition of ethanol this absorption immediately disappeared and the ab-



Scheme 1.

Table 1. Experimental data on the thermal reversion of the intermediate 4 to starting material, 1, at ambient temperature. Left series: Reappearance of 1 at 370 nm. Right series: Disappearance of 4 at 440–450 nm. Solutions were 10^{-5} M.

	Degassed		Aerated		Degassed k/s^{-1}	Aerated k/s^{-1}
	Reversibility/%	k/s^{-1}	Reversibility/%	k/s^{-1}		
Absolute ethanol	36	170	56	187	116	144
96 % ethanol	26	146	50	174	101	136
Cyclohexane	24	290	53	248	214	230

sorption increased at 285 nm due to benzo[c]-1,2,5-thiadiazoline 1,1-dioxide. The 463 nm absorption was assigned to the *S*-oxide, 2 (see Discussion).

Photolysis (350 nm) at 0 °C of an aerated 10^{-5} M solution in pentane followed by evaporation at the same temperature led to an insoluble polymeric substance. A black polymeric substance also resulted from photolysis in methylene chloride, deaerated with argon.

Flash photolysis of benzo[c]-1,2,5-thiadiazole 2-oxide in ethanol and cyclohexane. Flash photolysis was performed both in aerated and degassed 10^{-5} M solutions using light of wavelengths greater than 230 nm* (see Experimental). In ethanol, two transient absorptions were observed, both decaying in a first order process. The longer lived transient showed an absorption maximum at 467 nm (Fig. 1) and decayed with $k \sim 100$ s $^{-1}$ (Table 1). When the

* This was chosen in order to improve the intensity of the signal. The same transients were observed using light of wavelengths greater than 300 nm.

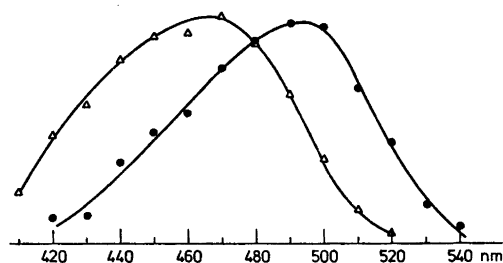


Fig. 1. UV spectra of 2-thionitrosobenzene (4) in 96 % ethanol (Δ), $\lambda_{\max} = 467$ nm, and cyclohexane (\bullet), $\lambda_{\max} = 493$ nm, at room temperature obtained by flash photolysis. Intensity in absorbance, arbitrary units.

result of flash photolysis was monitored at 370 nm, where only the starting material absorbs light, it could be shown that the starting material was re-formed at the same rate as the transient ($\lambda_{\max} = 467$ nm) decayed (Table 1). This clearly shows that the photo-process is reversible. The quantum yield for the formation of this transient was found to be unaffected by the presence of oxygen. The transient was identified as 2-thionitrosobenzene (4, Chart 1), *vide infra*. The second transient could be monitored at 410 nm where both the starting material and transient 4 absorb only weakly. It decayed with $k = 3.7 \times 10^3$ s $^{-1}$ in both absolute and 96 % ethanol. The process was irreversible. Unlike 4, the formation of this transient was partly quenched by the presence of oxygen (~ 50 %). In agreement with this, the photoreaction was less reversible in degassed ethanolic solution (36 %) than in an aerated solution (56 %, Table 1). The process observed at 410 nm is assigned to solvolysis of photochemically-formed benzo[c]-

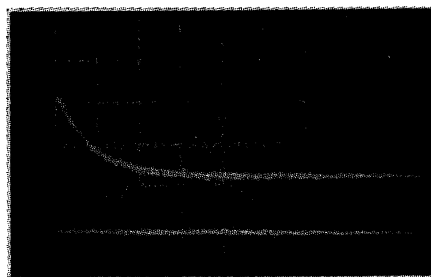


Fig. 2. Flash photolysis of benzo[c]-1,2,5-thiadiazole 2-oxide (1) in aerated cyclohexane, 10^{-5} M. Abscissa: time, 5 ms/division, ordinate: Intensity in mV ($\sim I_0 - I$). The picture shows the decay of compound 4 at 440 nm and the time independent absorption of compound 2 relative to the I_0 -line lowest.

Table 2. Thermodynamic data on the thermal reversion of the intermediate 4. Temperatures varied from 15 to 51 °C in ethanol and from 10 to 35 °C in cyclohexane. Solutions, 10⁻⁵ M, were not degassed.

	96 % ethanol	Cyclohexane
E_a /(kcal/mol)	12.8 (0.8)	16.1 (0.6)
A /s ⁻¹	2.77×10^{11}	1.06×10^{14}
ΔS^\ddagger /(cal/deg. mol at 25 °C)	-8.1 (2.5)	3.7 (1.9)
ΔH^\ddagger /(kcal/mol at 25 °C)	12.2 (0.8)	15.5 (0.6)
ΔG^\ddagger /(kcal/mol at 25 °C)	14.7 (0.2)	14.4 (0.2)

1,2,5-thiadiazole 1-oxide (2), which ultimately leads to benzo[c]-1,2,5-thiadiazoline 1,1-dioxide (3).

The results of flash photolysis in cyclohexane are similar to the results in ethanol. Due to the nature of the solvent however, 2 was observed as a permanent absorption (Fig. 2) with λ_{\max} at 463 nm. This absorption was also observed during steady state photolysis in cyclohexane (see above). As in ethanol, compound 4 reverted to the starting material in a first-order process (Table 1) and the quantum yield for the formation of 4 was unaffected by oxygen. The absorption spectrum of 4 with λ_{\max} at 493 nm

is shown in Fig. 1. The reaction parameters for the thermal reversion of compound 4 in ethanol and cyclohexane were evaluated (Table 2) from the Arrhenius plot (Fig. 3).

Photolysis of benzo[c]-1,2,5-thiadiazole 2-oxide at low temperature. This was performed in a variety of media (diethyl ether, isopentane, ethanol, 5:5:2 (EPA), poly(vinyl chloride) (PVC), argon) and the reactions studied with absorption spectroscopy (Table 3).

Spectra recorded during irradiation of compound 1 at 85 K in EPA ($\lambda_{\max}=408$ nm, $\epsilon=8400$ M⁻¹ cm⁻¹) with 400 nm light showed the appearance of two new absorptions at 458 and 485 nm (Fig. 4). The relative intensities of these were not constant. This means that the two absorptions are due to different products. When the sample was warmed up, products could still be detected at 145 K, above the melting point of EPA.

On prolonged photolysis at 400 nm all of the starting material and the absorption at 485 nm gradually disappeared and the final spectrum had absorptions at 447 and 285 nm (Fig. 5). This spectrum was unaffected by further photolysis at 450 nm. This result indicates that the species ($\lambda_{\max}=485$ nm) can be photolysed back to starting material which is then re-photolysed. The irreversible product ($\lambda_{\max}=447$ nm) will therefore dominate after some time. The 447 nm absorption is assigned to benzo[c]-1,2,5-thiadiazole 1-oxide, 2. The spectral shift of λ_{\max} from 458 to 447 nm in EPA is due to overlap of absorption profiles. Provided that no other products are formed, the estimated absorption coefficients are ϵ_{447} and $\epsilon_{285}=3000$ M⁻¹ cm⁻¹.

A further investigation of the photochemically reversible formation of compound

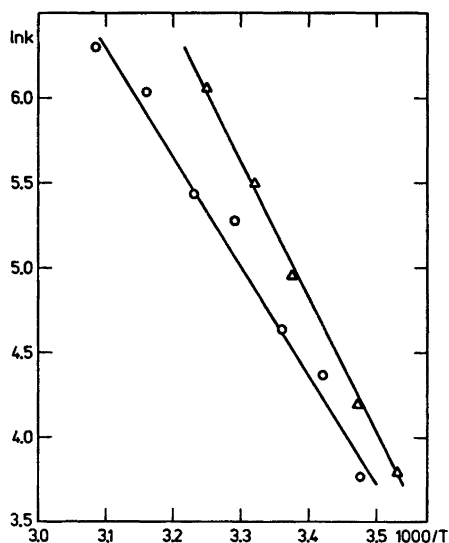


Fig. 3. Arrhenius plots of the first-order rate constants for the thermal reversion of 2-thionitrosobenzene (4) to benzo[c]-1,2,5-thiadiazole 2-oxide (1) in ethanol (O) and cyclohexane (Δ).

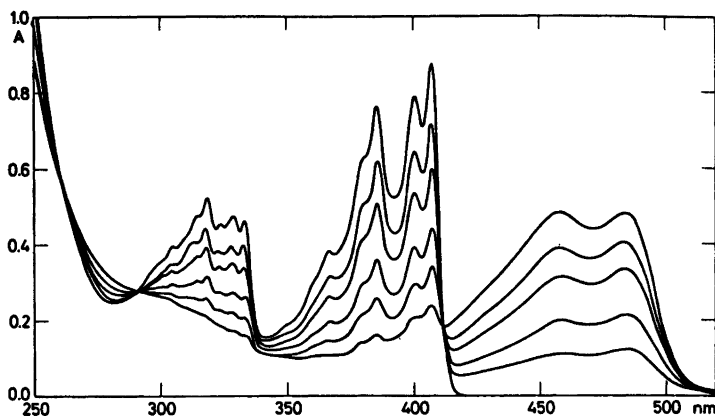


Fig. 4. UV spectra after photolysis at 85 K of benzo[*c*]-1,2,5-thiadiazole 2-oxide (1, $\lambda_{\max} = 408$ nm), 10^{-4} M, in EPA with 400 ± 20 nm light. Product absorptions at 458 and 485 nm can be seen.

4 was undertaken in a PVC film, 10 μm thick, ~ 0.1 M. Irradiation (400 nm) was carried out at 85 K until 50 % of the starting material had been converted into products (spectra not shown). At this stage, the absorptions at 470 and 485 nm were equal in intensity. Irradiation was then continued at 515 nm. This removed the absorption at 485 nm and regenerated ca. 25 % of the starting material. Compound 2 now absorbed at 453 nm. This absorption disappeared quite rapidly at room temperature when the film was exposed to water vapour. The final product, benzo[*c*]-1,2,5-thiadiazoline 1,1-dioxide (3), absorbed at 286 nm.

Some further studies were undertaken in PVC (Fig. 6). After photolysis at 400 nm, the

same two products were observed ($\lambda_{\max} = 473$ and 492 nm). The sample was then slowly warmed to room temperature. The 492 nm absorption could not be detected above 240 K. The other photoproduct, 2, hydrolysed rapidly at room temperature. The sample was then re-cooled to 85 K and the spectrum recorded (Fig. 6). This procedure allows one to calculate the degree of thermal reversibility. It showed that ~ 65 % of the starting material was reformed.

From these low temperature experiments it is clear that identical photochemical processes occur both at low temperatures and at room temperature.

A further lowering of temperature to 20 K

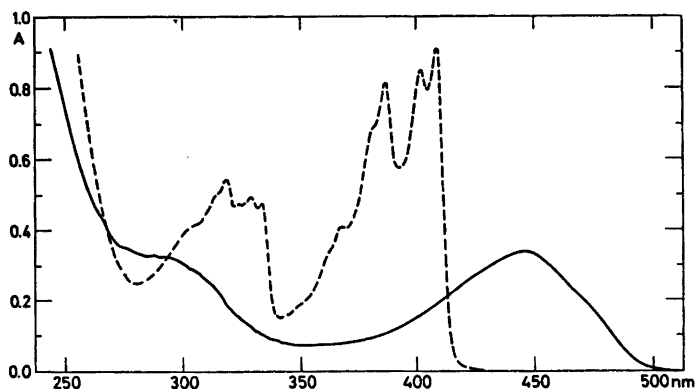


Fig. 5. UV spectrum of benzo[*c*]-1,2,5-thiadiazole 1-oxide (2, $\lambda_{\max} = 285$ and 447 nm) obtained by prolonged photolysis at 85 K of benzo[*c*]-1,2,5-thiadiazole 2-oxide (1, - - -), 10^{-4} M, in EPA with 400 ± 20 nm light.

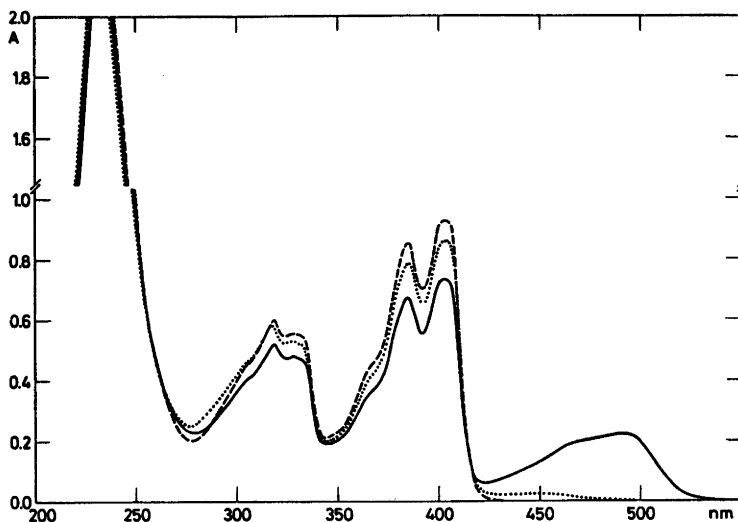


Fig. 6. UV spectra after photolysis at 85 K of benzo[*c*]-1,2,5-thiadiazole 2-oxide (1) in PVC film, 10 μm thick, with 400 ± 20 nm light. - - -, starting material at 85 K. —, after photolysis, product absorptions at 473 and 492 nm. . . ., after heating the photolysed sample to room temperature and recoiling to 85 K. The absorption near 300 nm is due to compound 3.

did not change the identity and approximate composition of the products: After deposition in solid argon at 20 K, the sample was photolysed at 386 nm (interference filter) and absorptions were seen at 463 and 486 nm (458 and 485 nm in EPA, Table 3). After consecutive matrix deposition and photolysis, a very intense band at 1185 cm^{-1} and weaker bands at 775 , 750 and 720 cm^{-1} , due to 2, were observed.

Table 3. UV absorptions in nm of compounds 1, 2 and 4.

Medium, temp.	1	2	4
PVC, 85 K	403	470 ^a 453	485 ^a
EPA, 85 K	408	458 ^a 447	485 ^a
Ethanol, 298 K	397	—	467
Cyclohexane, 298 K	406	463	493
Argon, 20 K	401	463 ^a	486 ^a

^a λ_{max} of overlapping absorption bands of compounds 2 and 4.

DISCUSSION

Identification of products. Benzo[*c*]-1,2,5-thiadiazole 1-oxide (2) was identified from its intense IR absorption at 1185 cm^{-1} (S—O stretching vibration⁴) in solid argon at 20 K and from its solvolytic reaction in ethanol and hydrolysis in a thin PVC-film, leading to benzo[*c*]-1,2,5-thiadiazoline 1,1-dioxide (3). Compound 2 has not been reported previously, but derivatives of 1,2,5-thiadiazole 1-oxide are known and stable compounds,⁵ viz. diphenyl-1,2,5-thiadiazole 1-oxide and phenanthro[9,10-*c*]-1,2,5-thiadiazole 1-oxide (intense absorption at 1130 cm^{-1} , (Ref. 4). The relative instability of 2, and in particular its ease of polymerization in dilute hydrocarbon solutions prevented its isolation. This instability is probably due to its *o*-quinoid structure.

The evidence for assigning structure 4 to the intermediate, which was formed reversibly, is as follows: (i) The lifetimes of the intermediate in ethanol and cyclohexane were not significantly different in aerated and degassed solutions. It is therefore unlikely that the intermediate is a free radical. (ii) The intermediate was also formed at temperatures down to 20 K. Thermal rearrangements following the primary

photochemical reaction are therefore unlikely. (iii) The intermediate reverts to the starting material at nearly the same rate in ethanol and cyclohexane. Also the starting material is re-formed at the same rate as the intermediate decays. The intermediate which absorbs intensely at ~ 500 nm can also be photolysed back to starting material.

As a system with two conjugated chromophores, one containing a weak π -bond, **4** would be predicted to have a $\pi-\pi^*$ transition in the visible. Nitroso compounds also exhibit an absorption at 700–800 nm, which is $n-\pi^*$ in character, but since this transition is weak (~ 50 M⁻¹ cm⁻¹; Ref. 6) and since a high concentration of **4** cannot be obtained, any absorption in this region could not be detected with conventional UV and flash spectroscopic methods. Compounds containing the thionitroso group have previously been described. *N*-Thionitroso compounds are stable,⁷ but the *C*-thionitroso compound thionitrosobenzene has only been trapped with butadienes,⁸ but never isolated.

The flash spectrum of compound **4** in ethanol (Fig. 2) is considerably blue shifted (467 nm) relative to cyclohexane (493 nm) probably indicating that different rotamers are present in polar and non-polar solvents at room temperature. At low temperatures in PVC, EPA and argon where continuous rotations are not possible **4** absorbs at 485–486 nm (Table 3). The absorption coefficient of this absorption can be calculated from the low temperature spectra by assuming that compound **2** is the only product formed by prolonged photolysis of compound **1** (Fig. 5, only two bands are present in the spectrum). Alternatively one can assume that the photochemical reversibility of compound **4** is quantitative. In both cases, an absorption coefficient of 8000–9000 M⁻¹ cm⁻¹ was calculated, indicating that the assumptions are correct.

Mechanistic results. The relative amounts of the two photoproducts **2** and **4** are approximately 3:1 at room temperature and 1:2 at low temperature, with small degrees of conversion. This means that the primary processes in compound **1** are dependent on temperature, but independent of the medium. The formation of **2** was partly quenched in liquid solution by oxygen (Table 1). The flash signal correspond-

ing to **2** was only enhanced when solutions were carefully degassed by pump – and – thaw cycles. Deoxygenation merely using argon was insufficient, indicating that a relatively long-lived triplet state of compound **1** is involved.* The effect of degassing indicates that **2** is formed from both the excited singlet and triplet states of **1** whereas **4** is formed only from the excited singlet since the absorption intensity of **4** was not significantly affected by oxygen. The quantum yield for the disappearance of **1** in aerated 96 % ethanol was measured as 0.014 by ferrioxalate actinometry.⁹ Flash photolysis of **1** in aerated ethanol showed that equal amounts of **2** and **4** were formed in the primary processes (Table 1). Thus, the quantum yield for the formation of **4** must also be 0.014.

EXPERIMENTAL

Benzo[c]-1,2,5-thiadiazole 2-oxide (1). The procedure of Pilgram⁴ was modified by using S₂Cl₂ instead of SCl₂ and dimethylformamide as solvent: *o*-Benzoquinone dioxime¹⁰ (1.00 g ~ 7.2 mmol) was dissolved in dimethylformamide (20 ml) and disulfur dichloride (2.0 g ~ 15 mmol) was added dropwise with stirring. During this, the reaction mixture was cooled externally with water to prevent the temperature exceeding 35 °C. The stirring was continued for $\frac{1}{2}$ h at room temperature and the mixture was poured into water and extracted with chloroform. The concentrated extract was separated by preparative layer chromatography (PLC) on silica gel (Merck_{PF254+366}) into benzo[c]-1,2,5-thiadiazole (0.31 g ~ 32 %) and benzo[c]-1,2,5-thiadiazole 2-oxide (**1**, 0.35 g ~ 32 %, m.p. 86–87 °C (methanol), Ref. 4, 78–80 °C). The plate was developed with a 7:7:1 mixture of benzene, light petroleum and acetone.

Flash photolysis. The flash lamp was filled with air and the light was filtered with aqueous NaBr in quartz ($\lambda > 230$ nm). Flash energies were 200 J. The analysing light beam was passed through a monochromator, through the reaction cell and through a second monochromator with a photomultiplier on the exit slit.

Steady state photolyses. For details concerning light sources, spectroscopic equipment and preparation of PVC films, see Ref. 11.

Photolysis of compound 1 in ethanol. Compound **1** (0.30 g) in aerated 96 % ethanol (500 ml, $\lambda_{\text{max}} = 397$ nm, $\epsilon = 6600$ M⁻¹ cm⁻¹) was photolysed with RUL 3500 Å lamps for 18 h. PLC on silica gel gave benzol[c]-1,2,5-thiadi-

* Compound **1** did not luminesce either at room temperature or at 85 K in EPA.

azoline 1,1-dioxide (3, 0.30 g ~90 %) identical with an authentic sample.³ The plate was developed with a 1:1:1 mixture of benzene, light petroleum and acetone.

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Note added in proof. With improved spectroscopic equipment a weak absorption around 700 nm ($\epsilon=10 \text{ M}^{-1} \text{ cm}^{-1}$) was detected by flash photolysis of compound 1 in ethanol. The reversible formed intermediate is therefore identified as 2-thionitrosobenzene.

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