R Mosher Ester of (*S*)-(trimethylsilyl)phenylmethanol: ^{1}H NMR ($CDCl_3$) major isomer 0.036, minor isomer 0.026 (s, 9 H), 3.52 (s, 3 H), 5.81 (s, 1 H), 7.00–7.59 (m, 5 H); ^{19}F NMR (470 MHz) ($CDCl_3$) major isomer −71.65, minor isomer −71.32.

3-(Hydroxyphenylmethyl)cyclohexanone. A solution of **9** (31 mg, 0.12 mmol) in 10 mL of a 5:1 methanol/water solution containing 4 drops of concd. HCl was refluxed for 6 h and neutralized via the addition of sodium bicarbonate solution (to pH 8). The crude reaction mixture was concentrated under reduced pressure and the residue was extracted with ether (3 × 50 mL). The combined ether fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified via radial chromatography, using a 10–25% ethyl acetate/petroleum ether gradient.

R Mosher ester of 3-(Hydroxyphenylmethyl)cyclohexanone: ^{1}H NMR ($CDCl_3$) δ 1.11–2.61 (m, 17 H), 3.44–3.52 (m, 4 H), 5.67 (m, 1 H), 7.1–7.8 (m, 10 H); ^{19}F NMR (470 MHz) ($CDCl_3$) δ −71.17, −71.25, −71.52, −71.60.

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Benzofuroxan Photochemistry: Direct Observation of 1,2-Dinitrosobenzene by Steady-State Spectroscopy. A New Photochromic Reaction

Nigel P. Hacker

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

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The synthesis of a 1,2-dinitrosoarene was first claimed in 1886. However it was clear from its physical properties that 1,2-dinitrosobenzene (II), and related arenes, were better represented by the benzofuroxan structure (I), which was first proposed in 1912.[1] Even to date there is still confusion between benzofuroxans and 1,2-dinitrosoarenes. For example, benzotrifuroxan is incorrectly depicted as hexanitrosobenzene.[2] Benzofuroxans substituted in the 5- and 6-positions are known and can thermally interconvert, presumably through the dinitrosobenzene intermediate, while the 4-substituted compound does not usually interconvert with the thermodynamically less stable 7-isomer. A number of studies on the photochemistry and thermochemistry of benzofuroxans have resulted in the proposal of 1,2-dinitrosoarenes as intermediates. Low-temperature ^{1}H NMR studies on the thermal isomerization of unsymmetrical benzofuroxans gave an activation energy ΔG^* for tautomerisation of about 15 kcal mol^{-1},[3] and anisyl azide has been successfully employed as a trap for 1,2-dinitrosobenzene from thermolysis of benzofuroxan at 155 °C.[4] A more recent report has found persistent radicals from benzofuroxan photolysis.[5] However, in all of the above studies there was no direct observation of the 1,2-dinitrosobenzene intermediate. Our recent studies on the photochemistry of matrix-isolated nitrosobenzene, which efficiently ejects nitric oxide and generates phenyl radical, prompted an examination of the photochemistry of benzofuroxan, which may undergo an analogous reaction via the 1,2-dinitrosobenzene intermediate and be a new precursor for benzyne.[6] We report here the photochemistry of benzofuroxan in inert matrices and as thin films at cryogenic temperatures, the direct observation of 1,2-dinitrosobenzene, and the photochromic behavior of this system at 12–80 K.

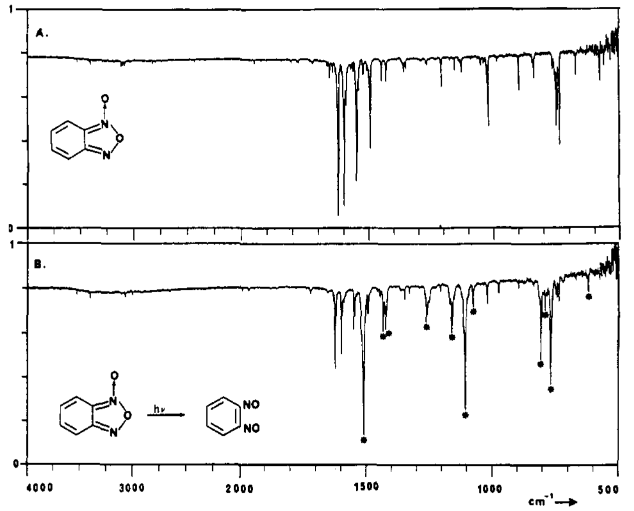
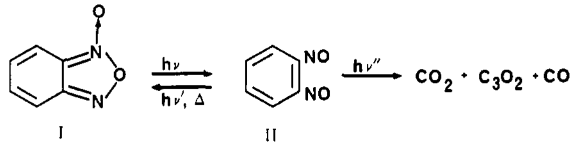


Figure 1. IR spectra recorded from photolysis of benzofuroxan in Xe at 14 K: (A) benzofuroxan; (B) after 2 h photolysis at 366 nm. (Bands in spectrum B that are marked with an asterisk appear after photolysis, disappear after warming the matrix to 70 K, and are assigned to 1,2-dinitrosobenzene.)

Scheme I. Products from Photolysis of Benzofuroxan at 14 K



Benzofuroxan was deposited from a side arm, at ambient temperature, with a constant stream of inert gas, onto a CsI window at 32 K (Ar) or 60 K (Xe) for about 20 min. The sample was cooled to 14 K at 1 K min^{-1} and gave a clear matrix. The infrared spectrum in xenon (Figure 1) shows principal bands at 1622, 1599, 1547, and 1492 cm^{-1}, typical for the furoxan ring, along with less intense bands at lower frequencies. Irradiation of this sample at λ = 366 nm for 0.5 to 2.0 h caused all of these bands to decrease and new bands centered at 1515, 1102, 805, and 795 cm^{-1} to appear. Warming the matrix to 80 K resulted in a minor loss of sample and caused the 1515 cm^{-1} band and related bands to disappear and the benzofuroxan bands to reappear. In separate experiments the 1515 cm^{-1} species was generated as above and photolysis of these samples with λ = 254 or 313 nm at 14 K resulted in almost complete reversion to benzofuroxan. Similar results were obtained in argon matrices except that the thermal reversion could not be completed due to sample loss above temperatures of 40 K. Thus this photochemically and thermally reversible process represents a new photochromic reaction. It is well known that monomeric aromatic *C*-nitroso compounds have a characteristic strong N=O stretching frequency at 1490–1520 cm^{-1} and bands at 1100 and 800 ± 50 cm^{-1} associated with C–N vibration.[7] The facts that

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[1] For a review of benzofuroxan chemistry, see: Boulton, A. J.; Ghosh, P. B. *Advances in Heterocyclic Chemistry*, Vol. 10; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1969; p 1.

[2] Aldrich Chemical Catalog, 1990–1991, p 702.

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[4] Bulacinski, A. B.; Scriven, E. F. V.; Suschitzky, H. *Tetrahedron Lett.* **1975**, 3577.

[5] Lin, S.-K. *J. Photochem. Photobiol. A. Chem.* **1988**, *45*, 243.

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[7] (a) Bradley, G. M.; Strauss, H. L. *J. Phys. Chem.* **1975**, *79*, 1953. (b) Gowenlock, B. G.; Luttke, W. *Q. Rev.* **1958**, *12*, 321.

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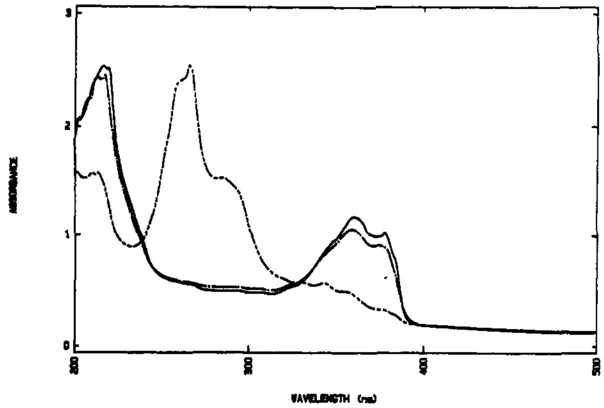

Figure 2. UV spectra recorded from photolysis of benzofuroxan in Xe at 14 K: (—) benzofuroxan; (- - - -) after photolysis at 366 nm, 1,2-dinitrosobenzene; (- · -) after warming to 70 K, regeneration of benzofuroxan.

strong peaks at 1515, 1102, 805, and 795 cm^{-1} are formed from benzofuroxan photolysis, and that this species reverts thermally and photochemically to benzofuroxan, suggest that this intermediate is 1,2-dinitrosobenzene (Scheme I). A similar IR spectrum has been recorded for II in a N_2 matrix from photolysis experiments with 2-nitrophenyl azide as a precursor.[8]

We recently reported that photolysis of nitrosobenzene in argon at 12 K gives phenyl radical and nitric oxide.[6] An analogous reaction with 1,2-dinitrosobenzene should give benzyne and nitric oxide via the 2-nitrosophenyl radical. Photolysis of 1,2-dinitrosobenzene at $\lambda = 254$ or $\lambda = 313$ nm only resulted in regeneration of benzofuroxan. However, photolysis of benzofuroxan at $\lambda > 280$ nm gave a steady state mixture of dinitrosobenzene and benzofuroxan. Prolonged photolysis of this mixture at $\lambda > 280$ nm resulted in a decrease of the IR bands due to the two precursors and new sharp bands at 2343 and 2137 cm^{-1} and a broad band at 2224 cm^{-1}. There were no bands detected that could be assigned to benzyne or at 1871 cm^{-1} for nitric oxide.[6,9] The two sharp bands are due to matrix-isolated carbon dioxide and carbon monoxide, respectively, whereas the broad band is due to carbon suboxide. The same carbon oxides were identified as minor photoproducts from nitrosobenzene photolysis. It is unclear why the main photodecomposition pathway is oxidative destruction of the aromatic nucleus for the dinitroso compound, while the mononitroso analogue efficiently photoejects nitric oxide.

The extinction coefficients of the UV absorptions are large relative to the vibrational absorption coefficients, making IR and UV spectroscopic analysis on the same sample impossible. The samples for UV absorption spectroscopy were deposited in a similar manner to the IR experiments except that shorter deposition times, quartz outer windows, and a sapphire sample window were used for UV analysis. The UV spectra in argon, xenon, and as thin films all gave similar results and exhibited identical behavior to the IR experiments. Benzofuroxan in xenon at 12 K gave UV absorptions at $\lambda = 378$ (sh), 362, and 214 nm. Photolysis at $\lambda = 366$ nm resulted in a decrease in intensity of the benzofuroxan absorptions and the formation of new absorptions at $\lambda = 280$ (sh), 266, and 260 (sh) nm (Figure 2). Heating the sample from 12–80 K caused the absorbances around 266 nm to decrease and the absorbances due to benzofuroxan to reappear, with some loss of the matrix.[10] In separate experiments argon or xenon matrices containing the 266-nm species were converted back to benzofuroxan by photolysis with $\lambda = 254$ nm. Similarly, a thin film of benzofuroxan was deposited at 60 K and gave broader absorbances at $\lambda = 379$, 363, and 218 nm. The film was cooled to 14 K and photolysed at $\lambda = 366$ nm to give 1,2-dinitrosobenzene, $\lambda = 300$ (sh), 272, and 218 nm. The broadened, red-shifted absorptions for thin films of I prevented complete photochemical conversion of I to II; however, heating the thin film to 80 K caused complete thermal reversion of II to I (Figure 3). Thus the absorbances observed at around 270 nm in all of the UV spectroscopic experiments behave in an identical manner as the new peaks for the intermediate observed in the IR experiments and are assigned to 1,2-dinitrosobenzene.

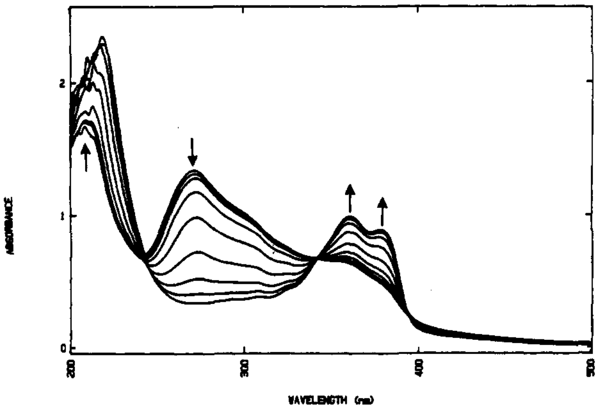

Figure 3. UV spectra recorded after photolysis of a thin film of benzofuroxan at 14 K and then warming to 80 K.

From the above IR and UV spectroscopic studies it is concluded that photolysis of benzofuroxan at $\lambda = 366$ nm gives 1,2-dinitrosobenzene, which can thermally or photochemically regenerate benzofuroxan. This new photochromic system operates only at cryogenic temperatures, 12–80 K.

Experimental Section

Benzofuroxan (98%) was purchased from Aldrich Chemical Company and used without further purification. Liquid Carbonics Ar (99.9995%) and Spectra Gases Xe (99.99%) were used for the matrix gases. Spectra were recorded at 1 cm^{-1} on an IBM Instruments IR44 FTIR spectrometer or at 2-nm resolution on a Hewlett-Packard 8451 diode array UV absorption spectrometer. An Air Products CS-202E Displex refrigerator was used to cool the matrix samples. The matrix isolation equipment will be described in detail in a later publication. Oriel 1-kW Hg/Xe or 500-W Hg arc lamps were used as light sources. The light was filtered through water, defocussed to prevent hot spots in the matrix sample, and filtered through UV–vis transmittance filters (Oriel 51152 for $\lambda < 300$ nm and 51154 for $\lambda > 300$ nm). In addition the individual Hg emission lines were isolated by using an interference filter, whereas broad band irradiations employed a cut-off filter.

Registry No. I, 480-96-6; II, 7617-57-4.

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(8) Dunkin, I. R., manuscript in preparation. The author thanks Dr. Dunkin for personal communication of his results.

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(10) The changes in quality and also some loss of the matrix prevented the observation of isosbestic points in the thermal transformation of II to I for the UV absorption spectra recorded in Xe.