Into a 100-mL three-necked flask, equipped with an N_2 inlet and a reflux condenser connected to a trap kept at −78 °C during the reaction, was introduced $Cu(OAc)_2 \cdot H_2O$ (0.1 g, 0.5 mmol), pyridine (1.16 g, 0.0147 mol), **10** (2. g, 0.0147 mol), and 15 mL of chlorobenzene. The mixture was stirred magnetically for 40 min at room temperature. To the resulting homogeneous solution was added 97% lead(IV) tetraacetate (2.5 g, 5.7 mmol, freshly recrystallized) and 15 mL more of chlorobenzene. The resulting mixture was stirred in the dark for 1 h at room temperature, and then it was heated gradually up to 80 °C and refluxed for 1 h. The product was mostly condensed in the trap at −78 °C, and more of the product was obtained by distilling it from the chlorobenzene. The total amount of the product obtained was 0.5 g (0.0055 mol, 37.7%). The spectroscopic data for **3** are identical with those described above.

1,1,2,2-Tetrachloro-3,3-difluorocyclobutane. This compound was prepared by similar procedure as for **7**, using 100 g (0.751 mol) of 1,1-dichloro-2,2-difluoroethylene and 70.1 g (60 mL, 0.73 mol) of vinylidene chloride at 180 °C for 9 h to give 34 g (0.147 mmol 20.1%) of the adduct, a white solid. Mp: 53–55°C. Bp: 60 °C (20 mm). NMR: ^1H, δ 3.59 (t, J_{HF} = 10 Hz); ^{19}F, ϕ 101.5 (t, J_{FH} = 10 Hz).

1,2-Dichloro-3,3-difluorocyclobutene (11). Dechlorination was carried out in refluxing ethanol (280 mL) using 29 g (0.126 mol) of 1,1,2,2-tetrachloro-3,3-difluorocyclobutane and 75 g (1.134 mol) of zinc powder to give 11 g (0.0691 mol, 55%) of **11**, a colorless liquid. Bp: 82–84.5 °C. NMR: ^1H, δ 3.2 (t, J_{HF} = 3 Hz); ^{19}F, ϕ 114 (t, J_{FH} = 3 Hz); ^{13}C, δ 48.5 (t, $^2J_{CF}$ = 29 Hz), 116.8 (t, $^1J_{CF}$ = 342 Hz), 122.5 (t, $^2J_{CF}$ = 34.2 Hz), 136.8 (t, $^3J_{CF}$ = 29 Hz).

1-Chloro-4,4-difluorocyclobutene (12). According to a published procedure,[10] 3 g (0.0188 mol) of **11** was reduced with 0.75 g (0.0197 mol) of lithium aluminum hydride in 100 mL of ether to give 0.3 g (0.0024 mol, 13%) of **12**. NMR: ^1H, δ 2.66 (t, $^3J_{HF}$ = 3 Hz), 6.3 (t, $^4J_{HF}$ = 13 Hz); ^{19}F, ϕ 114 (dt, $^4J_{FH}$ = 13 Hz, $^3J_{FH}$ = 3.0 Hz).

1,1,2-Trichloro-3,3-difluorocyclobutane. The procedure followed was similar to that described for **7**. 1-Chloro-2,2-difluoroethylene (26 g, 0.264 mol) and 21.34 g (0.22 mol) of vinylidene chloride were heated at 220 °C for 22 h, giving 1.45 g (0.0074 mol, (3%) of product, a colorless liquid. Bp: 80–84 °C (40 mm). NMR: ^1H, δ 3.51 (dd, midpoint AB, J_{AB} = 6 Hz, $\Delta\nu$ = 16 Hz, 2 H), 5.1 (td, $^3J_{HF}$ = 9 Hz, J_{HF} = 2 Hz, 1 H); ^{19}F, ϕ 102 (midpoint AB, J_{AB} = 210 Hz, $\Delta\nu$ = 1410 Hz, upfield F, d of octet, J_{FF} = 210 Hz, $^3J_{FH}$ = 10 Hz, $^3J_{FH}$ = 6 Hz, downfield F, d of sextet, J_{FF} = 210 Hz, J_{FH} = 10 Hz).

1-Chloro-3,3-difluorocyclobutene (13). The procedure was similar to that described for **11**. 1,1,2-Trichloro-3,3-difluorocyclobutane 1.4 g, 0.0071 mol) was utilized along with 4.3 g (0.064 mol) of powdered zinc in 30 mL of ethanol to give 0.2 g (0.0016 mol) (22.6%) of **13**. NMR: ^{19}F, ϕ 106.92 (td, $^3J_{FH}$ = 2.83 Hz, $^3J_{FH(vinylic)}$ = 1.39 Hz).

3,3-Difluorocyclobutene (3) by Reduction of 13. The reduction was achieved by a procedure similar to that used for **12**. The reaction of 0.2 g (0.0016 mol) of **13** and 0.8 g (0.021 mol) of lithium aluminum hydride in 20 mL of ether at room temperature for 22 h gave **3** with spectral data as described above.

7,7- and 6,6-Difluoro-2,3-diazabicyclo[3.2.0]hept-2-ene. An ether solution of diazomethane (70 mL) was prepared from 7.14 g (0.0285 mol) of *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide and was allowed to react with 0.828 g (0.0111 mol) of 3,3-difluorocyclobutene for 20 h at room temperature to give 0.335 g (0.00372 mol, 33.5%) of an oily faint yellow liquid. IR: 2945, 1545 cm^{-1} (main peaks). NMR: ^1H, δ 5.8 (m, 1 H), 5.2 (m, 1 H, **5**), 4.6 (br s with fine splitting, 2 H), 1.5–2.9 (m, 3 H); ^{19}F, ϕ 95.55 (midpoint AB, **4**, J_{AB} = 207.73 Hz, $\Delta\nu$ = 1055.48 Hz, upfield F, dddd, J_{FF} = 207.73 Hz, J_{FH} = 20 Hz, J_{FH} = 10.5 Hz, J_{FH} = 4.51 Hz, downfield F, ddddd, J_{FF} = 207.73 Hz, J_{FH} = 18.99 Hz, J_{FH} = 9.99 Hz, J_{FH} = 3.42 Hz, J_{FH} = 1.79 Hz), 93.98 (midpoint AB, **5**, J_{AB} = 197.39 Hz, $\Delta\nu$ = 2486.46 Hz, upfield F, dddd, J_{FF} = 197.39 Hz, $^3J_{FH}$ = 21.26 Hz, $^3J_{FH}$ = 11.11 Hz, $^4J_{FH}$ = 4.34 Hz, downfield F, dm, J_{FF} = 197.39 Hz, J_{FH} = 18.84, 14.94, 7.33, and 4.86 Hz).

Acknowledgment. We acknowledge with thanks support of this research in part by the National Science Foundation.

Registry No. **3**, 29507-09-3; **4**, 107496-59-3; **5**, 107496-58-2; **7**, 107496-53-7; **8**, 1735-42-8; **9**, 1801-08-7; **10**, 107496-54-8; **11**, 14851-11-7; **12**, 107496-55-9; **13**, 107496-57-1; $ClHC{=}CF_2$, 359-10-4; $F_2C{=}CHCH{=}CH_2$, 590-91-0; $H_2C{=}CH_2CN$, 107-13-1; $Cl_2C{=}CF_2$, 79-35-6; $H_2C{=}CCl_2$, 75-35-4; 1,1,2-trichloro-3,3-difluorocyclobutane, 107496-56-0; 1,1,2,2-tetrachloro-3,3-difluorocyclobutane, 697-16-5; CH_2N_2, 334-88-3.

Supplementary Material Available: ^1H, ^{13}C, and ^{19}F NMR for compounds **10** and **3** (10 pages). Ordering information is given on any current masthead page.

(10) Fuller, G.; Tatlow, J. C. *J. Chem. Soc.* **1961**, 3198.

Thioquinones. A Reinvestigation of Perkin and Green's Diaminodithioquinone

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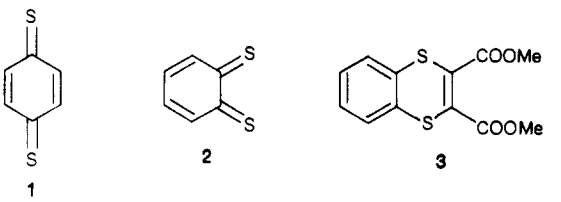
Received December 15, 1986

In contrast to the vast and rich chemistry of the quinones, the chemistry of their thione analogues remains practically unexplored.[1,2] Although the first futile attempt to synthesize *p*-dithiobenzoquinone (1) was reported in



1909,[3] this highly labile molecule was successfully generated only in 1983 using a flash pyrolysis reaction; it was studied spectroscopically in a frozen argon matrix, but it was observed to decompose in an unknown manner, on moderate warming of the matrix.[4] The isomeric *o*-dithiobenzoquinone (**2**) has proven to be even more elusive. Two attempts have been recorded to generate this compound by either a photochemical or a thermal fragmentation of an appropriate precursor. The matrix-isolated product from the pyrolysis route showed an ultraviolet spectrum suggestive of the unknown benzodithiete rather than that expected of dithione **2**.[5] The photolysis route also did not afford **2** as an isolable product, but its transient generation was proven by trapping it with DMAD to give adduct **3** in modest yield.[6]

As a part of a broad program concerning thioquinone chemistry,[7,8] we have been interested in the possibility of

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(2) Patai, S., Ed. *The Chemistry of Quinonoid Compounds*; Wiley: New York, 1974.
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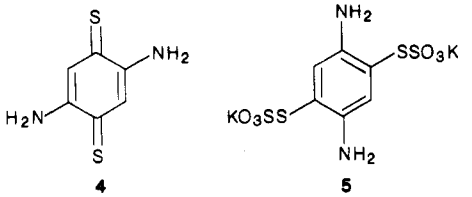
0022-3263/87/1952-1874$01.50/0

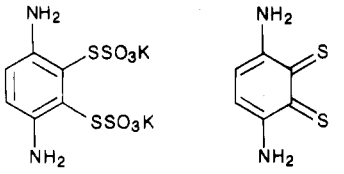
stabilizing various types of thioquinones by a push–pull mechanism using electron-donating substituents. A perusal of the literature indicated that a structure of the desired type had in fact been assigned to a compound more than 80 years ago by Perkin and Green.[9] The work reported here concerns our reinvestigation of this presumed dithioquinone.

Results

The Perkin and Green paper of 1903 described the oxidation of *p*-phenylenediamine in the presence of 2 equiv of sodium thiosulfate to give a diamino dithiosulfonic acid; this material was isolated as its yellow dipotassium salt, which was assumed to have the sulfur substituents in the para relationship as in structure **5**. Treatment of **5** with



4 **5**



6 **7**

warm hydrochloric acid produced both sulfuric and sulfurous acids, with the separation of a yellow dihydrochloride. Basification of the latter salt afforded a deep red material that was assigned the *p*-dithioquinone structure **4** on the basis of elemental analysis. Although the literature records no further account of this red compound, the structure of the dithiosulfonate from which it is derived was modified in 1968 to that of the ortho isomer **6** on the basis of a ^{13}C NMR study of a derived benzodithiazole.[10] Consequently, one may modify the presumed structure of the Perkin and Green compound to that of the *o*-dithioquinone **7**.

Repetition of the literature procedure afforded the desired material as deep red microcrystals, which melt with decomposition above 225 °C and are highly insoluble in most organic solvents. The mass spectrum of the compound was not in accord with a monomeric structure such as **7** but rather with a *dimeric* structure. Crystallization from DMF or aqueous DMA afforded small shiny plates reminiscent of Venus copper. Although these crystals were not suitable for an X-ray crystallographic analysis, suitable crystals in the form of heavy garnet rhombs were eventually obtained, by slow equilibration of a warm solution of the compound in DMF and water separated from it by a porous disk. An X-ray crystallographic analysis led to the unambiguous assignment of the tetrathiocin structure **8** (Figure 1; for details, see the Experimental Section).

In accord with structure **8**, warm hypophosphorous acid afforded the dithiol **9**, whereas sodium borohydride reduction followed by methylation yielded the bis(thiomethyl) compound **10**. Both **9** and **10** were extremely

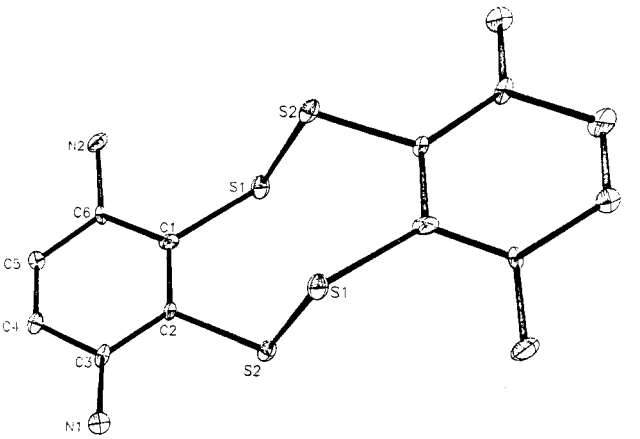
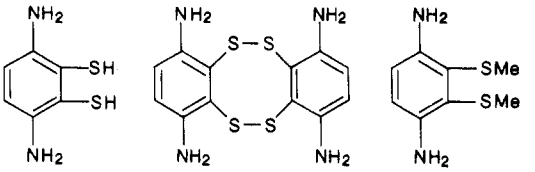
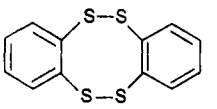


Figure 1. Compound 8.

susceptible to oxidation by air but were readily isolable as the colorless crystalline hydroiodides.



9 **8** **10**



11

Discussion

The known[11,12] parent dibenzotetrathiocin **11** is a lemon yellow compound. We have determined that its longest wavelength maximum lies at 299 nm, indicating that its visible color is a result only of end absorption. In contrast, the dark red dilute solutions of **8** in DMF show that the color is due to an intense maximum (log ϵ 4.02) at 491 nm.[13] Since the position and intensity of this band cannot be rationalized on the basis of structure **8**, we suggest that it is due to *the reversible dissociation of 8 in the polar solvent to the diamino-o-benzoquinone 7*. Structure **7** should be quite polarized, since it would be stabilized in a push–pull manner as indicated by the contributor **7a**. In the solid state, dimerization of **7** back to **8** is taking place, although the garnet color of the crystals of **8** suggests that a small number of the red monomer molecules **7** may be randomly frozen into the crystal matrix, but in insufficient number to be detected by X-ray crystallography.

Addition of hydrochloric acid to a red solution of **7** in DMF produces a yellow solution of the protonated species; this reaction can be reversed on neutralization of the acid. The deep yellow protonated species shows a strong maximum (log ϵ 3.93) at 410 nm. This band cannot be due to the protonated form of **8**, since this species should, like the parent heterocycle **11**, absorb at about 300 nm. We propose, therefore, that this species is either the diprotonated form (**7b**) of the dithioquinone **7** or the monoprotonated species **7c**.

One might expect that **7** would undergo a 4 + 2 addition to an olefinic or acetylenic center. No reaction with either

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(9) Green, A. G.; Perkin, A. G. *J. Chem. Soc.* **1903**, *83*, 1201. For an analogous example of push–pull stabilized α-dithione. Kusters, W.; deMayo, P. *J. Am. Chem. Soc.* **1974**, 96, 3502.

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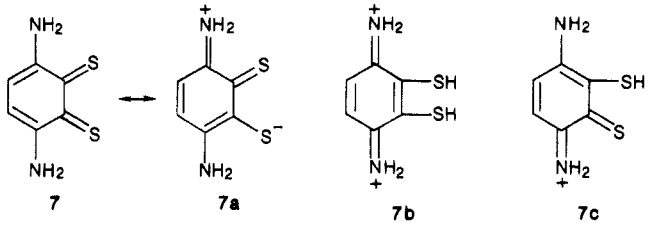
(12) Sato, M.; Lakshmikantham, M. V.; Cava, M. P.; Garito, A. F. *J. Org. Chem.* **1978**, *43*, 2084.

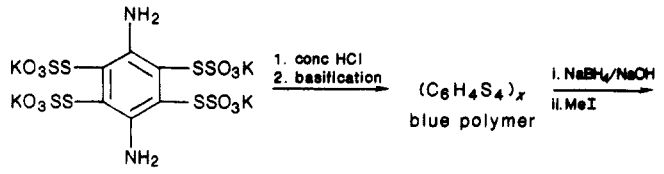
(13) The parent *o*-benzodithioquinone is predicted to have an absorption maximum at 482 nm (see ref 5).



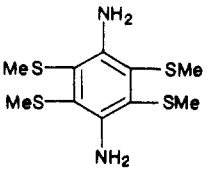
7 7a 7b 7c

norbornene or dimethyl acetylenedicarboxylate could be effected, indicating considerable push–pull stabilization of the thione functions.

Green and Perkin also reported that oxidation of *p*-phenylenediamine in the presence of excess of sodium thiosulfate afforded a tetrathiosulfonic acid, readily isolable as its potasssium salt **12**. Heating **12** with hydrochloric



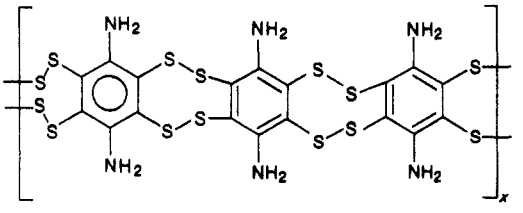
12



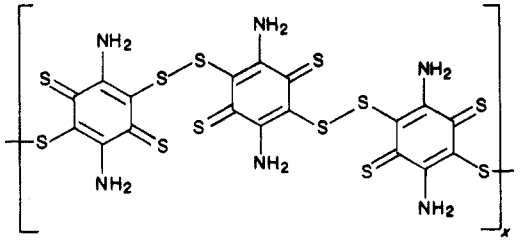
13

acid gave an insoluble deep red salt, which, on basification, yielded a blue–black material having the empirical composition $C_6H_4S_4$. We have now confirmed these observations and have obtained the blue–black material, which is *completely* insoluble in all organic solvents and apparently polymeric in nature. The units of this polymer must be linked only by disulfide bonds, since it can be reductively solubilized by sodium borohydride to a thiolate solution which, on mild methylation, affords the highly fluorescent, yellow 2,3,5,6-tetrakis(methylthio)-*p*-phenylenediamine (**13**).

Since the intense dark color of the polymer seems inconsistent with the polymeric tetrathiocin structure **14**, we propose that at least some regions of the material may contain diamino-*p*-dithiobenzoquinone units as in **15**. The synthesis of monomeric units related to those in **15** is under current study in our laboratory.



14



15

Table I. Crystal Data and Data Collection Parameters for 8

compd	$S_4N_4C_{12}H_{12}$
mol wt	340.52
space group	*Pbca*
cell constants	
a, Å	14.02 (1)
b, Å	14.29 (2)
c, Å	6.92 (1)
cell vol, Å^3	1386
molecules/unit cell	4
ρ(calcd), g cm^{-3}	1.64
μ(calcd), cm^{-1}	6.55
radiation	Mo Kα
max cryst dimens, mm	0.02 × 0.05 × 0.05
scan width, deg	0.8 + 0.2 tan θ
std reflcns	200, 020
decay of stds, %	21
reflcns measd	801
2θ range	2–40
obsd reflcns	322
no. parameters varied	91
GOF	4.1
R	0.0848
R_w	0.0755

Table II. Atomic Coordinates for 8

atom	*x*/*a*	*y*/*b*	*z*/*c*
S(1)	0.4707 (4)	0.4204 (5)	0.791 (1)
S(2)	0.4939 (4)	0.6373 (4)	0.945 (1)
N(2)	0.641 (1)	0.351 (1)	0.559 (3)
N(1)	0.674 (1)	0.731 (1)	0.799 (3)
C(1)	0.571 (1)	0.490 (1)	0.724 (4)
C(2)	0.580 (1)	0.584 (2)	0.783 (3)
C(3)	0.656 (1)	0.640 (1)	0.729 (3)
C(4)	0.723 (1)	0.597 (2)	0.599 (4)
C(5)	0.714 (1)	0.508 (2)	0.546 (3)
C(6)	0.641 (2)	0.449 (2)	0.614 (3)

Experimental Section

General Procedures. All melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Ultraviolet–visible spectra, IR spectra, mass spectra, and NMR spectra were determined on Perkin-Elmer λ_4, Perkin-Elmer 781, Finnigan, and Bruker 90-MHz spectrometers, respectively. δ values are reported downfield from Me_4Si. Elemental analyses were carried out by Atlantic Microlabs, Atlanta, GA.

X-ray Crystallography. A crystal of **8** of size of 0.02 × 0.05 × 0.05 mm was mounted on an Enraf-Nonius CAD-4 diffractometer. Final unit cell parameters, given in Table I, were obtained by a least-squares fit of the angles of 24 accurately centered reflections (2θ > 25°). A total of 801 reflections with 2 < 2θ < 40° were collected by the method previously described,[14] of which 322 were considered observed. The data were corrected for Lorentz and polarization effects, but not for absorption. A summary of data collection parameters is given in Table I.

Application of the direct-methods program MULTAN[15] revealed the positions of most of the non-hydrogen atoms, and subsequent difference maps generated by the SHELX system of computer programs[16] readily provided the remaining positions. Refinement of the non-hydrogen atoms with anisotropic thermal parameters and inclusion of hydrogen atoms at calculated positions converged at $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.085$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2} = 0.076$. The largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. Neutral atom scattering factors were from usual sources.[14] Final positional parameters are given in Table II, and final solid lengths and angles, in Table III.

Tetraamino Tetrathiocin 8. This compound was made es-

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(16) Sheldrick, G. SHELX—A Program System for Crystal Structure Determination, 1976.

Table III. Final Bond Lengths and Angles in 8

atoms	distance	atoms	distance
S(1)-S(2)	2.064 (9)	S(1)-C(1)	1.78 (2)
S(2)-C(2)	1.81 (2)	N(1)-C(3)	1.42 (3)
N(2)-C(6)	1.45 (3)	C(1)-C(2)	1.42 (3)
C(1)-C(6)	1.38 (3)	C(2)-C(3)	1.38 (3)
C(3)-C(4)	1.43 (3)	C(4)-C(5)	1.34 (3)
C(5)-C(6)	1.41 (3)		
atoms	**angle**	**atoms**	**angle**
S(2)'-S(1)-C(1)	105.3 (9)	S(1)'-S(2)-C(2)	102.5 (8)
S(1)-C(1)-C(2)	122 (2)	S(1)-C(1)-C(6)	119 (2)
C(2)-C(1)-C(6)	120 (2)	S(2)-C(2)-C(1)	121 (2)
S(2)-C(2)-C(3)	116 (2)	C(1)-C(2)-C(3)	123 (2)
N(1)-C(3)-C(2)	125 (2)	N(1)-C(3)-C(4)	120 (2)
C(2)-C(3)-C(4)	116 (2)	C(3)-C(4)-C(5)	121 (2)
C(4)-C(5)-C(6)	123 (2)	N(2)-C(6)-C(1)	123 (2)
N(2)-C(6)-C(5)	119 (2)	C(1)-C(6)-C(5)	117 (2)

sentially according to literature procedure.[9] The red material was conveniently recrystallized from DMF instead of boiling aniline–ethanol: mp >225 °C dec; IR (KBr) 3400, 3300, 1600, 1595, 1590, 1460, 1285, 1220, 1155, 918, 810 cm^{-1}; UV–visible (DMF) λ_{max} (log ϵ) 276 nm (4.14), 313 (3.58), 4.91 (4.02), (DMF/HCl) 267 (3.95), 410 (3.93); mass spectrum, *m/e* (rel intens, %) 340 (0.3), 276 (35), 243 (26), 202 (100), 169 (44).

1,4-Diaminobenzene-2,3-dithiol (9). Tetrathiocin 8 (100 mg) was heated cautiously with hypophosphorus acid (25%, 5 mL) for 20 min at 100 °C until a pale yellow solution resulted. The mixture was concentrated to half its volume in vacuo. Hydriodic acid (48%) was added dropwise until the HI salt precipitated (150 mg). This was recrystallized best from CH_2Cl_2–MeOH–Et_2O: mp >150 °C dec; mass spectrum; *m/e* (rel intens, %) 172 (M^+, 2.4%); IR, 2800 br, 1560, 1510, 1400, 1280, 830, 725 cm^{-1}. Anal. Calcd for $C_6H_{10}I_2N_2S_2$: C, 16.83; H, 2.12. Found: C, 16.79; H, 2.48.

2,3-Bis(methylthio)-1,4-benzenediamine (10). A suspension of tetrathiocin 8 (350 mg) in THF–water (3:17, 20 cm^3) containing aqueous sodium hydroxide (1 cm^3) was stirred under nitrogen after the addition of excess $NaBH_4$. After 3 days of stirring, a yellow solution resulted. Methyl iodide (excess, 1 cm^3) was added, and stirring was continued. The product was extracted into ether and after standard workup was obtained as a dark gum. Its solutions in organic solvents were highly fluorescent, and it turned rapidly blue in air and light. It was best isolated as the HI salt by treatment with ethanolic hydriodic acid: the white crystalline salt (340 mg) decomposed above 200 °C; mass spectrum, *m/e* (intens, %), 200 (M^+, 100), 185 (16.7), 184 (11.7), 152 (36.1), 139 (13.8), 121 (15.8); IR (KBr) 2850, 1490, 1450, 1110, 1035, 980, 965 cm^{-1}. Anal. Calcd for $C_8H_{14}I_2N_2S_2$: C, 21.07; H, 3.09. Found: C, 21.32; H, 3.16.

The Blue Polymer.[9] A filtered solution of diamino tetrathiosulfonate **12** (0.96 g) in hot water (30 mL) was treated with concentrated HCl (30 mL), and the dark mixture was boiled until no more SO_2 evolved. The resulting red precipitate of hydrochloride was filtered, washed with concentrated HCl and ether successively, and dried. Trituration of the foregoing hydrochloride with dilute sodium hydroxide solution yielded the blue polymer which was filtered, washed with water, alcohol, and ether, and dried: 0.3 g (94.6%); IR (KBr) 3450, 3350, 1600, 1400, 1250, 1020 cm^{-1}.

2,3,5,6-Tetrakis(methylthio)-*p*-phenylenediamine (13). Reduction of the above polymer (0.12 g) in THF–water–NaOH suspension with excess sodium borohydride (300 mg) at 45 °C over a period of 48 h followed by methylation with Me_2SO_4 (0.8 mL) under nitrogen yielded a light yellow precipitate (0.08 g) that is extremely susceptible to oxidation in air and light leading to soluble blue polar material. A pure sample of **13** (30 mg) was isolated by careful chromatography on alumina under inert atmosphere and crystallization from ether–hexane. It formed light yellow fluorescent prisms: mp 115 °C (30 mg); mass spectrum, *m/e* 292 (M^+, 100%); IR (KBr) 3400, 3300, 3000, 2900, 1570, 1400, 1250, 1160, 985 cm^{-1}. Anal. Calcd for $C_{10}H_{16}N_2S_4$: C, 41.10; H, 5.50. Found: C, 41.11; H, 5.60.

Acknowledgment. This work was supported by a grant from the National Science Foundation (85-14876).

Registry No. 8, 107474-48-6; 9·2HI, 107474-49-7; 10·2HI, 107474-50-0; 12, 107474-51-1; 12 (hydrochloride), 107474-52-2; 12 (hydrochloride homopolymer), 107474-54-4; 13, 107474-53-3.

Supplementary Material Available: Listings of anisotropic thermal parameters (1 page); listings of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

Stereochemistry of the Ring Opening of Chiral Epoxides Derived from Allylic Alcohols Having Two Substituted-Phenyl Groups

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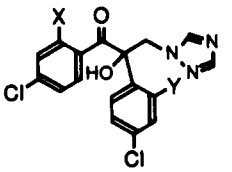
Received August 7, 1986

The antifungal activity of imidazole- and triazole-containing compounds has led us to study their synthesis over the past few years.[1] We have found that 2,3-diphenyl-3-oxo-1-(1*H*-1,2,4-triazol-1-yl)propan-2-ol derivatives such as **1** are orally active against fungi.[2,3] As generally ob-



1a X=Y=H
1b X=H, Y=Cl
1c X=Y=Cl

served with biologically active compounds, only one of the two enantiomers of the imidazole-containing compounds is active against fungi.[3,4] We were interested in synthesizing optically active isomers of **1** by using the Sharpless asymmetric epoxidation to introduce chirality.[5] The asymmetric epoxidation of allylic alcohols has been extensively studied and widely applied[6] to syntheses of optically active compounds. However, few examples of the epoxidation of allylic alcohols having two substituted-phenyl groups have been reported.[7] Moreover, although there are many reports of ring-opening epoxides that have aliphatic side chains, there are few examples of ring-opening epoxides with two aromatic substituents.[8-10] We

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(2) In formula **a**, **b**, and **c**, X = Y = H,X = H,Y = Cl, and X = Y = Cl, respectively, throughout this paper.

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(5) (a) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. (b) For a recent paper, see: Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922.

(6) Review: Pfenninges, A. *Synthesis* **1986**, 89.

(7) For the asymmetric epoxidation of α-phenylcinnamic alcohol: Lu, L. D.-L.; Johnson, R. A.; Finn, M. G.; Sharpless, K. B. *J. Org. Chem.* **1984**, *49*, 728.

(8) Rosowsky, A. In *Heterocyclic Compounds with Three and Four-Membered Rings*, Weissberger, A., Ed.; Wiley: New York, 1964; pp 1-523. Bartbk, M.; Lång, K. L. In *Small Ring Heterocycles, Part 3*, Hassner, A., Ed.; Wiley: New York, 1985; pp 1-196.

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