Conclusion

Complexation of the lanthanide reagent to N-5 in the NNO moiety and the attendant modification of the NMR spectra have several consequences. Our earlier Eu(dpm)$_3$ and ^{13}C determination that *cis*-azoxyalkanes are unsymmetrical[2b] in spite of coincident bridgehead proton chemical shifts is fully confirmed. Moreover, both carbon and hydrogen α to trivalent nitrogen experience the greatest overall lanthanide induced shifts (Figure 1). Since certain bicyclic azo *N*-oxides undergo sequential base-catalyzed deuterium exchange at the bridgehead positions,[4] the site of deprotonation can now be specified with certainty. If the intermediate bridgehead anions prove exploitable as synthetic entities, isomeric substitution sites should also be readily identifiable.

The LIS analysis of *N*-oxide 4 allows a comparison of the diamagnetic anisotropy of the double bond vs. the NNO unit. Figure 2 indicates that protons lying over the carbon unsaturation are shielded by 0.4–0.5 ppm more than those positioned over the nitrogens. This outcome obtains even though hydrogens syn to NNO are slightly closer to nitrogen than those syn to C=C are to carbon.[26] Reduced shielding by the hetero unit is undoubtedly due to orbital shrinkage at the relatively electronegative nitrogen compared to carbon and to the unsymmetrical dispersal of π-electron density away from nitrogen by virtue of conjugation with oxygen.

Acknowledgment. We are grateful to the National Institutes of Health (GM 15927) and the Robert A. Welch Foundation (Grant E-143) for support of the work and to Dr. Michael Heyman for furnishing some of the *N*-oxides.

Registry No.—**3a**, 22509-00-8; **3b**, 25926-96-9; **3c**, 26081-83-4; **4**, 37436-17-2; **5**, 25926-99-2; **6**, 34098-80-1; Yb(dpm)$_3$, 15492-52-1.

References and Notes

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(3) *cis*-Azo *N*-oxide derivatives in which the protons α to nitrogen are forced out of the C–N=N(O)–C plane, unlike **3–6**, exhibit separate bridgehead proton resonances. The effect is proportional to the degree of aplanarization.[4]

(4) M. Heyman and H. Olsen (University of Copenhagen), unpublished results.

(5) The X-ray structure determination of azoxyalkane **3c** has been carried out.[1a]

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(8) (a) M. R. Willcott III, R. E. Lenkinski, and R. E. Davis, *J. Am. Chem. Soc.*, **94**, 1742 (1972). (b) For a reasonable but extensive set of lanthanide locations, the experimental and the calculated shift values are sorted and matched by the PDIGM subprogram AUTOASSIGN. The lowest resulting *R* factor corresponds to the best fit. Numerical control experiments have been conducted on a variety of substrates; the technique consistently provides assignments in agreement with independent identification criteria. In the case of the azo *N*-oxides described here, automatic assignment was carried out under the constraint that certain nuclei were held fixed. The assignments were then varied within appropriate subsets. For example, the two bridgehead resonances were treated as a single group and the assignments permuted to give the best possible *R* factor. Copies of the current and soon-to-be updated versions of PDIGM and a description of the AUTOASSIGN algorithm are available from R.D.

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(22) Cf. G. Klopman, Ed., "Chemical Reactivity and Reaction Paths", Wiley, New York, 1974, pp 55–82. For a general review on nucleophilic reactivity, see R. F. Hudson, *ibid., pp 167–252.*

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(26) This has been demonstrated for **3b** by X ray[1a] and derives from the shorter C–N bond lengths. A full geometry optimization for bicycles **3a** and **4** with MINDO/3 yields the same result.[1a]

Low-Temperature Photochemical Matrix Aposynthesis of an Oxathiete and Its Valence Tautomerism with the Corresponding α-Ketothione[1]

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London, Ontario, N6A 5B7 Canada

Received November 21, 1978

Photochemical elimination of carbon monoxide from 5-methyl-1,3-benzoxathiol-2-one (**5b**) yields the transient monothio-*o*-benzoquinone **6b**. This, at 77 K, can be reversibly photoisomerized into a species identified as the benzoxathiete **7b** containing the previously unobserved oxathiete ring. When **5b** is irradiated in ethyl vinyl ether at room temperature, trapping occurs regiospecifically to give the adduct **11a**, which then undergoes a photochemical rearrangement to yield **12**. Spectroscopic evidence suggests that the transients may experience a second elimination of carbon monoxide to give the cyclopentadienethione **9a**. Monothiobenzil (**1b**) and monothiopivaloyl (**1a**) do not appear to undergo an analogous photoisomerization to give the corresponding oxathietes. 1,3-Benzodithiol-2-one (**5e**) also loses carbon monoxide photochemically to give a transient identified as benzodithiete (**7e**), which can be trapped by dimethyl acetylenedicarboxylate.

There have been few descriptions of α-ketothiones;[2–7] those so far reported are α-ketothiocamphor,[3] monothiopivaloyl[2] (**1a**), and monothiobenzil[6] (**1b**). Their spectroscopic properties indicate that, to at least a large degree, **1a** and **1b** exist as α-ketothiones rather than the oxathietes **2a** and **2b**, and attempts to demonstrate the existence of oxathietes have been unsuccessful.[5,6] Recently we reported[2,8] the preparation of α-dithiones **1c**, **1d**, and **1e** and were successful in observing

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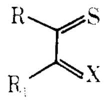
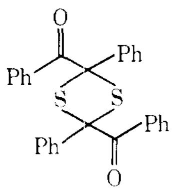


1

2

a, $R_1 = R = Me_3C$, X = O; b, $R_1 = R = Ph$, X = O; c, $R_1 = R = H$, X = S; d, $R_1 = R = p\text{-}Me_2NC_6H_4$, X = S; e, $R_1 = H$, $R = Me_3C$, X = S



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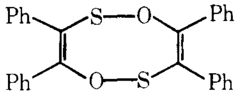


4

their light, temperature, and solvent dependent tautomerism with the corresponding 1,2-dithietes **2**, **2d**, and **2e**. We describe here the results of an examination of α-ketothiones for evidence of a similar tautomerism with 1,2-oxathietes.

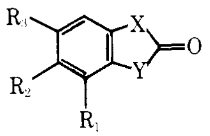
Results and Discussion

Diaryl and Dialkyl α-Ketothiones. Following removal of solvent, blue solutions of monothiobenzil (**1b**) yield a green glassy solid, described as polymeric;[7] redissolution produces a green solution which gradually regenerates the original blue color.[7] In order to examine the possibility that the green material might in fact be a mixture of 2,3-diphenyloxathiete (**2b**) and a small amount of blue monothiobenzil, freshly dissolved samples of the green glass in carbon tetrachloride were monitored by visible spectroscopy and vapor phase osmometry as a function of time. An initial average weight of 440 was observed (monomeric monothiobenzil has a molecular weight of 226), and this decreased simultaneously with the intensification in the visible spectrum of the blue band at 608 nm assigned to monothiobenzil.[6] Competing decomposition of monothiobenzil[9] did not allow accurate kinetic analysis of the results in order to determine the degree of polymerization, but they do appear to be consistent with the presence of a dimeric species for which structures such as **3** and **4** may be reasonable, based upon analogy with the behavior of α-dithiones[2,8] and the products of reaction of benzil and benzoin with hydrogen sulfide.[9] However, these observations provide no evidence for a tautomerism with the oxathiete **2b**.

Selective irradiation of α-dithiones and 1,2-dithietes results in their reversible interconversion.[2,8] However, irradiation of the long wavelength band of monothiobenzil (**1b**) and of monothiopivaloyl (**1a**) in ether-isopentane-ethanol (5:5:2) at both room temperature and 77 K resulted in no observable change in their electronic spectra, indicating that no detectable concentrations of oxathietes **2a** and **2b** were formed. Assuming that, as do α-dithiones, the α-ketothiones can cyclize photochemically and also that the closure occurs from a singlet state, then the failure to observe cyclization here may be due to rapid intersystem crossing competing successfully with intramolecular rotation of the ketothione into a conformation suitable for closure (for example, α-diketones exist in a twisted or trans-planar conformation[10]). Alternatively, the oxathietes could be formed, but rapidly open thermally and revert to the α-ketothiones.

Monothio-o-benzoquinones. Chapman has claimed[11] that the benzoxathiolone **5a** eliminates carbon monoxide photochemically to give a mixture of the tautomers **8** and **6a**. The absence of a hydroxyl group in **5a** would eliminate the possibility of an equilibrium between **8** and **6a** and possibly would allow the observation of valence tautomerism with a benzoxathiete. Accordingly, we investigated the products of irradiation of the benzoxathiolone **5b** for evidence of such a tautomerism.

Prior to irradiation of **5b**, the mass spectrum was recorded; fragments corresponding to successive loss of two molecules of carbon monoxide were observed which can be interpreted as being due to the formation of the radical cations of the monothio-*o*-benzoquinone **6b** or the benzoxathiete **7b** and cyclopentadienethione **9a**. No fragments corresponding to loss of carbon dioxide from **5b** were observed.[12] As will be seen, this behavior mimics the photolytic reactions of **5b**. In the mass spectrum of monothiobenzil a weak intensity ion corresponding to loss of SO was observed,[6] and this was presented as evidence that the radical cation might exist as 3,4-diphenyloxathiete (**2b**). In the mass spectrum of **5b**, no loss of SO from the daughter ion assigned to **6b** or **7b** was observed.



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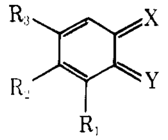

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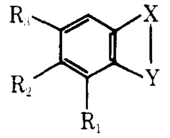
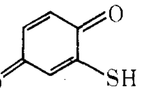


7

a, X = O, Y = S, $R_1 = R_3 = H$, $R_2 = OH$; b, X = O, Y = S, $R_1 = R_3 = H$, $R_2 = Me$; c, X = O, Y = S, $R_1 = R_3 = Me_3C$, $R_2 = H$; d, X = Y = O, $R_1 = R_2 = R_3 = H$; e, X = Y = S, $R_1 = R_2 = R_3 = H$

Irradiation through quartz of benzoxathiolone **5b** in ether at room temperature resulted in partial conversion to, apparently, polymeric material. However, in ethyl vinyl ether as solvent only clean formation of the dihydrobenzoxathiin **11a** and the 2*H*-benzoxathiole **12** occurred. Prolonged irradiation did not result in complete conversion, probably because the products (**11a**, λ_{max} 290, 299 nm; and **12**, λ_{max} 293, 301 nm) absorb in the same region as their precursor, **5b** (λ_{max} 282, 289 nm).



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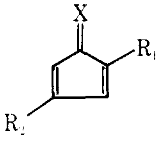

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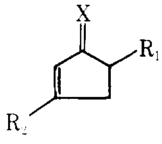

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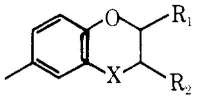
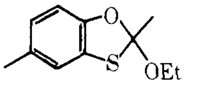
a, X = S, R_1 = H, R_2 = Me; b, X = S, $R_1 = R_2 = Me_3C$; c, X = CH_2, $R_1 = R_2 = H$; d, X = O, R_1 = H, $R_2 = Me_3C$; e, X = S, R_1 = H, R_2 = Me; f, X = C=O, $R_1 = R_2 = H$; g, X = C=S, R_1 = H, R_2 = Me, or $R_1 = R_2 = Me_3C$; h, X = S, $R_1 = R_2 = H$; i, X = O, $R_1 = R_2 = H$

The dihydrobenzoxathiin **11a** was differentiated from the possible alternative, the isomeric structure **11b**, by oxidation to the sulfone **11c**; the ring methylene protons experienced a much greater downfield shift than the ring methine in the ^{1}H NMR spectrum, implying that the ethoxyl group was adjacent to the oxygen atom. The structure of the benzoxathiole **12** followed from its spectral data; as with **11a**, the ethoxyl methylene group resonated as an AB system as a consequence of the adjacent asymmetric center.



11a, X = S; R_1 = OEt; R_2 = H
b, X = S; R_1 = H; R_2 = OEt
c, X = SO_2; R_1 = OEt; R_2 = H



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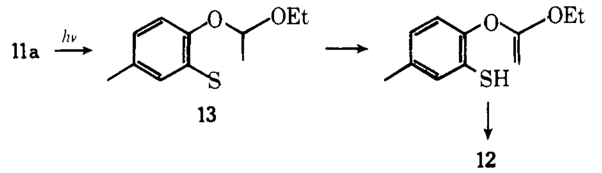
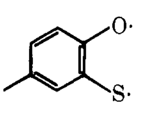
Scheme I





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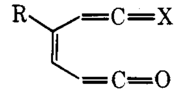
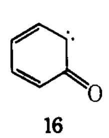


15a, R = H; X = O
b, R = Me; X = S



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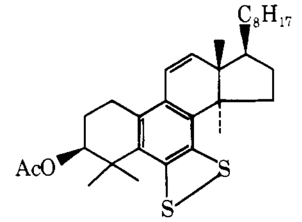

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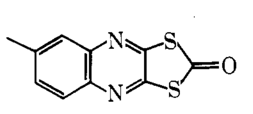

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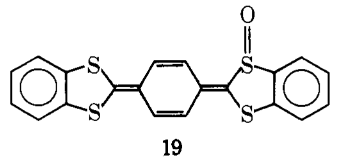

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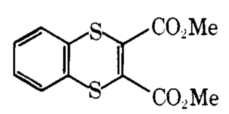

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Irradiation through quartz of the benzoxathiin **11a** in ethyl vinyl ether generated the benzoxathiole **12**, demonstrating that the origin of this compound is possibly by the process illustrated in Scheme I.

The formation of **11a** is consistent with the thermal $2\pi + 4\pi$ trapping of the monothio-*o*-benzoquinone **6b**; the direction of addition (i.e., formation of **11a** rather than **11b**) is in accord with the regiochemistry of Diels–Alder additions of polarized species.[13] However, other mechanisms of formation cannot be excluded; these include, for example, the reaction of photoexcited **6b** or **7b** with olefin, the reaction of photoexcited **5b** with olefin followed by extrusion of carbon monoxide, and stepwise reaction of the triplet biradical **14** (formed photochemically from **6b**, **7b**, or **5b**) with olefin to give both **11a** and **12** via the biradical **13**.

An attempt was made to distinguish between some of these possibilities by generation of **6b** and/or **7b** in an inert matrix[14] at 77 K and subsequent dark addition of ethyl vinyl ether simultaneously with destruction of the matrix by warming. However, none of **11a** was isolated, probably because of rapid reaction of **6b** (or **7b**) with itself or solvent before the ethyl vinyl ether could diffuse into the solution.[15]

More information about the transients formed by irradiation of **5b** was gleaned by their generation in a low-temperature organic matrix under conditions where they were unreactive and observable spectroscopically.

Irradiation with light of wavelength 280–340 nm of a 10^{-4} M solution of **5b** in an alcohol[14] glass at 77 K and monitoring of the electronic absorption spectrum until all of the starting material band around 280 nm had disappeared resulted in the appearance of intense absorption bands at 450 and 290 nm, the latter possessing vibrational structure, along with weak bands at 320 and 500 nm, the latter visible as a shoulder (Figure 1). Repetition of the irradiation at 100-fold higher concentration allowed the observation of an additional, weak, very broad band centered around 750 nm. All of these absorption maxima rapidly disappeared when the matrix was allowed to soften, indicating the reactivity of the species generated. However, at 77 K the maxima were stable in the absence of light, indicating that no thermal reactions occur at this temperature. The absorption bands are attributed to the presence of the monothio-*o*-benzoquinone **6b**, the benzoxathiete **7b**, and more tentatively to the cyclopentadienethione **9a**; we believe that the first absorbs at 500 and 450 nm and also in the region 280 to 340 nm and that the last absorbs at 750, 450, and 320 nm, while the benzoxathiete absorbs at 290 nm. It will be noted that both the monothiobenzoquinone and the cyclopentadienethione possess maxima coincident at 450 nm. Selective irradiation of these absorption bands resulted in the observation of a reversible photochemically induced tautomerism between the oxathiete **7b** and the monothioquinone **6b** and their conversion to the cyclopentadienethione **9a** on prolonged irradiation. The absorption maxima and the photochemical relationships of the transients described are summarized in Scheme II and illustrated in Figure 1; the bases of these assignments, that is the results of the selective irradiations, are discussed below.

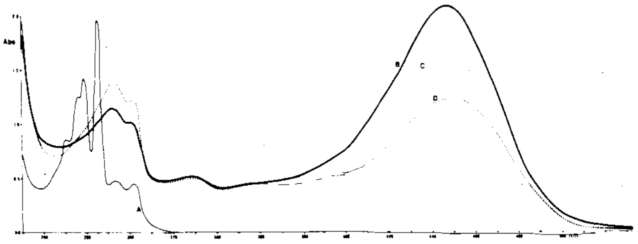
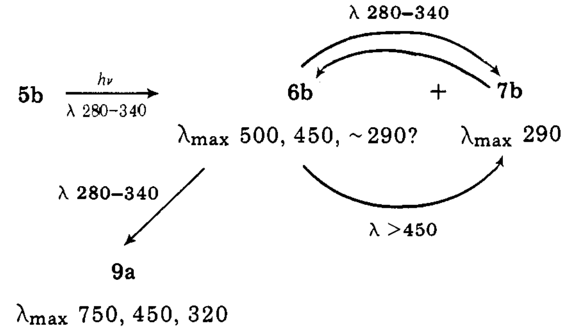


Figure 1. Electronic absorption spectrum for **5b** → **6b** + **7b** + **9a** in alcohol glass (10^{-4} M) at 77 K: (A) before irradiation; (A → B) irradiating at 280–340 nm; (B → D) irradiating at >440 nm; (D → C) irradiating at 280–340 nm.

Scheme II



Selective irradiation into the band attributed to cyclopentadienethione at 750 nm produced no change in the spectrum. Irradiation into the monothio-*o*-benzoquinone bands at 450 and 500 nm using light of wavelengths longer than 440 nm resulted in their partial disappearance and an intensification of the maximum at 290 nm assigned to the benzoxathiete, with the band at 320 nm remaining unchanged. Continued irradiation into the 450-nm band led to its further diminution in intensity, but the rate of disappearance declined more rapidly than would be expected after making proper allowance for the fact that the species responsible for the 450-nm band was absorbing less light as its concentration was reduced. Given that no dark reaction was occurring (leading to reversion of the benzoxathiete to the monothioquinone) and assuming that the benzoxathiete possesses no absorption maxima at wavelengths longer than 440 nm, then this must imply that a second band is present at 450 nm. This band is assigned to the cyclopentadienethione **9a**.

Following irradiation into the monothioquinone band at 450 nm and its conversion to the benzoxathiete, absorbing at 290 nm, the system was irradiated with light of wavelength

280–340 nm. This resulted in regeneration of the band at 450 nm and a decrease in intensity at 290 nm as the benzoxathiete was transformed into the monothioquinone. This cycle was reversible and was repeated several times. It was noted that prolonged irradiation into the benzoxathiete band at 290 nm did not result in complete conversion to the monothioquinone; in the absence of dark reactions this must mean that the quinone also possesses an absorption in the irradiated region (280–340 nm) and that a photostationary state between **6b** and **7b** is being set up. It was also noted that irradiation into the benzoxathiete band at 290 nm led to a rate of diminution which was not fully matched by the rate of increase of the monothioquinone band at 450 nm and also that the weak maximum at 320 nm slowly increased in intensity. This is attributed to photochemical elimination of a second molecule of carbon monoxide to yield the cyclopentadienethione **9a**. Such behavior has precedent; photolysis of 3,5-di-*tert*-butyl-*o*-benzoquinone at 254, 546, or 579 nm results in elimination of carbon monoxide and formation of isolable 2,4-di-*tert*-butylcyclopentadienone.[16] An alternative, competing photochemical fragmentation of *o*-benzoquinones to give bis ketenes such as **15a** has been reported.[17] Photolysis of **6b** and **7b** to give an analogous bis ketene **15b** is ruled out here by the electronic absorption spectrum observed for the species assigned as **9a**; a thioketene n → π* maximum would lie in the region of 500 to 570 nm.[18]

The fate of the transients **6b**, **7b**, and **9a** when the matrix softens is not known, and since in a matrix it is necessary to work at concentrations of 10^{-4} M in order to irradiate all of the sample and to observe spectra, it was not feasible to isolate any of the products. In an attempt to circumvent this problem, the di-*tert*-butylbenzoxathiolone **5c** was prepared in the hope that the expected products **6c**, **7c**, and **9b** might be sufficiently unreactive to allow their generation in solution rather than a matrix and also their isolation. Benzoxathione **5c** was irradiated in a diethyl ether/methylcyclohexane (2:3) matrix at 77 K utilizing the conditions used for **5b**; the electronic absorption spectrum of the products was similar to that obtained from **5b**, except that the absorption maximum attributed to the cyclopentadienethione now appeared at 440 nm and the monothiobenzoquinone band appeared at 485 nm. Prolonged irradiation with light of wavelength 280–340 nm resulted in an irreversible decrease in intensity of the band at 480 nm and an increase in intensity of the absorption at 440 nm as the monothiobenzoquinone **6c** was converted to the cyclopentadienethione **9b**. When the matrix was allowed to soften, the absorption maxima all rapidly disappeared, indicating that despite the steric protection **6c**, **7c**, and **9b** were all too reactive to permit their isolation.

A comparison of the absorption spectrum suggested to be that of cyclopentadienethione **9a** with those of related compounds supports the assignment; fulvene (**9c**) and 3-*tert*-butylcyclopentadienone (**9d**) possess moderately weak maxima at 360 and 280 nm, respectively, which have been assigned as π → π* transitions,[19] and this correlates with the band at 450 nm for **9a**. The n → π* absorption of 2-cyclopentenone (**10i**) at 324 nm[20] experiences a bathochromic shift in going to 3-*tert*-butylcyclopentadienone (**9d**), where the band is presumably situated underneath the 380-nm absorption. A similar energy bathochromic shift from 3-methylcyclopent-2-enethione (**10e**), where the n → π* maximum is reported[21] to be in the region of 550 nm, correlates well with the position of the n → π* maximum observed for **9a** at 750 nm.

The *o*-phenylene carbonate **5d** has been reported[12] to lose both CO_2 and CO thermally, the former process leading to the intermediate **9f** by way of the keto carbene **16**. It could be argued that the absorption bands assigned to cyclopentadienethiones **9a** and **9b** in the photolyses of **5b** and **5c** are in fact due to formation of analogous structures **9g**, generated by photochemical extrusion of carbon dioxide from the benzoxathiolones. However, this is not supported by the fact that the rates of formation of **9a** and **9b** were slow at the start of irradiation and increased at high conversion; furthermore, **9a** was still being formed after all of the precursor **5b** had been photolyzed.

Dithio-*o*-benzoquinones. Recently, Barton and colleagues reported the isolation of the benzodithiete **17** and confirmed its structure by X-ray crystallographic analysis.[22] We decided to attempt to generate the parent member of this series, **7e**, by irradiation of the benzodithiolone **5e** in order to observe its possible tautomerism with the dithio-*o*-benzoquinone **6d**.

The preparation of benzodithiete has been claimed by oxidation of dithiocatechol.[23] However, later work has shown that the reaction product was probably a polymeric mixture.[24] Subsequently, the quinoxaline-2,3-dithiocarbonate **18** has been irradiated to give a mixture of carbon monoxide, sulfur, and dithiin and thiophene derivatives which can, at least in part, be explained in terms of photochemical extrusion of carbon monoxide to give a 1,2-dithiete followed by dimerization and subsequent loss of sulfur.[25] More recently the sulfoxide **19** has been thermolyzed[26] and some of the products rationalized in terms of the intermediacy of dithio-*o*-benzoquinone **6e**.

In the mass spectrum of the benzodithiolone **5e**, fragmentation corresponding to consecutive loss of carbon monoxide and carbon monosulfide (CS) was observed. The charge-bearing fragments can be assigned to the desired benzodithiete **7e** (or the quinone **6e**) and cyclopentadienethione **9h**. The fragmentation could be partially reproduced thermally; flash thermolysis of **5e**[27] at temperatures up to 1000 °C in an apparatus previously described[28] and collection of the thermolysate yielded carbon monoxide, identified by its infrared spectrum. No carbonyl sulfide (COS) was detected. When **5e** was irradiated with light of wavelength 240–400 nm in the presence of dimethyl acetylenedicarboxylate, the benzodithiin **20** was obtained as the only product. The isolation of **20** is consistent with trapping of the proposed intermediates, **6e** and **7e**. Evidence for such trappable intermediates was obtained by irradiation of a 10^{-2} M solution of **5e** in an alcohol[14] matrix at 77 K using light of wavelength 275–330 nm. A weak band at 370 nm was generated, and no absorptions at longer wavelength ascribable to dithio-*o*-benzoquinone were observed. Selective irradiation into the new band at 370 nm with light of wavelength 350–380 nm produced no change in the spectrum. When the matrix was allowed to melt, the band at 370 nm disappeared, indicating that it was associated with a reactive species. In conjunction with the chemical trapping evidence supplied, these observations are consistent with the formation of benzodithiete **7e**, which when irradiated under the conditions described either does not open to give dithio-*o*-benzoquinone **6e** or, if it does, then rapidly reverts to the dithiete.

Experimental Section

Irradiations at room temperature were conducted under a positive pressure of dry, oxygen-free nitrogen gas using an Hanovia 450-W medium-pressure mercury lamp mounted in a water-cooled quartz well. Low-temperature experiments were performed on an optical bench using light from an Hanovia HBO 200-W high-pressure mercury lamp suitably filtered to isolate wavelength ranges described in the text. Samples for low-temperature experiments were degassed by at least three freeze–pump–thaw cycles to a residual pressure of better than 3×10^{-5} mmHg and were sealed under vacuum in quartz cells. The cells were mounted in a cryostat capable of being cooled to temperatures down to 77 K and designed to allow periodic monitoring of the electronic absorption spectrum of the sample undergoing irradiation. Monothiobenzil (**1b**) and monothiopivaloyl (**1a**) were prepared by the methods previously described for these compounds.[2,7]

5-Methyl-1,3-benzoxathiol-2-one (5b). KSCN (40 g, 0.4 mol) in water (50 mL) was added to a solution of $CuSO_4 \cdot 5H_2O$ (51 g, 0.2 mol) and *p*-cresol (10.8 g, 0.1 mol) in water (250 mL), and the black suspension was heated with stirring on a steam bath until the precipitate became white. The mixture was filtered, and the precipitate and filtrate were extracted with CH_2Cl_2 (500 mL). The extract was washed with 10% aqueous NaOH, dried, and evaporated to yield crude 5-methyl-1,3-benzoxathiol-2-imine, which was hydrolyzed directly using aqueous ethanolic HCl. Aqueous workup and crystallization of the product from diethyl ether gave **5b** (1.5 g, 9%): mp 83–84 °C (lit.[29] 83 °C); UV (hexane) 289 nm (ϵ 3520), 282 (2950), 278 shoulder, 273 shoulder, 222 (10 500); MS (70 eV) *m/e* 166 (M^+, 62), 138 (16), 121 (19), 110 (100).

6-Methyl-2,3-dihydro-2-ethoxy-1,4-benzoxathiin (11a) and 2,5-Dimethyl-2*H*-2-ethoxy-1,3-benzoxathiole (12). A solution of **5b** (194 mg, 1.17 mmol) in ethyl vinyl ether (6 mL) in a quartz tube was irradiated at room temperature for 26 h. Evaporation gave a yellow oil which was separated by preparative TLC on silica gel to give back unreacted **5b** (57 mg, 0.34 mmol) along with **11a** (110 mg, 0.52 mmol, 63% allowing for reclaimed **5b**) as an oil and **12** (38 mg, 0.18 mmol, 22% allowing for reclaimed **5b**) also as an oil. Irradiation of **5b** (368 mg) in ethyl vinyl ether (15 mL) for 100 h gave 44 and 25% yields of **11a** and **12,** respectively.

For **11a:** UV (hexane) 299 nm (ϵ 3480), 290 (3770), 252 (7540), 242 (8300), 215 (39 700); ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 3 H, X′ of $A'B'X'_3$, $J_{A'X'/B'X'}$ = 7 Hz), 2.22 (s, 3 H), 3.04 (2 H, AB of ABX, J_{AB} = 12.5 Hz, J_{AX} = 2.5 Hz, J_{BX} = 4.5 Hz), 3.82 (2 H, A′B′ of $A'B'X'_3$, $J_{A'B'}$ = 9.5 Hz, $J_{A'X'/B'X'}$ = 7 Hz), 5.36 (1 H, X of ABX, J_{AX} = 2.5 Hz, J_{BX} = 4.5 Hz), 6.85–7.10 (m, 3 H); MS (70 eV) *m/e* 210 (M^+, 100), 195 (2), 181 (15), 165 (19), 153 (80), 149 (57); M^+ *m/e* 210.0713 (calcd for $C_{11}H_{14}O_2S$, 210.0714).

For **12:** UV (hexane) 301 nm (ϵ 4050), 293 (4640), 241 (6430), 209 (24 200); ^{1}H NMR ($CDCl_3$) δ 1.18 (t, 3 H, X of ABX_3, $J_{AX/BX}$ = 8 Hz), 2.04 (s, 3 H), 2.26 (s, 3 H), 3.06 (2 H, AB of ABX_3, J_{AB} = 9.4 Hz, $J_{AX/BX}$ = 8 Hz), 6.96–6.76 (m, 3 H); MS (70 eV) *m/e* 210 (M^+, 44), 195 (3), 165 (61), 140 (100); M^+ *m/e* 210.0711 (calcd for $C_{11}H_{14}O_2S$, 210.0714).

6-Methyl-2,3-dihydro-2-ethoxy-1,4-benzoxathiin 4,4-Dioxide (11c). The oxathiin **11a** (55 mg, 0.26 mmol) was stirred in $CHCl_3$ (5 mL) and *m*-chloroperbenzoic acid (175 mg, 52% purity, equivalent to 0.53 mmol of peracid) in $CHCl_3$ (10 mL) was added over 15 min, and the mixture was stirred overnight. An aqueous workup yielded the crude, crystalline sulfone **11c** (68 mg, 97%). Crystallization from acetone/hexane gave pure **11c:** mp 88–89 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (t, 3 H, X of ABX_3, $J_{AX/BX}$ = 7 Hz), 2.35 (s, 3 H), 3.56 (2 H, A′B′ of A′B′X′, $J_{A'X'/B'X}$ = 3 Hz, $J_{A'B'}$ = 3 Hz), 3.96 (2 H, AB of ABX_3, J_{AB} = 9.8 Hz, $J_{AX/BX}$ = 7 Hz), 5.63 (X′ of A′B′X′, $J_{A'X'/B'X'}$ = 3 Hz), 6.89–7.69 (m, 3 H); MS (70 eV) *m/e* 242 (M^+, 50), 214 (44), 186 (18), 171 (25), 154 (62), 123 (84), 108 (65), 77 (100); M^+ *m/e* 242.0615 (calcd for $C_{11}H_{14}O_4S$, 242.0613).

4,6-Di-*tert*-butyl-1,3-benzoxathiol-2-one (5c). 3,5-Di-*tert*-butylphenol (2 g, 9.7 mmol) and dry $Cu(SCN)_2$ (8 g, 45 mmol, freshly prepared by mixing aqueous solutions of KSCN and $CuSO_4$ and filtering off the precipitate) were stirred together in AcOH (50 mL) at 70 °C for 1 h, after which time the black precipitate of $Cu(SCN)_2$ had become colorless. The reaction mixture was poured into water (100 mL) containing NaOH (35 g), stirred for 30 min, and filtered. The precipitate and the filtrate were extracted with diethyl ether (450 mL), and the extract was washed with water. The ethereal solution was extracted with dilute HCl (7 × 100 mL), and the combined acidic extracts were neutralized with aqueous NaOH to liberate the crude 4,6-di-*tert*-butyl-1,3-benzoxathiol-2-imine (180 mg), which was hydrolyzed by stirring in MeOH (60 mL) containing dilute HCl (25 mL) for 2 h. Aqueous workup and crystallization from aqueous MeOH gave pure **5c** (63 mg, 3%): mp 51–52 °C; UV (EtOH) 280 nm (ϵ 1900), 272 (1900), 266 shoulder, 226 (10 300); IR (Nujol) 1735, 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9 H), 1.30 (s, 9 H), 6.9–7.1 (AB, J = 1.5 Hz, 2 H); MS (70 eV) *m/e* 264 (M^+, 20), 249 (100), 221 (5), 205 (4), 193 (10); M^+ *m/e* 264.1186 (calcd for $C_{15}H_{20}O_2S$, 264.1184).

1,3-Benzodithiol-2-one (5e) (with Dr. N. Toshima). 1,2,3-Benzothiadiazole was prepared by the method of Jacobsen and Janssen[30] from 2-aminobenzenethiol and nitrous acid and was converted to 1,3-benzodithiol-2-thione using the method of Huisgen and Weberndörfer[31] (heating with CS_2 in an autoclave). 1,3-Benzodithiol-2-thione (5.53 g, 30 mmol) in $CHCl_3$ (75 mL) was added dropwise to $Hg(OAc)_2$ (19.13 g, 60 mmol) in AcOH (500 mL), and the mixture was stirred for 2 h before being poured into water. The resulting suspension was filtered, and the filtrate was extracted several times with $CHCl_3$. The combined extracts were washed with saturated aqueous $NaHCO_3$ solution and water and dried. Removal of solvent and crystallization from EtOH gave **5e** (2.93 g, 58%): mp 78–78.5 °C (lit.[32] 78–79 °C); MS (70 eV) *m/e* 168 (M^+, 53), 140 (100), 96 (64).

2,3-Bis(carbomethoxy)-1,4-benzodithiin (20). **5e** (110 mg, 0.65 mmol) was dissolved in dimethyl acetylenedicarboxylate (1.19 g, 8.4 mmol) in a quartz tube and irradiated at room temperature through a Corning 7-54 glass filter for 42 h. Removal of excess dimethyl acetylenedicarboxylate by reduced pressure evaporation at room temperature gave an orange residue which was purified by preparative TLC on silica gel to yield unchanged **5e** (19 mg, identified by mixture melting point and IR) and the product **20** (64 mg, 42% allowing for recovered **5e**) as a light yellow oil: UV (cyclohexane) 355 nm (ϵ 895), 273 (9300), 241 shoulder, 237 (10 800), 229 shoulder; IR (film) 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.92 (s) and 7.38 (m) in a ratio of 3:2, MS (70 eV) *m/e* 282 (M^+, 100), 251 (25), 250 (36), 223 (17), 219 (52); M^+ *m/e* 282.0014 (calcd for $C_{12}H_{10}O_4S_2$, 282.0020).

Registry No.—5b, 15062-74-5; **5c,** 69652-82-0; **5e,** 62576-04-9; **11a,** 69652-83-1; **11c,** 69652-84-2; **12,** 69652-85-3; **20,** 69652-86-4; *p*-cresol, 104-93-8; ethyl vinyl ether, 109-92-2; 3,5-di-*tert*-butylphenol, 1138-52-9; 1,3-benzodithiol-2-thione, 934-36-1.

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